

Waste Plastics as Fuel Additives: Study of Solubility in Biodiesel and Performance of Plastic-Biodiesel-Diesel Blends in a Diesel Engine

by

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Thesis

Submitted in fulfillment of the requirements for the degree of

Doctor of Philosophy

School of Engineering and Technology (SET), Higher Education Division CQUniversity Australia Rockhampton, QLD Australia

November 2020



CRICOS Provider Code: 00219C | RTO Code: 40939

ABSTRACT

This study investigated the suitability of using waste plastics as an additive in biodiesel through assessing the performance, emissions and combustion characterises of a diesel engine. Firstly, the waste plastics were dissolved into different biodiesels. Then, the dissolved solution was mixed with standard diesel to make diesel-biodiesel-plastic blends. These plastic blends were then tested in a 4-cylinder, 4-stroke, diesel engine. These analyses indicated that waste plastics can potentially be used as fuel additives along with the diesel-biodiesel blends in diesel engines. There exists little research in this field, so the comprehensive study reported in this thesis is important and significant.

The novelty of this work lies in identifying the biodegradable solvents that can properly dissolve waste plastics and demonstrate the beneficial effects of plastics in reducing harmful gas emissions and improving engine performance.

Three different thermoplastics, namely polyethylene (PE), polypropylene (PP) and polystyrene (PS) were chosen for investigation in this study. These thermoplastics were dissolved into nine different biodiesels. Six of these were produced from beef tallow (WTB), waste cooking oil (WCB), castor oil (CaB), poppy seed oil (PB), canola oil (CB) and sunflower oil (SB). Another three were made as binary biodiesels by blending biodiesels from beef tallow, waste cooking oil and poppy seed oil, in different proportions.

The biodiesel production process was optimised through response surface methodology (RSM) using statistical software Minitab 18 along with analysis of variance (ANOVA). Chemical compositions of the biodiesels were determined to investigate the impact of these fuels on diesel engine performance.

Both analytical and experimental investigations were carried out to dissolve plastics in biodiesels (biodegradable solvents). The solubility parameters were determined using various analytical methods sourced from the literature. A reaction kinetic model of biodiesel production was developed to calculate the energy required to initiate the reaction. The solubility rates were determined using the developed kinetic models. All these analyses were undertaken to identify a suitable solvent (biodiesel) for a given solute (plastic). The dissolution process was then experimentally investigated using all three thermoplastics. Both experimental and analytical results indicated that, amongst PE, PP and PS, only PS was suitable to remain dissolved at

ambient conditions. Both CaB and WTB were found as two most suitable biosolvents for dissolving PS. Therefore, PS was dissolved in castor oil biodiesel and tallow biodiesel to produce diesel-biodiesel-PS blends for analysis and engine testing. In addition, two binary biodiesel blends defined as WTC (binary blend of 30% waste cooking and 70% waste tallow biodiesel) and PWC (binary blend of 70% poppy and 30% waste cooking biodiesel) were chosen to investigate the effect of binary biodiesel fuels in engine's performance analyses. The biodiesel-PS fuel blends were prepared by dissolving 5% (w/v), 10% (w/v) and 15% (w/v) of PS in four biodiesel fuels of WTB, WTC (binary blend of 30% waste cooking and 70% waste tallow biodiesel), CaB, and PWC (binary blend of 70% poppy and 30% waste cooking biodiesel) respectively. The diesel-biodiesel-PS fuel blends were then made by blending various proportions of diesel and biodiesel-PS fuels.

The study found that the brake power (BP) decreased by up to 6% with diesel-biodiesel blends compared to diesel, however it decreased by up to 7% when PS was added with diesel-biodiesel blends. BSFC increased by up to 17% with diesel-biodiesel blends compared to diesel, however it increased by up to 19% when PS was added. Overall, brake thermal efficiency (BTE) decreased by up to 14% for diesel-biodiesel blends compared to diesel and by up to 12% when PS was added. Both the biodiesel and PS have higher viscosity and lower calorific value than the diesel fuel. As a result, combustion of diesel-biodiesel-PS fuels reduced both the torque and brake mean effective pressure (BMEP). The brake specific fuel consumption (BSFC) also increased with compared to diesel.

The increase of CO₂ emissions for diesel-biodiesel blends was 11% as compared to 10% when PS was added into diesel-biodiesel blends. The PM emissions doubled with diesel-biodiesel blends compared to diesel, but only increased by up to 60% when PS was added. This indicates that adding PS with diesel-biodiesel blends will decrease the PM emissions. The CO emissions for diesel-biodiesel blend were reduced by about 50%, as compared to 73% when PS was added. The NOx emissions increased by up to 51% with diesel-biodiesel blends, however, they decreased by up to 41% when PS was added. The HC emissions increased by up to 90% with diesel-biodiesel blends as compared to 50% when PS was added. Clearly, the addition of PS has reduced most of the harmful gas emissions.

The experimental results indicated that, due to the addition of biodiesel and PS into the diesel fuel, the peak in-cylinder pressure (CP) was increased. The CP was higher at higher loading conditions but kept decreasing with the increase in engine speeds at any given loading

condition. The peak heat release rate (HRR) was observed to be the highest for diesel combustion at 2400 rpm at full load condition compared to all other blends.

Amongst all the fuels, at full load (100% load) and 1500 rpm, the CaB15PS15 (blend of 70% diesel and 15% castor biodiesel with 15% (w/v) PS) fuel performed well because it showed the minimum reduction of BTE (6%) and BSFC (11%) and only 2.5% more CO₂ emissions than diesel fuel. On the other hand, WTB15PS15 (blend of 70% diesel and 15% tallow biodiesel with 15% (w/v) PS) fuel blend performed well as it reduced CO, NOx, PM and HC emissions by 72%, 34%, 8%, and 48% respectively in comparison to diesel fuel. While reducing these emission components significantly, the WTB15PS15 fuel showed increases in CO₂ emissions by 9% and BSFC by 19%, with a reduction in BTE by 11% in comparison to diesel fuel. Though these fuels had higher BSFC and lower BTE than diesel fuel, turning the waste plastics into fuel offers an environmental and economic benefit.

Clearly, use of the waste plastics, namely, PS in any of the diesel-biodiesel blends that improve overall engine performance, emissions and combustion characteristics provides several advantages. It will compensate the increasing demand of fossil fuel and reduce environmental pollution that are essential for our society and government.

CANDIDATE'S STATEMENT

By submitting this thesis for formal examination at CQUniversity Australia, I declare that it meets all requirements as outlined in the Research Higher Degree Theses Policy and Procedure.

Signature

(Md Hazrat Ali)

STATEMENT AUTHORSHIP AND ORIGINALITY

By submitting this thesis for formal examination at CQUniversity Australia, I declare that all of the research and discussion presented in this thesis is original work performed by the author. No content of this thesis has been submitted or considered either in whole or in part, at any tertiary institute or university for a degree or any other category of award. I also declare that any material presented in this thesis performed by another person or institute has been referenced and listed in the reference section.

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Signature

(Md Hazrat Ali)

I am grateful to Almighty Allah for His blessings with good health, ability to earn knowledge and conduct this research work study successfully.

I would like to express my gratitude towards my academic supervisors, Professor Mohammad Rasul, Professor Masud Khan and Associate Professor Nanjappa Ashwath. I have always found Professor Rasul, my principal supervisor, beside me to guide me with constructive suggestions in both professional and personal issues that I wanted to discuss. Throughout my candidature, I have been impressed by his availability and amiable attitude to listen and help that helped to deal with the key research challenges and stay focused. I must treasure these attributes to look forward in my professional journey. Especially, I would like to acknowledge the guidance of Professor Khan on engine testing, analysis, and discussions. In addition, Associate Professor Ashwath's contribution in the area of biodiesel production, optimisation and characterisation are highly acknowledged. I am really grateful to all three of you for advising me in my study with your expertise and scholarly inputs in order to achieve the research goals.

I would like to specially acknowledge Pattrick O'Grady and Heather Smyth, who were very enthusiastic to assist me on my laboratory work implementation and to follow relevant workplace regulations to remain safe. I am also thankful to both the School of Engineering and Technology and the School of Graduate Research officials who helped me unfeignedly from their respective position of responsibilities.

I must appreciate my parents, Mr Abdur Rahim, and Mrs Rawshan Ara Begum, for their relentless faith on motivating me to keep me focused on my goals. I would like to express my gratitude to my siblings who shared my part of the family responsibilities towards my parents in Bangladesh and allowed me to conduct study here in Australia. I would like to take the opportunity to thank my friends, acquaintances, and a few of the community members in Rockhampton for helping me to adjust with the society and never feel lonely.

Finally, I would like to remember the lady in my life, my wife, Dr Mabruka Islam, who has shown her best possible mental strength to support me during any of the crises I have faced in last few years. Thank you very much Mabruka for always keeping your faith on me and inspiring me with your lovely attitudes.

ACKNOWLEDGEMENT OF SUPPORT PROVIDED BY THE AUSTRALIAN GOVERNMENT

This RHD candidature was supported under the Commonwealth Government's Research Training Program/Research Training Scheme. I gratefully acknowledge the financial support provided by the Australian Government.

ACKNOWLEDGEMENT OF FINANCIAL SUPPORT

I gratefully acknowledge the funding received from Strategic Research Scholarship (SRS) sponsored by the CQUniversity, High Cost Research Fund, and Candidate research support funds from the School of Graduate Research (SGR) of the CQUniversity, which have supported this research.

I also acknowledge the kind financial support from Professor Masud and DDR of the School of Engineering & Technology of the CQUniversity, that substantially helped me to acquire necessary research equipment.

ACKNOWLEDGEMENT OF PROFESSIONAL SERVICES

Professional editor, Dr Peter Kurg, provided copyediting and proof-reading services, according to the guidelines laid out in the University-endorsed national guidelines, 'The editing of research theses by professional editors".

LIST OF PUBLICATIONS

The list of publications have been sorted based on the recent publication year. The first author (Hazrat M A) would like to declare that these articles have never been submitted for examination purpose by any of the co-authors.

Article No. 1	
Title of the Paper	Emission Characteristics of Polymer Additive Mixed Diesel-Sunflower Biodiesel Fuel
Full bibiliographic reference	Hazrat, M. A., M. Rasul, M. Khan, N. Ashwath, and T. Rufford, <i>Emission Characteristics of Polymer Additive Mixed Diesel-Sunflower</i> <i>Biodiesel Fuel</i> . Energy Procedia, 2019. 156 : p. 59-64. <u>https://doi.org/10.1016/j.egypro.2018.11.090</u>
Status	Accepted. Available online 18 January 2019.
Nature of candidates's contribution	While producing this article, I came up with the concept of the paper's content, conducted the experiment, analysed data, interpreted the results, drafted for review, and prepared the final article for submission. My contribution was 70%.
Co-authors' contribution	My co-authors, Rasul, Khan, and Ashwath reviwed the article, helped finalising the draft, and respond to the reviewers' comments. Annother co-author, Rufford worked as assessor of the experimental process methodology section as I needed expert's comment on the reliability of the chemical process work adopted in this article. Overall co-authors' contribution was 30%

Article No. 2	
Title of the Paper	Emission characteristics of waste tallow and waste cooking oil based ternary biodiesel fuels
Full bibiliographic reference	Hazrat, M. A., M. Rasul, M. Khan, N. Ashwath, and T. Rufford, <i>Emission characteristics of waste tallow and waste cooking oil based</i>

	ternary biodiesel fuels. Energy Procedia, 2019. 160: p. 842-847.
	https://doi.org/10.1016/j.egypro.2019.02.149
Status	Accepted. Available online 12 March 2019.
Nature of	While producing this article, I produced the key concept, collected
candidates's	literature data, designed the methodology, conducted the experiments,
contribution	analysed data, interpreted the results, drafted for review, and prepared the
	final article for submission.
	My contribution was 75%.
Co-authors'	My co-authors, Rasul, Khan, Ashwath, and Rufford reviwed the article,
contribution	helped me finalising the draft by giving key instructions and expert
	knowledge sharing, and respond to the reviewers' comments.
	Overall co-authors' contribution was 25%

Article No. 3	
Title of the Paper	Experimental Investigation of Dissolution of Plastic Polymers into Biodiesel
Full bibiliographic reference	Hazrat, M. A., M.G. Rasul, and C. Bode, <i>Experimental Investigation of Dissolution of Plastic Polymers into Biodiesel</i> . WSEAS Transactions on Environment and Development, 2017. 13 : p. 33-42. <u>http://www.wseas.org/multimedia/journals/environment/2017/a105815-050.php</u>
Status	Accepted. Available online 2017.
Nature of candidates's contribution	While producing this article, I produced concept, collected literature data, designed the methodology, conducted the experiments, analysed data, interpreted the results, drafted for review, and prepared the final article for submission.
	My contribution was 50%.
Co-authors' contribution	My co-authors, Rasul, and Bode helped producing the concept into reality by helping with the experimental activities along with me, provided key instructions, and shared expert knowledge to respond to the reviewers' comments for final submission.
	Overall co-authors' contribution was 50%

Article No. 4	
Title of the Paper	Study of combustion and emission characteristics of fuel derived from waste plastics by various waste to energy (WtE) conversion processes
Full bibiliographic reference	Hazrat, M. A., M. Rasul, and M. Khan, <i>Study of combustion and</i> <i>emission characteristics of fuel derived from waste plastics by various</i> <i>waste to energy (WtE) conversion processes.</i> in <i>AIP Conference</i> <i>Proceedings.</i> 2016. AIP Publishing. <u>https://doi.org/10.1063/1.4958429</u>
Status	Accepted. Available online 12 July 2016.
Nature of candidates's contribution	While producing this article, I produced key concept of the article's content, collected literature data, analysed the information to find answers of the key research questions, drafted for review, and prepared the final article for submission.
Co-authors' contribution	My contribution was 80%. My co-authors, Rasul, and Khan also helped developing the key research questions, and shared expert knowledge to respond to the reviewers' comments for final submission.
Co-authors' contribution	 article for submission. My contribution was 80%. My co-authors, Rasul, and Khan also helped developing the key research questions, and shared expert knowledge to respond to the reviewers' comments for final submission. Overall co-authors' contribution was 20%

Article No. 5	
Title of the Paper	Lubricity improvement of the ultra-low sulfur diesel fuel with the biodiesel
Full bibiliographic reference	Hazrat, M. A., M. Rasul, and M. Khan, Lubricity improvement of the ultra-low sulfur diesel fuel with the biodiesel. Energy Procedia, Volume 75, 2015, Pages 111-117. <u>https://doi.org/10.1016/j.egypro.2015.07.619</u>
Status	Accepted. Available online 28 August 2015.
Nature of candidates's contribution	While producing this article, I produced key concept (research gaps and novelty) of the article's content, collected literature data, analysed the information to find answers of the key research questions, drafted for review, and prepared the final article for submission.
Nature of candidates's contribution	While producing this article, I produced key concept (research gaps and novelty) of the article's content, collected literature data, analysed the information to find answers of the key research questions, drafted for review, and prepared the final article for submission.My contribution was 80%.

Co-authors' My co-authors, Rasul, and Khan also helped developing the key research contribution questions, and shared expert knowledge to respond to the reviewers' comments for final submission. Overall co-authors' contribution was 20%

Article No. 6	
Title of the Paper	A Study on Thermo-catalytic Degradation for Production of Clean Transport Fuel and Reducing Plastic Wastes
Full bibiliographic reference	Hazrat, M. A., M. Rasul, and M. Khan, <i>A Study on Thermo-catalytic Degradation for Production of Clean Transport Fuel and Reducing Plastic Wastes</i> . Procedia Engineering, 2015. 105 : p. 865-876. https://doi.org/10.1016/j.proeng.2015.05.108.
Status	Accepted. Available online 11 June 2015.
Nature of candidates's contribution	While producing this article, I produced key concept (research gaps and novelty) of the article's content, collected literature data, analysed the information to find answers of the key research questions, drafted for review, and prepared the final article for submission. My contribution was 70%.
Co-authors' contribution	My co-authors, Rasul, and Khan also helped developing the key research questions, and shared expert knowledge to respond to the reviewers' comments for final submission. Overall co-authors' contribution was 30%

Article No. 7	
Title of the Paper	Biofuel: An Australian Perspective in Abating the Fossil Fuel Vulnerability
Full	Hazrat, M. A., M. Rasul, and M. Khan, Biofuel: An Australian
Full bibiliographic	Hazrat, M. A., M. Rasul, and M. Khan, <i>Biofuel: An Australian Perspective in Abating the Fossil Fuel Vulnerability</i> . Procedia
Full bibiliographic reference	Hazrat, M. A., M. Rasul, and M. Khan, <i>Biofuel: An Australian Perspective in Abating the Fossil Fuel Vulnerability</i> . Procedia Engineering, 2015. 105 : p. 628-637.

Status	Accepted. Available online 11 June 2015.
Nature of candidates's contribution	While producing this article, I produced key concept (research gaps and novelty) of the article's content, collected literature data, analysed the information to find answers of the key research questions, drafted for review, and prepared the final article for submission. My contribution was 60%.
Co-authors' contribution	My co-authors, Rasul, and Khan also helped developing the key research questions, and shared expert knowledge to enrich the contents of the article as well as respond to the reviewers' comments for final submission on acceptance. Overall co-authors' contribution was 40%

Article No. 8	
Title of the Paper	Utilization of Polymer Wastes as Transport Fuel Resources-a Recent Development
Full bibiliographic reference	Hazrat, M. A., M. Rasul, M. Khan, A. Azad, and M. Bhuiya, <i>Utilization</i> of Polymer Wastes as Transport Fuel Resources-a Recent Development. Energy Procedia, 2014. 61 : p. 1681-1685. <u>https://doi.org/10.1016/j.egypro.2014.12.191</u>
Status	Accepted. Available online 12 January 2015.
Nature of candidates's contribution	While producing this article, I produced key concept (research gaps and novelty) of the article's content, collected literature data, analysed the information to find answers of the key research questions, drafted for review, and prepared the final article for submission.
	My contribution was 60%.
Co-authors' contribution	My co-authors, Rasul, and Khan checked the draft, and shared expert knowledge to enrich the contents of the article to state the research questions and novelty succinctly. My other co-authors, Azad and Bhuiya helped me collecting the updated information and analyse the data to organise the article's contents.
	Overall co-authors' contribution was 40%

Article No. 9	
Title of the Paper	Prospective use of antioxidants in 2nd generation biodiesel for diesel engines in Australia
Full bibiliographic reference	Hazrat, M. A., M. Rasul, and M.M.K. Khan, <i>Prospective use of</i> <i>antioxidants in 2nd generation biodiesel for diesel engines in Australia.</i> 9th Annual Green Energy Conference in Tianjin China (IGEC-IX), May 25-28, 2014.
Status	Accepted and presented in the conference in May 2014.
Nature of candidates's contribution	While producing this article, I produced key concept (research gaps and novelty) of the article's content, collected literature data, analysed the information to find answers of the key research questions, drafted for review, and prepared the final article for submission. I have also produced the draft presentation content for the conference presentation. My contribution was 60%.
Co-authors' contribution	My co-authors, Rasul, and Khan also helped developing the key research questions, and shared expert knowledge to respond to the reviewers' comments for final submission. Rasul presented the article in the conference by improving the presentation content of the draft that I wrote.
	Overall co-authors' contribution was 40%

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LIST OF SYMBOLS AND A	ABBREVIATIONS
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%wt. or wt.%	Percentage weight amount	EGT	Exhaust gas temperature
Adj.	Adjusted	FAME	Fatty acid methyl ester (biodiesel)
AgNO ₃	Silver nitrate	FFA	Free fatty acid
BMEP	Brake mean effective pressure	GCM	Group contribution method
Bn	Billion	GHG	Greenhouse gas
BP	Brake power	GL	Giga litres
BP	Brake power	G_m	Mixing free energy
BSEC	Brake effective energy consumption	Н	Enthalpy
BSFC	Brake specific fuel consumption	H ₂ O	Water
BTE	Brake thermal efficiency	H_2SO_4	Sulphuric acid
CA	Crank angle	HC	Unburnt hydrocarbons
CaB	Castor oil biodiesel	HRR	Apparent heat release rate
CB	Canola oil biodiesel	HSP	Hansen solubility parameter
CED	Cohesive energy density	ID	Ignition delay
CH ₃ OH	Methanol	IEA	International energy agency
CN	Cetane Number	Κ	Kelvin
CO	Carbon monoxide	kg, g, mg	Kilogram, gram, milligram
CO_2	Carbon dioxide	КОН	Potassium hydroxide
CP, P	In-cylinder pressure, Pressure	М	Molar weight
E_{coh}	Cohesion energy	M tonnes	Million tonnes
m, km	Metre, kilometre	S, ms	Second, millisecond

ML	Million litres	SB	Sunflower oil biodiesel
NaHCO ₃	Sodium bicarbonate	SFC	Specific fuel consumption
NaOH	Sodium hydroxide	t	time
NOx	Oxides of nitrogen	Т	Torque
O ₂	Oxygen	Т	Temperature
°С	Degree Celsius	T_{g}	Glass transition temperature
PB	Poppy oil biodiesel	\mathbf{V}_{m}	Molar volume
PBD	plastic-biodiesel-diesel	\mathbf{V}_{w}	van der Waals volume
PE	Polyethylene	WCB	Waste cooking oil biodiesel
PIC	Plastic identification code	WTB	Waste tallow biodiesel
РМ	Particulate matters	WTC	Mix of waste tallow and waste cooking oil biodiesel
PP	Polypropylene	WTP	Mix of waste tallow and poppy biodiesel
Pred.	Predicted	Δ	Change of any parameter
PS/EPS	Polystyrene/Extended polystyrene	δ	Solubility parameter
PWC	Mix of poppy and waste cooking oil biodiesel	ΔH_{vap}	Evaporation enthalpy
rpm	Engine speed (revolution per minute)	δ_t	Total solubility parameter
S	Entropy	ρ	density

Chapter 1 INTRODUCTION

1.0 Motivation and Background

Use of biofuel has been increasing steadily in recent times in providing renewable energy input in the global transport sector by either as direct liquid mix with the diesel/petrol or by generating renewable electricity to power the electric powered vehicles. A report from the International Energy Agency (IEA) stated that, the energy input from the renewable sources into the transport sector was about 3.7% (i.e. about 4 exajoules) of the total energy consumed in this sector globally in 2018 is expected to increase its share to about 4.6% by 2024 [1]. Despite its own production capacity, the Australian domestic petroleum market has been leaning towards import dependency of refined petroleum products, which has increased about threefold within the last decade [2]. As a result, the vulnerability of the Australian fuel supply chain has been aggregating [3-6]. In 2017-2018, oil accounted 38.7% (2387.8 petajoules) and renewables accounted for 6.2% (382.1 petajoules) from a total of 6171.7 petajoules of energy consumed in Australia [7]. There was about 3.2% increase in oil consumption, 9.9% increase in bioethanol consumption but 85.2% reduction in biodiesel consumption compared with the previous year (2016-2017). Additionally, the transport sector consumed about 28.1% of total energy, in electricity supply the increase was 26.3%, and that in the mining sector was 11.8% in the year 2017-2018. About 36.19% of the total energy consumed was supplied from imported energy products. Such an alarming situation has made the Australian petroleum supply chain management vulnerable. Figure 1-1 and Figure 1-2 show the total energy supply in the Australian energy stream by sources and oil consumed by the various sectors for energy production in Australia from 1990 to 2018/2017. These figures give brief information about the energy demand and supply trends in Australia.



Figure 1-1 Total Energy Supply in the Australian Energy Stream by Sources (Data Collected from **[8, 9]**



Figure 1-2 Oil consumed by various sectors for energy production in Australia from 1990-2017 (data collected from **[8, 9]**)

There is always a threat of declining the overall fossil fuel reserves worldwide due to increased consumption and political unrest in the oil producing regions. Energy security has been turning into one of the key issues of concern in Australia. Renewable energy, which is considered as low or zero emission emitter, could be a potentially effective source in reducing Australia's greenhouse gas (GHG) emission and to boost energy security. Biofuels (biodiesel and bioethanol), which are produced from regionally available feedstocks, could develop market strength if these can be commercialised and standardised for vehicular engines.

The biofuel feedstocks are mainly obtained from agricultural farming or forests. These feedstocks can be either edible or inedible, and classified as first generation, second generation, third generation or fourth generation feedstocks [10]. Production of second generation biodiesel will not only meet the fuel demand but also potentially improve overall ecological condition as a result of establishing deep-rooted and inedible feedstock farming in saline and degraded lands left over from mining, grazing and coastal lands [11]. It is essential to set up a substantial policy mix in the development of reliable biofuel production and marketing in order to reduce the greenhouse gas related pollution.

On the other hand, economic growth and changing consumption and production patterns are resulting into the rapid increase in generation of waste plastics in the world. The world's annual consumption of plastic materials has increased from around 5 M tonnes in the 1950s to nearly 360 M tonnes in 2018; thus, about 71 times more plastics are produced nowadays than 68years ago. This implies that, more resources are being used to meet the increased demand for plastic. As a result, more plastic wastes are being generated. Although plastic production is increasing rapidly, the rate of recovery or recycling of the waste plastics has been very slow. The global average recycling rate of waste plastics was about 9 % wt. in the year 2015 [12, 13]. In 2017-2018, about 3.41 M tonnes of plastics were used in Australia and only 9.4% of these were recovered and recycled [14]. About 54% of the collected recyclable waste plastics were exported after collection during this financial year (2017-2018).

Conventional plastic polymers, which are mainly produced (~99%) from hydrocarbon feedstocks [15], are of predominant interest as renewable raw material for energy production. These plastics also possess equivalent heating value comparable to fossil and biomass-based fuels. Unfortunately, refineries are technologically limited to accepting only a very narrow range of liquid hydrocarbons with very specific properties and minimal contaminates [16].

Due to complexities, high cost, detection issues and labour intensiveness in the sorting steps, plastic recycling has not received the same attention as glass or metals. Unlike other recycled materials, accurate sorting of plastics based on their types is essential for recycling and reuse due to their distinct performance characteristics. It is a gruelling task to clean and decolourise the contaminated waste plastics after collection even when the plastics are of same category [17]. However, in terms of the cost of saving the environment, the investment in collection, sorting and converting them in preparation for recycling, reuse or convert into energy could be a better trade off.

On the other hand, the looming fossil fuel scarcity threat has evidently shifted the world energy scenario from the sole dependence on fossil fuels into various alternative energy resources. Therefore, various thermal treatment processes like pyrolysis, gasification, hydrolysis, have been evolving for several decades to ensure a yield of alternative energy resources for various industries, e.g. automotive, power plants, etc. Thus the thermo-chemical recycling of the waste plastics through various processes has been encouraged to convert the plastic polymers into liquefied or gaseous products to be effectively used as energy resources [18]. If the plastic wastes can be converted into fuels, they will not only reduce the complexities of non-biodegradable polymers wastes from the earth but also could be recognised as another alternative fuel resource [19].

In recent years, new methods of converting waste plastics into fuel have been investigated. One of the potential and most attractive methods is dissolving these plastic wastes into biodiesel, an effective biodegradable solvent for polymer dissolution **[19-21]**. In this way, the waste polymers can be treated as one of the effective additives to boost the fuel quality instead of recycling or reprocessing only. The array of predicted consequences includes: more input towards nation's renewable fuel supply, less dependence on international market supply, reduction of environment pollution and finally, the beneficial development of methods for recycling of waste.

1.1 Prospects of Biofuels and Waste Plastics on Achieving Australian Fuel Security

Countries like the United States of America (USA), Brazil, European Union (EU), United Kingdom (UK), China, Indonesia, Thailand, Canada, India and Japan have progressed towards establishing large scale biofuel production and consumption policies to reap the benefits of the renewable and sustainable clean fuels in the transport sector **[22, 23]**. The rate of progress of world biofuel production has experienced a positive gradient in last two decades. Between 2000 and 2017, the total global biofuel production increased from 16 GL to 143GL **[24]**. Among biofuel producers, the USA and Brazil are the leading producers of bioethanol (about 87% of the global production in total) but biodiesel production has been evenly spreading product among Asia, Europe and America continents **[24]**. Liquid biofuels are mostly consumed by the transport sectors around the world to reduce their contribution of pollutants emission due to combustion of fossil fuels. The International Energy Agency (IEA) has reported the share of renewable energy sources being used in the transport sector in various countries in 2016 **[23]**. Apparently, Brazil and Sweden are the two countries that could meet the transport sector energy

demand by more than 15% with biofuels. Also, USA, Norway, France, Denmark, and Austria achieved the goal of more than 5% contribution of biofuel to their individual transport energy demands.

Development of biofuel policies has opened the gateway to consider these fuels as one of the key components of the bioeconomy, which may turn into world trade feature within the next decade [24]. Creation of new jobs (direct and indirect employments), reduction of environmental pollution, utilisation of biodegradable feedstocks, advancement of technical efforts, and improvement of quality of social life. could be considered as key ingredients of sustainable bioeconomy development. While the countries like USA and Brazil are setting benchmarks with proper and timely national level mandates for biofuel based economic development, Australia is far behind that track [25, 26]. Australia has been working on improving the biofuel mandates since 1980 [27, 28]. Biofuel consumption in Australia has been increasing since 2003-04 and it was expected that with significant support it may contribute a good share of nation's total fuel consumption by 2020 [29]. Though biofuel has not been able to achieve the desired prospects between 2014-2019, it is anticipated that implementation of efficient renewable fuel policy will help this industry to emerge [30]. Various Australian states have their own source of feedstocks to produce biofuel without disrupting the ecosystem and colliding with the food supply chain [25]. Following demonstrated successful models from other developed countries, biofuel policies in Australia may turn into effective investment in near future.

Figure 1-3 shows the overall diesel fuel import and sales in Australia since 2010 [**31**]. The figure shows that, about 49.33% and 133% increases in sales and import have been observed respectively in 2018 compared with 2010. In addition, the domestic supply started losing its competitive track since 2013-14 after reaching to its peak of 12,130 ML in 2012-13. In the year 2018-19, about 70.34% of the total diesel fuel demand was met by importing from other countries by the establishment of efficient supply chain management systems by key fuel importers in Australia. If 5% -15% biodiesel fuel could be supplied to the Australian diesel consumer market, there would need to be about 1.46-4.39 GL of biodiesel produced and consumed.



Figure 1-3 Australian diesel oil (overall) statistics from 2010-2018 [31]

Fossil fuels are still contributing about 98% of the total transport industry demand, therefore, they are one of the major sources of greenhouse gas emissions **[32, 33]**. Biodiesel has the least contribution to the transport sector energy consumption in Australia **[33]**. However, biofuels can be an effective way to overcome the liquid fuel security risk and to reduce net GHG emission from transport engines by making optimal use of regionally suitable feedstocks, which could be grown in dry lands as well **[34-39]**.

Apart from the potential resourcing of energy from the biodiesel feedstocks, waste polymers could become an effective catalyst in achieving sustainable economic development. Following the world trend, the rate of plastic consumption has been increasing in Australia. Though the overall waste recycling rate has been increasing in Australia [40, 41], the nonbiodegradable waste plastic recycling rate is very low. Table 1-1, which shows the waste plastic data in recent years in Australia, shows only a 9.4% recycling rate out of 3.4073 M tonnes of plastics consumed in the year 2017-2018 [14]. One of the key reasons is the complexities linked with the waste plastic recycling processes [42]. The rest of the unrecovered or unrecycled waste plastics are sent to the landfill sites. Proper infrastructure support from government along with modified technology related to plastic waste recycling processes can be helpful for exploiting these leftover wastes. Since the waste plastics are mainly generated from very good level of calorific value-based hydrocarbon raw materials, waste to energy production could be very helpful in achieving 100% waste recycling and establishing a circular economy [40]. Though waste plastics to energy production has not yet begun in Australia, about 1.97 M tonnes of waste was fed into waste-to-energy production processing plants in 2016-2017 in Australia [41]. One of the Australian companies, named IGESolutions, has patented a plastic-to-liquid fuel processing method, that claimed the fuel could reduce about 38% of the greenhouse gas

(GHG) emission generated by use of fossil diesel fuel **[43]**. More investigation into fuel conversion efficiency may substantially encourage consideration of waste plastics as feedstocks for the purpose of liquid fuel production.

Year	Plastic Consumed (tonnes)	Plastic Recovered (tonnes)	Recycling Rate (%)
2017-2018	3407300	320000	9.4
2016-2017	2955400	291000	9.8
2015-2016	2912000	328900	11.3
2014-2015	3167000	341800	10.8

Table 1-1 Australian plastic consumption and waste plastic recovery trends [14]

Hence the establishment of sustainable and potentially environmentally friendly renewable and alternative energy resources are necessary to minimise the gradual increase of nation's fuel import demand. Protecting the environment from any hazardous threats and thus assuring an appropriate waste management policy is another important aspect of sustainable development.

1.2 Research Problems

Based on the discussions on previous section it has been found that the fossil fuel demand has been increasing with the increase in various applications. Due to various alternative energy producing sources, demand for fossil fuels is not increasing as rapidly as it would otherwise be. Combustion of fossil fuels is one of the leading reasons for GHG emissions, thus environment pollution to a great extent. Transport sectors are consuming major proportion of the liquid fuels. Biodiesel could be one of the renewable fuels alternatives to meet the demand of diesel fuel for energy production. To avoid the food vs fuel conflict and the threat to destroy the ecological balance, it is essential to use inedible, waste resources and high oil yielding feedstocks to produce biodiesel fuels. In order to produce the required amount of biodiesel most efficiently from a feedstock, it is essential to determine the optimal process parameters and understand the process kinetics.

In fact, overall energy demand will always keep rising. Hence, further supply of fuels from alternative sources will help to lessen the excessive demand on fossil fuel production facilities. Sustainable, less expensive, and environmentally friendly alternative fuel production from waste plastics may be considered as one of the alternative resources for liquid fuel supply. Notably, the waste plastics are becoming environmental threat and very much an uneconomic investment for reprocessing in many countries. Though plastic wastes are non-biodegradable,

a bigger chunk of these wastes is still going to the landfill and to the rivers/oceans due to higher costs of cleaning and sorting the wastes. Since plastics are mainly originated from hydrocarbons, they have higher calorific values which could be used as alternative source of energy production. Among several industrial processes, also known as waste management or recycling processes, chemical conversion of the plastics into liquid hydrocarbons may potentially turn into an effective way of reducing non-biodegradable wastes. There are various chemical solvents to chemically treat the plastics to convert them into liquid [44], but it is essential to use biodegradable and diesel compliant solvents in order to use the solution to make diesel fuel blends.

Solubility analysis of plastics in biodiesel is a promising way to produce fuel by dissolving optimal amount of plastics. There is limited research and results available on this applicability analysis. There is a need and it is highly desirable to study and develop an efficient and cost-effective methodology to produce the fuel mixture. In this research, a simplified technical principle has been adopted to dissolve the waste plastics in biodiesel, which is already a conducive bio-solvent in the form of renewable fuel.

The proposed process of dissolving the plastics in the biodiesel is deemed a simple, economic, and effective process to be installed in commercial purposes. The detailed process is discussed in the methodology section along with the solubility analyses. While conducting the solubility analysis of the plastics in the biodiesel solvents, it is also essential to understand their dissolution kinetics. The main focus of this study is not only to derive PBD (plastic-biodiesel-diesel) fuel, but rather to study how to make the best use of PBD fuel in the diesel engines and get the desired results of acceptance of the PBD as a transport grade fuel. So, these fuel blends need to be assessed in the diesel engine test bed to investigate their combustion, emission, and performance characteristics.

Therefore, this discussion shows that there exists several significant research-topics to be researched in order to use the biodiesel and waste plastics as fuel alternatives in diesel engines. It is expected that the analyses conducted will be helpful to further progress in supplying fossil fuel alternatives to reduce the continual demand pressure on diesel fuels around the world and choosing a sustainable waste management/recycling process. As a result, the bulk content of the untreated waste plastics could be reduced and the related risks of environmental pollution can be minimised.

While looking for the research problems and setting up the expected outcomes of this study, the following research questions were taken into consideration.

How to find a suitable, economic, and achievable process method to convert the waste plastics into liquified solutions. What is the purpose of using biodiesel fuels as biosolvent to dissolve the plastics? How much economic the biodiesel production will be in terms of the production method used in this study? Will there be any engine modification requirement to use the diesel-biodiesel-plastic fuel blends in the diesel engine? How can this method be helpful to the waste management/waste plastic recycling industries?

The following chapters will present the solution of these questions based on intensive analytical and experimental investigations.

1.3 Aims and Objectives

The primary aim of this study is to investigate the possibility of using waste plastics as liquified fuel in the diesel engine, thus increasing the amount of alternative fuel supply for the internal combustion engine. Successful accomplishment of the primary aim will help to reduce bulk amount of waste plastics that are not recovered due to recycling complexities and higher processing expenditures.

The key objectives of the research are to:

- I. Optimise and develop the reaction kinetics for biodiesel production processes from various edible and inedible biodiesel feedstocks.
- II. Analyse the solubility of plastic dissolution into biodiesel and develop the reaction kinetics of the dissolution process.
- III. Identify the type of waste plastic polymers to be used as fuel with the biodieseldiesel fuel blends by investigating various waste-to-energy conversion technologies.
- IV. Characterise various biodiesel-diesel and polymer-biodiesel-diesel blends.
- V. Assess performance, emission, and combustion characteristics of various polymer additive mixed diesel-biodiesel fuel blends in a diesel engine.

1.4 Expected Outcomes of the Research

First expected outcome will be production of the plastic-biodiesel-diesel (PBD) fuel blend through a simplified and less expensive process methodology. While the plastics are turning into fuel, use of biodiesel will be increasing due to inherent solvent quality of the biodiesel fuels. There will be further opportunities to turn the biodiesel industries into profitable ones.

The novel method used in order to convert the wastes into liquid fuel will help the recycling industries. The proposed technology may be acceptable to the national and international alternative fuel processing and plastic waste management industries simultaneously.

Expected outcomes from this study include, but not limited to:

1.4.1 Intermediate Outcomes and Benefits

- Reduce annual tonnes of waste plastic polymers produced annually and are dumped into the landfill sites or sent to incinerators.
- Reduce greenhouse gas emission.
- Reduce consumption of fossil fuel via an increase in sustainable fuel production capacity, thereby increasing the renewable fuel consumption for energy production.
- Minimise the ways of reducing contamination of the soil, water, air, and the food by microplastics.

1.4.2 End Outcomes and Benefits

- Characterise emissions of PBD fuels for better environmental policy development.
- Achieve health benefits as the wastes will be reduced from the Earth.
- Optimise biodiesel production processes and develop reaction kinetics for economic benefits.
- Understand dissolution kinetics of biodiesel-plastics which will help with the energy economy of the processes.

1.4.3 Potential Outcomes and Benefits

- An increased understanding of the environmental or economic effectiveness of the implemented technology
- Increased public awareness of alternative utilisation of resources

• National and international acceptance of the proposed technology

1.5 Scopes and Limitations of the Study

1.5.1 *Scopes*

This study strives to experimentally investigate conversion of a range of thermoplastics (PE, PP and PS) into liquefied fuel by the thermochemical process, commonly known as solvolysis. Altogether 9 biodiesel fuels, namely, waste tallow biodiesel (WTB), waste cooking oil biodiesel (WCB), castor oil biodiesel (CaB), poppy seed oil biodiesel (PB), sunflower oil biodiesel (SB), canola oil biodiesel (CB), binary mix of poppy and waste cooking oil biodiesel (PWC), binary mix of waste tallow and poppy seed oil biodiesel (WTP) and binary mix of waste tallow and waste cooking oil biodiesel (WTC), which are produced from various edible and inedible feedstocks, are used as solvent for this solvolysis process. The experimental results are analysed to develop plastic-biodiesel fuel blends have been chosen to conduct fuel performance study in the diesel engine with comparison to pure fossil-derived diesel fuel. As a result of these extensive investigations, the proposed methodologies and objectives of this study will evidently bolster scientific and technical arguments in favour of mass scale investment in efficient plastic waste management industries (i.e. recycling and waste-to-fuel conversion).

Plastics are currently used in various industrial applications as alternatives to several other materials and to produce less expensive products. It is impossible to deny the benefits from plastics. However, plastic wastes are accumulating in the land and ocean at an alarming rate and posing a threat to the ecology. By converting plastics into fuel or pure reusable raw materials, the world will benefit from the reduction in unwanted environmental pollution, less expensive and simplified plastic recycling method, as well as fulfilling the energy demand for liquified fuel.

1.5.2 Limitations

Though theoretical solubility analyses are conducted for 6 types of thermoplastics (PIC 1-PIC6) out of the 7 types of thermoplastics, the experimental investigations were performed with only three, namely, PE, PP and PS. The theoretical analysis was modelled for 25 $^{\circ}$ C

temperature only, whereas the experimental dissolution processes are conducted at higher temperatures.

1.6 Outline of the Thesis

The thesis contains 10 chapters, whose outlines are given below:

Chapter 1 introduces the potential of both the biodiesel and waste plastics as alternative fuel for diesel fuelled internal combustion engines. Global renewable liquid fuel and Australian energy production conditions have been presented. The research gaps have been identified and expected outcomes have been listed in this chapter.

Chapter 2 reviews the plastics, their properties, global plastic production and recycling data, target wastes, various thermochemical processes for converting the plastics into fuels and several of the existing recycling processes. The effectiveness of each of the processes is also presented.

Chapter 3 presents theoretical considerations of analyses of solubility parameters of the polymer in solvents. The factors affecting solubility, thermodynamic criteria of solubility and methodologies for determining the solubility parameters are discussed briefly. A brief discussion on solubility criteria is also presented in this chapter.

Chapter 4 reviews the various biodiesel production processes, the fuel quality parameters and relevant standards used globally and in Australia. Brief theoretical considerations on optimisation and development of reaction kinetic modelling of both esterification and transesterification processes are presented in this chapter.

Chapter 5 presents a detailed description of methods of biodiesel production (i.e. both esterification and transesterification processes) for studied biodiesel feedstocks. Also, this chapter presents statistical analyses for optimising both the esterification and transesterification processes of all of these biodiesel fuels. These analyses are followed by the optimisation processes, and a detailed description of developing reaction kinetic models for each of the processes for the studied fuels are also presented. Finally, this chapter presents few of the key fuel characteristics as determined for the studied fuels.

Chapter 6 presents the detail for the experimental investigations of the dissolution of plastics (PE, PP and PS) into various studied biodiesel solvents. Relevant experimental

methodologies are also presented in this chapter. Dissolution profile (temperature vs dissolution time) for plastics into biodiesel solvents, variation of solution viscosities and reaction kinetic models of dissolution processes are also discussed in this chapter.

Chapter 7 presents the analytical procedures for determining solubility parameters and criteria for thermoplastics (i.e. PE, PP, PET, PVC, and PS) into various studied biodiesel fuels. Detailed mathematical procedures for determining solubility parameters of both solute and solvents using various theoretical models and solubility criteria are discussed in this chapter.

Chapter 8 presents the experimental analysis of the emission characteristics of the studied fuel blends in a diesel engine. This chapter also presents the experimental methodology and total matrix of fuels selected for the study carried out in both chapter 8 and chapter 9.

Chapter 9 presents the performance and combustion characteristics of PS polymer additivebased diesel-biodiesel fuel blends in the diesel engines with relevant experimental analysis. These results contributed to assessment of the quality of diesel-biodiesel-PS solution as fuel with comparison to diesel and diesel-biodiesel fuel blends.

Chapter 10 briefly presents the key findings of this study. It also concludes by presenting a few future lines of research works, which may increase the effectiveness of industrial expansion of converting waste polymers into fuels as one of the widely acceptable ways to improve the world.

The reference section presents the list of the cited works, publications, and information, which were essential precursors to developing related knowledge and skills presented in this thesis.

The appendices present the supplementary data to support various analyses in this study.

Chapter 2

REVIEW ON PLASTIC WASTES AND WASTE-TO-ENERGY CONVERSION PROCESSES

2.0 Introduction

This chapter briefly discusses plastics wastes, their properties as fuels or source of energy, and environmental pollution due to existing recycling processes. This chapter also reviews the conditions of plastic production and recovery status. The thermal and microstructure characteristics of plastic materials are reviewed to enable us to investigate their potential use as solute for biodiesel solvents.

2.1 Global Plastic Production and Recycling

There are extensive variations of plastic materials based on their different characteristics and types of applications. Plastics are mainly produced from various hydrocarbons (e.g. ethylene, propylene, naphtha, natural gas) produced in the refineries while refining the crudes [45]. Salt like minerals and renewable materials like sugarcane, complex carbohydrates, oil, or fats are also used to produce plastics for various applications. The worldwide total plastic production trend is presented in Figure 2-1. This information is evidently indicating the rapid growth in production of plastics in last five decades. There were only about 1.5 million tonnes of plastics produced globally in the year 1950, which had risen about 359 million tonnes in the year 2018 [46]. Rapid population growth, modern industrial revolution together with economical and durable manufacturing systems, and diverse acceptance of plastic materials to replace expensive metals, etc. are the key factors driving this increase. In Table 2-1 [47, 48], worldwide total annual production of most of the consumable thermoplastics is shown. Production of thermoplastics is higher due to increased consumption in the industrial and retail sectors. For this reason, Asia is now producing more than 50 % wt. of worldwide plastic with China's leading contribution of 30 %wt. The European Union produced about 17%wt. and NAFTA produced about 18 %wt. (Figure 2-2) in the year 2018 and the remainder was contributed by the other regions of the world.



Figure 2-1 Worldwide total plastic production scenario [46]

Table 2-1 Worldwide Annual	Thermoplastic	Production	[47,	48]
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Plastic	LDPE	LLDPE	HDPE	PP	PS	PVC	PET	Total	Percent of Total Plastic Production
World Production (M tons) in 2011	23.3	7.4	25.5	52.2	14.6	43.0	53.3	219.3	78.32%
World Production (M tons) in 2015	(LDPE	64 +LLDPE)	52	68	25	38	33	280	86.95%



Figure 2-2 Comparison of worldwide regional plastic production share in the year (a) 2012 [49] and (b) 2018 [45]

It has been estimated that about 8-9% of the worldwide oil and gas production are used for production of virgin plastic polymers including the half of these hydrocarbons consumed as the fuels required to produce these plastic materials **[50, 51]**. Global cumulative plastic

production (excluding fibres and additives) doubled just between years 2000 (~3.39 Bn tonnes) and 2015 (~7.82 Bn tonnes) [52]. By 2018, the overall global plastic production was about 8.862 Bn tonnes [53]. Though the amount of plastics production is increasing rapidly, the rate of recovery or recycling of the waste plastics has been found to be very poor. The global average recycling rate of waste plastics was less than 5 % wt. of the total new plastics produced in the year 2012 [49], and had risen to 9 % wt. in the year 2015 [12, 13]. The lion's share of the rest of the plastics goes into landfill (as collected and discarded and dumped form) and a portion goes to the incineration plants to produce energy, but with the risk of producing toxic fumes to pollute the environment [54, 55].

The plastic waste stream observed in the total municipal solid waste (MSW) stream in the USA is presented in Table 2-2. This table presents a brief overview of waste plastic generation within the MSW stream from 1960 to 2017. Themelis and Mussche **[56]** stated that, theoretically, if all the landfilled non-recyclable plastics (NRP) (~ 34.4 million tons) in the USA in the year 2011 were used for energy recovery, it could help to reduce the use of 48 million tons of coal, or 180 million barrels of oil, or 1 trillion standard cubic feet of natural gas.

Waste plastic	Plastic materials in the waste stream from 1960 to 2017, (Thousands of US tons)								
management data	1960	1980	1990	2000	2010	2015	2016	2017	
Generated	390	6830	17130	25550	31040	34500	34870	35370	
Combustion with energy recovery	-	140	2980	4120	4530	5330	5340	5590	
Recycled	Negligible	20	370	1480	2550	3140	3240	2960	
% of total MSW stream	0.4	4.5	8.2	10.5	12.5	13.2	13.1	13.2	
Landfilled & Waste-to- energy (WTE)	390	6670	13780	19950	24370	26030	26290	26820	

Table 2-2 Plastic materials present in the waste stream in the USA [57]

These small percentages of recycling indicate a grave loss of extracting potential resource value from the waste products. Most of the developed countries are not focusing on reprocessing the waste plastics; rather they have been focusing on clean collection of wastes to export them outside their own borders due to the cost involve in reprocessing. Both the overall recycling process and process of eliminating toxic fumes from the recycling plants are very complex processes because of the diverse plastic products invented using various chemical processes and additives **[55, 58-64]**. Nevertheless, with the advent of technology and increased

awareness, the average increase of annual plastic polymer recycling rate has been 0.7% over the period 1990 to 2014, which extrapolates to about 44 % wt. of waste plastic recycling rate by the year 2050 if this rate of increase continues **[13]**.

Plastic waste export and import business also controls the recycling industry's fate and related environmental effects. Though it does not reflect the waste management status of a country but developed countries like, Kuwait, Guyana, Germany, Netherlands, Ireland and the USA generate almost 10times of the daily plastic wastes per person than that by the countries like India, Tanzania, Mozambique and Bangladesh (Figure 2-3) [52, 65]. Waste plastics export-import trend has indicated that the highly developed countries with well-structured waste collection facilities have been exporting waste plastics to the low-income countries who are not capable of establishing a good waste management plan [49, 52]. Such waste import trend by the low-income countries can lead to the cumulative growth of discarded and mismanaged waste plastics in both landfills and oceans. In most cases, there is lack of awareness of what sort of waste plastics are just discarded anywhere, thus creating severe pollution.





China has been the prime importer of waste plastics since 1992. It accounted about 56 wt.% of the total global imports in 2012 **[49]**. As well, Hong Kong plays the role of one of the biggest exporters of waste plastics to the China as it imports waste plastics from various countries of the world and then reexport them to China **[13, 49, 52]**. At that the same time, European Union

(EU) exported almost 46 wt.% of the collected waste plastics (~87 wt.% of the total exported plastics) outside of their region (e.g. to China and Hong Kong) **[49]**.



Figure 2-4 Waste plastics export to China in the year 2016 [52, 66]

Figure 2-4 shows the import trend of waste plastics by China in the year 2016, which shows that among the total import of 7.13 million tonnes of waste plastics from around the world, the top 10 countries (Hong Kong, Japan, USA, Thailand, Germany, Belgium, Philippines, Australia, Indonesia, and Canada) export about 76.44% wt. of the waste plastics to China. Since China has been producing a lot of quality plastic products which are exported worldwide with increased demand since last few decades, it imports only high quality waste plastics from the other countries in addition to their domestic supply to avoid the higher production cost of virgin plastics. To avoid the inconvenience of recycling of diverse sources of waste plastics and the resulting environmental pollution risks, China has permanently ceased importing non-industrial plastics from 2017 **[52, 66]**. Brooks *et al.* **[66]** estimated that the Chinese import ban could divert from the waste stream up to 110 M tonnes by 2030 if the 100% ban is imposed. Alternatively, such shifts may encourage the waste exporting countries to develop their own recycling industry as well as encouraging the evolution of more effective technologies.

2.2 Categories of Plastics

Plastics are classified into two main categories, namely, thermoplastics and thermoset plastics. In this research, only few of the thermoplastic materials are studied to investigate and analyse the research objectives. The plastic polymers are extensively classified as

thermoplastics, thermosets, and elastomers (Figure 2-5) based on their inherent molecular structure and polymer formation methodologies **[67]**.



Figure 2-5 Classification of Plastic Polymers [67]

Thermoplastic polymers **[67-69]** are very responsive to the temperature and heat. They change their solid phase into liquid phase when enough heat is applied and turns into solids if cooled. These plastic polymers can be recycled by remelting and remoulding processes. Typically, these polymers are of high molecular weights and the chains are formed of weak van der Walls forces (e.g. PE, PP, PET, etc.), strong dipole-dipole interactions as well as hydrogen bonding (e.g. nylon). Table 2-3 shows few key physical characteristics and their applications of thermoplastics. The table shows that the HDPE, LDPE, and PP are used in rubbery state (soft/flexible state) as these plastics have glass transition temperatures below than room temperature. Plastics like PS, PET, PVC, and Nylon are used at temperature below the glass transition temperatures and are therefore glassy state materials.

Plastic Type	Density (g/cm ³)	Crystallinity	Glass Transition Temperature (°C)	Crystal Melting Temperature (°C)	Applications (Typical)
HDPE	0.95-0.97	High	-120	137	Milk bottles, Insulation for cables, Toys, etc.
LDPE	0.92-0.93	Moderate	-120	110	Agro mulching, Shopping bags, Packaging films, etc.
PP	0.90-0.91	High	-20	176	Food storage containers, carpet, chemical tanks, Toys, Furnitures, automotive body parts, etc.
PS	1.0-1.1	Nil	100	210-249	Foamed food containers, Packing materials, etc.
PET	1.3-1.4	Moderate	69	265	Engine covers, Glass replacement, Transparent components, etc.

Table 2-3 Physical Properties of Various Thermoplastics [70-72]

PVC	1.3-1.6	Nil	85	100 - 260	Piping material, Frames, Conduits, etc.
Nylon 6	1.1-1.2	Moderate	50	210-220	Gears, Bearing, Pulleys, fibres, etc.

The thermoset plastic **[67-69]** polymers are formed due to chemical decomposition on applied heat. Hence, these cannot be remoulded or melted for recycling purposes. These plastics are stronger than thermoplastics and can sustain substantially high heat. Mostly, these plastic polymers are formed by cross linking of molecules at certain temperature and pressure to produce desired thermoset plastic. So, these are hard and brittle by nature. Typical thermosetting polymers are Phenolics (1.27 g.cm⁻³), Amines (1.50 g.cm⁻³), Polyesters (1.28 g.cm⁻³), Epoxies (1.25 g.cm⁻³), Urethanes (1.30 g.cm⁻³) and Silicones (1.55 g.cm⁻³) **[67-69]**.

2.3 Energy Content of Thermoplastics

Energy content, as measured by, lower heating value (LHV), of various thermoplastic materials is shown in Table 2-4. The comparative energy values of some other renowned fuels are shown in the Table 2-5. Based on the observations, it is obvious that the conversion of waste plastics into any form of energy resources can be regarded as beneficial to the energy consumers, consequently, helping to meet the ever-growing energy demand in the world.

Table 2-4 Energy content / lower heating values (LHV) of various plastic materials [56]

Plastic material	Polyethylene Terephthalate (PET)	High Density Polyethylene (HDPE)	Polyvinyl Chloride (PVC)	Low Density Polyethylene (LDPE & LLDP)	Polypropylene (PP)	Polystyrene (PS)
LHV (MJ/kg)	23.9	44.3	19.2	44.3	44.3	41.5

Table 2-5 Energy content / lower heating values (LHV) of various fuels [56]

Fuel type	Natural Gas	Crude Oil	Non-recycled plastics (avg.)	Petroleum coke	US coal-1	US coal-2	Wood
LHV (MJ/kg)	47.3	42.9	35.7	29.6	26.1	22.8	14.0

2.4 The Plastic Identification Code (PIC)

The Society of Plastic Industries (SPI) has categorised the plastic materials in order to make the recycling process simpler **[73]**. There are many types of plastics produced around the world to serve the requirement of industries and consumers. If the recycling of the waste plastics is to be performed to obtain products of similar quality of the virgin plastics, both the collection and sorting of the waste plastics should be performed strictly. Any minor amount of different type of plastics can severely deteriorate the quality of the reprocessed plastics, thus putting the commercial investment into risk **[74]**. The SPI has introduced the codes according to the similarity of the properties of the plastics. Recently this code has been revised by the ASTM standardisation system. The recognised standard for plastic or resin identification code is ASTM D7611 / D7611M-13e1 **[75]**. Due to classification and standardisation worldwide reprocessing industries are able to recognise and categorise the required plastic materials so that the desired products can be built after the reprocessing. In Australia, the plastic identification code (PIC) has been revised by the Plastics and Chemicals Industries Association (PACIA) **[73, 74]** for commercial advantage in recycling and recovering the plastic wastes. Table 2-6 is the representation of the universally identified and coded plastics as recognised by the PACIA and SPI.

Plastic	Repeat Unit	Molecular weight of repeat unit, M (g/mol)	Density, ρ (gm.cm ⁻³)	Melting temp. T _m (^o C)	Glass transition temp. T _g (^o C)
PIC-1. Polyethylene Terephthalate (PET) $(C_{10}H_8O_4)_n$	- [0 - (CH ₂) ₂ - 0 - C C] -	192.2	1.36	212~265 semi- crystalline	66~80
PIC-2. HDPE High Density Polyethylene (HDPE) (C ₂ H ₄) _n	-(CH ₂ -CH ₂)-	28.05	0.96	130~137 semi- crystalline	-110
PIC-3. v Polyvinyl Chloride (PVC)- Unplasticized (UPVC) & Plasticized (PPVC)	-† СН ₂ — СН-] С1	62.50	1.4 (UPVC) 1.35 (PPVC)	175~212 amorphous	87
PIC-4. LDPE	Unit: LDPE chain structure	28.05	0.925	98~115 semi- crystalline	-90 ~ -25

Table 2-6 Various plastics as categorised by the ASTM D7611M-13e1 [68, 73-76]

Low Density Polyethylene (LDPE) (C ₂ H ₄) _n Linear Low- Density Polyethylene (LLDPE)	Снь снь снь снь снь снь снь снь с				
Â	-[CH ₂ -CH(CH ₃)]-	42.08	0.9 (average)	160~180	-25 ~ -20
PIC-5. PP Polypropylene (PP)			0.85 (Amorphous, at 25°C)	semi- crystalline	
-[CH ₂ -			0.95		
CH(CH ₃)] _n –			(Crystalline, at 25°C)		
A	- [CH ₂ - CH] -	104.1	1.06 (PS)	180~280	85~125
PIC-6. PS Polystyrene (PS) -[CH ₂ -			0.90-0.93 (EPS)	amorphous	
$CH(C_6H_5)]_n$					
Expanded Polystyrene (EPS)					
Other					
Includes all other resins and	-	-	-	-	-
multi-materials.					

Observing both Table 2-1 and Table 2-6, it could be found that the first 6 types of coded plastic materials are highly produced in the world and they are all classified as thermoplastics. The repeated units of the plastic polymers, molecular weight of the repeated units, density, melting as well as glass transition temperature are shown in the Table 2-6 [68]. All other types of plastics which are not identified by the PIC codes 1 to 6 are coded as "PIC-7 (Other)". Several of the thermoplastics which are identified as PIC-7 are, Liquid crystal polymer (LCP), Polyphenylene sulphide (PPS), Polysulfone (PSF), Polybutylene terephthalate (PBT), Polyurethanes (PUR), Denatured polyphenylene ether (PPE), Polycarbonate (PC), Polyacetal (POM), Polyamide (PAI), Methyl acrylic resin (PMMA), Acrylonitrile-Butadiene-Styrene copolymers resin (ABS), and Styrene acrylonitrile resin (AS/SAN). which have wide spread industrial applications in the modern world [70, 73].

2.5 Plastics as alternative sources of energy production

Though all the thermoplastic materials are classified and sorted with identification numbers, not all of these are easily recyclable. There are both economic and technical reasons are there, which pull back the complete recovery of all post-consumer plastics . Different plastics possess distinct properties and they are mixed with various chemicals to produce certain consumable products **[45, 69, 77-79]**. Plastic wastes come from various streams. The essential steps before processing the waste plastics in the recycling plants are collection, cleaning, sorting, and removing added chemicals from those plastics. These are very complex steps to produce high quality recycled virgin plastics from the available wastes. PET and HDPE are mainly easy to recycle polymers. However, the overall rate of recovery and recycling is lower than the wastes accumulated. These potential energy producing polymers are thrown out for dumping in the landfills or left as mismanaged wastes in the open environment in many countries.

The negative impacts of waste plastics could be reduced if we can identify the great potential of resource recovery by converting the waste plastics into a valuable resource.

The type of the targeted wastes can indicate the selection of conversion/recycling method of those collected wastes. Thermoplastics possess significant energy values (Table 2-4), thus provide enough argument to either recycle them into their original states or produce energy rather than wasting them into the dumping yards [80]. Besides, the average energy content of the thermosets varies between 10 MJ/kg and 20 MJ/kg which lead to the consideration of using these plastics for energy recovery options with the modern advent of thermal processing technologies [81, 82].

The other factors like the selection of less expensive and appropriate technology, consumer demand of alternative energies, and the effect on environment can greatly influence the effectiveness of the plastic to fuel production processes [80]. Since plastics are used to make various consumer level products, they contain various additives (i.e. Fillers, Pigments, Stabilisers, Antistatic Agents, Flame Retardants, Plasticisers, Reinforcements, and Catalysts, etc.) comprising of bromine or antimony-based compounds. They may contain nitrogen, halogens, sulphur or some of the hazardous substances, which could potentially pose threats to the human being as well to the environment [68, 69]. When the waste plastics are collected by the waste collection companies, the waste hierarchy presented in the following figure (Figure

2-6) is followed to process the wastes. With an organised waste recycling methodology, the target wastes for energy recovery process can be easily determined.



Figure 2-6 Waste hierarchy of waste plastics (Adopted from [83])

As per the UNEP report, polymers that contain carbon and hydrogen molecules (e.g. thermoplastics like PE, PP, PMMA and PS, etc.) only can be regarded as good feedstocks to produce liquefied fuel [80]. Fuels produced from these plastics also lead to cleaner exhaust emission that the refined petroleum diesel and petrol produced from crude oil, which is the most desirable features of alternative fuel production in this modern world. But Plastics containing nitrogen and sulphur (e.g. polyamide, polyurethane, polyphenylene sulphide, etc.) can generate increased amount of nitrogen oxides and sulphur oxides, which are unwelcomed due to stringent emission standards [84]. Halogenated molecule containing polymers (e.g. PVC, flame retardant type polymers made of bromine and fluorocarbons, etc.) can be highly corrosive to the fuel process plant as well as the fuel flow system in the vehicles, as well. Recently, in various thermochemical processes, these feedstocks are used to produce fuel by adding few chemical additives to remove the halogen molecules from the final product [85, **86**]. Contrarily, various thermosetting plastics which does not contain any hydrocarbon (e.g. Polyvinyl alcohol (PVA), Polyoxymethylene (POM), etc.) are not suitable for fuel production as they may form water, alcohol or aldehyde compounds during their thermal conversion [80, 87]. PET can form terephthalic acid and benzoic acid; Acrylonitrile-Butadiene-Styrene copolymers (ABS) may release nitrogen and cyanide-based compounds in the fuel [87].

Thus, the PE, PP and PS based thermoplastics are most preferable and PVC and PET are moderately preferable as feedstocks to produce liquid hydrocarbon fuels. Also, liquid fuel production from the waste thermoplastics with the help of various processes has shown better efficiency than production of liquid fuels from thermoset waste plastics **[88-93]**. But those can be used as solid fuels in stationary controlled incinerators to obtain energy as an effective means of waste recycling.



2.6 Thermo-chemical Conversion Processes of Waste Plastics to Energy Production

Figure 2-7 Schematic representation of various thermo-chemical conversion processes and their products **[94, 95]**

Various methods are currently under exploration to produce petrochemicals from plastic wastes. Pyrolysis, hydrogenation, gasification, catalytic degradation, thermo-catalytic conversion processes are being considered extensively to adopt in the industrial establishment **[96]**. In general, when the plastics are used as feedstocks in the non-catalytic processes, these are known as thermolysis process **[97]**. Chemical recycling along with controlled thermal processing has been considered as a method of producing various hydro- carbon fractions from plastic solid wastes (PSW) for few decades **[98]**. Depolymerisation occurs in these processes and the desired conversion rate is very high **[97]**. These processes are known as thermo-chemical recycling processes of plastic wastes, which convert the plastics into desired gaseous or liquid or mixed of liquid and gaseous petrochemical products. Later these yields are treated further to produce liquefied fuels or monomers to produce new plastics. Such thermo-chemical processes are now commercially in operation in several countries for the purpose of effective

solid and non-degradable plastic wastes. Figure 2-7 is a brief schematic representation of the various thermo-chemical conversion processes by which the plastic wastes can be treated to produce respective products.

2.6.1 Gasification

Gasification process of PSW occur at higher than 800 $^{\circ}$ C and practically at 1000 $^{\circ}$ C in a lean air (20%-40% air) or oxygen-deficient reactor [99]. The reactors are mostly moving-bed, fluidized-bed, and entrain-bed types. The final product yields of a gasification process are mainly combustible gas mixture (producer gas or syngas) and solid residue as char [100]. Figure 2-7 shows the pathway of using this syngas as feedstock for energy production. Components of gasification of 100% waste plastic yields more gaseous products but in different compositions like increase of methane, light hydrocarbon and CO; but H₂ and CO₂ production diminished up to 10 vol% [101]. The syngas can be converted into diesel fuel by either the Fischer-Tropsch (FT) reaction or by methanol to gasoline (MTG) process for transport application [102, 103]. In MTG process, the syngas is first converted into methanol and then the methanol is processed to produce gasoline liquids [104].

Gasification process is also considered as an alternative and cleaner process to the incineration process **[99, 105]**. Controlled amount of oxygen in the gasification process does not allow the formation of toxic compounds like dioxins, furans and other hazardous aromatics which are formed in the later process **[99, 105]**. The gasification process yields syngas that can be cleaned up as well. The utmost disfavouring fact of this process is production of tar, metals, halogens, and alkaline compounds along with the syngas product. If this mixture is used as fuel it will lead to formation of pollutants that can harm lives. Further treatments are performed to reduce this problem by either syngas treatment (primary method) inside the gasification reactor or removing hot gas from the downstream of the gasifier (secondary method) **[100]**.

Prolonged residence time for the gas products and temperature beyond 500 °C also increase the gas yield from the gasification process reaction of plastic wastes [106]. Mainly the syngas is used as fuel in boilers and gas engines/turbines, but can be further processed to produce liquified fuels like gasoline (Figure 2-7) [94, 95, 107]. A secondary reactor (catalytic reactor) has been used to catalytically crack the produced tar after the gasification in presence of calcined dolomite (at 800–900 °C) to purify the producer gas [108-110].

Hirn [111] presented a report on a large scale pilot plant of waste plastic gasification (shaft kiln) process, where CaO works as a very efficient catalyst. CaO trapped the halogens from PVC wastes, cleaned the flue gas emissions and reduced the quantity of the tar production, thus ensures a total plant efficiency of about 80%. On the other hand, high impact polystyrene (HiPS, produced by adding polybutadiene rubber to polystyrene) was fed into a gasifier containing supercritical water as oxidant/gasification agent (known as supercritical water gasification process) by Bai et al. [112] and operating parameters were optimised. The optimisation of process operating conditions (i.e. supercritical water, 800 °C, 60min, 23 MPa, and 3 wt.% of feed rate, etc.) yielded about 94.48 wt.% of conversion efficiency of syngas from the system [112]. Onwudli and Williams [113] conducted supercritical water gasification of plastics (LDPE, HDPE, PP and PS) at a lower temperature (450 °C) than the process followed by Bai et al. [112] in presence of RuO₂/γ-Al₂O₃ catalyst (20 wt.%) [114]. The process showed very high level of gas production efficiency. Thus, supercritical water gasification process encourages thermal processing of waste plastics to obtain petroleum resources for energy production at a very high efficiency. However, co-gasification of coal (60 wt.%), wood (pine, 20 wt.%) and plastic (PE, 20 wt.%) wastes also reduce the amount of tar and char and increases the H₂ gas yield from the process within temperature profile of 750-890 °C [106]. Use of steam instead of lean air also made this process successful by reducing further dilution of the gaseous products. Straka and Bičáková [115] has investigated co-gasification of mixed waste plastics (LDPE, LLDPE, HDPE, PP, and PS) and lignite at 1200 °C. Reduction in conversion of polycyclic aromatic hydrocarbons (PAHs) and soot from tar was observed due to this high temperature operation. As a result, hydrogen rich gaseous products increased. Baloch et al. [116] conducted co-gasification of ternary blend prepared from rice straw (RS, 20%), PE (40%), and PVC (40%), which yielded hydrogen and methane enriched syngas of about 48.7 mmol/g of fed materials in a fixed bed reactor at 900 °C. The other two syngas compounds were CO and CO₂ as well. This experimental investigation showed that higher temperature has positive influence on syngas production but steam to biomass ratio has less effect on yield quantity. But this experiment did adopt any entrapment process of halogen molecules present in the PVC waste.

Brems *et al.* **[117]** conducted gasification reaction of PSW samples (mixture of PET, PE, PP and PS) in a bubbling fluidised bed reactor by injecting steam ($110 \,{}^{\rm O}$ C, 5 bar) at temperature profile of 550 ${}^{\rm O}$ C to 800 ${}^{\rm O}$ C. The researchers also considered the gasification process as a first

order reaction process. The following table (Table 2-7) summarises the results of their experimental analysis.

PSW	T (K)	A (s ⁻¹)	Ea (kJ/mol)
PE	1008	5.12×10^{15}	289
PP	1018	1.99×10 ¹³	187
PET	968	2.94×10^{16}	238
PS	953	2.94×10^{14}	212

 Table 2-7 Reaction temperature, activation energy and pre-exponential factor of PSW gasification process (Collected from [117])

Though gasification is a high temperature process, optimisation of various operating parameters will surely pave an efficient pathway to convert the waste plastics into usable energy resources. The development of supercritical water gasification has a potential in terms of efficient output and desired end products. If the wastes are considered as a raw material for both energy production as well as ingredient to be removed from environment seriously, the investment cost will be a great trade off.

2.6.2 Pyrolysis

Pyrolysis process is a type of thermochemical recycling technique, which can convert waste plastics into three main products – bio-oil, bio char, and syngas **[118]**. Also, the reaction process mainly occurs in absence of oxygen ensuring no combustion occurs inside the pyrolysis reactors. The primary product of the pyrolysis process is mix of gas and residual by-products. This mixture is then sent to the cyclone chamber to obtain cleaned gas mixture, which are quenched to derive the bio-oil as liquid product. A fraction of the gas mixture is sent back to the combustor of the pyrolytic reactor. The by-products are removed through the bottom of the cyclone chamber as tar, char and ash contents **[97]**.

The bio-oil derived from condensation of pyrolytic gases possesses almost the similar properties of the solid feedstocks. It has vulnerable stability for long-term storage **[119, 120]** as it is intricately mixed with oxygenated compounds **[121]**. Such hydrocarbon oil is also immiscible with the conventional hydrocarbon petroleum fuels **[94]**. This bio-oil can be further processed to obtain polymer derived gasoline, diesel as crude oils are refined in the refineries. The carbon chain distribution of bio-oil can widely vary due to temperature inside the reactor

as well as the resident time **[118]**. For instance, petroleum fuel like liquid and gases are produced from both PE and PP at higher temperature pyrolysis operation; but the same plastics yield waxes, paraffin, olefins and vaseline type products due to low temperature pyrolysis process **[118]**. Besides, the lower temperature increasing rate (about 6 ⁰C/min) in the pyrolysis process influences the higher production rate of liquid portions **[122]**. For instance, 6 ^oC/min of temperature increase rate of LDPE, PP and PET can produce liquid products up to 80.41 wt.%, 82.12 wt.%, and 38.89 wt.% of liquid products respectively for the operating temperature profile between 300-500 ^oC **[122]**. Miandad *et al.* **[123]** also mentioned that the diesel like liquid yields can be obtained (about 80 wt.%) from waste plastics if the temperature and other operating parameters are controlled optimally. A recent publication by Tulashie *et al.* **[124]** also observed pyrolysis reaction (350 ^oC, 160 minutes) of mixed waste plastics of pp, HDPE and LDPE, which yielded major portion of liquid content within the diesel fuel range.

Types of the fed plastic polymers, feeding conditions, rate of heating, residence timing, type of reactors used and gas condensation process, etc. effectively governs the performance criteria of a pyrolysis process. Polymers of both biomass and tyre have undergone through pyrolysis process for a long time, but that of waste plastics to obtain fuel like compounds is still evolving. Al-Salem *et al.* [125] and Sharuddin *et al.* [126] have reviewed various published results on thermal cracking of waste plastics based on the type of plastic feedstock, reactors, temperature profile, conversion efficiency and corresponding final products. Few of the key information obtained from the reviews are:

Not all gases produced from the pyrolysis process can be converted to useful liquid fuel through condensation, rather the non-converted gas is used as fuel for heating purposes to the reactor. Besides, the composition of yield gas and liquids are mostly influenced by the type of plastics used. Most of the fast pyrolysis processes are performed at a heating rate of 10 $^{\circ}$ C/min.

Fast pyrolysis of PS usually yields higher amount of aromatic type liquids (e.g. styrene, ethylbenzene, benzene, toluene), a little amount of aromatic gas and no char if operated at not more than 500 ^OC. Operating beyond that temperature may generate some char thus reducing the liquid yield quantity.

PET, being a multi-purpose raw material, may turn into an expensive item to sort and clean for the recycling process. Fast pyrolysis of PET may always produce more liquid yield than those of non-liquified gas contents. Also, about half of the liquid content is benzoic acid, which is corrosive, and may cause clogging to the fuel transmission line. Furthermore, ethane gas is the major constituent of the gaseous contents.

HDPE pyrolysis process temperature may vary with the reactor type while observing the optimal liquid yield. Semi batch reactor has demonstrated higher yield of liquid oil (80-90 wt.%, 440-460 °C, [127]) than that of the batch reactors (80.88 wt.% at 350 °C [128]; 88 wt.% at 515 °C [129]). HDPE also shows a very high-quality fuel yield with further treatment. On the other hand, LDPE can yield up to 95 wt.% of liquid from non-catalytic pyrolysis process in the fixed bed reactor [130, 131]. Due to diverse applications, various additives are used with HDPE and LDPE plastics. These additives also can affect the yield efficiency of the process.

In general, a wide temperature profile between 250 °C and 400 °C in a batch reactor (micro steel) can yield about 70 wt.% of liquid fuel from PP plastic pyrolysis process **[128]**. But, Thahir *et al.* **[89]** conducted pyrolysis reaction (fixed bed, 500-650 °C) of PP plastic, which yielded optimal 88 wt.% of liquid fuel at 580 °C. Though increasing temperature beyond this optimal condition increases the total conversion efficiency, the liquid yield reduced beyond this temperature. Being high energy content polymer, the PP waste plastics also need to explore to be used in fuel production.

PVC, being resistant to fire to some extent due to about 57% chlorine within the constituents, needs treatment to remove chlorine to avoid environment pollution during thermal conversion. Dechlorination process has been adopted by researchers to remove chlorine with help of some chlorine adsorbent (e.g. CaCO₃, NaOH) [**129**, **132**, **133**] at lower temperature (220–240 °C) considering first stage of the pyrolysis process. Then the heating rate and temperature are increased to produce hydrocarbon from the polymer in the second stage of the polymer process. No carbon is lost during dichlorination process. Due to dichlorination process, PVC losses most of its weight (about 57%). Hence, the hydrocarbon production efficiency of the total pyrolysis process is very low. Zhou *et al.* [**134**] used wire-mesh reactor to conduct pyrolysis of PVC which occurred within 200-500 °C. The optimal dechlorination occurred at around 400-450 °C, which about 88% of dechlorination and 12% converted into hydrocarbon out of overall ~66% conversion efficiency of the process. Due to mass loss of the PVC feedstock, the pyrolysis process of PVC is advised to be performed by mixing with other plastics as waste stream contains to make the overall process efficient enough [**132**].
2.6.3 Thermo-catalytic process

In the thermo-catalytic process (cracking–catalytic reforming / the two-step process) [135], plastics are fed into the reactor to be thermally cracked at medium temperatures and then go through the catalytic reforming. Therefore, the catalytic reforming accepts the residue liquefied bio-oil or quenched syngas converted into liquid. The ratio between catalyst and the polymer waste also controls the liquid fuel conversion efficiency of the process. Though several research outputs have shown that the increase of catalyst content increases the amount of desired fuel like liquid products, there is an optimal range. The conversion efficiency even decreases after the optimal range of catalyst to waste plastic ratio based on the type of catalysts, plastics, and reaction temperature [136]. Acidity of the catalysts governs the quantity of the desired liquid yield. Highly acidic active catalysts can lead to further cracking of the liquid hydrocarbon in the reaction chamber resulting into more gaseous products and coke [136]. Hence, in this process, the optimal amount of catalysts can be mixed well with the pyrolysis process yields in the second stage resulting into relatively higher quality of oil products.

Mainly hydrocarbons are the constituents of the liquid fuel products obtained from thermal cracking, which have boiling points in a varied range. Among the yield compounds such as gasoline and diesel oil are low in fractions. Also, the quality of these oils is poor. To raise the RON, the isomers, cycloparaffins as well as the aromatics should be improved via catalytic reforming. Catalysts are also added to accelerate the reaction rate during thermal cracking for quality purpose, though the products undergo catalytic reforming in later step. As a result, this methodology has been considered suitable to treat the mixed waste plastics. Also, the most beneficial part of this two-stage process is the recoverability of the catalysts used. Further runs may require fewer refills of catalysts in the reactor. All these benefits have led to develop this technology in a faster rate and acceptable to the industries for commercial purpose.

A further review on these processes can be obtained from the author's review article indicated below:

"Hazrat, M.A., M.G. Rasul, M.M.K. Khan, A.K. Azad, and M.M.K. Bhuiya, *Utilization of Polymer Wastes as Transport Fuel Resources- a Recent Development*. Energy Procedia, 2014. **61**: p. 1681-1685.DOI: <u>http://dx.doi.org/10.1016/j.egypro.2014.12.191</u>."

2.6.4 Incineration of Plastic Wastes

Incineration of wastes has been considered as the highly effective method to reduce the volume of wastes by producing energy, thus contributing to reduction of non-biodegradable wastes globally [137]. Apparently, there are about 1179 municipal solid waste incinerators (MSWI) plants around the world which are capable of burning about 700,000 Million Tonnes of wastes per day but still struggling to deal with the ever-increasing trend of waste stream [137]. China (268), Taiwan (24) EU(469), USA (80), Japan (234), South Korea (39) are the countries mostly utilising the incinerators among which China produces the most pollutant emissions from the incinerators [138]. In most countries, energy production from incinerators is one of the traditionally adopted technologies. Recycling industries have been struggling with mixed plastics to economically recycle these from waste stream. That is why, energy production from mixed plastic waste stream could be worthy option [139]. So, there is a widespread concern about the methodologies regarding incineration process and the emissions related to it. Air pollutants like CO, CO₂, NO_x, SO_x, particulate matters (PM), volatile organic compounds (VOCs), and polycyclic aromatic hydrocarbons (PAHs) are found from the plastic waste incinerations [86, 140]. Almost 30% by weight of waste plastics are converted into CO₂ due to this process with a factor of 25 gm/MJ fuel to be compared with other fuels [141]. With the effective use of modern technologies, pollutant emissions can be controlled or totally isolated to enhance feasibility of the MSWI plants in order to produce energy, thus abating environment pollution through burning as well as through waste accumulation around the world.

Gradus *et al.* **[142]** investigated the economic effectiveness between recycling and incineration of Dutch waste plastic stream from households. These researchers have mentioned that still about 25% mixed waste plastics are sent to the energy production sectors and incineration process costs less than that of recycling costs. Though the incineration process converts the waste into energy for industrial uses in some extent, the conversion efficiency and the emitted pollutants are endangerment concerns. Plastic wastes are generally burnt for few seconds in high temperature (e.g. 2 s, 850 °C or higher) incinerators with an excess air ratio between 1.0 and 1.8 **[86, 143]**. The ash by-products of incineration process are generally landfilled and are of risk based concerns due their carcinogenic threat **[144]**. Enforcement of new legislations, increased expense, social as well as ecological awareness, stringent strategies

of environment protection, etc. are the restricting factors to the disposals of both organic as well as plastic wastes in the landfills and incinerators **[145]**.

2.7 Landfilling of Plastic Wastes

Waste plastics are not biodegradable; they remain for long period into the landfill. The lack of landfill sites and assessments of the environmental consequences of landfilling have led many countries to ban landfilling of combustible wastes, including wet organic waste [146, 147]. Geyer *et al.* [13] have mentioned that about 79% of the total accumulated plastic wastes between 1950 and 2015 have been discarded as land-filled wastes. Complete degradation of plastic may require more than 4000 years if land filled. So, the amount of plastic wastes is just increasing cumulatively.

Landfilling of plastic wastes causes pollution by emitting toxic gases like furanes and dioxins to the environment which are carcinogenic. Various types of additives, i.e. fillers, plasticizers, colorants are used with virgin plastics to make them user friendly, hygienic, durable, UV resistant and economic for the consumers. Hence, plastics can pollute the environment due to presence of various additives. Mostly Nonylphenols, Polybrominated diphenyl ethers (PBDEs), di-(2-ethylhexyl) phthalate (DEHP), and Bisphenol A (BPA), are mixed with the monomers of virgin plastics to act as catalyst in producing polymers and thus enhance other desired properties. Some of these used chemicals are found responsible as hormone-disrupters [148]. Bisphenol A, which is extensively used with the epoxy resins of food and beverage containers and as monomer in the polycarbonate plastic of many consumer products, is alarmingly related to cardiac diseases, diabetes as well as abnormal increase of certain liver enzymes [149]. PBDEs may be responsible for lowering the immune system, thyroid disruptions, and troubles in fertility issues of human being. So, when plastics are used or discarded, the emissions based on these additives are undesirable from an environmental point of view [140]. The American Chemistry Council (ACC) reported that if all of the landfilled municipal solid wastes in USA could be diverted into waste to energy production processes it could reduce the coal consumption by 108 million tons. This is equivalent to the production of 162 million MWh of electricity for 16.2 Million households for one year [144]. Even the biodegradable plastics are liable for methane-based greenhouse gas emission to the environment. Leachate forming is also another threat that can pollute the ground water being soaked by the soil.

An economically feasible recycling thus revenue sourcing strategies have been under investigation to reclaim these land-filled plastic wastes, which are termed as landfill-recovered plastics (LRP) **[150]**. With such strategies, already left land-fill sites are treated as mines (i.e., landfill mining) to pull out the non-biodegradable polymers, mainly plastics, which can be used as energy producing sources by making the best use of currently available evolutionary waste-to-energy production technologies **[151, 152]**. Most of the waste plastics collected from landfill mines obviously contain impurities. Soil-type, ashes, sands, cellulosic wastes, etc. along with various chemicals are the common contaminants of waste plastics, which only paves the energy production **[152-155]**. As a result, tertiary recycling of the waste recycling can be established as one of the economical sources of waste valorisation **[153]**. Besides, the metals obtained from these waste mines can be treated as another source of metal extraction as well as recovery **[153]**.

2.8 Chemical Treatment of Waste Plastics as Tertiary Recycling Process

Chemical recycling processes of waste plastics can be one of the efficient precursors for sustainable development, though such process can be expensive in small scale operating plants [156, 157]. The impact of landfilled or left alone plastic wastes can turn into microplastic hazards, that can be more expensive by harming human health conditions than the investment costs avoided for efficient waste management purposes [158]. Based on the type of solvents and adopted techniques, chemical dissolution process of waste plastics can be effective for both recycling as well as energy production purposes. If the waste plastic polymers can be easily converted into liquid, it will be easy to transport and handle rather than handling a bulk quantity. This process requires the waste plastics to be cleaned before being treated. Indeed, dissolution process of waste plastic polymers into appropriate solvents can be considered as one of the types of chemical or ternary recycling processes [159-161]. Several researchers [79, 162-166] have used benzene, toluene, xylene and trichloroethylene as solvent for polyolefin recovering and recycling successfully. Wong et al. [162] pointed out that, is spite of benzene being an effective solvent for olefins it is not suitable for its threat of toxicity in the environment. The solubility of the olefins was characterised based on their film surface area per unit molar mass. This has been also explained by Zhang et al. [21] through detail solubility analysis and determination of solubility parameters of both PS and LDPE into biodiesel and their fatty acid methyl esters individually.

Use of appropriate co-solvent can reduce the dissolution temperature and increase the rate of dissolution in the solvent mixture **[163]**. Determination of optimal ratio of the solvent and co-solvent for optimal dissolution is of the solute plastics is necessary to reduce the energy consumption of the process. Otherwise, the target of reducing the reaction temperature will lead to loss of solute particles in the process. Also, an optimal ratio between solvent and co-solvent may only benefit one type of plastic. This idea has engendered the application of selective dissolution process in polymer recovery and recycles process.

According to selective dissolution process demonstrated by Nauman and Lynch [79, 165], individual liquefied plastic polymers can be separated based on their melting points from mixed plastics. This distillation process is equivalent to the fractionating distillation process in the chemical industries. The plastics are cleaned, chopped, shredded, and dried after collection to avoid excessive solvent loss. Then the unsorted mixed plastics are dissolved into a common solvent under a wide range of temperature so that individual plastics could be melted at their distinct melting temperatures. Later, the liquid polymers can be separated by fractionating distillation process to be reused as raw material in the plastic manufacturing industries. The contaminants of unsorted waste plastics of all coded plastics could be drained later from the distillation column. The researchers could recycle the PS, LDPE, LLDPE, HDPE, PP, and PVC polymers by using Xylene at 15 °C, 75 °C, 85 °C, 105 °C, 118 °C, and 138 °C respectively at 1 atm. pressure. After that, the PET was brought out as undissolved which was purified by the tetrahydrofuran (THF) solvent at 190 °C at 17 atm. pressure. As per the dissolution kinematics, the temperature and the working pressure have effect on vapour-liquid characteristics of pure solvent irrespective of the polymers used in the dissolution process. Moreover, the percentage of polymers to be dissolved was limited between 5% and 20% by weight. This technic is economically compatible, too against the virgin plastics prepared from hydrocarbons [17] and it can encourage more establishment of recycling processes.

Moreover, the selective dissolution process can be made economic with the help of sinkfloat principle by sorting the mixture of plastics in cleaning stage based on their density [167, 168]. The density ranges of the olefins (PP, LDPE, HDPE) and non-olefins (PS, EPS, PVC, PET) are mentioned in the Table 2-6. Later the sorted mixtures can be sent to selected solvent based dissolution process achieving higher process efficiency. Since mixture of a little amount (ppm scale) of PVC with the PET can ruin the quality of PET, these can be also sorted by the commercially benefitted micro-sorting technic [78]. Mixed solvent-based polymer waste dissolution process has also demonstrated better polymer recovery from the waste stream with the help of sequential distillation/extraction process. Weeden *et al.* **[159, 169]** recovered (>95%) pure polycarbonate(PC) from electronic waste plastics made of combination of the acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polystyrene (PS), and styrene acrylonitrile (SAN) polymers in addition to resorcinol-bis-diphenyl phosphate (RDP) bisphenol-A-bis-diphenylphosphate (BPADP) additives with sequential extraction process by using dichloromethane (DCM) and acetone.

However, the prospect of dissolving waste plastics into bio-solvent (e.g. biodiesels/vegetable oils from edible and non-edible feedstocks) opens up prospective opportunities of waste plastic disposal processes [20, 21, 170]. Thus, the polymer-biodiesel solutions can be used as clean alternative fuel in the internal combustion engines. At least, few of the major thermoplastic polymer wastes can be easily dissolved well into a B100 biodiesel due to their good solvent behaviour [171]. Because of the attraction between polymers and biodiesels, this can influence the loosening or dissolving of varnish/paints. The biodiesel and vegetable oil contents can leave some sediment in the fuel tanks used for storing purpose. For such characteristics, fatty acid methyl esters have been used as low-VOC (volatile organic compound) cleaners as well as solvents for last few decades. As the B100 comprises of methyl esters that meet ASTM D6751 standard, it may dissolve the accrued sediments in the diesel storage and in the engine fuel tanks [172].

Industrial expansion of using biodiesel as solvent for the solvolysis process of the waste plastics can demonstrate several benefits, namely, waste reduction, investment cost reduction on infrastructure development for plastic recycling and increase of clean alternative fuel production [173-176]. Arjanggi and Kansedo [177] stated that the use of biodiesel as solvent could turn the chemical recycling process into a cost-effective one. When plastics are dissolved into biodiesel solvent, these non-biodegradable resources can enhance fuel properties and easily convert the wastes into purified virgin materials [177], as can be schematically presented as in the Figure 2-8. When biodiesel-PS solutions are used by blending with diesel fuel, it can overcome several of the shortcomings that occur due to diesel-biodiesel fuel blends, namely, reduction of NOx emission and increase in thermal efficiency [178, 179].



Figure 2-8 Dual benefit of liquefaction of waste plastics into biodiesel solvents (modified from [177])

Several researchers [20, 172, 180, 181] have reported about the dissolution behaviour of low density polyethylene, polystyrene, expanded polystyrene, etc. in soy bean derived, waste cooking oil derived and rape seed derived biodiesels. They observed promising solubility behaviour of the plastic polymers into the biodiesel, which improved the fuel quality by reducing the engine's emission products except NOx. Also, brake thermal efficiency increases with the slight decrease of brake power at full load with reduction of brake specific fuel consumption rate significantly [20].

Mohammadi *et al.* [181] investigated the EPS solubility in the waste cooking oil derived biodiesel in presence of a homogenized co-solvent, acetone (5 wt. % of used biodiesel). The EPS sample quantities were 2.5, 5.0 and 7.5 gm respectively in 100 ml of biodiesel solvent at 60 °C. The reaction times were set at 40, 50, 60 min, respectively for these three solute EPS samples for a complete dissolution. The researchers prepared 5% blend of EPS-Biodiesel to diesel fuel (EPS-Biodiesel-Diesel blend) to observe the engine performances. At highest speed, increased EPS quantity-based biodiesel blend reduced the CO, CO₂, NOx, and smoke emission. Also, the fuel blend increased the brake thermal efficiency by 7.8% with increased specific fuel consumption (SFC) (7.2%) and reduction of brake power (BP) (3.2%). Reduction of brake power could be overlooked as it is minimal in comparison to the increased thermal efficiency.

Increased SFC was predictable due to the lower heating value discrepancy between plastic and diesel fuel. But, Kuzhiyil and Kong **[20]** observed that the biodiesel with PS (up to 10 wt.% dissolved into the biodiesel) dissolved, can lead to increased NOx in the emission. Though the other emission parameters reduced up to 10 % wt. PS dissolved biodiesel, they start increasing with the increase of PS concentration beyond that quantity.

2.9 Summary

The research on producing transport grade fuels from waste plastics (as they possess substantial calorific value) has been going on for few decades. Results are promising and several processes are under investigation to convert waste plastics into fuel like product efficiently.

Gasification process can handle mixed plastics and produces more gaseous products. Those gases can be used for gas engines as fuel. Instead, the gas can be hydroprocessed to produce fuel like liquid products. Due to higher temperature and pressure concern, this process may not be economical for every nation. But this process is a better option than the incinerators. The syngas is the yield of the gasifier, which is clean and non-toxic. Contrarily, the incinerator burns the feedstock, for which the energy demanding instrument needs to take safety measures to save the components from corrosion. The combustion gases are impure and impose threat on human health as well as to the environment. The produced ash from gasifier is unlike that of incinerator. Therefore, the ash from incinerators is sent to the landfills. And the ash from the gasification process undergoes molten stage due to high temperature, which can be used in the cement industries, asphalt filler and for sandblasting.

Pyrolysis (thermal cracking) process of waste plastics alone has been facing few obstacles to produce fuels according to the fuel standards. Thermal liquefaction in presence of hydrogen gas pressure system can produce more liquefied hydrocarbons than the nitrogen based thermal cracking system.

The catalytic cracking followed by the thermal liquefaction can facilitate the effective conversion of those waste plastics. Only catalytic process faces the obstacles with mixed and uncleaned plastics. That causes production of more residual solids. But if the waste plastics are liquefied in presence of hydrogen and then the catalysts are introduced in the yield of this process, the combined process provides better process efficiency. Also, the consumption of

catalysts is optimized with this mixed mechanism. Moreover, the problem with the mixed plastics is resolved in this thermo-catalytic process.

Thermo-catalytic process can reduce the process temperature of the thermal cracking process alone. The liquefied and the gaseous hydrocarbons from the liquefaction process can be easily mixed with the catalysts. Therefore, the less catalyst consumption reduces the process expenditure. Besides, the problem with the PVC, PS type plastics can be resolved in the thermo-catalytic process with an optimal solution of NaOH, NaHCO₃, and AgNO₃. As a result, most of the unprocessed waste plastics can be fed into the thermal liquefaction chamber for fuel production purpose.

These processes are very big in size and due to investment issues, most of the countries are not adopting it in large scale to show any effective improvement in the plastic recycling process. Though the incineration can reduce the volume of the plastic and provide energy, the process is very harmful to the environment. On the other hand, landfilling is not encouraging due to non-degradable nature of the plastics and pollution continuity. Dumping and putting them under the earth is not the good solution as that can pollute the underground ecology and water by leaching.

So, it is highly recommended from this literature review to consider some other options of converting waste plastics into usable products. In such situation, the dissolution of waste plastics into some hydrocarbon category solvents may encourage recycling industry to work along with the energy sectors. Chemically treated waste plastics are turned into cleaner hydrocarbon-based petroleum without wasting much energy in comparison to the available thermal conversion processes.

For this study, the chemical recycling process is investigated through theoretical and experimental analyses of plastic dissolution into biodiesel solvents. In addition, feasibility, and effectiveness of use of biodiesel-diesel-plastic fuel blends in diesel engine are investigated in terms of performance, emissions, and combustion characteristics.

Chapter 3

THEORETICAL CONSIDERATIONS OF SOLUBILITY OF PLASTIC DISSOLUTION

3.0 Introduction

This chapter presents the analytical procedures to determine the solubility parameters of the polymers and solvents. Detailed mathematical expressions are presented to conduct the relevant calculations. Besides, the methodology of dissolving the polymers into the organic solvents is presented. Furthermore, mathematical presentation of determining the reaction rate of the dissolution process is also presented to interpret the reaction kinetics of dissolution of the polymers.

3.1 Dissolution of Polymers

There is an obvious difference between non-polymeric and polymeric materials while dissolving into a solvent. In case of non-polymeric materials, the resistance created by the external mass transfer through the liquid layer that is created adjacent to the solid-liquid interface and the process is very much instantaneous. On the contrary, the solvent diffusion in addition to chain disentanglement are involved while polymer solutes are dissolved into any solvent, as schematically presented in figure (Figure 3-1) [182-185]. As a result, the polymer dissolution process does not happen instantaneously and the time required can be designated as induction time for total diffusion of polymer into solvent by dissolution [186]. The solvent which dissolves the polymer solute must be thermodynamically compatible [187]. While the dissolution is occurring, the thermodynamic conditions remain constant [188]. Polymer structure variations, i.e. (i) Amorphous (e.g. PS, PVC, ABS), (ii) Crystalline (e.g. Nylon), and (iii) Semi-Crystalline (LDPE, HDPE, PP, PET); stiffness (i.e. glassy or rubbery state) and degree of crosslinking (i.e. linear or crosslinked) determine the steps required to complete the dissolution of polymer solutes into thermodynamically compatible solvent. The abovementioned polymer dissolution process is a transport phenomenon for amorphous (linear and glassy) polymer. However, in the case of semicrystalline polymers, the crystal chins are unfolded at the beginning and then follows solvent diffusion in addition to polymer chain disentanglement, as schematically presented in Figure 3-2 [189]. Detailed mathematical explanation of this transport phenomena and solvent-polymer diffusion mechanism can be obtained from the theses of Mallapragada **[190]** and Miller-Chou **[185]**. With all other governing parameters of dissolution process being constant, Mallapragada **[190]** has mentioned that, (i) the intensity of solvent penetration is reduced remarkably when the crystal unfolding rate is reduced by an order of one magnitude, (ii) the dissolution rate is increased by 50% if the polymer chain disentanglement rate is increased by a factor of 10 due to more participation of polymer-solvent interface into the dissolution process.



Figure 3-1 Schematic transport phenomena of solvent diffusion into polymer for dissolution (adapted from **[189]**)



Figure 3-2 Crystalline chain unfolding of semicrystalline polymers during dissolution (Redrawn from [190])

The dissolution mechanism of polymers is an intricate process based on various parameters. The most imperative parameters are molecular weight of the polymers, polydispersity, degree of crystallinity, polymer–solvent interactions, as well as temperature variation [191]. When the temperature is increased the rate of solubility of the polymers increases. But the solubility of the polymers decreases with the growing molecular weight number of the polymers.

3.1.1 Factors Affecting Polymer Solubility

There are some internal and external factors related to the solubility of solutes into solvents [192]. These factors are mentioned briefly based on the discussions from Senichev and Tereshatov [192]:

Chemical structure, molecular weight, size of the molecules as well as the degree of crosslinking of the polymer solute are the internal factors related to dissolution. However, temperature, pressure, free volumes are the external parameters. Both the solute and the solvent are noticeably recognised based on the external factors. The solvent effectiveness is mostly affected by variations of these factors.

The polymer solution in a chemically matching solvent ought to have unequal free volumes of components. It reasons significant thermodynamic consequences. Among the thermodynamic effects, phase separation is one of the key incidents, which is due to compatibility reduction between solute and solvent at higher temperatures.

The polarity properties based on chemical structure of the polymers regulate the solubility of the solute. When there is similar type of chemical bonds within the solvent and the polymer solute, the interaction energies of both homogeneous and heterogeneous molecules become almost equal. As a result, the polymer solution is facilitated by the chemical characteristics of polymers and solvents. On the other hand, the solubility does not happen if there is a huge difference of polarity between solute and solvent. This property reflects the empirical "like dissolves like" axiom. For instance, the polybutadiene (nonpolar polymer) is highly soluble in alkanes (e.g. hexane, octane) but insoluble with polar type solvent like water or alcohols. Also, PS does not dissolve in water and alkanes but easily dissolves in aromatic hydrocarbons and ethers.

On the other hand, when the molar mass of the polymer increases with the chain length to the result is an increase of interaction energy between the chains. There will be more energy demand in order to break these long chains. Solubility of long chain polymers is an energy intensive process as well. The same thing happens when the chains are very rigidly linked. So, the additional input of energy is required by the solvent to be strong enough to break such strong chain bonding. Nevertheless, addition of functional groups in the long chain increases the chain flexibility of the long chain molecules, which facilitate better solubility. Due to flexible chains, thermal energy easily influences the dissociation of chains from one another. Then the separated chains can easily penetrate through the solvent to be diffused by swelling and thus dissolution takes place.

Amorphous polymers dissolve in solvents more promptly than the crystalline polymers. Since the crystalline polymers are rigidly bonded, it requires more energy to allow chain dissociation. For instance, polyethylene (semi-crystalline polymer) swells up with the hexane solvent at room temperature but dissolves properly at higher temperature.

The presence of trace amount of crosslinking causes hinderance in chain dissociation of the polymers and deters diffusion of chains into the solvent. The density or quantity of crosslinking determines the swelling degree of the solute into solvent, thus can indicate the solubility compatibility between solvent and polymer. The temperature increase can also dissolve the crystalline polymers by improving the compatibility. For the combination of liquid solvent-amorphous solute or liquid–liquid system, increasing temperature can greatly enhance the solubility of the system. Also, it requires more energy if the polymer has higher melting point. Such demand for energy may categorise these polymers as less preferable for dissolution process at room temperature. For instance, PE and PVC are insoluble at room temperature but can readily dissolve at elevated temperature with compatible solvents.

3.1.2 Viscosity Effect on Dissolution of Polystyrene (PS)

Dissolution of polymers into a solvent causes increase of viscosity of the solution. This parameter sets the limit of quantity of PS in a solvent in case of using the solution as fuel for internal combustion engines. For instance, the solubility of polystyrene [PS, $(C_6H_5CHCH_2)_n$] can be presented as follows in which the viscosity variation with the temperature and PS quantity has been observed well in a patent publication [193]. According to this patent, the solubility of PS could be accelerated by heating the fatty acid methyl ester that is very slow at room temperature. Besides the pressure (atmospheric pressure) and stirring speeds for dissolution, the temperature profile (between 100 °C and 180 °C) could be varied based on

heating arrangements. During the observation of the dissolution of PS at an amount of 1-80% (w/w) of fatty acid methyl ester, the dissolution period was negligible beyond 150° C due to rapid solubilisation of PS into the solvent **[193]**. The viscosity change of the polystyrene-fatty acid ester (biodiesel) solution is presented in the Table 3-1.

Table 3-1 Change of viscosity of the polystyrene-biodiesel solution due to increased solubility of Polystyrene [193]

Wt.% Polystyrene	0	10	20	30	40	50	60	70	80
Viscosity (centipoise)	0.0664	1.15	3.45	16	40	100	150	260	390

While polystyrene quantity is increasing in the solution, viscosity increases exponentially [193]. Since the limiting value of viscosity of diesel and biodiesel fuels are lower than <5.5 Centipoise [194, 195], if the polymer-biodiesel solution is to be used in the diesel engines, the maximum allowable concentration of PS in biodiesel could be between 20% and 30% (w/w) of biodiesel quantity. The viscosity profile of PS-biodiesel solution has been found to be exponential. Calder *et al.* [178] conducted a dissolution experiment of expanded polystyrenes (EPS) in canola oil biodiesel at a rate of 50 g/L and observed that the viscosity of the EPS dissolved in 5%, 20% and 50% diesel-biodiesel blend fuels were 4.15, 5.36 and 7.55 cSt respectively. These researchers also observed little reduction of viscosity with increase in density of these solutions while adding acetone as stabilising agent. Some more researchers [20, 181] have also worked with such solution for the purpose of alternative fuel applications. This methodology is advantageous due to reuse and recycling opportunity of the polystyrene in its pure form, whereas disposal in a landfill is substantially eliminated.

3.2 Analysis of Solubility of Polymers

3.2.1 Solubility Behaviour

The solubility behaviour of a polymer depends mainly on the chemical structure of the polymer and on the interactions of solvent and polymer [196]. The solubility of a given polymer in each solvent is favoured if the solubility parameters of polymer and solvent are equal. The solubility parameter (δ) is an indicator to determine the usability of certain polymers in required technical applications [197]. Some empirical rules have been proposed to determine the solubility of polymers in solvents. Based on the behaviour of other solute-solvent system analysis, it is also likely to deduce certain solubility features of polymer-solvent systems.

The compatibility between two materials assures that the mixing molecules must coexist than the tendency of being separated. In this case, the forces of attraction between the molecules of solvent and the solute are brought into consideration. If material "A" possesses the intermolecular forces " F_{AA} " and that of "B" is " F_{BB} ", then the compatibility of the solution system will occur if F_{AB} > F_{BB} and F_{AB} > F_{AA} [**69, 198**]. If any of the forces F_{AA} and F_{BB} is greater than the intermolecular forces of the solution system (F_{AB}), it will turn into an incompatible system to make a solution. If both the forces, i.e. F_{AA} and F_{BB} are equal, the system will be considered a good solution. The average intermolecular forces between the solvent and solute are given by $F_{AB}=(F_{AA}F_{BB})^{1/2}$. The result will be separation of the system molecules, creating multiphase system. If there is deficiency of any specified interaction forces (e.g. hydrogen bonding forces) in the solution system produced by the solute and solvent, the geometric mean of the intermolecular forces should be assumed to define the compatibility of the solution system.

The chemical structure of the solute and solvent also determines the solubility relation as the similar chemical structure favours solubility [196, 199]. Besides, the higher the molecular weight of the solute the lesser its tendency to be dissolved well in a given solvent. The solubility characteristics of a polymer are also related to the cohesive energy density (CED) parameter (i.e. vaporisation energy of molecules per unit volume), free volume fraction and internal pressure [196, 200-205]. In addition, the change in molar enthalpy, molar volume of the number of repeat unit volume of the long chain polymers (i.e. solubility parameter-segment number relation of polymer fraction) are related to the solubility determination of solutes [200, 206-209]. Due to lack of authentic and direct method for determining the solubility parameters for the polymers, the relationship between intrinsic viscosity of the polymer and temperature can be used to alternatively determine the solubility parameters of the polymers [209]. Both the glass transition temperature (T_g), surface tension (γ) and heat capacity of solute are much related to the cohesive energy (E_{coh}) , which enhances the prominence of this thermophysical parameter [210]. The solubility parameter (δ) is the official term used to indicate the solubility of any substance [204]. A solvent is categorised as a good solvent for a particular solute if the intermolecular forces or the cohesive forces are of similar strength between the molecules of solute and solvent [206].

3.2.2 Determination of the Solubility Parameters

Direct determination of solubility parameters of the polymers is difficult due to unavailability of heat of vaporisation at dissolution temperature or boiling point for the polymers. The solubility parameter of the polymers is always defined as the square root of the cohesive energy density in the amorphous state at room temperature [211]. Cataldo [212] referred Hildebrand and Scott [213], Hansen [207] and van Krevelen [196] to determine the solubility parameter of desired molecules in an effective way to complement the experimental analyses.

The solubility parameter can be determined [213] by,

Here ΔH_{vap} = Evaporation enthalpy (J/kg)

RT= Thermal energy (J)

 V_m = Molar volume (cm³/mol) = (Molar mass (M)/ Molar density (ρ))

The unit of the solubility parameter is expressed in $(cal^{\frac{1}{2}}cm^{-3/2})$ or $(J^{1/2}m^{-3/2})$ or $(MPa)^{1/2}$.

Generally, 1 cal^{1/2} cm^{-3/2} = 2.046 (MPa)^{1/2}=2.046 (MJ/m³)^{1/2}

The Cohesion energy of the molecules at any temperature (T) can be expressed as,

$$E_{coh} = \left[\Delta H_{vap} - RT\right] \qquad \dots \qquad (Eq. 3.2)$$

Polymers start degrading prior to reaching their vaporisation temperature, for which reason determination of E_{coh} (J) by a direct method is impossible. Measurement methods for the enthalpy of evaporation can be found in "Handbook of Solvents" [214] and in the cited thesis [215]. Conveniently, the following empirical formula by Watson [216] can be used to determine the ΔH_{vap} at any given temperature if it is known for one other temperature [217].

$$\frac{\Delta H_{vap,T_2}}{\Delta H_{vap,T_1}} = \left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38}$$
(Eq. 3.2a)

Here, T_c is the critical temperature of the substance.

Also, another convenient empirical formula to determine ΔH_{vap} at 25 ^oC from the normal boiling point T_b for non-polar liquids **[214, 218]** can be used as follows (usually the normal boiling points for substances are available in various publications):

In case of polymers (e.g. amorphous high molecular weight polymers), the above equations (equation 3.2a or equation 3.2b) are not applicable directly, rather the atomic and group contribution methods described in a paper by Fedors [217] can be used to determine the enthalpy of vaporisation of the high molecular weight polymers. In this case, the ΔH_{vap} is replaced by the term $\sum_i \Delta h_i$ in the equation 3.1 as follows to determine the solubility parameter [217]:

$$\delta = \left[\frac{(\Sigma_i \Delta h_i - RT)}{V_m}\right]^{0.5} = \left(\frac{\Sigma_i \Delta h_i}{V_m} - \frac{RT}{V_m}\right)^{0.5} = \left(\frac{2\Delta h_{ie} + \Sigma_i \Delta h_{ir}}{V_m} - \frac{RT}{V_m}\right)^{0.5} = \left(\rho \frac{\Sigma_i \Delta h_{ir}}{M_r}\right)^{0.50}$$
.....(Eq. 3.2c)
Where, $\rho = \frac{M}{V_m} = \frac{2M_e + nM_r}{V_m}$ (Eq. 3.2d)

Here, Δh_{ir} and M_r are the atomic and group contribution to the heat of vaporisation and molecular weight of the polymer's repeating units respectively, M_e is the molecular weight of the end units of the polymers. Notably $\frac{2\Delta h_{ie}}{M} \rightarrow 0$ as M>>>2 Δh_{ie} , and $2M_e \rightarrow 0$ as 2Me<<M_r.

Therefore, the solubility parameter can be expressed in terms of cohesive energy as follows,

$$\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5} \tag{Eq. 3.3}$$

Here, (E_{coh}/V_m) is also known as the cohesive energy density (CED), (MJ/m^3) ,

i.e.
$$\delta = (CED)^{1/2}$$
 (Eq. 3.4)

The above formula does not consider the effect of polar forces in addition to the hydrogen bonding.

Fedors [217] presented that the solubility parameter δ for large molecular weight molecules at temperature T= 25 °C can be determined as follows from the equation 3.3:

Where the Δe_i and Δv_i are the additive atomic and group contribution for the energy of vaporisation and molar volume, respectively. Also, e_{ir} and v_{ir} are the repeating units of the additive atomic and group contribution to the energy of vaporisation and molar volume, respectively. These group contribution data are applicable at temperature of 25 °C. Increase of temperature also influences the solubility, thus the solubility parameter also gets affected.

3.2.2.1 Hansen Solubility Parameters

The total energy required for vaporisation of any liquid comprises several energy component, i.e. (i) dispersion (contribution from the non-polar bonding forces) (ii) polar forces and (ii) the hydrogen bond effect [211, 213, 219]. As a result, the Hildebrand solubility parameter (δ) can be expressed in a more explicit way known as Hansen solubility parameters as follows [220].

Where,

 δ_d is the energy due to dispersion forces between the molecules (atomic level, van der Waals) (Jm⁻³),

 δ_p is the energy due to dipolar intermolecular forces between the molecules (Jm^-3), and

 δ_h is the energy due to hydrogen bonding between the molecules (Jm⁻³).

These three parameters can also be treated as co-ordinates, i.e. the Hansen solubility parameter (HSP) components in the Hansen space to determine solubility for a solute in a solvent [207], as shown in the Figure 3-3. It has been reported that the Hansen solubility sphere should be scaled as a $(2\delta_d, \delta_p, \delta_h)$ coordinate system [207, 221, 222]. The centre of the threedimensional sphere in the Hansen space is the solubility component coordinate of the polymer solute (i.e. the centre's coordinate should be $(2\delta_{d,solute}, \delta_{p,solute}, \delta_{h,solute})$.



Figure 3-3 Coordinates of Hansen Solubility Parameters in Hansen Sphere (Adapted from [223, 224])

The solvents which can dissolve the solute are called the "good solvents" and these are located within the volume covered by a sphere of interaction radius (R_0) from the centre in Hansen space. The nearer the solute and solvent within that sphere, the better is the solubility of the solute in the solvent. The distance (R_a) between solute or polymer to be dissolved and the potential solvent can be determined from the following expression if the solubility parameter components are known already.

$$R_{a} = \left[4\left(\delta_{d,solute} - \delta_{d,solv}\right)^{2} + \left(\delta_{p,soute} - \delta_{p,solv}\right)^{2} + \left(\delta_{h,solute} - \delta_{h,solv}\right)^{2}\right]^{0.5}$$
.....(Eq. 3.6)

The interaction radius (R_0) and the distance between the two points within the Hansen space (R_a) can be related to define relative energy difference (RED) as follows:

$$RED = {\binom{R_a}{R_o}}$$
 (Eq. 3.6a)

It is obvious that a good solvent meeting criterion of $R_a < R_0$ will ensure complete miscibility of the polymer solute.

The cohesive energy, E_{coh} (unit, J/mol.) can is also calculated from three components,

$$E_{coh} = E_d + E_p + E_h$$
 (Eq. 3.7)

Where,

 E_d = contribution of dispersion forces (unit, J/mol.),

 E_p = contribution of polar forces (dipole-dipole permanent forces) (unit, J/mol.), and

 E_h = contribution of hydrogen bonding (unit, J/mol.).

Since molecules are built up from atoms, all molecules will contain non-polar type of attractive forces. In case of saturated aliphatic hydrocarbons, for instance, these non-polar atomic forces are essentially the only cohesive interactions, i.e. both the E_p and E_h are zero. Therefore, the energy of vaporisation is assumed to be the same as the dispersion cohesive energy, E_d [207].

So, the cohesive energy density (CED) can be related to the solubility parameters as follows:

$$\frac{E_{coh}}{V_m} = \frac{E_d}{V_m} + \frac{E_p}{V_m} + \frac{E_h}{V_m}$$
 (Eq. 3.7a)

i.e. using Eq.3.3 and Eq.3.7a, $\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$ (Eq. 3.8)

The total solubility parameter (δ_t) is related to the room temperature (25 ^OC), i.e. the molar volume is measured at room temperature **[196]**. It demonstrates the intensity of cohesive energy density rather than the individual type of the energies.

The Hansen solubility parameter (HSP) components have extensive applications and adaptations in various industrial fields (e.g. cleaning, paint, to determine the solubility or miscibility of the respective polymer compounds in target solvents [225]. Also, the chemical resistance of any product to another product can be determined. Some other fields include but not restricted are the pharmaceuticals industry, mineral oil analysis, packaging industry, cleaning, surface tension analysis, carbon nanotube, supercritical fluids, bitumen, and asphalt.

The Hansen solubility parameter components and the resultant total solubility parameters for the repeating units of the thermoplastics as per the HSP method are presented in Table 3-2.

Monomer	Solubility parameters (cal ^{1/2} cm ^{-3/2})				Solubility parameters (MPa) ^{1/2}			
	δ _d	δ _p	δ_h	δ_t	δ _d	δ _p	δ_h	δ_t
Ethylene	8.022	0	0	8.02	16.413	0.000	0.000	16.41
Propylene	7.665	0	0	7.67	15.683	0.000	0.000	15.68
Styrene	8.88	0.55	0	8.90	18.168	1.125	0.000	18.20
Vinyl Chloride	8.65	5.95	1.45	10.60	17.698	12.174	3.567	21.77
PET	8.84	2.40	4.83	10.36	18.09	4.90	9.89	21.19

Table 3-2 Solubility parameter components (HSP method) of several plastic polymer repeating units [198]

In case of the solubility parameters of biodiesels, the Table 3-3 is a list of available literature reports of Hansen solubility parameters (HSP) and the interaction radius of Hansen space. From Table 3-3, it can be seen that the castor biodiesel displayed higher values of the solubility parameter components (δ_d , δ_p , δ_h , $\delta_t = 16.1$, 6.72, 9.11 and 19.68 MPa^{1/2} respectively). Due to presence of hydroxyl group (i.e. Methyl Ricinoleate) in this biodiesel it can show the solubility with strongly hydrogen bonded molecules. Besides, the lubricity of the castor biodiesel increases due to presence of this hydroxyl group. Therefore, it may be deemed as one of the appropriate lubricant additives [**226**].

Biodiesels	δ_d (MPa) ^{1/2}	$\begin{array}{c} \delta_p \\ (MPa)^{1/2} \end{array}$	$\frac{\delta_h}{(MPa)^{1/2}}$	$\frac{\delta_t}{(MPa)^{1/2}}$	R _o (MPa) ^{1/2}
Soybean biodiesel [225]	15.03	3.69	8.92	17.86	11.33
Soybean Oil [212]	15.4	1.5	4.6	16.2	ND (not determined)
Soybean biodiesel (group contribution method) (section 3.2 and Table 4 of [225])	16.1	1.6	3.8	16.8	ND
Coconut oil biodiesel [225]	15.12	3.99	9.25	18.17	10.92
Palm oil biodiesel [225]	15.43	5.28	6.61	17.60	10.54
Castor oil biodiesel [225]	16.10	6.72	9.11	19.68	11.78
Castor Oil [212]	15.8	1.2	9.1	18.3	ND
Sunflower Oil [212]	16.0	1.5	4.6	16.2	ND
Peanut Oil [212]	15.3	1.5	4.6	16.1	ND
Linseed Oil [212]	15.7	1.5	4.7	16.4	ND
Brassica Oil [212]	16.2	1.5	4.4	16.9	ND

Table 3-3 HSPs and interaction radius of various biodiesels and vegetable oils

3.2.2.2 Group Contribution Method to Determine the Solubility Parameters 3.2.2.2.1 van Krevelen-Hoftyzer Methodology

Hoftyzer and van Krevelen [227] proposed a set of equations to calculate the components of the solubility parameter using the molar attraction constant and additivity rules, known as the group contribution methodology to determine the solubility parameters.

The molar attraction constant (ϕ) (unit: cal^{1/2}cm^{3/2}mol⁻¹) can be related with the cohesive energy as follows,

$$\varphi = (E_{coh}V_m)^{0.5}$$
 (Eq. 3.9)

The above correlation can be also related to the solubility parameters as follows,

$$\varphi = (E_{coh}V_m)^{0.5} = \left(\frac{E_{coh}}{V_m}\right)^{0.5} V_m = \delta V_m \quad \dots \quad (Eq. 3.10)$$

i.e. $\delta = \frac{\varphi}{V_m} \qquad \dots \quad (Eq. 3.11)$
 $=> \delta = \frac{\rho\varphi}{M} \qquad \dots \quad (Eq. 3.12)$

Hence, the group contribution methodology can be expressed as follows to determine the components of the solubility parameters **[196, 219]**.

$$\delta_d = \frac{\sum \varphi_d}{V_m} \qquad \dots \qquad (Eq. \ 3.12a)$$

$$\delta_p = \frac{\left(\sum \varphi_p^2\right)^{0.5}}{V_m} \qquad \dots \qquad (Eq. \ 3.12b)$$

$$\delta_h = \left[\frac{\sum E_h}{V_m}\right]^{0.5} \qquad \dots \qquad (Eq. \ 3.12c)$$

Notably, the energy due to hydrogen bonding (δ_h) cannot be determined from the molar attraction, rather it is measured by using additivity rules of the hydrogen bonding energy E_h [212, 219].

Therefore, the total solubility parameter can be calculated using these above set of values in the following equation,

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5}$$
 (Eq. 3.13)

Once the V_m [i.e. Molar volume = (Molar mass/ Molar density)] is determined from the analytical or experimental procedures, the solubility parameter components are obtained from the above equations. Also, the corresponding φ values for group increments are obtained from the tabulated data (Table A1-1 to Table A1-2) in the Appendix A1. Thus, the solubility parameter of a given material can be calculated either from the cohesive energy, or from the molar attraction constant.

Also, a similar methodology can be applied to the polymers at the temperature of solution to be produced [69]. Thus, in case of a polymer having amorphous density (ρ) at solution temperature, the sum of all molar attraction constants of all components in the repeating unit ($\Sigma \phi$), and the molar mass (M_r) of the repeating unit, the solubility parameter of that polymer can be expressed as follows according to Small [217, 228].

This group contribution type methodology can be utilised as one of the effective tools to select a potential good solvent **[229]**. It also reduces the waste of experimental time period when lot of solvents are to be analysed for a solute's solubility behaviour. This methodology helps reducing the anomalies in the data fit in Hansen space during the application of the Hansen methodology. The Hansen space provides a set of appropriate solvents for a solute **[230]**.

The polymers can be amorphous, glassy, or completely crystalline, for which their molar volumes are also varied with the variation of temperature differently. Van Krevelen [208] proposed the following equations to determine the molar volumes.

Crystalline polymer: $V_{m,c}(T) = V_w(1.30 + 0.451 \times 10^{-3}T)$ (Eq. 3.14c)

Here, T is the temperature, T_g is the glass transition temperature, and V_w is the van der Waals volume of the repeating units.

Appendix A1 shows molar attraction constants, contribution to cohesive energy and molar volume of group contribution, which are used to determine the solubility parameters in this study. Table A1-1 shows molar attraction constants and Table A1-2 shows contribution to the cohesive energy and molar volume of group contributions. The values in Table A1-2 differ from those Table A1-3 though the data sources are same. In this study, the values presented in the Table A1-2 will be used for result analyses. Researchers **[212, 225, 231]** have worked on determining the Hansen solubility parameter components and the corresponding total solubility parameters of various fatty acid methyl esters (FAME) by following the van-Krevelen-Hoftyzer methodology. Though these results are not same for the same FAME, the obtained values are within a close range of variations. The results are tabulated in the Table A1-4.

3.2.2.2.2 Hoy's Methodology

Hoy **[232, 233]** proposed two different sets of group-contribution method formulae (system of equations) to determine the solubility parameters. Each of the system of equations contain four additive molar functions, several auxiliary equations, and a set of expressions to determine the total solubility in addition to the solubility parameter components. These are presented in the Table 3-4.

Formulae	For solvents	For amorphous polymers
	(Eq. 3.15)	(Eq. 3.16)
Additive molar functions	$\varphi_t = \sum N_i \varphi_{t,i} ; \ \varphi_p = \sum N_i \varphi_{p,i}$	$\varphi_t = \sum N_i \varphi_{t,i}; \ \varphi_p =$
	$V_m = \sum N_i V_i$; $\Delta_T =$	$\sum N_i \varphi_{p,i}$
	$\sum N_i \Delta_{T,i}$	$V_m = \sum N_i V_i$; $\Delta_T^p =$
		$\sum N_i \Delta_{T,i}^p$
Equations to determine solubility parameters	$\delta_t = \frac{\varphi_t + B}{V_m} \qquad ; \mathbf{B} = 227$	$\delta_t = rac{\varphi_t + rac{B}{\overline{n}}}{V_m}$; $B = 227$
boluoliky parameters	$\delta_p = \delta_t \left(\frac{1}{\alpha} \times \frac{\varphi_p}{\varphi_t + B} \right)^{0.5}$	$\delta_p = \delta_t \left(\frac{1}{n} \times \frac{\varphi_p}{p} \right)^{0.5}$
	$\delta_h = \delta_t \left(\frac{lpha - 1}{lpha}\right)^{0.5}$	$\varphi = \left(\left(\alpha^{p} - \varphi_{t} + \frac{B}{\overline{n}} \right) \right)$
	$\delta_d = \left(\delta_t^2 - \delta_p^2 - \delta_h^2\right)^{0.5}$	$\delta_h = \delta_t \left(\frac{\alpha^p - 1}{\alpha^p}\right)^{0.5}$

Table 3-4 Set of equations used to determine the solubility parameters by Hoy's method [208,232]

$$\delta_{d} = \delta_{t} \left[\frac{1}{\alpha} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + B} \right) \right]^{0.5} \qquad \delta_{d} = \left(\delta_{t}^{2} - \delta_{p}^{2} - \delta_{h}^{2} \right)^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right) \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d} = \delta_{t} \left[\frac{1}{\alpha^{p}} \times \left(1 - \frac{\varphi_{p}}{\varphi_{t} + \frac{B}{n}} \right]^{0.5} \\ \delta_{d}$$

The molar volume and molar attraction constants can be determined from the Table A1-5 in the **Appendix A1**. Van Krevelen **[196]** has proposed that the average values of the solubility parameter components determined by the Hoftyzer–Van Krevelen and Hoy methods could be a safest way to investigate the solubility of the polymers into any organic solvents. The molar attraction constants of the molecular groups can be used to determine the solubility parameters of targeted thermoplastics. The difference between calculated values from van Krevelen methodology and the Hoy's methodology are due to variation of molecular wight numbers in the same polymers. In the van Krevelen methodology **[196]**, all the components of molecular attraction constants and the molar volume were determined from the group contribution values. Alternatively, in Hoy's methodology **[232, 233]**, only the total molecular attraction parameters were determined from the group contribution chart and the density and molar mass were used which are based on the repeating unit's characteristics.

3.2.3 Thermodynamic Criteria of Solubility

The solubility can be also specified based on the mixing of free energy (ΔG_m) [196, 207]. The free energy for mixing (known as Gibbs free energy) of two substances which mutually produce a good solution is a negative quantity by relating with enthalpy change (ΔH_m) and entropy change (ΔS_m) of the mixing at temperature T. So, the relationship can be expressed as follows:

Both the enthalpy and entropy of mixing terms are mutually dependent and linked to the polar as well as hydrogen bonding energy fraction of the total free energy of mixing within a system [220]. An explanatory derivation of equation 3.17 can be found in the chapter entitled, "Free energy and Chemical Thermodynamics" by Schroeder [235].

In the case of polymers to be dissolved in a solvent, the change of entropy occurs in two stages, which are disorientation (i.e. polymers turning into amorphous states, ΔS_{dis}) and dissolution of amorphous polymers in the solvent to create the mix (ΔS_{mix}). The combination of these two entropy parameters is known as the configurational mixing of entropy (S_c). The change of entropy for a polymer solute in a solvent has been derived by Flory and Huggins [236-238] with the consideration that the mixing of entropy is combinatorial (i.e. pure polymers dissolving in pure solvent), which can be expressed as follows:

Here, n_1 is number of identical solvent molecules, n_2 is number of identical polymer molecules, v_1 and v_2 are the volume fraction of the solvent and solute respectively, and k is the Boltzmann constant.

In that case, the equation 3.18a can be expressed as follows:

$$\Delta S_{mix} = -R[x_1 \ln v_1 + x_2 \ln v_2] \quad \dots \quad (\text{Eq. 3.18b})$$

Also, the above equation (equation 3.18j) can be expressed as follows for the case of heterogenous polymer which is comprised of a range of homologous molecular groups.

$$\Delta S_{mix} = -k(n_1 \ln v_1 + \sum_{i}' n_i \ln v_i) \quad \quad (\text{Eq. 3.18c})$$

Where, $\sum_{i}' v_i = v_2 = 1 - v_1$ = total polymer concentration.

The heat of mixing (ΔH_{mix}) of the two interacting ingredients (polymer and solvent) can be thus derived from Flory-Huggins theory [237-239] (commonly known as van Laar

expression for two interacting component systems), when the system solvent contains r segments of polymer chains within the solution.

$$\Delta H_{mix} = kT\chi_1 n_1 v_2 = \frac{R}{n} (T\chi_1 n_1 v_2) \dots (Eq. 3.18d)$$

Here, the new parameter, χ_1 , is the characteristic of interaction energy commonly known as Flory-Huggins interaction parameter and it is a dimensionless quantity.

Thus, Eq. 3.17 can be also expressed as follows:

$$\Delta G_m = RT(x_1 \ln v_1 + x_2 \ln v_2 + \chi_1 v_1 v_2) \quad \dots \quad (\text{Eq. 3.19})$$

Or, $\frac{G_m}{RT} = (x_1 \ln v_1 + x_2 \ln v_2 + \chi_1 v_1 v_2) \quad \dots \quad (\text{Eq. 3.19a})$

Where, $v_1 = \frac{n_1}{n_1 + rn_2}$ and $v_2 = \frac{rn_2}{n_1 + rn_2}$ are the volume fraction of the solvent and solute respectively and the molecule number fraction of solvent is, $x_1 = \frac{n_1}{(n_1 + n_2)}$, that of polymer is, $x_2 = \frac{n_2}{(n_1 + n_2)}$ and total molecule number is, $n = (n_1 + n_2)$, then the Boltzmann constant (k) can be expressed as $k = \frac{R}{n}$. Here, R= universal gas constant= 8.314 J.K⁻¹.mol⁻¹

Also, r is the number of solvent molecules replaced by the solute during mixing of the solute in the solvent lattice (degree of polymerisation or the length of the polymer chain in the lattice), and $r = \frac{\text{molar volume of solvent}}{\text{molar volume of solute}}$.

To make a good solution, equation 3.19 should be a negative quantity. It is only possible when the value of Flory-Huggins interaction parameter (χ_1) is reduced as much as possible. Van Krevelen [208] has mentioned that the high molecular weight polymers will dissolve only if $\chi_1 \leq 0.5$, whereas, for a regular low molecular weight solute the mixing can happen for $\chi_1 \leq 2.0$.

In the case of polymer-solvent interaction, the Flory-Huggins interaction parameter (χ_1) is considered as a summation of the enthalpic component (χ_H) and the entropic component (χ_S) of the polymer-solvent interactions as per the Bristow-Watson method [240]. The relation is presented as follows:

$$\chi_1 = \chi_H + \chi_S$$
 (Eq. 3.19b)

Van Krevelen **[196]** referred to previous literatures from which the entropic contribution of the Flory-Huggins interaction parameter can be considered as a constant entity within the value of $\chi_s = 0.35 \pm 0.1$ (for polar solution) and $\chi_s = 0.34$ (for non-polar solution).

Therefore, the total interaction parameter for polar or non-polar solution (from Eq.3.19b) can be expressed as follows:

$$\chi_1 = \chi_H + \chi_S \approx 0.35 + \frac{V_{sol}}{RT} (\delta_p - \delta_s)^2$$
(3.19c)

Since the solvent-polymer dissolution criterion for the interaction parameter is $\chi_1 \leq 0.5$ and equation 3.19c is a positive quantity, the difference of solubility parameter between the polymer and solvent must be very small to ensure the solubility. That is why, if the solubility parameters of solute and solvent are equal or almost equal the polymer is dissolved well in that solvent. If the difference between solubility parameters for the polymer and solvent increases, the solubility rate is reduced remarkably.

Thus, substituting equation 3.19c into equation 3.19, the following expression of free energy of mixing can be obtained [207]:

$$\Delta G_m = RT \left(x_1 \ln v_1 + x_2 \ln v_2 + \left[0.35 + \frac{V_{sol}}{RT} \left(\delta_p - \delta_s \right)^2 \right] v_1 v_2 \right) \dots (3.19d)$$

Equation 3.19d is a complete expression of a solution in which the enthalpy and entropic change of interaction energy is considered. It is also a one-dimensional expression for solubility analysis. In general, the polarity level of esters, ethers and alcohols can be shown as, alcohol>esters>ethers. So, within the tolerance of entropic component of Flory-Huggins interaction parameter, the equation 3.19d is a valid expression for both the polar and non-polar substances.

The value of mixing enthalpy is positive (i.e. endothermic) and increases quadratically. The difference between the solubility parameters determines the consumption of heat in the solution. When the ΔH_{mixing} increases, due to limiting value of solubility criteria, only rise of the temperature can drive the entropy of the solution sufficiently to meet the solubility conditions. The entropy is changed during the dissolution of polymers and the enthalpy is key parameter to decide the change in the Gibbs energy [207]. Only if the change of free energy becomes zero or negative, the dissolution occurs spontaneously.

In case of solutions which contain polar-bonding and hydrogen-bonding components, the enthalpic component of the Flory-Huggins parameter does not hold a very good relationship with the interaction parameter. Then Hansen's solubility parameters components are used to estimate the Flory-Huggins parameter (χ_1) for these solution systems. This model is commonly known as the Flory-Huggins/Hansen (FH-Hansen) model for interaction parameter.

$$\chi_1 = \alpha_1 \frac{V_{sol}}{RT} \left[\left(\delta_{pd} - \delta_{sd} \right)^2 + 0.25 \left(\delta_{pp} - \delta_{sp} \right)^2 + 0.25 \left(\delta_{ph} - \delta_{sh} \right)^2 \right] \dots \dots (Eq. 3.19e)$$

Hansen [220] proposed the value of α_1 to be 1, which generates good correlation compensating the missing entropic term in the equation 3.19e for the systems having dominant dispersive energy bonding over the polar and hydrogen bonds. Lindvig *et al.*[241] used volume-fraction based combinatorial form and obtained the optimal value of the α_1 -parameter as 0.6 instead of 1 which was proposed by Hansen. Thus, Hansen [207] reported the FH-Hansen model using the optimal value proposed by Lindvig *et al.* [241] as follows:

$$\chi_1 = 0.6 \frac{V_{sol}}{RT} \left[\left(\delta_{pd} - \delta_{sd} \right)^2 + 0.25 \left(\delta_{pp} - \delta_{sp} \right)^2 + 0.25 \left(\delta_{ph} - \delta_{sh} \right)^2 \right] \dots \dots \dots (Eq. 3.19f)$$

Hence, equation 3.19 can be rewritten as follows:

Since the solubility criteria for a polymer-solvent solution system in terms of interaction parameter is $\chi_1 \leq 0.5$, the equations 3.19f or 3.19g can be used as a first point of analysis of polymer-solvent miscibility when the Hansen solubility parameters are available. On the other hand, the group contribution method requires the detailed information of the molecular structure of the system constituents to determine the solubility criteria. That is why, available Hansen parameters are used to determine the system compatibility in most commercial paintsolvent analysis [241].

3.2.4 Determining the Solubility Parameter of Fatty Acids and Fatty Acids Esters

Vegetable oils and biodiesel derived from vegetable oils are mixture of various fatty acids and fatty acid alkyl esters. It is a very complex process to determine the solubility parameters of the oils/fuels by group increment methodology. Cataldo [212] has presented the following steps to determine the solubility parameters of these compounds using the group increment methodology. In this case, the molar volume of the oil/fuel (mixture of various fatty acids/esters) has been determined by the considering average molecular weight (M) as well as the density (ρ) determined from experiments.

The generalised expression for the three components of the solubility parameter can be as follows,

$$\delta_{d} = (\sum_{i} x_{i} \varphi_{di}) / (M\rho^{-1}) \qquad \dots \qquad \text{(Eq. 3.20a)}$$

$$\delta_{p} = \frac{(\sum_{i} x_{i} \varphi_{pi}^{2})^{0.5}}{M\rho^{-1}} \qquad \dots \qquad \text{(Eq. 3.20b)}$$

$$\delta_{h} = [(\sum_{i} x_{i} E_{hi}) / (M\rho^{-1})]^{0.5} \qquad \dots \qquad \text{(Eq. 3.20c)}$$

So, the total solubility parameter can be calculated using these above set of values in the following equation,

$$\delta_t = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5}$$
 (Eq. 3.21)

Here, x_i is the weight fraction of the respective component (triglycerides/fatty acid esters) of the vegetable oil/biodiesel fuel.

Once the compositions, average molecular weight, density of the oil/fuel components are known, the relative parameters can be calculated to determine the total solubility parameter. The chemical formula and molecular weight of various fatty acids, and fatty acid methyl esters which are generally available are presented in the Table A1-6 and Table A1-7 respectively [242] in the Appendix A1. The molecular weight and the chemical formulae are the important key factors to determine the solubility parameters following the (analytical methodologies) group contribution methodology in the result analyses. Furthermore, both the Figure A1-1 and Figure A1-2 in the Appendix A1 [208] show group contributions to molar mass and van der Waals volume of functional group increments for bivalent and non-bivalent group molecules.

3.2.4.1 Alternate Methods of Determining Solvent Capacity of Biodiesel

Other than the already mentioned solubility analysis process, there are several more parameters which may indicate the solvent capacity of biodiesel. Biodiesel fuels possess inherent lubricity due to their constituent fatty acid profile. Therefore, it is anticipated to make the waste plastic-biodiesel-diesel blends to be more amenable for the engines [243]. Along with the fuel and lubricant applications of biodiesels, the other applications could be summarised as: resin cleaning and removal, cleaning up oil spills, metal working fluids, and career solvent, etc. [244].

Apparently, the solubility of a solute correlates with the unsaturation level of the vegetable oils, in terms of the Iodine value (IV) of the oil. The unit of solubility is milligrams per litre (mg/l). Cataldo and Braun [245], observed that the saturated fatty acid alkyl esters can influence better solubility of the C_{60} (fullerenes) molecule than that of higher level of unsaturation. The higher IV shows that the double bond or the unsaturation level increases with the rise of IV in the fuel/oil.

Solvent power of various hydrocarbon solvents could be another way of measuring solubility criterion of biodiesel solvent. Usually, solvent power is measured in terms of kauributanol value (K_b value) as per ASTM D1133 [192, 246]. The higher the K_b value, the more aggressive is the solvent for a range of solutes. Hu *et al.*[246] and Kerton [247] observed that the pure methyl esters possess higher K_b values than those having some amount of glycerides due to biodiesel conversion inefficiency. Other observations made by those researchers are that the glycerides deteriorate the solvent power of the biodiesel. The saturation and unsaturation level of fatty acids have effect on this value. The unsaturated fatty acid esters have higher K_b values than the saturated esters. The number of double bond or unsaturation position does not govern anything regarding this. But the longer chain fatty acid compositions have weaker K_b values than the shorter ones.

Thus, the biodiesels which have more unsaturated esters or shorter chain esters can show better solvent ability. The type of alcohol used in the transesterification process also governs the solvent power. The shorter chain alcohols help to have higher K_b values of the biodiesel. Biodiesel also act effectively as a co-solvent with ethyl lactate, another bio derived solvent [246-248]. The combination showed synergic effect as solvent combination. Hence, when the biodiesels are used as solvent for the dissolution of plastics, the use of co-solvent may expedite the dissolution process.

3.2.5 Solubility Criteria of a Solute in a Solvent

Ideally, a solute polymer will only dissolve in a solvent that possess similar or lower solubility parameter in comparison to the solute. A solubility criterion determines the extent of

solubility of certain molecule (solute) in a certain solvent. The following criterion has been proposed by van Krevelen [196, 219]:

$$\Delta \delta = \left[\left(\delta_{d,solute} - \delta_{d,solv} \right)^2 + \left(\delta_{p,solute} - \delta_{p,solv} \right)^2 + \left(\delta_{h,solute} - \delta_{h,solv} \right)^2 \right]^{0.5} \le 5MPa^{\frac{1}{2}}$$
..... (Eq. 3.22)

In case of molecules having the solubility parameter $\delta_t = \delta_d$ with all the other components being zero, the above solubility criteria should not be applied. Rather the total solubility parameter of the solute ($\delta_{t,solute}$) and the solvent ($\delta_{t,solvent}$) are determined and then the following equation is used to calculate the solubility criteria.

$$\Delta \delta_t = \left[\left(\delta_{t,solute} - \delta_{t,solvent} \right)^2 \right]^{0.5} = \left| \delta_{t,solute} - \delta_{t,solvent} \right| \le 5MPa^{\frac{1}{2}} \dots (Eq. 3.23)$$

Increasing temperature beyond the room temperature can reduce the time required for dissolution of the solute in the solvent. However, in that case, even if the solution is cooled to room temperature to determine the overall solubility parameter, the results will vary than that of the dissolution occurred at room temperature for a prolonged period [212, 245]. Cataldo [212] has mentioned that this above criteria can be effective in terms of calculating polymer solubility in the biodiesel or their oils as they are mainly constitute of several long chain fatty acid (both saturated and unsaturated). In their analysis of determining the solubility of fullerene (C_{60}) in several biodiesels and oils, they found that the HSP components-based condition of solubility was showing limited solubility of this compound. However, experimental investigation showed good solubility as was indicated by this condition.

In an another criterion of solubility [207, 221, 230], the interaction radius (R_o) and the distance between the Hansen solubility parameters in the Hansen space (R_a) can be related to define relative energy difference (RED) as follows,

$$RED = \binom{R_a}{R_o}$$
 (Eq. 3.24)

Where,

$$R_{a} = \left[x\left(\delta_{d,solute} - \delta_{d,solv}\right)^{2} + y\left(\delta_{p,soute} - \delta_{p,solv}\right)^{2} + z\left(\delta_{h,solute} - \delta_{h,solv}\right)^{2}\right]^{0.5}$$
.....(Eq. 3.25)

Based on several empirical tests, it was suggested that the value of the constants could be x=4, y=z=1, which are most usable values. Thus,

$$R_{a} = \left[4\left(\delta_{d,solute} - \delta_{d,solv}\right)^{2} + \left(\delta_{p,soute} - \delta_{p,solv}\right)^{2} + \left(\delta_{h,solute} - \delta_{h,solv}\right)^{2}\right]^{0.5}$$
.....(Eq. 3.26)

Here, R_o is measured from the Hansen sphere. The interaction radius (R_o) is the radius of the sphere in the Hansen space for the solute. It represents a region of high solubility, i.e. the solvents which have centre within that radius are good solvent for that solute. The distance between the centre of the solute's sphere and the location of the solvent in the Hansen space is also a measure of solubility of the solute [198, 207]. This distance is also known as solubility parameter distance, R_a . The value of R_a is always smaller than that of R_o of a good solvent.

RED is a quick indication of whether the solvent is likely to be within the solubility sphere. With this criterion, the dissolution of a solute in a solvent can be described as,

If, RED < 1 the molecules are alike and will dissolve

RED = 1 the system will partially dissolve

RED > 1 the system will not dissolve and inappropriate solvent

Later, researchers also observed that several compounds are soluble to particular solvents which are shown as insoluble through the above criteria. Batista *et al.* [225] and Cataldo [212] observed these for biodiesels. Batista *et al.* [225] referred the comparative solubility methodologies presented by Greenhalgh *et al.* [249] and Bagley *et al.* [250], which are as follows respectively,

Solubility condition defined by Greenhalgh methodology:

If $\Delta \delta_t < 7$ MPa^{1/2}, the solute is soluble.

If $\Delta \delta_t > 7$ MPa^{1/2}, the solute is insoluble.

Here, Bagley at el.[250] defined $\delta_v = (\delta_d + \delta_p)^{\frac{1}{2}}$ as a volume dependent solubility parameter.

Then the solubility condition has been defined as follows:

For $12.3 \le Rv \le 13.9$ MPa^{1/2} the solute is soluble, whereas, for $13.4 \le Rv \le 14.2$ MPa^{1/2} the solute is insoluble.

Hansen [207] cited Hildebrand solubility criteria for polymers as,

Equation 3.28a is valid for polymer and solvent system having the same δ_p and δ_h .

On the other hand, Lindvig [241] cited Seymour [251], who stated that the solubility criterion for regular solution of polymer and solvent system as follows (Eq. 3.28b),

$$\Delta \delta_t = \left| \delta_{t,solute} - \delta_{t,solvent} \right| \le 1 \sim 1.8 \left(\frac{cal}{cm^3} \right)^{0.5} or \ 2.045 \sim 3.681 \text{MPa}^{\frac{1}{2}} \dots (\text{Eq. 3.28b})$$

There are some other methodologies **[182, 252]** to determine the solubility criteria of a solute in a solvent, or to determine a good solvent for a particular solute.

3.3 Concluding Remarks

In this chapter, analytical methodology of solubility of polymers in appropriate solvents is presented. The key focus was presented to analyse the analytical dissolution behaviour of plastics in biodiesel. Based on the type of solvents and adopted techniques, the dissolution process can be effective for both recycling as well as energy production purposes. The feature of selecting a biodiesel fuel as solvent for plastics has been presented through theoretical analysis of solubility parameters. Averaging solubility parameters from the van Krevelen-Hoftyzer and Hoy methods may be deemed efficient combination in order to determine the solubility parameter components to assess the solubility of the polymers in organic solvents as per Van Krevelen **[196]**.

The knowledge of solubility from chapter 3 and the optimised production of biodiesel from chapter 4 were utilised to progress towards experimental and analytical activities for this thesis. Chapter 5 explains how optimal yield of biodiesel was obtained. Then both the chapter 6 and

chapter 7 explain the experimental and analytical investigations of solubility of plastics into biodiesel, respectively. Chapter 6 presents the dissolution kinetic models of PE, PP and PS into 9 selected biodiesel fuels as described in chapter 5. Whereas chapter 7 presents application of theoretical models presented in the chapter 3 to determine the solubility of thermoplastics into the selected biodiesel solvents. The information from both chapter 6 and chapter 7 indicated which plastic can be used as fuel along with diesel-biodiesel blends in an unmodified diesel engine. Both chapter 8 and chapter 9 explains the assessment of application of plastic-biodiesel-diesel fuel blends in the diesel engine.

Chapter 4

BIODIESEL PRODUCTION METHODOLOGY, ITS PROCESS OPTIMISATION AND REACTION KINETICS MODEL DEVELOPMENT

4.0 Introduction

This chapter presents the relevant experimental methodologies for biodiesel production process (both esterification and transesterification processes), optimisation of the experimental process parameters and reaction kinetics model development for this study. The reason of optimising and reaction kinetics determination for production process is to understand the process efficiency as well as the required energy consumption in order to accomplish these reaction processes.

4.1 Experimental Methodologies for Biodiesel Production

Transesterification process **[253-255]** has been performed for all the feedstocks used here in a batch reactor. Though conventional transesterification process in the batch reactors have been reported to be one of the most efficient processes, several steps **[256, 257]** have to be followed strictly to successfully complete the process and increase process yield efficiency. Key experimental processes followed in this study are presented in the flowchart provided in Figure 4-1. The physical-chemical properties of the fuel should abide by the established standards (ASTM D6751 and EN 14214) **[258-261]** irrespective of the feedstocks selected or methodologies applied to produce the fuel. The success of conversion to biodiesel depends on the type of catalysts, the methanol to oil ratio, temperature, reaction time, purification process, etc. **[256, 257, 262, 263]**. Determining an optimal operating parametric condition for all types of feedstocks is very complex. Even for the same type of feedstock, the operating conditions can be varied time to time **[263]**.

The key steps followed in this study are described as follows:

4.1.1 Preheating and Removal of Moisture from Oil

Once the feedstock (raw material) is collected, moisture or water content within the oil/fat/waste oil has to be removed to avoid the formation of more FFA by hydrolysis reaction (Figure 4-2) in presence of alkaline catalysts. Moisture also results in loss of conversion
efficiency. Moisture removal is done by heating the oil at 110 $^{\text{O}\text{C}}$ for more than 30 minutes. The heating systems used in this process was equipped with feedback-controlled temperature management system. Therefore, managing desired temperature was convenient within the \pm 1 $^{\text{O}\text{C}}$ tolerance. To facilitate the water vapour to be removed well from the heating containers, wide-open faced glass beakers were used within a fume hood zone. Besides, magnetic stirring was continued at 600 rpm or more to assure better convection heat transfer to the liquid. Once the temperature reached at 110 $^{\text{O}\text{C}}$, the timer was "ON" for 30 minutes and visual observation was performed for any vapour formation or any bubble within the oil during the last 10 minutes to decide if further heating was required beyond 30 minutes period. A traditional but convenient process was also performed to inspect moisture to vapour formation was to cover the heating containers with a paper towel for a few seconds to see if it gets wet. Since total available moisture/water content within oil is limited to 0.5% (w/w), complete or best possible removal of moisture from the raw material assures better transsetrification reaction and conversion efficiency.

If there is more than 0.5% (w/w) moisture present within the raw material, hydrolysis process occurs to produce FFA (Eq. 4.1) that increases the total FFA level in the system [**264**]. Usually, the FFA has a fatty acid profile of C16:0, C18:0, C18:1, C18:2, and C18:3. A typical example for rapeseed oil shows that the quantification level of FFA could be C18:1>C18:2>C18:3>C18:0>C16:0 [**265**].

Triglycerides (TG) + water (H₂O)
$$\stackrel{\Delta,\text{NaOH}}{\longleftrightarrow}$$
 FFA (RCOOH) + Diglycerides (DG)(Eq. 4.1)

In presence of water, the alkaline catalyst, NaOH, reacts with water (dissociation reaction) to form Na^+ and OH^- radicals. Then, Na^+ encounters the FFA (RCOOH) to form soap.

$$NaOH + H_2O \xrightarrow{\Delta} Na^+ + OH^- \dots (Eq. 4.1a)$$
$$Na^+ + OH^- + RCOOH \xrightarrow{\Delta} H_2O + RCOONa(soap) \dots (Eq. 4.1b)$$

During the process of dissolution of NaOH pellets in methanol, the NaOH dissociates the methanol (CH₃OH) to form Na⁺, CH₃O⁻ and H₂O in the solution. It has been reported that there are both steric and electronic interactions between the alkyl esters and the alkali hydroxides which mainly controls the saponification of the esters [266, 267]. Besides, the saponification

of FAME compounds occurs 5-7 times faster with the ethanol than that of the methanol during the transesterification reaction [266]. So, excessive methanol is a better way to push the reaction in the forward direction.



Figure 4-1 Bidoiesel Production Process Flowchart

C ₃ H ₅ (OCOR) ₃ + H ₂ O triglyceride water	\longleftrightarrow	C ₃ H ₅ (OH).(OCOR) ₂ + RCOOH diglyceride free fatty acid (FFA)
C ₃ H ₅ (OH).(OCOR) ₂ + H ₂ O diglyceride water	← →	C ₃ H ₈ (OH) ₂ . (OCOR) + RCOOH monoglyceride FFA
C ₃ H ₅ (OH) ₂ .(OCOR) + H ₂ O monoglyceride water	$\leftarrow \rightarrow$	C3H5(OH)3 + RCOOH glycerol FFA

Figure 4-2 Hydrolysis of triglycerides in presence of water [264, 268]

4.1.2 FFA Determination

It is important to determine the FFA content and moisture content in the vegetable oil/animal fat triglycerides prior to conduct any base-catalysed alcoholysis (preferably, methanolysis) to produce FAMEs. Any lean content of FFAs and moisture in the triglyceride content causes severe loss of final product content (i.e. less efficient conversion efficiency, %CE) in terms of saponification. Hence, the conversion process is done in two steps [269, 270] if the feedstock derived oil contains higher FFAs (e.g. jatropha, beauty leaf tree, waste cooking oil, beef tallow) or moisture (e.g. waste cooking oil). The first step is known as esterification, which is a pre-treatment process to reduce impurities by acid catalysts. Then the derived content undergoes base-catalysed transesterification [271].

Chemical titration known in the form of potentiometric titration was conceived to determine the acid value (AV) and then %FFA content of the samples following procedures described in ASTM D664 [272] (maximum limit 0.50 mg KOH/g of sample)

To perform the titration process, 0.1M KOH (molar weight 56.11 g/mol) solution was prepared by dissolving 5.611 g KOH in 1000 ml of propan-2-ol. The mixture was stirred well to dissolve solid KOH in the solvent and gentle heating (not more than 65 ^oC) for up to 10 minutes was applied to expedite the dissolution. The solution was stored in a chemically resistant bottle. The prepared solution was not used for more than 2 weeks to avoid concentration changes. The concentration was checked at the beginning of day of testing the samples. A change of more than 0.0005 mol/L was the maximum limit of concentration variation to decide on discarding titrant.

The titration solvent was made by mixing 1000 ml of toluene, 990 ml of propan-2-ol and 10 ml of distilled water. While mixing these compounds together, magnetic stirring was

performed to mix these well. The prepared solution was neutralised against phenolphthalein and stored in a chemically resistant bottle.

Phenolphthalein solution was prepared by dissolving 1.0 g of phenolphthalein in100 ml of propan-2-ol.

Method of titration: A 250 ml Erlenmeyer flask, burette and a precision weighing scale were required to perform the analyses.

About 5-10 g of oil was weighed and mixed well in an Erlenmeyer flask with 125 ml of solvent. Necessary mixing methods like stirring and heating up to 65 ^oC were applied accordingly. Several drops of phenolphthalein solution were added in the solution and shaken well to observe the colour change. Once the solution had settled, the reaction agent solution was mixed drop by drop from a burette while shaking the flask well to facilitate the reaction. Once the reaction is done for certain amount of solution reactant, there was a sustained colour change. The volume of the 0.01N KOH was recorded and the calculation was performed by the respective equations to determine the AV (acid value) and %FFA for further processing with the sample.

Acid value
$$\left(\frac{mg \ KOH}{gm \ of \ sample}\right) = \left[\frac{volume \ 0.1N \ KOH \ (ml) \times Normality \ of \ KOH \left(\frac{mol}{L}\right) \times 56.1 \left(\frac{g}{mol}\right)}{sample \ weight \ (gm)}\right]$$

Empirically, the relation between FFA (%FFA) value and the Acid value (AV) has been expressed as follows [273]:

$$\% FFA = AV \left(mg \frac{KOH}{g} \right) \times 0.503 \qquad (Eq. 4.1d)$$

$$AV = 1.99 \times \% FFA$$
 (Eq. 4.1e)

Also, the amount of FFA conversion into fatty acid methyl ester (FAME) can be calculated from the following formula, (Eq. 4.1f).

FFA Conversion (%) =
$$\frac{A_0 - A_t}{A_0} \times 100 = \left(1 - \frac{A_t}{A_0}\right) \times 100$$
 (Eq. 4.1f)

Here, A_0 = the initial acid value; and A_t = the acid value at a certain reaction time, t.

4.1.3 Catalysts Used for Biodiesel Production

In this study, sulphuric acid (H₂SO₄) was used as catalyst for the esterification reaction and the alkali hydroxides (NaOH and KOH) were used for the transesterification process in the batch reaction systems. Compounds like alkali hydroxides (NaOH, KOH) and alkali metal alkoxides (CH₃ONa, CH₃OK) are categorised as strong alkali catalysts for successful transesterification process with the latter categories claiming higher yield efficiencies [253, 270, 274].

Acid catalysts are mainly used as first stage reaction (esterification) catalysts for the twostage esterification-transesterification process. Hydrochloric acid (HCl), sulphuric acid (H₂SO₄), phosphoric acid (H₃PO₄), carboxylates (PbCH₃COOH) and sulphonic acid (RSO₃H) (e.g. methane-sulphonic acid, H₃C-SO₂-OH), etc. are the higher strength acid catalysts for efficient acid esterification to remove FFA from the feedstocks (oil/fats) without worrying about soap formation [**253**, **275**]. But in case of very high FFA in the feedstocks (e.g. waste cooking oil, vegetable refinery wastes, etc.) acids like p-toluene-4-sulphonic acid could be an effective homogeneous acid catalyst following KOH based transesterification.

While washing the biodiesel with warm water, neutralisation with sulphuric acid is also a good option to refine the biodiesel **[253, 276]**. In addition, use of co-solvents can accelerate the reaction processes by enhancing solubility between oils and methanol for both acid esterification and alkali transesterification reactions. Tetrahydrofuran, acetone, cyclohexane, hexane, methyl tertiary butyl ether, are effective influence to accelerate the reaction processes with doses ranging less than 10% **[253, 277, 278]**.

In many cases, heterogeneous catalysts are chosen over the homogeneous catalysts due to some of their beneficial contribution to the transesterification process: cost effectiveness (4-20% less than that of homogeneous catalysts), less pollutant generation, green chemistry, easy to recover, reusable, high tolerance to high water and FFA content, high temperature and pressure, non-corrosive and may support both he esterification and transesterification reactions with the same catalyst **[253, 254, 275, 277, 279-282]**. Due to reusability, heterogeneous catalysts can be used preferably and efficiently in batch reactors rather than using them in continuous reactors **[281, 282]**. Among numerous heterogeneous catalysts BaO, CaO (e.g. eggshell), MgO, SrO, Sr(NO₃)₂/ZnO, KI/Al₂O₃, Na/NaOH/Al₂O₃, KCaF₃, KCaCO₃F, CaAl₂F₄(OH), Ca(OCH₃)₂, CaTiO₃, CaMnO₃,Ca₂Fe₂O₅, CaZrO₃ and CaO–CeO₂, Alkaline

hydrotalcite of Mg/Al and Li/Al, Fe₃O₄/MCM(Mobil Composition of Matter)-41, Zeolites, Anionic Clays, nano-catalysts (e.g. Li-doped CaO, CaO–MgO, etc.), nano-porous catalysts (e.g. [HSO₃-BMIM]HSO₄, Tungsten loaded bovine bone, Sulphated niobium oxide, etc.), etc. have shown many successful applications to convert feedstocks into biodiesel by transesterification process [**253**, **254**, **279**, **281-283**]. Due to numerous availabilities, the heterogeneous catalysts can be also categorised as solid acid and solid base catalysts. Also, these two categories can be classified into various groups, i.e. solid based catalyst groups are: alkaline earth metal oxides, alkali doped materials, transition metal oxides, hydrotalcites, mixed metal oxides, etc. and the solid acid catalysts are grouped as: mesoporous silicas, hetero-polyacids, acidic polymers and resins, waste carbon-derived solid acids, range of additional solid acids, etc. [**253**, **254**, **279**, **281**, **283**, **284**].

4.1.4 Acid-Catalysed Esterification Process

When the %FFA content in the oil (various edible and inedible oils, fats, and waste oil, etc.) is detected to be more than 1% (w/w), the acid-catalysed esterification is performed to convert the free fatty acids into respective esters (Figure 4-3). Water is produced as a by-product of this reaction and separated through separation process.



Figure 4-3 Esterification reaction equation [285]

4.1.4.1 Esterification Parameters

To conduct esterification reaction in this study, about 6 M-12 M methanol (alcohol) was measured against 1 M oil. The acid catalyst for the esterification process was always H₂SO₄, which was measured as 1-3 % wt. (w/w) of the oil. Usually, the temperature was varied between 50 $^{\circ}$ C and 65 $^{\circ}$ C for various oil samples. Finally, the reaction period was selected within the range of 60 minutes to 180 minutes based on the FFA content of the oil. Since there are four parameters (i.e. methanol content, quantity of acid catalyst, reaction temperature and reaction period) to conduct the reaction, optimal quantification for highest efficiency of the conversion process was determined for each of the type of oil used in this study.



Figure 4-4 Various stages of biodiesel production processes from Tallow, (a) melting tallow, (b) tallow oil after moisture removal, (c) tallow esterification, (d) separation of FFA from esterified oil, (e) transesterification process, (f) separation of glycerine, (g) tallow biodiesel (WTB) after washing, (h) centrifugal separation of debris after drying process, (i) purified WTB

4.1.4.2 Reactor Setup for Esterification Process

To construct the experimental batch reactor, a three-necked round bottom thick walled reactor flask (capacity varied between 250 ml to 2000 ml) was used. The flask was placed within a water bath which was kept on the heating surface of the hot plate. The reason for putting the reactor flask in a water bath was to assure proper heat transfer to the reacting samples from all the possible heat transfer surfaces in contact of the sample. The temperature probe of the heating system was inserted through one neck of the flask which measured and controlled the temperature through a temperature control system integrated with the hot plate magnetic stirrer system. Usually, the middle neck of the flask was connected with a condenser which was cooled by continuous water flow to cool the evaporated reactants back to the reactor. The third neck was used to feed the reacting agents, raw material, and catalysts into the reactor. All these necks were made firmly air-tight by appropriate glass stoppers and connectors. Then the overall flask and condenser unit was fixed firmly with the help of laboratory stand and support clamps as required after balancing the flask within the water bath. An appropriate size of magnetic stirrer was fed in the reactor to perform the stirring which was set from the hot plate magnetic stirrer control system. The same experimental setup was also used for the transesterification process. Figure 4-4 (a-i) shows various stages of the biodiesel production processes from tallow based on the experimental set up adopted in this study.

4.1.4.3 Procedure for Conducting the Esterification Reaction

A standard operating procedure (SOP) was followed in all the esterification reaction processes in order to perform the reaction safely and efficiently. All the reactor equipment was cleaned and dried well to set up the reactor. Considering the moisture content has been removed by preheating and the oil is cooled down to safely handle for further processing, the oil sample was measured and poured in the flask. Heating system was set at desired temperature and the stirring with the magnetic stirrer also started at a set stirring speed (usually 600 rpm). While the oil was being heated, the required amount of methanol and sulphuric acid were calculated. Then methanol was poured the flask and observed mixing and temperature changes. When the mixing temperature rose near to the set temperature (i.e. about 2-3 ^oC less than the set temperature), the acid catalyst was poured slowly in the system. The reason for pouring sulphuring acid in the reactor before reaching the set temperature was an observation of sudden temperature rise and agitation during mixing of acid catalyst with the reactant (Figure 4-4(c)). Time recording started from the time of pouring acid catalyst in the system. Though the

condenser was used to cool down any evaporation of reacting agents, this precaution of pouring acid catalyst in the system helped controlling temperature of reaction within a desired level efficiently. When the reaction is done and pre-set time period ended, the temperature probe was carefully removed along with the condensing unit from the flask necks. Then the product and by-product mixtures were put in a clamped separating funnel to rest for a period between 5 hours and 24 hours as convenient. Once the impurities are removed the esterified sample was treated following the flow chart in Figure 4-1.

4.1.5 Alkali-Catalysed Transesterification Process

Generally, methanol or ethanol is used to react with the triglycerides to produce the methyl or ethyl esters (alcoholysis) of the corresponding fatty acids available in the oil or fat. There is a stoichiometric calculation that total of 3M methanol is required to complete the total transesterification. Indeed, the total process can be mathematically simplified as a shunt reaction [**286-288**]. To conduct this reaction (Figure 4-4(e)), about 5M-7M methanol (alcohol) was measured against 1M oil. The base catalysts for the esterification process were either sodium hydroxide (NaOH) or potassium hydroxide (KOH) at a level of 1-3% (w/w) of the oil. Usually, the temperature was varied between 50 °C and 65 °C for various oil samples. The reaction period effect on the biodiesel conversion process. Since there are four parameters (i.e. methanol content, alkali catalyst content, temperature and the reaction period) to conduct the reaction, optimal quantification for highest efficiency of the conversion process was determined for each of the type of oils used in this study.

A standard operating procedure (SOP) for the transesterification reaction process was also followed for all the transesterification reactions in this study in order to perform the reaction safely and efficiently. All of the reactor equipment was cleaned and dried well to set up the reactor. Considering the FFA content has been removed by esterification process and is within the allowable limit (%FFA \leq 1 %wt.), the sample was measured and poured in the reactor flask. Heating system was set at desired temperature and the stirring with the magnetic stirrer also started at a set stirring speed (usually 600 rpm). While the oil was being heated, required amount of methanol and alkali catalyst were calculated and measured. To use KOH/NaOH solution in the reactor for better catalytic activity, 100-200ml of methanol was used to dissolve the solid catalyst. Sufficient stirring and heating (less than 65 $^{\circ}$ C) were used to expedite the dissolution process. Part of the methanol was already poured in the reactor to mix well with

the oil sample and achieve desired heating level. Then the stopper was opened from the third neck to pour the alcoholic KOH/NaOH solution to perform the reaction. Time recording started from the time of pouring alcoholic KOH/NaOH solution in the system. When the reaction was done and pre-set time period is finished, the temperature probe was removed carefully along with the condensing unit from the flask necks. Then the product and by-product mixtures were put in a clamped separating funnel to rest for a period between 5 hours and 24 hours as convenient. Once the clear different layers were formed in the separating funnel, further treatment was carried out following the flow chart in Figure 4-1.

4.1.6 Post-treatment: Removal of Impurities and Preparing to be Used as Fuel

Removing glycerol and methanol from the biodiesel are the first two steps after the transesterification reaction substances have settled in a separation funnel. Biodiesel is lighter than the glycerol-methanol mixture. Hence bottom layer separation of the glycerol and methanol mixture was performed based on visual inspection of the layer differences. Only the biodiesel mixed with fraction of methanol and other impurities are left in the funnel. Methanol recovery was not in consideration for this study and that is why, the fractionating distillation process was not performed to the biodiesel-methanol mixture or glycerol-methanol mixture.

After removing the glycerols (flowchart in Figure 4-1), the rest of the substances in the funnel underwent vigorous washing and settling processes several times until any visible foam, bubble and very clear water layer is formed. Warm supplied water was used to wash the biodiesel rather than using distilled water to infuse trace elements of water in the fuel. Once a clear fuel and water layer were visible, water was removed as final washing process. Any trace amount of soap, catalysts, and methanol would make the water murky. So clear water layer is essential in the washing phase. Later the fuel was centrifuged for 10 minutes to remove the rest of the impurities.

Since the biodiesel fuel is hygroscopic by its nature, washing phase infuses moisture content within the fuel. Drying is necessary to remove any extent of water from the fuel. Usually the drying was performed at between 110 °C and 115 °C. Initial heating started with 115 °C temperature setting for first 10 minutes to quickly heat and remove more moisture from the fuel. Then the rest of the time the temperature was set at 110 °C until complete drying process was assured. The drying process is important to maintain the limit of moisture content within biodiesel to meet either ASTM D6751-12 or EN14214:2012 standards.

Once the fuel is dried, it is ready to be tested in the diesel engines as well as characterisations. To protect the fuel from photo-oxidation, usually the biodiesel fuels were stored in coloured and air tight containers with proper labelling along with standard hazard codes following the biodiesel handling policy guide [289].

Fuel conversion efficiency was recorded at this stage by following the equation:

$$\% CE = \frac{Weight of biodiesel fuel}{Weight of initial amount of oil} \times 100 \quad \dots \quad (Eq. \ 4.1g)$$

4.1.7 Fuel Characterisation

Fuel characterisation is necessary to determine the fatty acid methyl esters and their mass composition within the fuel of interest. Among many of the standard characteristic parameters, density, viscosity, calorific value, acid value, oxidation stability, cold flow properties (i.e. pour point, cloud point, and cold filter plugging point), flash point, cetane number were measured to observe the fuel quality effect on combustion quality and emission characteristics. Table 4-1 is a brief list of the standard test methods used to determine the physio-chemical properties of biodiesel fuel.

Properties measured	Equipment used	Method standard	Accuracy
Density (kg/m ³)) at 40 °C	SVM 3000 (Anton paar, UK)	D7042	0.0005 kg/m ³
Kinematic Viscosity at 40 °C	SVM 3000 (Anton paar, UK)	D7042	±0.35%
Flash point (^o C)	Pensky-Martens flash point— automatic NPM 440	D93	±0.1 °C
Oxidation stability (hr)	Metrohm 873 Rancimat	D675	±0.01 h
Higher heating value (MJ/kg))	IKA C200 calorimeter	D240	±0.1%
Cloud point (^o C)		D2500	±0.1 °C
Pour point (⁰ C)	NTE 450 cloud and pour point tester	D97	±0.1 °C
CFPP (^o C)	NTL 450 CFPP (Normlab)	D6371	±0.1 °C
Acid value (mg KOH/g)	Potentiometric titration method	D664	±0.001

Table 4-1 Fuel characterising equipment used to determine properties of biodiesel fuels

Countries using biodiesel as fuel for diesel engines have adopted biodiesel fuel standards as per the adaptability factors (e.g. blending factors of biodiesel and diesel, additives, engine and fuel handling materials) and necessities (e.g. fuel necessity, fuel import impact on respective country's economy and environment protection) [289-292]. Two of the most common and widely accepted standards are known as ASTM D6751[195] and EN 14214 [293]. ASTM D6751 standards can be applied to any fatty acid alkyl esters (i.e. methanol or ethanol) if the fuels properties fall within the standardised ranges, EN14214 strictly applies to the fatty acid methyl esters only. The automobile manufacturers and the fuel producers around the world mostly comply with these standards [290]. These standards were set to make a safe handling of the newly invented biodiesel fuel in the diesel engines before blending pure biodiesel with diesel fuel. The report titled "Biodiesel Handling and Use Guide" explains all these quality parameters in brief [289]. It has been observed that the B5 blends (Up to B5 must follow ASTM D6751 [289]) of biodiesel with the diesel fuel does not degrade the diesel's energy density and that of B20 (B6-B20 blends must comply with ASTM D7467-15 [289]) has equivalent to around 98% of the diesel fuel's energy density [294]. So, most modern diesel engines may be running on B5 fuels as this blend does not require any labelling to comply with vehicle manufacturers' policies. Biodiesel fuels used in Australia should comply with the Australian version of biodiesel fuel quality standards which are assessed and updated regularly by the relevant authorities of the Australian Government [194].

4.1.7.1 GC-MS (Gas Chromatography and Mass Spectrometry) Analyses of Biodiesel

GC-MS analyses gives the fatty acid methyl ester (FAME) compositions of the biodiesel. The test is performed following EN14103 standard [295, 296]. In Addition, ASTM E2997-16 standards can be also applied to analyse the FAME composition within a biodiesel fuel sample [297]. Table 4-2 presents the detailed operating conditions to conduct the GC-MS analysis. The sample is prepared by weighing about 100 mg (\pm 10 mg) biodiesel in a 10 ml screw cap vial and mixing with 2.0 ml methyl heptadecanoate solution. The internal standard solution was methyl heptadecanoate. 1µL volume of sample was injected into the GC column (HP-INNO Wax) and the carrier gas was helium (He) at 83 kPa. The temperature profile was managed as described in the Table 4-2. Once the area and FAME contents are identified the weight percentage of FAME compounds (%C) in the biodiesel were determined by following the formula in equation.

$$\%C = \frac{(\sum A - A_{mhd})}{A_{mhd}} \times \frac{(C_{mhd} \times V_{mhd})}{m} \times 100 \dots (Eq. 4.1h)$$

Where, $\sum A$ is the total peak area of the detected methyl esters,

 A_{mhd} is the peak area of the methyl heptadecanoate,

 C_{mhd} is the concentration of methyl heptadecanoate solution,

 V_{mhd} is the volume of methyl heptadecanoate solution used, and,

m is the mass of sampel used.

Table 4-2 Detailed operating parameters of the GC-MS analysis

Parameters	Specification
Carrier gas	Helium, 83 kPa
Injector	Split/Split less 1177, full FEC control
Temperature	250 °C
Linear velocity	24.4 cm/sec
Injection volume	1 μL
Column	HP-INNO Wax (crossed-linked PEG), 0.32 mm \times 30 mm, 0.25 μm
Column 2 flow	Helium at 1 mL per min. constant flow
Oven	210 °C isothermal
Column temperature	First 2 minutes at 60 °C. Then 10 °C/minute until 200 °C. Then 5 °C/minute until 240 °C. Then hold at 240 °C for 7 min.
Split flow	100 mL/min
Detector	250 °C, FID, full EFC control

Since GC-MS provides the exact amount of FAME present within the biodiesel, the yield of FAME from the oil that underwent transesterification process can be determined by the following formula:

$$Y_{Biodiesel} = (\Sigma \% C) \times \frac{W_{biodiesel}}{W_{oil}} = (\Sigma \% C) \times (CE) \dots (Eq. 4.1i)$$

Here, $Y_{Biodiesel}$ is the yield percentage of biodiesel. $W_{biodiesel}$ is the quantity of biodiesel obtained, and W_{oil} is the quantity of oil.

The detailed quantification of FAMEs available within a biodiesel can help determining other properties of the biodiesel based on available correlations. Several correlations used are as follows **[298-301]**:

Saponification number,
$$SN = \sum \left(\frac{560 \times A_i}{M_{wi}}\right)$$
 (Eq. 4.1j)

Iodine value,
$$IV = \sum \left(\frac{254 \times N_{double \ bond} \times A_i}{M_{wi}}\right)$$
 (Eq. 4.1k)

Cetane number,
$$CN = 46.3 + \left(\frac{5458}{SN}\right) - (0.0225 \times IV)$$
 (Eq. 4.11)

4.2 Optimisation of Biodiesel Production

The kinetic parameters of a chemical reaction show the rate at which the reaction takes place. They also show the effectiveness of the variables (nature, phase and concentration of the reactants, temperature, types of catalysts, and pressure, etc.) which govern the reaction along with the detailed reaction mechanism (such as the reaction order) [302]. Usually, the reaction kinetics give the information about the required energy to initiate the reaction as well as the required time to reach to equilibrium. Based on recent research findings, it can be observed that there has been a development of esterification kinetic models for both homogeneous and heterogeneous catalysts, and non-catalytic or supercritical conditions [303]. The system of chemical kinetic determination is a nonlinear process and there are available nonlinear regression models in the statistical system to help solving such real time problems [304, 305]. On the other hand, determination of the optimal process development for efficient yield output is essential. In the conventional biodiesel production process, the dependent variable is the yield of the reaction, whereas, the independent variables are the quantity of alcohol, catalyst loading, temperature, and the duration of the reaction. When a wide range of such independent variables are selected and varied to analyse and determine the optimal reaction condition, the statistical analysis renders better analysis than those performed in a conventional optimisation system [34, 35, 306, 307]. Since the feedstock cost is the biggest portion of the biodiesel production cost, it is essential to determine an optimal process design to get highest possible yield of the process output without any loss of efficiency. Response surface methodology (RSM) is one of the effective and convenient statistical analysis method to analyse large variations of the independent variables over a dependent variable, investigating the mutual effectiveness of the variables and determine the optimal reaction condition for efficient mass production [308, 309].

In order to optimise the biodiesel production process, both the esterification and transesterification processes need to be optimised if a raw material contains higher amount of FFA. But if the FFA content is on favour of conducting only transesterification process, then the same transesterification optimisation process can be used. Besides, the reaction process kinetics and activation energy were determined from the optimised process parameters

obtained by response surface method (RSM) and analysis of variance (ANOVA) of individual process.

4.2.1 Kinetic Modelling of Esterification Process

Determining the reaction kinetics give an idea on how the reactants turn into the desired products following the certain reaction mechanism and learning about the rate of reaching into equilibrium state by the mixture of the reactants in the reaction [310]. Also, when the rate constant is determined, it gives an idea how the concentration of the reactants and the reaction parameters influence the rate of getting the products [311, 312]. In order to analyse the reaction kinetics, with the rate of reduction of the concentration of the reactants in addition to the reaction operation parameters, e.g. temperature, catalysts are determined [313]. Number of effective collisions among the reactants in a unit time period (frequency/ pre-exponential factor), reaction temperature, minimum energy required to make the intermolecular collisions effective (activation energy) to produce the product, etc. are the key concern of reaction kinetic modelling. In this study, the reaction kinetic modelling for both esterification and transesterification will be developed for various biodiesel feedstocks.

4.2.1.1 Mechanism of Acid –Esterification

In an acid-esterification reaction of any oil or fat substance, a heterogeneous chemical reaction takes place between the free fatty acids (FFA) of the oil or fat and the alcohol (predominantly, methanol- CH₃OH) in presence of a strong acid (for instance, sulphuric acid H₂SO₄) as homogeneous catalyst [**314**]. In absence of the acid catalyst, the esterification reaction occurs very slowly as if there is no reaction taking place [**315**]. Due to limited solubility of oil or fat with methanol, it is essential to stir (about 600 rpm) the mixture of methanol and oil well to avoid the dominance of mass transfer within the mixture [**316**].

The chemical reaction mechanism of the acid catalysed esterification can be explained as per the Fischer esterification mechanism [**317**] as in the Figure 4-5:



Figure 4-5 Fischer Esterification Mechanism [317, 318]

Here, Figure 4-5 schematically shows that the strong acid (e.g. H_2SO_4) catalyst donates a proton to protonate the carboxylic acid (FFA) at the beginning of the reaction. Then the carbonyl carbon is added with the nucleophilic alcohol and develop bonds with the SP² bonding. As a result, the alcoholic proton is sacrificed and a new ester bond is formed between the carbon from carbonyl group and oxygen from the alcohol. In the next stage, H_2O is formed and eliminated. At the last stage, the extra proton leaves the ester and regenerates the acid catalyst.

4.2.1.2 Kinetic Reaction Modelling of Acid-Catalysed Esterification

Oil (triglycerides) phase is nonpolar and the methanol (alcohol) is a polar compound. So, during the esterification process, these two different types of reactants react through a heterogeneous reaction system. In this case, there are two factors, hydrodynamic effect between two phases and the kinetics of the chemical reaction govern the total reaction rates [314]. In the esterification process, the hydrodynamic effect can be ignored as the faster mixing speed within the reactor reduces that effect within the reaction system [319]. But the kinetics of the chemical reaction system [319].

There is not much of information available about the esterification mechanism for the biodiesel production process in comparison to those of the control parameter-based publications about two stage processes for biodiesel production. But determination of kinetics of the esterification process can effectively help to find quantitative evaluation of the process

(i.e. effect of type of reactor, reaction system, catalysts, etc.) adopted for the esterification reaction [303]. The esterification process can be explained as a reversible heterogeneous process [315, 320-322], or pseudo-first order pseudo-heterogeneous process [314, 323, 324], pseudo-homogeneous second order reaction [325]or a pseudo-homogeneous process [323, 324]. In these distinctive processes the reaction orders are also determined along with reaction kinetic parameters. Among the available research articles, a few are presented here in the following subsections to determine the reaction kinetics for the considered fuels from their relevant esterification processes.

4.2.1.2.1 Kinetic Parameters for a Reversible Heterogeneous Process

To describe the kinetics of a reversible heterogeneous reaction, the assumptions of the kinetic model described by Berrios *et al.* **[315]** are followed as follows:

- The reaction process is a reversible *heterogeneous* process,
- Under the given operation conditions, the rate of the esterification process is controlled by the rates of the reversible heterogeneous process.
- The reaction rate of the acid catalysed reaction is so high that the non-catalysed reaction rate can be considered as negligible. The esterification reaction process does not occur if catalysts are not mixed.
- The esterification reaction process completely occurs within the oil phase.
- The concentration of the methanol used in the reaction is considered to be constant due to very high molar ratio rather than that of stoichiometric molar ratio with the reactant triglycerides.

Based on these assumptions, the reaction process has been defined as a *pseudo*-homogeneous process in which the forward reaction is characterised as first order and the reverse directional reaction is characterised as second order kinetic reaction [**314**, **315**]. As a result, the esterification reaction kinetics can be expressed as follows:

$$-\frac{d[A]}{dt} = K_1[A] - K_2[C][D] \dots (Eq. 4.2a)$$

Here, [A] is the acid value (mg KOH/g oil) (i.e. the concentration of FFA in oil);

[C] and [D] are the concentrations of fatty acid methyl ester (FAME) and water, respectively, which are generated due to the esterification reaction of FFA;

 K_1 and K_2 are the kinetic reaction constants for forward reaction and reverse reaction, respectively.

At the beginning of the reaction (time, t=0), the concentration of FAME [C] and water [D] are considered to be zero. Also, if A_0 denotes the initial FFA concentration and E BE the total amount of removed acidity from the reactant, then $A=(A_0-E)$ and C=D=E at any time t. As a result, the Eq. 4.2b can be presented as follows:

$$\frac{dE}{dt} = K_1(A_0 - E) - K_2 E^2 \dots (Eq. 4.2b)$$

Eq. 4.2b can be also expressed as follows:

$$\frac{dE}{K_1 A_0 - K_1 E - K_2 E^2} = dt \dots (Eq. 4.2c)$$

Integrating the above equation (Eq. 4.2c) based on the integral formula table as follows:

$$\int \frac{dx}{ax^2 + bx + c} = \frac{1}{\sqrt{b^2 - 4c}} ln \frac{[2ax + b - \sqrt{b^2 - 4c}]}{[2ax + b + \sqrt{b^2 - 4c}]} \dots (Eq. 4.2d)$$

Now, integrating Eq. 4.2d the following are obtained:

$$2K_2. \alpha. t = \ln \frac{|A_0 + E.(\beta - \frac{1}{2})|}{|A_0 - E.(\beta + \frac{1}{2})|} \dots (Eq. 4.2e)$$

Here,
$$\alpha = \sqrt{\left(\frac{K^2}{4}\right) + K} A_0$$
(Eq. 4.2f)

And,
$$\beta = \frac{\alpha}{K}$$
, $K = \frac{K_1}{K_2}$(Eq. 4.2g)

Here, with the given operation conditions of the esterification reaction (i.e. methanol to oil ratio, temperature, acid catalyst's concentration and the reaction period), only the parameters A_0 , E and t are known for the Eq. 4.2e. To obtain the other parameters, trial and error based numerical analysis can be performed. In this study, a non-linear regression analysis was performed to obtain the possible solution and to determine the other parameters the numerical solution process of Levenberg-Marquardt (L-M) algorithm was followed [**304**].

Eq. 4.2e can also be expressed as a function of time as follows for a given reaction condition:

$$E = \frac{A_0(e^{2K_2.\alpha t} - 1)}{\beta(1 + e^{2K_2.\alpha t}) + 0.5(e^{2K_2.\alpha t} - 1)} \dots (Eq. 4.2h)$$

The feasibility of a reaction is determined from the thermodynamic parameters. The influence of temperature on the specific reaction rate was determined by fitting K_1 and K_2 to the Arrhenius equation,

 $K = A_f \cdot e^{\left[-\frac{E_a}{RT}\right]} \dots (Eq. 4.3a)$

Here, A_f = frequency parameter of the reaction (min⁻¹),

 $R = 8.314 \text{ jmol}^{-1} \text{k}^{-1}$ (universal gas constant),

and T = reaction temperature (K).

Therefore, the Eq. 4.3a can be rewritten as follows:

$$K_1 = A_{f1} \cdot e^{\left[-\frac{E_{a_1}}{RT}\right]}$$
.....(Eq. 4.3b)
 $K_2 = A_{f2} \cdot e^{\left[-\frac{E_{a_2}}{RT}\right]}$(Eq. 4.3c)

Thus, the reaction rate (Eq. 4.2b) for esterification process can be expressed as follows:

$$-\frac{d[A]}{dt} = \frac{dE}{dt} = K_1(A_0 - E) - K_2E^2 = A_{f1} \cdot e^{\left[-\frac{E_{a_1}}{RT}\right]}(A_0 - E) - A_{f2} \cdot e^{\left[-\frac{E_{a_2}}{RT}\right]}E^2 \dots (Eq. 4.2i)$$

4.2.1.2.2 Kinetic Parameters for a Pseudo-homogeneous Irreversible Process [323, 324]

The kinetic modelling for the pseudo-homogeneous irreversible process has been described as per the cited articles from [323, 324].

The overall reaction rate of an esterification process involving reversible reaction can be expressed as follows:

$$R_{1}-COOH + R_{2}-OH \stackrel{H_{2}SO_{4}}{\longleftrightarrow} R_{1}-COO-R_{2} + H_{2}O....(Eq. 4.4a)$$

The reaction rate, $r_A = k_1 C_A^a C_B^b - k_2 C_{ME}^e C_W^w$ (Eq. 4.4b)

Here, C_A, C_B, C_{ME}, C_W are the molar concentrations of the FFA, Methanol (i.e. alcohol), Methyl Ester and Water molecules, respectively.

The superscripts, a, b, e, and w are the orders for the reaction with respect to the molecules C_A , C_B , C_{ME} , and C_W , respectively. Besides, k_1 and k_2 are the rate constants for the forward and reverse reactions, respectively.

Assumptions for the pseudo-homogeneous reactions [323, 324] are as follows:

- Excessive methanol dominates the reaction rate to be driven towards the product side only. So, the reversible reaction rate could be considered as negligible.
- Higher molar ratio of methanol to triglycerides indicates that the change of methanol due to the esterification reaction of the available FFA in the triglycerides can be considered as constant in a batch reactor.
- Thus, the overall reaction is considered to be a constant density and constant volume reaction system.

Based on these assumptions, the reaction rate equation (Eq. 4.4b) can be expressed as follows:

Here, k is the reaction rate constant and n is the reaction order.

In a constant density and constant volume batch reactor, considering x be the fraction of FFA removed and C_{A0} be the initial constant of the FFA, the available FFA concentration at any time t can be expressed as,

$$C_A = C_{A0}(1-x)$$
 (Eq. 4.4d)

Then, the (Eq. 5.4c) can be expressed as follows:

$$r_A = -\frac{dC_A}{dt} = -\frac{d[C_{A0}(1-x)]}{dt} = k[C_{A0}(1-x)]^n \dots (Eq. 4.4e)$$

Now (Eq. 4.4e) => $\frac{dx}{dt} = {\binom{k}{C_{A0}} [C_{A0}(1-x)]^n} = k' [C_{A0}(1-x)]^n$(Eq. 4.4f)

Here,
$$k' = \frac{k}{C_{A0}} = \text{constant}$$

Now, the following expression can be obtained by using logarithm on both sides of the Eq. 4.4f:

$$\ln\left(\frac{dx}{dt}\right) = n\ln[\mathsf{C}_{\mathsf{A0}}(1-\mathsf{x})] + \ln k' \dots (\mathsf{Eq.}\ 4.4\mathsf{g})$$

Or, in another way, calculating logarithm on (Eq. 4.4e), it can be expressed as follows:

$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + n \ln[C_{A0}(1-x)] \dots (Eq. 4.4h)$$

Here, to determine the parameters n, and k, a linear relationship occurs if a plot between $\ln(\frac{dx}{dt})$ and $\ln[C_{A0}(1-x)]$ is plotted as per the studies of the experimental data. As a result, (Eq. 4.4g) can be compared with the following empirical straight-line equation:

Here, (Eq. 4.4i) indicates the straight line with tangent m and intercept c.

Hence, the comparison between (Eq. 4.4i) and (Eq. 4.4g) can be performed to determine the values of 'n' and 'k' accordingly.

Similarly, (Eq. 4.4i) and (Eq. 4.4h) can be also used to determine the values of k and n.

Also, the value of k determined from (Eq. 4.4g) at a constant methanol to oil ratio, catalyst ratio, and time, but different temperature values can be put in the logarithm form of Arrhenius equation (Eq. 4.3a), then the expression of Arrhenius equation becomes.

$$\ln k = \ln A_f + \left(-\frac{E_a}{R}\right)\frac{1}{T} \dots (\text{Eq. 4.3d})$$

When the different k values are plotted against different T values, a straight line can be obtained for the ln(k) vs 1/T relation in (Eq. 4.3d). As a result, the values of A_f and E_a are determined respectively for the considered reaction process.

Hence, the overall reaction rate and order of a pseudo-homogeneous reaction [323, 324] can be expressed as follows:

$$r_A = -\frac{dC_A}{dt} = C_{A0} \frac{dx}{dt} = A_f \cdot e^{\left[-\frac{E_A}{RT}\right]} [C_{A0}(1-x)]^n \dots (Eq. 4.4j)$$

4.2.1.2.3 Kinetic parameters for a second order pseudo-homogeneous irreversible process

In case of a pseudo-homogeneous esterification reaction that follows a second order (i.e. n=2) reaction rate [325], reaction rate determined in the (Eq. 4.4f) can be expressed as follows:

$$r_A = -\frac{dC_A}{dt} = -\frac{d[C_{A0}(1-x)]}{dt} = C_{A0}\frac{dx}{dt} = k[C_{A0}(1-x)]^2 \dots (Eq. 4.5a)$$

Here, x is considered to be the fraction of FFA removed, and C_{A0} is initial FFA concentration.

Then the (Eq. 4.5a) can be rewritten as follows:

$$\frac{dx}{dt} = kC_{A0}(1-x)^2 = k'(1-x)^2 \dots (Eq. 4.5b)$$

Here, $k' = kC_{A0}$ =constant.

Now, the reaction rate constant can be determined from the plot between $\frac{dx}{dt}$ and $(1 - x)^2$, where the slope of the lines are the reaction constants.

Thus, the overall reaction rate can be expressed as follows:

$$r_A = -\frac{dC_A}{dt} = C_{A0} \frac{dx}{dt} = A_f \cdot e^{\left[-\frac{E_a}{RT}\right]} [C_{A0}(1-x)]^2 \dots (Eq. 4.5c)$$

4.2.1.2.4 Determination of reaction kinetics when the esterification process is pseudohomogeneous first order irreversible reaction process

When both the methanol and oil are mixed together with a sufficient mixing process, then the hydrodynamic effect on the reaction rate can be eliminated **[314]**. The esterification process may occur in the methanol phase as the acid catalyst is available within the methanol phase. So, the FFA has to be moved from the oil phase and pass through the oil/methanol liquid/liquid interface (Figure 4.6) (from **[326]** as cited in **[314]**).



Figure 4-6 Schematic explanation of mass transfer of FFA from oil phase to methanol phase as per two-film theory (modified from **[314]**)

However, the esterification process is an instantaneous process which results the reaction between methanol and FFA to occur at the oil-methanol interphase **[326]**. So, the mass flow resistance of FFA will take place within the oil phase. The flow rate of FFA to overcome the oil phase resistance and react with the methanol at the interphase can be expressed as follows (Eq. 54.6a):

$$F_{FFA} = -r_{FFA}V_R = k_{FFA-o}a(C_{FFA-o} - C^*_{FFA-i})V_R$$
(Eq. 4.6a)

Here, V_R is reaction volume, r_{FFA} is the mass transfer rate of FFA to the interface, a = reaction order of FFA, and k_{FFA-o} is the mass transfer rate coefficient of FFA.

So, overall reaction rate at the interface can be expressed as follows (Eq. 4.6b):

$$-r_R = k_R C_{FFA-i}^{*a} C_{Al}^{b}$$
 (Eq. 4.6b)

Here, r_R is the overall reaction rate, k_R is the reaction rate constant, a and b are the reaction orders for with respect to the C^*_{FFA-i} and C_{Al-I} , respectively.

Since excessive methanol has been used to conduct this reaction, the concentration of methanol remains almost constant. So, considering $k_s = k_R C_{Al}^b$, Eq. 4.6b can be expressed as follows:

$$-r_R = k_s C_{FFA-i}^{*a} \dots (Eq. 4.6c)$$

Here, $k_s = pseudo-rate constant$.

So, the flow rate of FFA at the interface should be as follows:

$$F_{FFA} = -r_{FFA}V_R = k_s C_{FFA-i}^{*a}V_R \dots (Eq. 4.6d)$$

Zhou [314], along with Sendzikiene *et al.* [327], Kocsisová *et al.* [328], and Cardoso *et al.* [329] have mentioned that the esterification reaction can be directly considered as a first order reaction due to the presence of excessive methanol in the reaction system.

So, combining (Eq. 4.6a) and (Eq. 4.6d), we obtain the following expression,

$$C_{FFA-o} = \frac{F_{FFA}}{V_R} \left(\frac{1}{k_{FFA-o}a} + \frac{1}{k_s} \right) \dots (Eq. 4.6e)$$

Rearranging (Eq. 4.6e), the following overall reaction rate of esterification process can be obtained,

$$\frac{F_{FFA}}{V_R} = -r = \left(\frac{1}{\frac{1}{k_{FFA-o}a} + \frac{1}{k_s}}\right) C_{FFA-o} \qquad (Eq. 4.6f)$$

Here, (Eq. 4.6f) is an expression of pseudo first order reaction, where the FFA quantity affect the overall reaction rate in the oil phase. The overall reaction rate is also affected by the mass transfer resistance in the oil film and the chemical reaction rate in the oil phase.

To simplify, due to constant high stirring mixing speed between alcohol and triglycerides the hydrodynamic effect is considered as negligible and it can be ignored. Therefore, the mass transfer resistance effect can be neglected in the (Eq. 4.6f). Thus, the equation is simplified as follows:

$$-r = \frac{dC_A}{dt} = k_s C_{FFA-o} = k_s C_A \quad \dots \quad (\text{Eq. 4.6g})$$

Here, due to esterification reaction in the oil phase only, the concentration of FFA at any time in the oil phase is considered as $C_A=C_{FF-o.}$ Also, k_s is the overall first order reaction rate constant.

So, integrating (Eq. 4.6g), the following first order reaction rate expression can be obtained,

$$\ln\left(\frac{c_{A0}}{c_A}\right) = k_s t \dots (Eq. 4.6h)$$

Here, C_{A0} is the initial concentration of FFA and C_A is the concentration of FFA at time t. Hence, the reaction rate constant k_s can be obtained from the plot between $\ln\left(\frac{C_{A0}}{c_A}\right)$ and t. Once the various values of k_s is obtained at various temperatures, the values can be put in the logarithmic form of Arrhenius equation (Eq. 4.3d) to determine the values of activation energy and frequency factor for that particular reaction process.

4.2.1.3 Optimal Reaction Condition Determination for Acid-Catalysed Esterification Process

4.2.1.3.1 Design of Experiment and Optimisation Method

Esterification is one of the critical pre-treatment processes to purify the triglycerides before transesterification process in order to produce biodiesel. The better the esterification process, the lesser existence of FFA in the triglycerides. The ultimate benefit of the esterification process is to ensure better yield efficiency of the transesterification process. The operation parameters, i.e. methanol to oil ratio, reaction temperature, quantity of acid catalyst, and duration of esterification process, etc. are to be set in the best possible way to convert FFA into respective fatty acid esters of the triglycerides.

To determine the optimal reaction condition for conventional batch reactor type esterification process, a number of distinct esterification and transesterification reactions were performed from the set of the following experimental conditions. The heterogenous mixture needed very good stirring, which was performed by a magnetic stirrer (usual mixing speed was 600 rpm).

4.2.1.3.2 Reaction Kinetics Determination Based on Optimal Parameters

A statistical optimisation model (Box-Behnken model) was chosen to determine the required distribution of parameters. The Statistical software Minitab 18.0 was used to perform Response Surface Methodology (RSM) analysis to obtain the optimal process operation parameters. The mixing speed was constant for all operation conditions. The optimisation process was performed before determining the kinetic parameters for the esterification process. It was found to be a good idea to determine the optimal process operation parameters before determination of kinetics for reactions to avoid clumsiness in the overall system analysis. Once the RSM analysis provides the optimal parameters, the reaction conditions were set to the nearest possible conditions to conduct the experiments for kinetic parameter determination. To

obtain the reaction frequency parameters and activation energy of the chemical reaction process, the kinetic constant was determined for various temperature conditions by keeping the other operating conditions constant at their individual optimal status. In this stage, necessary regression plot studies and non-linear regression analyses were performed to determine the parameters for the system.

Several more assumptions were made to simplify the reaction kinetics.

- All of the FFA contained within the sample oil/fat was converted into biodiesel.
- Hydrodynamic effect was ignored due to negligible contribution.
- The overall reaction rate is impacted by the FFA concentration within oil bulk, the mass transfer resistance of FFA within oil film and the chemical reaction rate.

In this study, the predicted yield values from the Box-Behnken model for response surface analysis were fitted under the quadratic equation model as follows (Eq. 4.7a).

$$Y = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 + a_4 x_4 + a_{11} x_1^2 + a_{22} x_2^2 + a_{33} x_3^2 + a_{44} x_4^2 + a_{12} x_{12} + a_{13} x_{13} + a_{14} x_{14} + a_{23} x_{23} + a_{24} x_{24} + a_{34} x_{34} \dots$$
(Eq. 4.7a)

Here, Y is the yield of the analysis, known as predicted value. The subordinate values 1, 2, 3, 4 indicate the 4 individual parameters in the model, 'x' is the variable parameters and 'a' is the corresponding term's coefficient.

Besides, analysis of variance (ANOVA) was performed for the set of data used for RSM analysis in order to determine the significance level of the parameters and their mutual interactions within the 95% confidence interval. The P-value in the ANOVA table shows significance level of influence of that particular parameter to the yield value. If P<0.05 for any parameter, then the parameter is a significant one in the model for prediction through RSM analysis. Then the RSM analysis was further analysed to determine the optimal yield condition. Once the optimal values were determined, the kinetic parameters were determined for the reaction process.

4.2.2 Process Optimisation and Kinetics of Transesterification

4.2.2.1 RSM Analysis and Process Optimisation

Either esterified oil or low FFA containing oil without esterification undergo transesterification process to produce biodiesel. Total of m factors and n levels were considered with the Box-Behnken model to conduct the statistical investigation on the experimental results for the purpose of optimisation through response surface methodology (RSM). To do this, statistical analyses software Minitab 18.0 was used. The quadratic model equation for the process yield of the transesterification process was considered to be similar to Eq. 4.7a as mentioned for the esterification process.

Once the RSM analysis was performed, the ANOVA table was investigated to check the significant contribution of the considered parameters in the predicted yield. Then the model was analysed to determine the parametric conditions for optimal yield of biodiesel from the transesterification process.

4.2.2.2 Models Used to Determine the Kinetic Parameters for the Transesterification Process

It is essential to understand the reaction mechanism of transesterification process to determine the kinetics of the process. As per the stoichiometry of transesterification process, one molar fat or oil (Triglycerides, TG) reacts with 3M methanol (CH₃OH, MeOH) in the presence of alkali catalyst (e.g. NaOH, KOH) to produce 3M fatty acid methyl esters (RCOOCH₃, FAME) and glycerols. This is a reversible chemical reaction and in actual practice, extra methanol is used to avoid the loss of the process efficiency due to reverse reaction effect. The process reaction (stoichiometric) can be presented as follows (Eq. 4.8a):

$$TG + 3MeOH \stackrel{NaOH,heat}{\longleftrightarrow} 3RCOOCH_3 + Glycerol$$
(Eq. 4.8a)

In fact, transesterification process is a combination of three steps of reaction mechanisms **[330]**. In each of the steps, a certain amount of fatty acid methyl ester (FAME) is produced along with the decomposed glycerides. In the first step, the triglycerides (TG) are converted into diglycerides (DG) reacting with a stoichiometric quantity of 1M methanol (MeoH), then another mole of MeOH is used to convert the DG into monoglycerides (MG) along with FAME in the second step, and in the third step, another mole of MeOH is used to convert the MG into glycerols (G) and FAME. The reaction steps can be presented as follows:

First step:
$$TG + MeOH \xleftarrow{catalyst,heat}{\longrightarrow} DG + R_1COOCH_3$$
.....(Eq. 4.8b)

Second step:
$$DG + MeOH \xleftarrow{catalyst,heat} MG + R_2COOCH_3$$
(Eq. 4.8c)

Third step:
$$MG + MeOH \xleftarrow{catalyst,heat} G + R_3COOCH_3$$
(Eq. 4.8d)

Due to excessive use of methanol in a batch reactor system, all of these above mentioned three steps (Eq. 4.8b-d) for transesterification processes can be considered as irreversible first order reactions (indeed, a pseudo-first order irreversible reaction) [330]. If the parameters k_1 , k_2 and k_3 are considered as the reaction constants for each of the steps respectively, then the reaction rates can be presented as follows [330]:

For first step:
$$\frac{dC_{TG}}{dt} = -k_1 C_{TG} C_{MeOH} \dots (Eq. 4.8e)$$

For second step:
$$\frac{dC_{DG}}{dt} = k_1 C_{TG} C_{MeOH} + k_2 C_{DG} C_{MeOH} \quad \dots \quad (Eq. 4.8f)$$

Determination of quantity of FAME produced in each of the three steps needs a very efficient chromatographic experimental analysis to determine the quantity of methyl ester and other products. Due to limited accessibility with the chromatography analysis facilities, the stepwise rate determination methodology was not adopted in this study.

Due to excessive use of methanol in a batch reactor system, all of these above mentioned three steps can be considered as irreversible first order reaction [330]. Figure 4-7 shows the steps of transesterification process mechanisms schematically.



Figure 4-7 Stepwise reactions occurred in transesterification process [270]

Then the reaction rate "r" for this shunt reaction can be presented by the rate of decay of TG with time and the reaction rate equation can be presented as follows in Eq. 4.8h:

$$r = -\frac{dC_{TG}}{dt} = kC_{TG}^m C_{MeOH}^n = k_1 C_{TG}^m$$
(Eq. 4.8h)

Here, k is the reaction rate constant, $k_1=kC_{MeOH}$ is the overall apparent reaction rate constant, C_{TG} is the molar concentration of triglycerides, C_{MeOH} is the molar concentration of methanol, m and n are the reaction orders from respective ingredients in the reaction.

Considering the use of very high amount of methanol than that of the stoichiometry indicates, the molar concentration of the methanol can turn into a constant parameter. Also, the transesterification process reaction is considered as an irreversible first order reaction [287, 288, 319, 331], the rate constant can be rewritten as follows:

$$r = -\frac{dC_{TG}}{dt} = k_1 C_{TG}$$
 (Eq. 4.8i)

Even though Andreo-Martínez *et al.* **[302]** presented the rate equations for transesterification process as pseudo-zero order, pseudo-first order and pseudo-second order reactions, they only explained the pseudo first order reaction kinetics to describe their results in the publication.

Also, during the transesterification process within a batch reactor, the mixture is a combination of converted methyl esters (ME) and unmethyl ester (uME) [286]. In general, the uME is the mixture of glycerides – TG, DG, MG and unreacted FFA. Therefore, the overall reaction process at any time, t, can be expressed as follows (Eq. 4.8j):

 $uME + xMeOH \xrightarrow{k} G + xME$ (Eq. 4.8j)

Then the transesterification process reaction rate can be written as,

$$r = -\frac{dC_{uME}}{dt} = k_1 C_{uME} \dots (Eq. 4.8k)$$

Integrating (Eq. 4.8i) with respect to t, we get,

 $-lnC_{TG,t} + lnC_{TG,0} = k_1 t....$ (Eq. 4.81)

Here, C_{TG,0} and C_{TG,t} are the molar concentration of TG at time t=0 and t=t respectively.

Similarly, (Eq. 4.8k) can be rewritten as follows:

$$-lnC_{uME,t} + lnC_{uME,0} = k_1t....$$
 (Eq. 4.8m)

When x is considered as a fractional conversion entity of methyl ester in the batch reactor, we get,

 $C_{uME,t} = C_{uME,0}(1-x)$ (Eq. 4.8n)

Hence the (Eq. 4.81) can be written as follows:

$$\ln(1-x) = -k_1 t$$
, or $-\ln(1-x) = k_1 t$ (Eq. 4.80)

Based on experimental results, a graphical plot can be depicted between " $-\ln(1-x)$ " and "t" in order to determine the value of reaction rate constant k_1 at given operation conditions. Then, the values of k_1 at various temperature can be plotted against 1/T to compare against the logarithmic form of the Arrhenius equation (Eq. 4.3d) to obtain the values of A_f and Ea. Thus,

the overall reaction rate (kinetic model of transesterification process) can be expressed as follows:

$$r = -\frac{dC_{TG}}{dt} = k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG}$$
(Eq. 4.8p)

4.3 Concluding Remarks

Experimental steps of the biodiesel production process, pre-treatment, and post-treatment of the respective compounds, which have been discussed in this chapter are relevant to the experiments conducted in this study. Detailed procedures of moisture removal, FFA level determination, selection of acidic catalyst (H₂SO₄) for esterification, and alkali catalysts (NaOH and KOH) for transesterification reactions in the batch reactor system and further refinement processes are presented, which were used throughout this study in order to produce biodiesel fuels from various feedstocks. Besides, optimisation and reaction kinetic modelling for biodiesel production processes (esterification and transesterification) for each of the feedstocks are presented briefly. Chapter 5 presents the analysis for biodiesel production process optimisation and determination of reaction kinetic models for considered feedstocks based on the information provided in this chapter.

Chapter 5

BIODIESEL PRODUCTION PROCESS OPTIMISATION AND DEVELOPMENT OF REACTION KINETIC MODELS

5.0 Introduction

Experimental results of both optimal esterification and transesterification reaction process parameters are presented in this chapter. Followed by the optimisation processes, reaction kinetic models for each of the esterification and transesterification processes are also developed. There are altogether six feedstocks, namely, tallow, castor oil, waste cooking oil, poppy, sunflower and canola, which are processed to produce biodiesel through optimisation of the respective processes. Later, reaction kinetics of the each of these fuels are also developed. Indeed, only detail procedures of the tallow biodiesel production, optimisation and kinetic modelling are presented in this chapter. Due to process similarities, only the summarised results for the rest of the fuels are presented. Finally, this chapter presents few of the key fuel characteristics which are determined for the studied fuels.

5.1 Biodiesel Production from Beef Tallow (WTB)

Beef tallow is one of the key animal fat-based resources to produce biodiesel. Mainly the high free fatty acid (FFA) containing inedible tallow portion of the overall tallow production from beef processing industries are considered as feedstock for this purpose and it can be considered as one of the effective and economical ways of waste management in the meat industry [**332**, **333**]. Biodiesel produced from the animal fat generally possesses higher cetane number (CN). Besides, the cold flow properties of the pure biodiesel (100%) are unfavourable to be used in the internal combustion engines (ICE) during winter seasons and in the cold climate countries [**334**, **335**]. Due to higher FFA content in the beef tallow, the conversion process of tallow into biodiesel requires two stages, i.e. acid-catalysed esterification, and alkalicatalysed transesterification to increase the conversion efficiency. The efficiency of FFA removal mainly depend on the amount of acid catalyst used in the reaction, which indicates that the higher the FFA the more acid catalyst should be required [**336**, **337**]. Chuah *et al.* [**336**] demonstrated succinctly that the two varieties of Rubber seed oil (RSO) having 23.2% and 42.5% of FFA required about 1.38 wt.% and 10.74 wt.% H₂SO₄, respectively to remove

optimal amount of FFA from the respective oil feedstock. The other factors which influence the efficiency of esterification process are molar ratio between oil and methanol, reaction temperature and reaction period, accordingly [**336**]. Chai *et al.* [**337**] have mentioned necessity of determining the optimal amount of acid catalyst based on the particular feedstock's FFA content, oil-to-methanol molar ratio, reaction temperature and period in the laboratory prior to the industrial processing. Encinar *et al.* [**334**] conducted acid-catalysed esterification (0.5 wt.% H₂SO₄, 18:1 methanol to oil, 65 °C, 4h reaction time) to reduce the high FFA content from the beef tallow followed by base-catalysed transesterification (1.5 wt.% KOH, 6:1 methanol to esterified fats molar ratio, 65 °C and 2 h of reaction time) for biodiesel production. They obtained 0.35 mg KOH/g of acid value after esterification and consequently 93.8% biodiesel yield efficiency in a conventional batch reactor system.

On the other hand, a direct transesterification reaction (1h preheating at 105-110 °C, cool down to 60 °C, 6:1 methanol to tallow, 0.5 wt.% NaOH, 3h reaction time) of tallow was performed by Öner & Altun [338] but they have not reported any level of yield efficiency. Peng-Lim *et al.*[339] mentioned that the presence of moisture and higher FFA content are the two negative factors for a feedstock to yield lesser amount of yield along with saponification loss of the feedstocks during homogeneous base-catalyst transesterification. Moreover, Ma *et al.* [340] mentioned that the transesterification of beef tallow is favoured by the NaOH and the FFA level should be less than 0.5% (w/w) along with moisture content be below 0.06% (w/w) of the tallow feedstock quantity to perform the reaction process efficiently. Indeed, if there is higher FFA and moisture the higher dose of base catalysts causes loss of yield efficiency (as soap) and increase in viscosity of the biodiesel [341, 342]. So, purity in the form of lesser FFA and moisture content is the key factor to determine the required amount of base catalyst in the optimisation of biodiesel production of the respective feedstocks [343, 344].

Heterogeneous catalysts systems for both the acid-esterification and basetransesterification processes have also been favoured by researchers. Peng-Lim *et al.* [339] conducted sequential esterification (0.16:1 ferric-alginate beads to lauric acid mass ratio, 15M:1M methanol to lauric acid, 65 °C, reaction period 3h) and transesterification (CaO-boiler ash mix, 15M:1M methanol to oil, 65 °C, and 0.5h of reaction period) process for high FFA oil (mixture of lauric acid and palm olein) with varying FFA level and obtained about 98% yield efficiency. Xinyu *et al.* [345] conducted transesterification of beef tallow with solid catalyst Cs_2O/γ -Al₂O₃ and they obtained the optimal conditions of the reaction process parameters with response surface (RSM) technology as 10.5:1 molar ratio between methanol and tallow, 5.3 wt.% of catalyst, 66 °C and 120 minutes of reaction period. The optimal process yielded about 95.6% of biodiesel from the single stage process.

Conversion of biodiesel from beef tallow does not compete with the food supply chain system. Rather, it economically helps the meat industry to get rid of their wastes in an environment friendly way. In this study, two stage conventional batch reactor-based biodiesel production system (acid-esterification and base-transesterification) was considered and both the systems were analysed statistically with the help of RSM to determine the optimal reaction conditions. The optimal conditions were used to determine the reaction kinetics for both the esterification and transesterification processes.

5.1.1 Methodologies for Esterification and Transesterification Processes of Beef Tallow

Before esterification reaction, the solid tallow was melted and the molten fat was heated at a temperature of 110 °C for 1 hour to remove moisture in the tallow. Once the liquefied tallow temperature cooled down to 50 °C, it was filtered and put in the reactor for esterification reaction. When the tallow temperature reached at a particular reaction temperature, methanol was mixed and the temperature drop was observed. Vigorous mixing was assured with a magnetic stirring rod by maintaining mixing speed of 600-650 rpm so that a well-developed vortex could be seen for the methanol-tallow mixture. Once the mixture temperature reached to the set temperature, designed amount of sulphuric acid was mixed in the reactor. Reaction period was recorded and intermittent samples (10ml-15ml) were taken out from the reactor after various time intervals. The samples were cooled off and later used for determination of acid values (i.e. FFA level). When the reaction was completed, the liquid mixture was put in a separating funnel for 8-12 hours to settle down. After settling down, the esterified oil was collected and dried again at 110 °C for half an hour to remove both remainder of the methanol as well as moisture.

For transesterification reaction, the dried esterified oil was taken in the reactor and heated up to desired temperature. While the oil was being heated, NaOH was dissolved in methanol in another beaker with the magnetic stirrer. For convenience, the methanol-NaOH mixture was heated up to the level of reaction temperature. After mixing methanol-NaOH with hot esterified oil, the reaction time was recorded and the yield mixture was put in a separating funnel to settle down. After 8-12 hours of settling time, the glycerine and other impurities were removed from the bottom, washed with warm water, and then dried again at 110 °C for 1 hour. Then the dried biodiesel was centrifuged to remove any further impurities. Once the biodiesel was obtained, a sample amount was labelled to determine the characteristics of the fuel and to conduct experimental works.

5.1.2 Optimisation and Kinetic Modelling of Esterification Process of Beef Tallow

5.1.2.1 Design for Optimal Esterification Reaction Experiments

To determine the optimal reaction condition for conventional batch reactor type esterification process, a number of distinct esterification reactions were performed from the set of the following experimental conditions in Table 5-1.

	Table 5-1 Ex	perimental	conditions	for the	acid-cat	alysed	esterification	reactions	of Tallor
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 Experimental Parameters	Conditions or Range
FFA (%)	4.9%
Acid value (AV, mg KOH/g)	9.82
Methanol (M): Oil (M)	6M:1M, 9M:1M, 12M:1M
H2SO4 (%wt./wt. of oil)	1%, 2%, 3%
Reaction temperature (K)	328K, 333K, 338K
Reaction temperature (^O C)	55 °C, 60 °C, 65 °C
Stirring speed of the chemical reactions	600 rpm with magnetic stirrer
 Reaction period (time in minutes)	60, 90, 120

5.1.2.2 Esterification Process Optimisation

The design of four-factors and three-levels $(4m \times 3n)$ Box-Behnken (BB) model is shown in the Table 5-2. The model was designed with 2 replicates that required 54 sampling experiments. Both the coded and un-coded values for all these 54 samples are presented (Table 5-3). Besides, the predicted values of acidity removed (%) are presented along with the experimentally (titration method) derived acidity removal in the Table 5-3. Due to double replicate model analysis, the optimisation result can be considered as sustainable with repeatability for the given operating conditions. The results varied from 71.9% acidity removal to maximum of 97.9% of acidity removal with the adopted experimental conditions. However, the predicted results show 71.9% minimum acidity removal at a different condition than that for experimentally derived minimum acidity removal. But the maximum predicted acidity removal of 98.2% was found with the similar conditions to that of the experimentally obtained maximum acidity removal conditions.

Operation Parameters	Unit	Symbol	Range	Range and coded leve		
			-1	0	+1	
Methanol: Oil	M/M	М	6	9	12	
Acid Catalyst (H ₂ SO ₄)	wt.%	А	1	2	3	
Temperature	⁰ C	Т	55	60	65	
 Time	minutes	D	60	90	120	

Table 5-2 Coded and un-coded values of levels and factors for BB design model (Tallow esterification)

Table 5-3 RSM analysis of esterification process with percentile quantity of experimental	and
predicted acidity removal	

Run	Blk	М	A	Т	D	Methanol: Oil (M/M)	H ₂ SO ₄ (wt.%)	Temperature (⁰ C)	Time (minutes)	Acidity removed, E (%)	Predicted Fit, Ep (%)
1	1	-1	-1	0	0	9	2	65	120	87.26	89.32
2	1	1	-1	0	0	9	2	65	120	87.67	89.32
3	1	-1	1	0	0	6	2	60	120	89.98	88.27
4	1	1	1	0	0	9	1	60	120	86.18	83.86
5	1	0	0	-1	-1	9	3	60	120	83.56	82.81
6	1	0	0	1	-1	6	2	60	120	91.85	88.27
7	1	0	0	-1	1	12	2	60	120	97.55	98.15
8	1	0	0	1	1	9	1	60	120	86.68	83.86
9	1	-1	0	0	-1	12	2	60	120	97.95	98.15
10	1	1	0	0	-1	9	3	60	120	83.14	82.81
11	1	-1	0	0	1	9	2	55	120	83	86.26
12	1	1	0	0	1	9	2	55	120	82.5	86.26
13	1	0	-1	-1	0	6	2	65	90	83.16	84.05
14	1	0	1	-1	0	9	3	65	90	77.85	75.31
15	1	0	-1	1	0	12	2	65	90	89.96	90.63
16	1	0	1	1	0	9	3	65	90	77.12	75.31
17	1	-1	0	-1	0	6	2	65	90	83.68	84.05
18	1	1	0	-1	0	9	1	65	90	78.93	79.64
19	1	-1	0	1	0	9	1	65	90	79.16	79.64
20	1	1	0	1	0	12	2	65	90	92.28	90.63
21	1	0	-1	0	-1	6	3	60	90	71.86	74.96
22	1	0	1	0	-1	6	1	60	90	77.58	79.02
23	1	0	-1	0	1	12	1	60	90	90.2	90.86
24	1	0	1	0	1	9	2	60	90	93.8	93.37
25	1	0	0	0	0	9	2	60	90	92.89	93.37
26	1	0	0	0	0	9	2	60	90	93.68	93.37
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27	1	0	0	0	0	12	3	60	90	81.45	83.12
28	1	-1	-1	0	0	6	3	60	90	72.28	74.96
29	1	1	-1	0	0	6	1	60	90	76.18	79.02
30	1	-1	1	0	0	9	2	60	90	93.2	93.37
31	1	1	1	0	0	12	3	60	90	82.87	83.12
32	1	0	0	-1	-1	12	1	60	90	91.1	90.86
33	1	0	0	1	-1	9	2	60	90	92.98	93.37
34	1	0	0	-1	1	9	2	60	90	93.64	93.37
35	1	0	0	1	1	6	2	55	90	79.14	78.83
36	1	-1	0	0	-1	9	1	55	90	79.92	79.40
37	1	1	0	0	-1	9	3	55	90	75.12	71.93
38	1	-1	0	0	1	9	1	55	90	79.58	79.40
39	1	1	0	0	1	12	2	55	90	93.6	92.24
40	1	0	-1	-1	0	9	3	55	90	74.98	71.93
41	1	0	1	-1	0	12	2	55	90	93.28	92.24
42	1	0	-1	1	0	6	2	55	90	78.69	78.83
43	1	0	1	1	0	9	2	65	60	85.6	84.72
44	1	-1	0	-1	0	9	2	65	60	84.65	84.72
45	1	1	0	-1	0	9	1	60	60	85.15	85.37
46	1	-1	0	1	0	12	2	60	60	94.69	94.92
47	1	1	0	1	0	6	2	60	60	87.67	84.80
48	1	0	-1	0	-1	12	2	60	60	94.9	94.92
49	1	0	1	0	-1	6	2	60	60	87.78	84.80
50	1	0	-1	0	1	9	1	60	60	85.65	85.37
51	1	0	1	0	1	9	3	60	60	72.56	74.61
52	1	0	0	0	0	9	3	60	60	72.68	74.61
53	1	0	0	0	0	9	2	55	60	82.85	84.16
54	1	0	0	0	0	9	2	55	60	82.98	84.16

5.1.2.3 Response Surface Regression

FFA content of the system was determined at 5 minutes, 30 minutes, 60 minutes, 75 minutes, 90 minutes, 100 minutes, 110 minutes, and 120 minutes by collecting samples from the reactors at a given experimental setup. Then the Box-Behnken model for the response surface (RSM) analysis was performed as in the Table 5-3 and the predicted yield values were fitted under the quadratic equation mentioned in Eq. 4.7a.

In this analysis process, double replica experimental system was conceived. That is why, a total of 54 experimental investigations (Table 5-3) were performed. Each of these test runs was performed with 50ml tallow collected from the dried (considering possible existing moisture removal) and filtered tallow liquid prepared earlier.

Based on the RSM analysis, the regression response for acidity removal due to esterification process can be expressed as per the following quadratic equation (Eq. 5.1). The equation shows the acidity removal is a dependent function of all the four considered parameters and their individual as well mutual interactions. Both the regression and the experimental fits are compared and shown in the Figure 5-1. Besides, the experimental fit and predicted fit of acidity removal are shown in Figure 5-2 as per the experimental run order designed in Table 5-2. Both the graphs are showing very good level of conformity between experimental and predicted data.



Figure 5-1 Regression fit between experimental data and predicted data for acidity removal



Figure 5-2 Acidity removed (experimental and predicted) as per the experimental run order

5.1.2.4 Response Optimisation

Statistical software Minitab 18.0 was used to determine the optimal response based on the RSM analysis presented earlier. The optimal conditions for acidity (FFA content) removal are presented in the Table 5-4 with 95% confidence intervals. The values of the coded parameters obtained for optimal conditions in the table 5-4 can be decoded as, methanol to oil molar ratio is 12M:1M, sulphuric acid (H₂SO₄) content is 1.89 wt.% of the tallow, reaction temperature 59.75 °C, and the reaction period is 108.49 minutes. Based on the optimisation analysis, the maximum removal of FFA from the tallow could be achieved as 98.34% with these given parameter conditions in a conventional batch reactor.

Variables	М	А	Т	D
Ranges	(6, 12)	(1, 3)	(55, 65)	(60, 120)
Optimal Values	12	1.89	59.75	108.485
Response	Fit	SE Fit	95% CI	95% PI
Acidity removed	98.34	0.85	(96.63, 100)	(93.907, 100)

Table 5-4 Optimal response analysis for esterification of tallow by RSM analysis method

5.1.2.5 Analysis of Variance (ANOVA) for Tallow Esterification Process

Analysis of variance (ANOVA) has been performed along with the RSM analysis to determine the statistical significance of the variables. The results are presented as in the Table 5-5 and Table 5-6. The P values obtained for the individual parameters are found to be less than the significance level (i.e. P<0.05), which implies that the parameters are statistically significant and rejects the null hypothesis of the experimental investigations. The F-value of the overall ANOVA model is 43.67 with P-value equal to zero, which indicates a higher significance in the regression analysis process. The quadratic effect of methanol to oil ratio (M*M) and reaction time period (D*D), along with interaction parameters for methanol content with catalyst content (M*A), methanol content with reaction time period (M*D), catalyst content with reaction temperature (A^*T), and temperature with reaction time period (T^*D) have higher P value than the significance level (i.e. P>0.05), which caused some adverse effect in the overall system. But the R-square value (0.94) indicates that the model could deal with 94% of the data within the fit and the adjusted R-square value (0.9185) in comparison to the R-square predicted value (0.8806) also shows better regression prediction in the system. The P-value of the lack of fit is zero, resulting in acceptance of the regression fit model within any set of combination of the parameters to predict the acidity removal for tallow in the conventional batch reactor. Also, from the Table 5-6, it can be seen that the highest variance inflation factor (VIF) was 1.25 for the quadratic forms of the parameters but the other parametric VIFs were just 1.00. This factor explains how much the multicollinearity (correlation between the predictors) can affect the regression fit by varying the variance of the regression coefficients. As a result, the overall response fails to recognise the distinct effect of correlated predictors. If VIF>5, then the regression coefficients are very badly estimated due to high multicollinearity effect [346].

Table 5-5 The ANOVA test of quadratic model for acidity removal of Tallow as a function of considered parameters (coded)

Model	14	2498.38	178.46	43.67	0
Linear	4	895.68	223.92	54.79	0
М	1	599.8	599.8	146.77	0
А	1	209.1	209.1	51.16	0
Т	1	19.58	19.58	4.79	0.035
D	1	67.2	67.2	16.44	0
Square	4	1517.5	379.37	92.83	0
M*M	1	6.06	6.06	1.48	0.231
A*A	1	1203.55	1203.55	294.5	0
T*T	1	406.53	406.53	99.48	0
D*D	1	12.41	12.41	3.04	0.089
2-Way Interaction	6	85.2	14.2	3.47	0.008
M*A	1	6.77	6.77	1.66	0.206
M*T	1	23.29	23.29	5.7	0.022
M*D	1	0.03	0.03	0.01	0.935
A*T	1	4.93	4.93	1.21	0.279
A*D	1	47.05	47.05	11.51	0.002
T*D	1	3.14	3.14	0.77	0.386
Error	39	159.38	4.09		
Lack-of-Fit	10	149.92	14.99	45.98	0
Pure Error	29	9.46	0.33		
Total	53	2657.76			
Model summary					
S	R-sq	R-sq(adj.)	R-sq(pred.)		
2.02156	94.00%	91.85%	88.06%		

Table 5-6 Coefficients of coded parameters and the VIF of the response model for esterification process of Tallow

Term	Coefficients	Standard Error	95% CI	T-Value	P-Value	VIF
Constant	93.37	0.83	(91.69, 95.03)	113.13	0.000	•
М	5.00	0.41	(4.16, 5.83)	12.11	0.000	1.00
А	-2.95	0.41	(-3.78, -2.11)	-7.15	0.000	1.00
Т	0.90	0.41	(0.06, 1.73)	2.19	0.035	1.00
D	1.67	0.41	(0.83, 2.50)	4.06	0.000	1.00
M*M	-0.75	0.62	(-2.00, 0.49)	-1.22	0.231	1.25
A*A	-10.62	0.62	(-11.87, -9.37)	-17.16	0.000	1.25

T*T	-6.17	0.62	(-7.42, -4.92)	-9.97	0.000	1.25
D*D	-1.08	0.62	(-2.33, 0.17)	-1.74	0.089	1.25
M*A	-0.92	0.72	(-2.36, 0.52)	-1.29	0.206	1.00
M*T	-1.71	0.72	(-3.15, -0.26)	-2.39	0.022	1.00
M*D	-0.06	0.72	(-1.50, 1.38)	-0.08	0.935	1.00
A*T	0.79	0.72	(-0.66, 2.23)	1.10	0.279	1.00
A*D	2.43	0.72	(0.97, 3.87)	3.39	0.002	1.00
T*D	0.63	0.72	(-0.81, 2.07)	0.88	0.386	1.00

5.1.2.6 Effects Plots for Tallow Esterification Process

Both the Pareto chart (Figure 5-3) and Normal chart (Figure 5-4) represent the relative scales of effects the parameters contributing to the predicted results. Here, the Pareto chart (Figure 5-3) indicates that the model includes the error terms for the response calculation. The reference line valued at 2.02 with the significance level of 0.05 shows that the terms BB (catalyst*catalyst), A (methanol to oil molar ratio), CC (temperature*temperature), B (catalyst), D (time), BD (catalyst*time), AC (molar ratio*temperature), C (temperature) are statistically significant respectively according to their level of effects to the response. The most significant terms catalyst concentration, methanol to oil ratio and the reaction temperature.









The Pareto chart only indicates the significance level of the parameters but does not provide information about whether the parameters are positively or negatively significant to the response determination. In such case, the normal plot (Figure 5-4) provides the magnitude as well as the direction of effect relative to the t-statistics values in determining the response. In this analysis, the normal plot indicates that the coded parameters A, D, BD, and C are positively

significant in determining the response; whereas, the coded parameters AC, B, CC, and BB are negatively significant (i.e. negative standardised effects) in determining the response. The negatively significant terms will reduce their effect if their respective values are increased from their lower value to the higher values. The blue dotted parameters in the normal graph are very near to the distribution fit line (where the standardised values effects are zero), that indicates that the insignificant terms are not much severe in the response development. Besides, the normal plot shows that the quantity of B (catalyst) could be increased to reduce the negative standardised effect in the response.

5.1.2.7 Response Surface Plots for Tallow Esterification Process

Both the 3D contour surface plots and the 2D contour plots are presented for the percentile quantity of acidity removal (E, %) against the independent variables: methanol to oil molar ratio (M), amount of catalyst (A), reaction temperature (T) and reaction duration (D). It is an effective way to explain the interaction between two independent variables on the response yield (% of acidity removal) in the esterification process of tallow. Figure 5-5 to Figure 5-10 show the interaction effect of six possible combinations of the interaction parameters on acidity removal. While demonstrating the effect of any two variables against the acidity removal quantity, the other variables were held constant at the optimal condition values of those respective parameters.

5.1.2.7.1 Interaction Between Reaction Time (D) and Reaction Temperature (T)



(a) 3D response surface plot of E vs T and D

(b) 2D contour plot between D and T

Figure 5-5 Interaction effect of temperature and time on acidity removal of tallow esterification process

Figure 5-5(a) and Figure 5-5(b) are the 3D response surface plot and the 2D response contour plot respectively for acidity removal (E, %) due to interaction effect between reaction time (D) and reaction temperature (T). The other two parameters, methanol to oil molar ratio (M) and acid catalyst content (A) were kept constant at 12:1M and 1.9 wt.% respectively. The figures show that the acidity removal content increases with the increase of temperature from 55 $^{\circ}$ C towards 60 $^{\circ}$ C at a level of maximum removal content and then start decreasing as the temperature increases towards 65 $^{\circ}$ C. Also, the increase in reaction time almost gradually increases the acidity removal content at these given conditions. Besides, the response curves show that the reaction time has a gradually increasing (small gradient) effect on acidity removal at any given temperature. The normal plot has indicated that the mutual effect of interaction between time and temperature (DT) is insignificant. With increasing temperature beyond 60 $^{\circ}$ C the yield efficiency starts decreasing even though the reaction time increases due to volatile methanol content.





(a) 3D response surface plot of E vs M and A

(b) 2D contour plot between M and A

Figure 5-6 Interaction effect of methanol to oil molar ratio and the acid catalyst content on acidity removal of tallow esterification process

The acidity removal rate (E, %) increases gradually with the increase of methanol to oil molar ratio (M) in the reaction system as shown in the Figure 5-6(a). At such condition, the acid catalyst content (A) has a positive gradient up to 1.9 wt.% from 1.0 wt.% of the oil quantity and then starts showing negative gradient for any given quantity of methanol to oil ratio. In this case, the other two parameters were set at their optimal conditions. Figure 5-6(b) shows the interaction between M and A on acidity removal through contours. It also shows that the maximum amount of acidity removal is possible within the range of methanol to oil ratio of 11.8:1 to 12:1 and acid catalyst content ranges between 1.7 wt.% to 2.1wt.%. Since the normal plot and Pareto chart are showing that the quantity of catalyst has a negative impact on the response model development, the quantity of acid catalyst should be increased up to their optimal condition.

Also, the positive effect of methanol content indicates the quantity of methanol should be increased to get better response. The methanol and catalyst contents have distinct effectiveness individually based on the content of the FFA in oil or fat. There is no synergy between the acid catalyst and methanol content. Figure 5-4 (normal plot) indicates that the increase in methanol content has the most positive effectiveness in achieving the better response yield, whereas the acid catalyst content has the highest negative effect on the response. In such case, the optimal catalyst content was found to be 1.9 wt.% for 12M methanol content to obtain the optimal

acidity removal of about 98.34%. Also, an insignificant effect was observed when the mutual interaction effect of MA (coded as AB in the Figure 5-3 and Figure 5-4) was observed.

5.1.2.7.3 Interaction Between Methanol to Oil Ratio (M) and Reaction Temperature (T)

The 3D response plot for acidity removal (E, %) is shown in the Figure 5-7(a) when the methanol to oil molar ratio (M) and the reaction temperature (T) are varied holding the other two parameters at their optimal values. When the reaction temperature starts increasing from 55 0 C towards 60 0 C, the acidity removal content increases at any given methanol content. But starts reducing at a slower rate when the temperature increases beyond 60 0 C.



(a) 3D response surface plot of E vs M and T

(b) 2D contour plot between M and T

Figure 5-7 Interaction effect of methanol to oil molar ratio and the reaction temperature on acidity removal of tallow esterification process

The contour graph in Figure 5-7(b) shows that the optimal range of temperature for achieving the optimal amount of acidity removal occurs between 59 °C and 61°C while the methanol content should be at its maximum level. The Pareto chart (Figure 5-3) shows that there is significant mutual effect between methanol content and reaction temperature in achieving the optimal FFA removal rate. The normal plot (Figure 5-4) indicates that both the methanol content and temperature have positive effect on the response, but their mutual effect is significantly negative to the response. So, when both these parameters are increased the mutual effect may significantly shift towards the positive direction. The contour plot shows that maximum level of acidity could not be possible for a wide range of temperature as the higher temperature can lead to waste of energy in vaporisation of the methanol.





(a) 3D response surface plot of E vs M and D



Figure 5-8 Interaction effect of methanol to oil molar ratio and the reaction temperature on acidity removal of tallow esterification process

The Figure 5-8(a) shows the response surface of acidity removal (E, %) against the methanol to oil molar ratio (M) and reaction time (D). Both the parameters work well in producing the response with positive significance as indicated in the normal plot (Figure 5-4). Also, the insignificance level of mutual effect of these two parameters is not very high as indicated in the Pareto chart (Figure 5-3). The contour graph between M and D is shown in the Figure 5-8(b), which indicates that the highest response can be achieved very near to the 12M methanol content and above 100 minutes of reaction time. Due to their positive significance, the optimal design values were found as 108.49 minutes against the 12:1 methanol to oil ratio.

5.1.2.7.5 Interaction between acid catalyst (A) and reaction temperature (T)

The effect of acid catalyst content and that of reaction temperature in developing the response of acidity removal is shown in the Figure 5-9(a) as a response surface. The mutual effect between A and T is shown in the contour graph in Figure 5-9(b). While producing this relationship, the other two parameters, methanol to oil ratio and the reaction time were kept constant at optimal conditions. The response plot shows that at any given catalyst concentration, the variation of reaction temperature shows varying behaviour in developing the response. The contour plot shows that the maximum level of response can be obtained at the centre of the graph between varying values of A and T. The range of varying the catalyst concentration is shown as very narrow even though the quadratic effect of both the reaction temperature and catalytic concentration content are in the negative side of the significance

effect development. The Pareto chart also indicates that the mutual effect of the catalyst concentration and reaction temperature is insignificant. Both these parameters are on the opposite side of the standardised effect's fit line in the normal plot. The contour plot shows that the temperature and the acid concentration level could not be varied within a wide range.



(a) 3D response surface plot of E vs A and T (b) 2D contour between A and T

Figure 5-9 Interaction effect of methanol to oil molar ratio and the reaction temperature on acidity removal of tallow esterification process

5.1.2.7.6 Interaction between acid catalyst (A) and reaction time (D)

Figure 5-10(a) is a response surface plot of acidity removal (E, %) with the change of acid catalyst content (A) and reaction period (D). It shows that the reaction time increase at any level of acid catalyst does not influence the acidity removal from tallow compared to the quantity variation of the acid catalyst at any given reaction time period. For any given reaction time period between 60 and 120 minutes, the initial level of acidity removal (>90%) for 1wt.% of acid catalyst increases with the increase of the catalyst content up to around 2 wt.%. The highest acidity removal contour lines (Figure 5-10(b)) indicates a very narrow range of catalyst content effectiveness at reaction time period greater than 90 minutes. The Pareto chart in Figure 5-3 also shows that the varying quantity of B, D and the mutual interaction BD have the standardised effect towards response model development.



(a) 3D response surface plot of E vs A and D (b) 2D contour between A and D

Figure 5-10 Interaction effect of methanol to oil molar ratio and the reaction temperature on acidity removal of tallow esterification process

On the other hand, the normal plot (Figure 5-4) indicates that the mutual interaction between B and D has positive significance along with reaction time itself. So higher reaction period was encouraged. In such condition, the contour plot indicates that the maximum reaction time could be achieved up to 120 minutes. To produce the optimal response amount of acidity removal, it is found that the acid content could be 1.9 wt.% along with reaction time more than 108 minutes.

5.1.2.8 Kinetic Parameter Determination for Esterification Process of Beef Tallow

The kinetic parameter determination was performed at the optimal design level obtained from the RSM analysis. In this section, reaction kinetics for the esterification process was determined by considering it, (i) pseudo-homogeneous irreversible process and (ii) a reversible heterogeneous process. Both the systems are presented as follows.

5.1.2.8.1 Determination of Kinetic parameters for a pseudo-homogeneous irreversible esterification process

In order to determine the kinetic parameters of the tallow esterification process, which is a pseudo-homogeneous irreversible esterification process [**323**, **324**] as described in the section 4.2.1.2.2, the following FFA conversion fraction data at various times can be obtained for 55 0 C, 60 0 C, and 65 0 C as in the Figure 5-11. The R-square values of these regression fits are shown in the Figure 5-11 for each of the operating temperatures, respectively. The reaction order, rate equation of the esterification reaction, activation energy and the related kinetic

equation were obtained in this kinetic model, as this process does not premeditate the reaction order.

Indeed, the FFA removal rates are non-linear functions of time at a given temperature and at other reaction conditions.

Here, the Eq. 4.4g from Chapter 4 could be rewritten as follows for convenience:

Here $k_2 = k^{C_{A0}}$ =reaction rate constant

Based on the regression equations found for FFA removal against time, the plot (Figure 5-12) between $\ln[C_{A0}(1-X_E)]$ and $\ln(dX_E/dt)$ can be used to determine both the reaction order and the reaction rate constant.



Figure 5-11 FFA removal vs time for tallow esterification process at various temperatures



Figure 5-12 Reaction order and kinetic reaction rate constant determination for tallow esterification

Thus, comparing the Figure 5-12 and the Eq. 5.2a, the results in the Table 5-7 can be constructed.

Table 5-7 Reaction order for tallow esterificatin process (pseudo-homogeneous irreversible)

Т ⁰ С	T K	n (order)	lnk'	k'	k=k'*C _{A0}	1/T	lnk	Average reaction order, n
65	338	0.9911	-3.31	0.03651982	0.1789471	0.00295858	-1.72066479	1.01997
60	333	1.068	-3.792	0.02255045	0.1104972	0.003003	-2.20276479	
55	328	1.0008	-4.101	0.01655114	0.0811006	0.00304878	-2.51206479	

Here, the values of 1/T and lnk from the Table 5-7 can be used to construct the Figure 5-13 in order to determine the activation energy and frequency factor of the esterification process.



Figure 5-13 1/T vs lnk graph for tallow esterification (pseudo-homogeneous irreversible) process

Now, comparing Figure 5-13 with logarithmic version of Arrhenius equation (Eq. 4.3d: $\ln k = \ln A_f + \left(-\frac{E_a}{R}\right)\frac{1}{T}$), the activation energy and the frequency factors can be determined as presented in the Table 5-8.

Table 5-8 Activation energy and frequency factor for the rection kinetics of tallow esterificaiton (pseudo-homogeneous irreversible) process

lnA _f	A_{f}	(-Ea/R)	Ea (J/mol)	Ea (kJ/mol)
24.176	3.16E+10	-8763.5	72859.739	72.859739

Now, from Figure 5-13, the linear regression between 1/T and lnk' can be shown as follows:

$$y = -8763.5x + 24.176$$
 (Eq. 5.2b)

Which is similar to the following logarithmic version (Eq. 4.3d) of Arrhenius equation,

$$\ln k = \ln A_f + \left(-\frac{E_a}{R}\right) \frac{1}{T}....(Eq. 5.2c)$$

Now, comparing the equation (Eq. 5.2b) with (Eq. 5.2c), the following results for activation energy and reaction frequency factor are determined, which are presented in the Table 5-8.

Thus, the reaction rate equation (Eq. 4.4j) for the pseudo-homogeneous irreversible esterification reaction can be expressed as follows:

$$r_{A} = -\frac{dC_{A}}{dt} = C_{A0} \frac{dx}{dt} = A_{f} \cdot e^{\left[-\frac{E_{a}}{RT}\right]} [C_{A0}(1-x)]^{n}$$
$$=> r_{A} = 3.16 \times 10^{10} e^{\left[-\frac{\frac{72.86kJ}{mol}}{RT}\right]} [C_{A}]^{1.02} \dots (Eq. 5.2d)$$

This Eq. 5.2d is the reaction kinetic model for tallow esterification process when the esterification reaction is an irreversible pseudo-homogeneous reaction process.

As the reaction rate is determined from the graphical process, the fractional values of reaction orders are plausible based on these differential processes.

5.1.2.8.2 Determination of Kinetic Parameters of Esterification Process of Beef Tallow for Reversible Heterogeneous Process

The optimal esterification reaction conditions obtained for methanol to oil ratio was 12M:1M, and quantity of acid catalyst (H₂SO₄) was 1.9% (w/w) of oil. The necessary readings were taken at reaction times 5, 30, 60, 75, 90, 100, 110, 120 minutes for each of the reaction temperatures 55 0 C, 60 0 C, and 65 0 C from a batch reaction reactor. Initial FFA content was 4.9%.

The reaction process could be also defined as a *pseudo*-homogeneous process in which the forward reaction is characterised as first order and the reverse direction reaction is characterised as second order kinetic reaction [**314**, **315**]. While the reaction was taking place for a given temperature, samples of partially completed reaction system were collected and cooled down to measure the FFA level by potentiometric method (alcoholic KOH solution-based titration method) described in the section 4.1.2. With this known set of parameters, a non-linear regression analysis was performed following the Levenberg-Marquardt algorithm with the statistical analysis software Minitab 18.0 [**304**, **346**].



Figure 5-14 Change of FFA (%) level in the tallow with time at the given reaction temperatures

Variation of the acid value (or %FFA contents) at a pre-set temperature with sulphuric acid concentration of 1.9 wt.% of oil and a methanol to oil molar ratio of 12:1 can be shown as follows in the Figure 5-14. Besides, the numerical analysis plot of the non-linear equation $Eq. 4.2e: \left(2K_2, \alpha, t = \ln \frac{|A_0 + E.(\beta - \frac{1}{2}|}{|A_0 - E.(\beta + \frac{1}{2}|)}\right)$ has been plotted in the Figure 5-15. The trial and errorbased analysis of Eq.4.2e required a few initial assumptions, which were then numerically solved by Levenberg-Marquardt algorithm (L-M algorithm) with several hundred iterations. The figure 5-15 shows that the R-square values are of good fit due to very high percentage of data within the fit of a straight line passing through the origin. The slopes of the linear fit lines in Figure 5-15 are approach unity, indicating the better match between the two sides of the Eq. 4.2e with the obtained values of the unknown parameters for this reaction's analysis purpose.



Figure 5-15 Determination of kinetic constants by non-linear regression L-M analysis

The comparison between the experimentally determined FFA removed values at various times and that of the predicted fit values (Eq. 4.2h) of the esterification process of tallow for the reaction conditions, 12M:1M methanol to oil ratio, and 1.9 wt.% H₂SO₄ are shown for temperatures of 55 0 C, 60 0 C and 65 0 C in the Figure 5.16(a-c) respectively. This goodness-of-fit of the experimental data with the predicted data has been performed to observe the percentage of data fit within the model considered. In this case, the experimentally derived data were mostly fitting with the adopted model and numerically derived parameters that the reproduced data had less than 1% error in the fitting curve.



Figure 5-16 Comparing the predicted values of FFA removed with the experimentally obtained FFA removed at (a) 55 °C, (b) 60 °C and (c) 65 °C for tallow esterification process

Based on the regression analysis and using the determined numerical analysis values in the other equations (Eq. 4.2f - Eq.4.2g) the following data were determined as in the Table 5-9.

1/T	$\ln k = \ln(\alpha/\beta)$	Alpha (a)	Beta (β)	k ₂	k1=k*k2	lnk ₁	lnk ₂
0.00304878	0.948927661	1.2862	0.49796	0.00532	0.013741232	-4.28735431	-5.23628197
0.003003003	1.373266903	1.85393	0.46956	0.00863	0.034073209	-3.37924387	-4.75251077
0.00295858	1.651861597	2.63865	0.50581	0.00962	0.050184482	-2.99204941	-4.64391101

Table 5-9 Determination of rate constants to obtain 1/T vs lnk, lnk1 and lnk2 plots

Now, Table 5-9 can be used to generate the graph in Figure 5-17. The slopes of each of the graphs then be used to determine the activation energy of the system.



Figure 5-17 1/T vs lnk, lnk_1 and lnk_2 graph for the kinetic modeling of tallow esterification process

Here, the regression fit equations of the Figure 5-17 can be compared with the logarithmic form of Arrhenius equation (Eq. 4.3d: $\ln k = \ln A_f + \left(-\frac{E_a}{R}\right)\frac{1}{T}$) to determine the activation energy (Ea), and reaction frequency parameter A_f. The values of the Ea and A_f for the overall reaction rate constant (k), forward rate constant (k₁) and reverse reaction rate constant (k₂) are shown in the Table 5-10.

Table 5-10 Determination of frequency factor and activation energy for the pseudohomogeneous reversible esterification process of tallow

lnAf	$A_{\rm f}$	(-)Ea/R	Ea (J/mol)	Ea (kJ/mol)	1/T (K ⁻¹)	k
24.753	5.62E+10	-7800.5	64853.357	64.853357	0.00304878	For K
39.661	1.68E+17	-14388	119621.83	119.62183	0.003003003	For K1
14.908	2.98E+06	-6587.6	54769.306	54.769306	0.00295858	For K2

Therefore, the total reaction rate equation (Eq. 4.2i) for a pseudo-homogeneous reversible process can be expressed as follows:

$$\frac{d[A]}{dt} = \frac{dE}{dt} = K_1(A_0 - E) - K_2 E^2 = 1.68 \times 10^{17} \cdot e^{\left[-\frac{119.62183\frac{kJ}{mol}}{RT}\right]} (A_0 - E) -$$

$$2.98 \times 10^6 \cdot e^{\left[-\frac{54.7693kJ}{mol}\right]} E^2 \qquad (Eq. 5.2e)$$

Where, A_0 and E are known at various times, t from the experimental investigations.

This (Eq. 5.2e) is the kinetic model for tallow esterification process for a pseudohomogenous reversible process on the basis of given optimal design of tallow esterification.

5.1.3 Optimisation and Kinetic Modelling of Transesterification Process for Tallow Biodiesel Production

5.1.3.1 RSM Analysis and Optimisation of Transesterification Process

The esterified tallow oil was processed through transesterification process to produce tallow biodiesel (WTB). The reaction conditions for transesterification process is mentioned in the Table 5-11. RSM analysis (with Minitab 18.0 software) of the transesterification was performed to determine the optimal operation conditions. The quadratic model equation was as in case of the esterification process model. Once the RSM analysis was performed, the analysis of variance (ANOVA) table was investigated to check the significant contribution of the considered parameters in the predicted yield. Then the model was analysed to determine the parametric conditions for optimal yield of biodiesel from the transesterification process.

Experimental Parameters	Conditions or Range
FFA (%)	0.10045%
Acid value (AV, mgKOH/g)	0.199895
Methanol (M) :Oil (M)	5M:1M, 6M:1M, 7M:1M
NaOH (%wt./wt. of oil)	1%, 1.5%, 2%
Reaction temperature (K)	328K, 333K, 338K
Reaction temperature (^o C)	55 °C, 60 °C, 65 °C
Stirring speed of the chemical reactions	600 rpm with magnetic stirrer
Reaction period (time in minutes)	60, 90, 120

Table 5-11 Experimental conditions for the alkali-catalysed transesterification reactions of Tallow

The experiments were designed to obtain sufficient data to perform the statistical analysis. To perform this analysis, a 4-factors and 3-level (4×3) matrix Box-Behnken algorithm was considered as per the Table 5-12. The factors are methanol to oil molar ratio (M/M, M), amount of alkali (NaOH) catalyst (wt.% of oil, A), reaction temperature (0 C, T) and the reaction time (minutes, D). The range of the respective factors considered for this purpose are presented in

the Table 5-12 with both coded and actual values. In this case, the Box-Behnken algorithm provided a design matrix of 27 runs. All those 27 experiments were performed accordingly and are presented in the Table 5-13. Based on the RSM analysis, the predicted yields are obtained and mentioned in the Table 5-13. The maximum predicted yield was obtained as 97.92% against the experimental maximum yield of 97.91% tallow methyl ester (WTB) for the operating condition set of 6:1M (M), 1.5 wt.% (A), 60 °C (T), and 90 minutes (D) of the transesterification process. On the other hand, the minimum predicted yield was found as 75.69% in comparison to that of experimental minimum yield of 76.29% for the experimental operating parameters of 6:1M (M), 2wt.% (A), 55 °C (T), 90 minutes (D). To observe the goodness of fit between the experimental yields and predicted yields, the Figure 5-18 has been plotted for experimentally derived methyl ester yields (%) vs RSM analysis based predicted yields (%), which shows a better linear regression fit.

Table 5-12 Box-Behnken (4-factors, 3-levels) algorithm for transesterification process of esterified tallow

Operation Parameters	Unit	Symbol	Range	Range and coded lev	
			-1	0	+1
Methanol : Oil	M/M	М	5	6	7
Alkali Catalyst (NaOH)	wt.%	А	1	1.5	2
Temperature	^{0}C	Т	55	60	65
Time	minutes	D	60	90	120

Table 5-13 RSM analysis of transesterification process of esterified tallo)W
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		Coded Values			Actual Values (symbols)			nbols)	_		
Run	Blk	А	В	С	D	М	А	Т	D	Yield, Y (%)	Predicted yield, Yp%
1	1	-1	-1	0	0	6	1.5	65	60	87.19	87.54
2	1	1	-1	0	0	6	1.5	65	120	90.23	91.01
3	1	-1	1	0	0	6	1	65	90	86.62	86.97
4	1	1	1	0	0	6	2	65	90	80.91	80.22
5	1	0	0	-1	-1	5	1.5	65	90	83.65	83.73
6	1	0	0	1	-1	7	1.5	65	90	87.56	86.69
7	1	0	0	-1	1	5	1	60	90	86.5	86.15
8	1	0	0	1	1	7	1	60	90	93.21	94.37
9	1	-1	0	0	-1	5	2	60	90	82.96	82.82
10	1	1	0	0	-1	7	2	60	90	81.16	82.53
11	1	-1	0	0	1	5	1.5	60	60	87.36	87.72

1	1	0	0	1	7	1.5	60	60	92.68	92.48
1	0	-1	-1	0	5	1.5	60	120	92.65	92.60
1	0	1	-1	0	7	1.5	60	120	96.39	95.78
1	0	-1	1	0	6	1	60	60	93.56	92.78
1	0	1	1	0	6	2	60	60	84.15	84.19
1	-1	0	-1	0	6	1	60	120	96.67	95.86
1	1	0	-1	0	6	2	60	120	89.26	89.28
1	-1	0	1	0	6	1.5	60	90	97.86	97.92
1	1	0	1	0	6	1.5	60	90	97.98	97.92
1	0	-1	0	-1	6	1.5	60	90	97.91	97.92
1	0	1	0	-1	6	1.5	55	60	82.99	83.23
1	0	-1	0	1	6	1.5	55	120	87.26	87.93
1	0	1	0	1	6	1	55	90	83.68	84.11
1	0	0	0	0	6	2	55	90	76.29	75.69
1	0	0	0	0	5	1.5	55	90	78.93	79.03
1	0	0	0	0	7	1.5	55	90	84.85	84.00
	1 1 1 1 1 1 1 1 1 1 1 1 1 1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1100171.5606092.6810 -1 -1 05 1.5 60 120 92.65101 -1 07 1.5 60 120 96.3910 -1 1061606093.561011062606084.1510110616012096.67110 -1 0616012096.67110 -1 061.5609097.861101061.5609097.9810 -1 0 6 1.5 60 9097.9110 1 0 -1 6 1.5 55 60 82.99 10 -1 0 1 6 1.5 55 90 83.68 1010 1 6 1 55 90 76.29 1000 0 7 1.5 55 90 84.85							





5.1.3.2 Response Surface Regression

The regression analysis was analysed to a full quadratic model to predict the yield of tallow based fatty acid methyl esters (WTB). The full quadratic model equation (Eq. 5.9h) can be expressed as follows, where catalyst content (A) has negative effect along with quadratic effects of methanol content (M^2), catalyst (A^2), reaction temperature (T^2), reaction time (D^2), and mutual interaction effects of methanol-catalyst (MA), methanol-temperature (MT), methanol-reaction period (MD) and temperature-time (TD). A brief explanation of these effects is presented with both the normal plot and the Pareto chart of standardised effects later. The un-coded regression fit of transesterification process of esterified tallow to predict the yield methyl esters is presented as follows.

Yield, Y_p (%) = 97.917 + 1.983M - 3.793A + 1.847T + 2.044D - 4.917M² - 6.533A² - 9.635T² - 0.856D² - 2.127MA - 0.502MT - 0.395MD + 0.42AT + 0.5AD - 0.308TD(Eq. 5.3a)

5.1.3.3 Response Optimisation

The regression equation used to determine the optimal fit is the quadratic model equation presented in Eq. 5.3a. The limiting values of the factors and the regression fit for the optimisation are shown in the Table 5-14. It shows that the optimal yield could be 99.8% with the reaction conditions 6.2M methanol, NaOH 1.35 % (w/w) of oil, 60.35 0 C reaction temperature and 120 minutes of reaction period in a batch reactor system. The 95% confidence interval also lies between 98.78 and 100.

Table 5-14 Determination of Optimal Response for the Transesterification Process with the RSM Analysis

Variables	М	А	Т	D
Ranges	(5,7)	(1, 2)	(55, 65)	(60, 120)
Optimal Values	6.21	1.35	60.35	120
Response	Fit	SE Fit	95% CI	95% PI
Acidity removed	99.80	0.47	(98.78, 100)	(97.65, 100)

5.1.3.4 Analysis of Variance (ANOVA) for Transesterification Process

The analysis of variance (ANOVA) has been performed (Table 5-15) for the multi variable data set presented in the Table 5-13 along with the RSM analysis in order to determine the statistical significance of the variables. The table shows that the P-values are mostly significant by being less than the significance level (i.e. P<0.05) except the 2-way mutual interaction effect of the parameters. Only significant 2-way mutual interaction effect has been observed for the mutual interaction between the methanol to oil ratio and the catalyst content. Table 5-15 also shows that the R-square value is 99.08%, adjusted R-square value is 98.01% and predicted R-square value is 94.70%. The higher level of R-square value indicates that the model can deal with more than 99% of the experimentally derived data in developing the prediction. The predicted R-square value and the higher level of adjusted R-square value explain the efficiency of the fit between the experimental fit and predicted fit. Here in this model, the regression fit

is well standardised and the P-value of the model is zero, which refers that the model can evaluate any predicted yield for any given set of reaction parameters within the given set of values.

Table 5-16 shows the values of the coefficients of the quadratic model developed by the RSM analysis. The coded parameters are shown in the table and relevant P values, T-values, 95% CI and the variance of inflation factors (VIF), etc. are presented there. Since the VIF values range between 1 and 1.25 (i.e. VIF<5), there is no multicollinearity effect and reflects that the multicollinearity effect could not have any adverse effect on the parameters in building up the regression model coefficients.

Source	DF	Adj SS	Adj MS	F- Value	P- Value
Model	14	974.18	69.58	92.26	0
Linear	4	310.87	77.72	103.04	0
М	1	47.20	47.20	62.58	0
А	1	172.60	172.60	228.83	0
Т	1	40.92	40.92	54.26	0
D	1	50.14	50.14	66.48	0
Square	4	641.49	160.37	212.62	0
M*M	1	128.95	128.95	170.96	0
A*A	1	227.65	227.65	301.82	0
T*T	1	495.07	495.07	656.37	0
D*D	1	3.91	3.91	5.18	0.042
2-Way Interaction	6	21.82	3.64	4.82	0.01
M*A	1	18.11	18.11	24.00	0.00
M*T	1	1.01	1.01	1.34	0.27
M*D	1	0.62	0.62	0.83	0.38
A*T	1	0.71	0.71	0.94	0.35
A*D	1	1.00	1.00	1.33	0.27
T*D	1	0.38	0.38	0.50	0.49
Error	12	9.05	0.75		
Lack-of-Fit	10	9.04	0.90	248.91	0.004

Table 5-15 The ANOVA test of Transesterification Process Yield Prediction (Coded Parameters)

Pure Error	2	0.01	0.004
Total	26	983.23	
Model Summary			
S	R-sq	R-sq(adj.)	R-sq(pred.)
0.868478	99.08%	98.01%	94.70%

Table 5-16 Coefficients of the regression fit and VIF values for Transesterification process of Tallow

Term	Coefficients	SE Coefficients	95% CI	T-Value	P-Value	VIF
Constant	97.92	0.50	(96.82, 99.01)	195.28	0	
М	1.98	0.25	(1.44, 2.53)	7.91	0	1
А	-3.79	0.25	(-4.34, -3.25)	-15.13	0	1
Т	1.85	0.25	(1.30, 2.39)	7.37	0	1
D	2.04	0.25	(1.50, 2.60)	8.15	0	1
M*M	-4.92	0.38	(-5.74, -4.10)	-13.08	0	1.25
A*A	-6.53	0.38	(-7.35, -5.71)	-17.37	0	1.25
T*T	-9.64	0.38	(-10.45, -8.82)	-25.62	0	1.25
D*D	-0.86	0.38	(-1.68, -0.04)	-2.28	0.042	1.25
M*A	-2.13	0.43	(-3.07, -1.18)	-4.9	0	1
M*T	-0.50	0.43	(-1.45, 0.44)	-1.16	0.27	1
M*D	-0.40	0.43	(-1.34, 0.55)	-0.91	0.381	1
A*T	0.42	0.43	(-0.52, 1.37)	0.97	0.353	1
A*D	0.50	0.43	(-0.44, 1.44)	1.15	0.272	1
T*D	-0.31	0.43	(-1.25, 0.64)	-0.71	0.492	1

5.1.3.5 Effect Plots Parameters for RSM Analysis of Tallow Transesterification Process

Here, Figure 5-19 and Figure 5-20 are the schematic presentation about how the parameters of a quadratic model influence the transesterification process output. The normal plot in the Figure 5-19 shows the positive and negative effect of significance of the quadratic model parameters in developing the predicted model of response. On the other hand, the Pareto chart in the Figure 5-20 only indicates which parameters are significantly effective and which are insignificant in developing the predicted model. It is only the normal plot which shows whether the significant terms are positively or negatively influencing the model prediction. The left-hand side of the t-statistics fit line are quantitative measures of significantly negative effect

developing parameters. If the values of these parameters are increased from lower values towards higher values, the negative effect is reduced. So, the normal plot is indicating that the catalyst content could be increased to observe positive effect of the NaOH catalyst. Also, the right-side values of the t-statistic line shows that the effectiveness of these parameters will increase if the values of these parameters are increased.









5.1.3.6 Response Surface Plots to Explain the Relative Effects of Parameters on %Yield from Transesterification Process

Both the 2D contour plot and the 3D response surface plots are produced to observe the effects of two independent variables on % Yield of WTB (Tallow fatty acid methyl ester) obtained from the transesterification process. When the effect of two variables were being observed the other two independent variables were kept constant at their optimal values in the process. Figure 5-21 to Figure 5-26 show the total of six combinations of two variables from four available variable parameters: namely, methanol to esterified tallow molar ratio (M), amount of NaOH catalyst (A), reaction temperature (T) and the reaction time (D).

5.1.3.6.1 Effects of Catalyst Content (A) and Methanol to Oil Ratio (M)

Figure 5-21 shows that the range of methanol content varied from 5M to 7M, whereas the catalyst content varied from 1.0 wt.% to 2.0 wt.% of esterified oil. The other parameters, reaction temperature was kept constant at 60 °C and reaction time was held constant at 110 minutes as obtained from the optimisation. The Figure 5-21(a) shows the contour lines and relevant region where that contour value (% yield) is valid for the set of (M, A). The inner contour (97.5%) shows that the methanol molar ratio can be varied from 5.6M to 6.8M and catalyst content could be varied from 1.05 wt.% to 1.6 wt.% to obtain those yield values. Figure

5-21(b) shows that the fatty acid methyl ester yields vary gradually from low to high and again decreases from high to the lower values for both the methanol content and catalyst content. The surface response shows that the maximum level of yield can be obtained at the intersection of the two dotted lines in Figure 5-21(b). The normal plot (Figure 5-19) shows that the catalyst content has negative effect on yield content and that the methanol content has positive effect. So, both the methanol and NaOH contents have to be increased to improve their effect on achieving higher yield of FAME.





(a) 2D contour plot between M and A



Figure 5-21 Interaction effect of methanol to oil molar ratio (M) and NaOH catalyst content (A) on FAME yield (%Y) of transesterification process

5.1.3.6.2 Effects of Catalyst Content (A) and Reaction Period (D)

Here, the figure 5-22(a-b) shows the contour plot and 3D surface plots for interaction effect of catalyst content and the reaction period, respectively. The interaction effect refers that the maximum output can be obtained within the range of 1.05 wt.% to 1.5 wt.% of catalyst and the time requirement is more than 70 minutes. In this case, the other parameters, methanol content and reaction temperature were kept constant at 6.2M and 60 °C, respectively. The normal plot in the Figure 5-19 shows that these two parameters have positive significance on the prediction quadratic model. But their mutual effect is insignificant. So, in the reaction system, the effect of catalyst content does not produce any synergic effect being indifferent to the influence of the reaction time period.



Figure 5-22 Interaction effect of NaOH catalyst content (A) and Reaction time period (D) on FAME yield (Y) of transesterification process

5.1.3.6.3 Effects of Reaction Temperature (T) and Reaction Period (D)



(a). 2D contour plot between T and D

(b). 3D response surface plot of Y vs T and D

Figure 5-23 Interaction effect of reaction temperature (T) and reaction period (D) on FAME yield (Y) of transesterification process

The 3D surface plot for yield against the reaction time and reaction temperature shows uneven maximum yield pattern for the variation of these two parameters (Figure 5-23). In this case, the other parameters were kept constant at 6.2M methanol and 1.35 wt.% NaOH catalyst. The temperature effectiveness is within very narrow range, i.e. about 58 ^oC to 62.5 ^oC. Whereas, the higher the reaction period the better yield efficiency was observed in an infrequent pattern. But the maximum contour line shows that to obtain higher FAME the reaction period should be higher than 70 minutes for the temperature ranging from 58 ^oC to

62.5 ^oC. The normal plot in the Figure 5-19 shows that both the parameters are individually effective in producing the FAME outputs. It also shows that the mutual interaction between time and temperature does have negative significance on the output of transesterification process.

5.1.3.6.4 Effects of methanol to esterified tallow content (M) and reaction temperature (T)

The methanol content and the reaction temperature have very narrow range of variation in producing higher FAME output from the transesterification process as shown in the Figure 5-24(a-b). In both the 2D contour plot and 3D surface plots, the maximum output ranges within 5.8M to 6.5M methanol for the approximate temperature zone of 59 ^oC to 61 ^oC. The normal plot shows that the mutual dependency of these two parameters is insignificant. Therefore, better conversion efficiency can be greatly dependent on the quantity of methanol and temperature within their narrow ranges.



(a). 2D contour plot between T and M

(b). 3D response surface plot of Y vs T and M

Figure 5-24 Interaction effect of reaction temperature (T) and methanol to oil molar ratio (M) on FAME yield (Y) of transesterification process

Also, the other two parameters were kept constant at their optimal reaction conditions, i.e. at 1.35 wt.% of NaOH and 120 minutes. The contour plot also shows the contour lines and area where the maximum output region is very close to the optimal response. The normal plot (Figure 5-19) refers that, the methanol content and the reaction temperature are positively significant in determining the maximum yield. But these two parameters are mutually insignificant in producing any synergistic effect.

5.1.3.6.5 Effects of Methanol to Esterified Tallow content (M) and Reaction Time (D)

The figures presented by Figure 5-25(a-b) are the response effectiveness plot for the varying parameters methanol content (M) and reaction time period (D). The regression model shows that maximum FAME can be obtained for the methanol content ranging 5.9M to 6.6M and the reaction period should be more than 80 minutes. Increasing quantity of methanol and reaction time can independently control the output of the process. The other two parameters were kept constant in their optimal production condition. Hence the lower values of the values ranging for both methanol content and reaction time period could not be just selected for the regression fit and obtaining optimal conditions.



(a). 2D contour plot between D and M (b). 3D response surface plot of Y vs D and M

Figure 5-25 Interaction effect of reaction period (D) and methanol to oil molar ratio (M) on FAME yield (Y) of transesterification process

5.1.3.6.6 Effects of Methanol to Reaction Temperature (T) and Catalyst Content (A)

Here, the Figure 5-26(b) shows that the independent parameters T and A can be varied within the given regions of 55 °C to 65 °C and 1.0 wt.% to 2.0 wt.% respectively. The maximum yield (FAME content) can be obtained within point of diminishing zone, i.e. after a certain value of both the T and A, the output starts reducing with the increase of these two parameters. The normal plot (Figure 5-19) shows that the increase of catalyst content will reduce the negative influence in the prediction model and that the increase in temperature will increase the yield response. But both the parameters are restricted within the range where maximum FAME output can be achieved. Here, the other two parameters, methanol content and reaction

time period were kept constant at 6.2M and 120 minutes respectively to observe the optimal effect of T and A in the maximum possible FAME production from the transesterification process. These plots are obtained based on the quadratic regression model.



(a). 2D contour plot between T and A



(b). 3D response surface plot of Y vs T and A

Figure 5-26 Interaction effect of reaction temperature (T) and catalyst content (A) on FAME yield (Y) of transesterification process

5.1.3.7 Determination of Kinetic Model for Transesterification Process of Tallow

Since the optimal transesterification temperature was found at around 60 0 C, further two temperatures were considered keeping other three variables constant to facilitate the graphical determination of kinetic model of the transesterification process. The reaction conditions for the transesterification process was considered from the values obtained in Table 5-14, where the optimal response condition is presented. The reaction was performed in the conventional batch reactor. Here, the temperatures variations were considered to be integers rather than considering any decimal fractions. The graph in Figure 5-27 refers to the FAME conversion from the transesterification process with respect to time at a methanol to oil ratio of 6.2M:1M, NaOH catalyst loading of 1.35wt.% of esterified oil, at time periods of 0 minutes, 60 minutes, 90 minutes and 120 minutes and for the temperature conditions of 50 0 C, 55 0 C and 60 0 C.



Figure 5-27 Biodiesel conversion at various times for the given temperatures

R-square values for these regression equations obtained for FAME production at various times for the given temperature conditions were, at 50 $^{\circ}$ C (R² = 0.9997), at 55 $^{\circ}$ C (R² = 0.9911) and at 60 $^{\circ}$ C (R² = 0.9922).

Here, the kinetic model was determined by following the discussion of kinetic mechanism of transesterification process in the section 4.2.3.2. When x is considered as a fractional conversion entity of methyl ester in the batch reactor, we get following the (Eq. 5.3b):

$$\ln(1-x) = -k_1 t$$
, or $-\ln(1-x) = k_1 t$ (Eq. 5.3b)

Hence, for various values of T, the plot between $-\ln(1-x)$ and time (t) can be plotted as in the Figure 5-28. The regression equations can for the given temperatures are presented as follows, which can be compared with the (Eq. 5.3c) to determine the corresponding reaction rate constant k₁ for each of the temperatures. The R-square values are of good to fit categories in the Figure 5-28.

At 60 0 C: $-\ln(1 - x) = 0.0407t$; R ² = 0.9722	(Eq. 5.3c)
At 55 0 C: $-\ln(1 - x) = 0.0243t$; $R^{2} = 0.9301$	(Eq. 5.3d)
At 50 0 C: $-\ln(1 - x) = 0.0135$; R ² = 0.941	(Eq. 5.3e)



Figure 5-28 Determination of reaction rate constant for the transesterification process

Now, the values of k_1 with respect to the values of T can be used to develop a plot (Figure 5-29) of 1/T vs lnk₁ as in the Table 5-17. From the Figure 5-29, the regression equation is found to compare with a straight line with an intercept from vertical axis. Comparing the regression equation with the logarithmic form of Arrhenius equation (Eq. 4.3d), the following parameters in the Table 5-18 can be obtained.

T (k)	k1 (L/mol.min)	1/T	lnk1
323	0.0135	0.003096	-4.30507
328	0.0243	0.003049	-3.71728
333	0.0407	0.003003	-3.20153

Table 5-17 Determination of 1/T and lnk1



Figure 5-29 1/T vs lnk1 plot to determine the activation energy (Ea) and frequency factor (A_f) for Transesterification process

Table 5-18 Determination of activation energy (Ea) and frequency factor (A_f)

lnA _f	A _f	(-Ea/R)	Ea (J/mol)	Ea (kJ/mol)
32.461	1.25208E+14	-11873	98712.12	98.712122

Therefore, following the Eq. 4.8p: $(r = -\frac{dC_{TG}}{dt} = k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG}$), the overall reaction rate (kinetic model of transesterification process) can be expressed as follows:

$$r = -\frac{dC_{TG}}{dt} = k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG} = 1.252 \times 10^{14} e^{\left[-\frac{98.712 \frac{kJ}{mol}}{RT}\right]} C_{TG} \quad \dots \dots \quad (Eq. 5.3f)$$

5.1.4 Summary of the Beef Tallow Biodiesel (WTB) Production Optimisation and Kinetic Modelling

Tallow with 4.9% FFA was analysed experimentally and analytically for this study. The tallow biodiesel (FAME) was produced by a two-stage conversion process, namely, acid-catalysed esterification process and base-catalysed transesterification process. The optimisation of process parameters for maximum possible yield of the respective processes was

performed with Box-Behnken algorithm and RSM analysis along with multivariable type ANOVA analysis to determine the effectiveness of parameters in the regression model. Even though the kinetic modelling of esterification process was performed with two types of assumptions (pseudo-homogeneous reversible and irreversible), the transesterification process was performed only as a first order reaction process. The stepwise reaction kinetics for the transesterification process could not be performed due to the limited access to the required equipment. The GC-MS facility was used to determine the fatty acid content only, which is not a part of this study. For both the esterification and transesterification processes, the kinetic models were developed based on the reaction conditions near to the optimal conditions obtained from the optimisation analysis with the response surface methodology. The results obtained in this analysis can be summarised as follows:

- For the esterification process, the optimal condition was found as Methanol to oil molar ratio 12M:1M, sulphuric acid (H₂SO₄) content 1.89 wt.% of the oil or tallow, reaction temperature 59.75 ⁰C, and the reaction period 108.49 minutes. Based on the optimisation analysis, the maximum removal of FFA from the tallow could be achieved as 98.34% with these given parameters in a conventional batch reactor system.
- Esterification process kinetic models were found as,

(i) $r_A = 3.16 \times 10^{10} e^{\left[\frac{-\frac{72.86kJ}{mol}}{RT}\right]} [C_A]^{1.02}$ for an irreversible pseudo-homogeneous reaction process.

1.1.7

(ii)
$$\frac{d[A]}{dt} = \frac{dE}{dt} = K_1(A_0 - E) - K_2E^2 = 1.68 \times 10^{17} \cdot e^{\left[-\frac{119.62183}{RT}\frac{KJ}{mol}\right]}(A_0 - E) - 2.98 \times 10^{6} \cdot e^{\left[-\frac{54.7693kJ}{RT}\right]}E^2$$
 for a pseudo-homogenous reversible process on the basis of given optimal design of tallow esterification process.

- The overall activation energy for both the assumptions were almost similar.
- For the transesterification process, the optimal process conditions were obtained as, Methanol to esterified oil molar ratio 6.2M:1M, NaOH catalyst content 1.35 %wt. of the esterified oil, reaction temperature 60.35 ^oC and of reaction period 120 minutes in
a batch reactor system; for which the optimal yield could be achieved as 99.8% with a 95% confidence interval between 98.78 and 100.00.

• The kinetic model for the transesterification process was found as, $r = -\frac{dC_{TG}}{dt} =$

 $k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG} = 1.252 \times 10^{14} e^{\left[-\frac{98.712 \frac{kJ}{mol}}{RT}\right]} C_{TG}$ for a conventional batch reactor system. The activation energy was found to be 98.712 kJ/mol for this process.

• Based on the yield efficiency from the esterification process and the transesterification process, the overall process conversion efficiency can be obtained by multiplying the optimal conversion rates obtained from both the processes, which was 97.48%. This level of conversion efficiency ensures the reliability of the adopted processes to convert the tallow into biodiesel.

Similar analyses were done for the other five biodiesel feedstocks. However, only the summary of each of the processes for the fuels are provided in section 5.2 to section 5.6 distinctly.

5.2 Summary of the Waste Cooking Oil Biodiesel (WCB) Production Optimisation and Kinetic Modelling

WCO with 6.89% FFA was analysed in this fuel conversion analysis study. The WCB was produced in two stages, namely, acid-catalysed esterification process and base-catalysed transesterification process. Acid catalyst was H₂SO₄ and the alkali catalyst was KOH. The optimal parameters for maximum possible yield of the respective processes were performed with CCD algorithm and RSM analysis. Also, multivariable type ANOVA analysis was determined to check the effectiveness of parameters in the regression model. Two types of kinetics modelling were performed for both esterification and transesterification processes, the reaction kinetics were determined.

The results obtained in this analysis can be summarised as follows:

For the esterification process, the optimal condition was found as, Methanol to oil molar ratio 8.12M:1M, sulphuric acid (H₂SO₄) content 1.9 wt.% of the WCO, reaction temperature 60 ^oC, and the reaction period 90 minutes. Based on the RSM analysis, the

maximum removal of FFA from the WCO was predicted as 98.85% with these given parameters in a conventional batch reactor system. The experimental amount of FFA removal was 98.62% with these parameters.

• Esterification process kinetic models were found as,

(i) $r_A = 2.38 \times 10^{19} e^{\left[-\frac{\frac{130.2471kJ}{mol}}{RT}\right]} [C_A]^{1.151}$ for an irreversible pseudo-homogeneous reaction process, and

(ii)
$$r = -\frac{dC_A}{dt} = k_1 C_A = A_f e^{\left[-\frac{Ea}{RT}\right]} C_A = 4.73 \times 10^7 e^{\left[-\frac{57.369}{RT}\frac{kJ}{mol}\right]} C_A$$
 for a pseudo-

homogenous first order irreversible process

- There is a big difference between the activation energies for these two different types of kinetic modelling due to previously mentioned conditions.
- For the transesterification process, the optimal process conditions were obtained as, Methanol to esterified oil molar ratio 6.1M:1M, KOH catalyst content 1.2 % wt. of the esterified oil, reaction temperature 60 °C and of reaction period 110 minutes in a batch reactor system; for which the optimal yield could be achieved as 99.77% with a 95% confidence interval (99.6025, 99.9411).The experimental yield was obtained as 98.81% for these optimised conditions.
- The kinetic model for the transesterification process were as follows:

(i)
$$r = -\frac{dC_{TG}}{dt} = k_1 C_B = A_f e^{\left[-\frac{Ea}{RT}\right]} C_B = 1.96 \times 10^8 e^{\left[-\frac{61.903 \text{ kJ}}{MO}\right]} C_B$$
 when the

transesterification process is considered to be a pseudo-first order irreversible process.

(ii)
$$r = kC_A^n = A_f e^{\left[-\frac{Ea}{RT}\right]} [C_A^n] = 1.43 \times 10^{11} e^{\left[-\frac{79.13348 \, kJ}{mol}\right]} C_A^{1.088133}$$
 for pseudo-
homogeneous irreversible process.

Due to difference in chemical order, these two pseudo-homogenous processes have different activation energies and frequency factors.

• Based on the yield efficiency from the esterification process and the transesterification process, the overall process conversion efficiency can be obtained by multiplying the optimal conversion rates obtained from both the processes, which is 97.44% based on the experimental maximum yields of the respective processes.

This study has comprised an overall experimental and analytical procedure to investigate the biodiesel production from a feedstock, inedible waste cooking oil. Further studies on this reaction kinetics will help to determine the accurate reaction process kinetic analysis in the near future.

5.3 Summary of Castor Oil Biodiesel (CaB) Production Optimisation and Kinetic Modelling

Castor oil having high FFA (13.9%) was analysed both experimentally and analytically in this study. The fuel conversion process from castor oil to castor oil biodiesel (CaB) required two stages of conversion processes, namely, esterification with strong acid catalyst (H₂SO₄) and transesterification with alkali catalyst (KOH) in presence of methanol. Box-Behnken algorithm used to design the required number of experiments is based on 4 factors and 3 levels. Then both the esterification process and the transesterification process were analysed with response surface methodology (RSM) to determine both data fits and the optimal process parameters to obtain best possible output from the considered processes. Also, multivariable type ANOVA analysis was determined to check the effectiveness of parameters in the regression model. Once the optimisation was performed and mutual effectiveness of these parameters to the respective process outputs are analysed, these optimised parameters were considered to determine the process reaction kinetics (i.e. reaction rate constants, reaction order and activation energy, etc.). It is expected that the detail process optimisation and the reaction kinetics of this feedstock to biodiesel production may contribute to conduct further comparative analyses with other available biodiesel conversion processes to adopt the most economic and less energy intensive processes.

The results obtained in this analysis can be summarised as follows:

• For the esterification process, the optimal condition was found as, Methanol to oil molar ratio 12M:1M, sulphuric acid (H₂SO₄) content 2 wt.% of the castor oil, reaction temperature 64 ⁰C, and the reaction period 120 minutes. Based on the RSM analysis, the maximum removal of FFA from the castor oil was predicted as 95.81% with these

given parameters in a conventional batch reactor system. But the experimental amount of FFA removal was 96.18% with these parameters.

• Esterification process kinetic models were found as,

 $r_A = 5.71 \times 10^{15} e^{\left[-\frac{110.35kI}{mol}\right]} [C_A]^{1.013}$ for the pseudo-homogenous irreversible process with a reaction order of 1.013.

- For the transesterification process, the optimal process conditions were obtained as, Methanol to esterified oil molar ratio 6.3M:1M, KOH catalyst content 1.0 % wt. of the esterified oil, reaction temperature 60 °C (~59.72 °C) and of reaction period 120 minutes in a batch reactor system; for which the optimal yield could be achieved as 98.4587% with a 95% confidence interval (99.6025, 99.9411).The experimental yield was obtained as 98.95% for these optimised conditions.
- The kinetic model for the transesterification process were as follows:

(i)
$$r = -\frac{dC_B}{dt} = k_1 C_B = A_f e^{\left[-\frac{Ea}{RT}\right]} C_B = 1.1208 \times 10^{17} e^{\left[-\frac{118.998282 \frac{K}{mol}}{RT}\right]} C_B$$
 when the

transesterification process is considered to be a pseudo-first order irreversible process.

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(ii)
$$r = kC_B^n = A_f e^{\left[-\frac{Ea}{RT}\right]} [C_B^n] = 7.45 \times 10^{14} e^{\left[-\frac{92.426738 \, kJ}{mol}\right]} C_A^{1.033167}$$
 for pseudo-
homogeneous irreversible process.

Due to difference in chemical reaction order, these two pseudo-homogenous processes have different activation energies and frequency factors.

 Based on the yield efficiency from the esterification process and the transesterification process, the overall process conversion efficiency can be obtained by multiplying the optimal conversion rates obtained from both the processes, which is 95.17% based on the experimental maximum yields of the respective processes.

This study has comprised an overall experimental and analytical procedure to investigate the biodiesel production from a feedstock, a very highly viscous and high FFA content feedstock. Further studies on this reaction kinetics will help determining the accurate reaction process kinetic analysis in near future.

5.4 Summary of the Poppy Seed Oil Biodiesel (PB) Production Optimisation and Kinetic Modelling

Since the poppy oil used for biodiesel production contained about 4.59% FFA the oil was processed by two stage biodiesel production processes, acid-esterification, and alkalitransesterification. Both the processes were performed on batch reactors. H₂SO₄ was used as a strong acid catalyst for the esterification process, and it was effective in almost completely removing the FFA from the oil. The alkali transesterification process was performed with strong alkali catalyst, KOH. Optimisation was performed by RSM analyses to determine the best possible parametric quantity within the considered range of operating parameters. Box-Behnken algorithm was used to design the required number of experiments based on 4 factors and 3 levels. Then both the esterification process and the transesterification process were analysed with response surface methodology (RSM) to determine both data fits and the optimal process parameters. Also, multivariable type ANOVA analysis was performed to check the effectiveness of parameters in the regression model. Once the optimisation was performed and mutual effectiveness of these parameters to the respective process outputs are analysed, these optimised parameters were considered to determine the respective process reaction kinetics (i.e. reaction rate constants, reaction order and activation energy, etc.). The models used for this case has been described properly. It is expected that the detail process optimisation and the reaction kinetics of this feedstock to biodiesel production may contribute to conduct further comparative analyses with other available biodiesel conversion processes to adopt the most economic and less energy extensive processes.

The results obtained in this analysis can be summarised as follows:

• For the esterification process, the optimal condition was found as, Methanol to oil molar ratio 11.65M:1M, sulphuric acid (H₂SO₄) content 1.5 wt.% of the poppy seed oil, reaction temperature 62.8 ^oC, and the reaction period 105 minutes. Based on the RSM analysis, the maximum removal of FFA from the poppy oil was predicted as 99.88% with these optimal parameters in a conventional batch reactor system. But the experimental amount of FFA removal was 99.23% with these parameters at a higher temperature than the optimal condition predicted.

- Esterification process kinetic models were found as,
- (i) $r_A = 8.56 \times 10^{16} e^{\left[-\frac{\frac{117.2773kJ}{mol}}{RT}\right]} [C_A]^{1.035}$ for pseudo-homogeneous irreversible process with reaction order of 1.035, and activation energy 117.277kJ/mol.

(ii) $r = 4.17 \times 10^{12} e^{\left[-\frac{90.0905 \text{ kJ}}{\text{RT}}\right]} C_A$ for a first order pseudo-homogeneous irreversible process with activation energy of 90.09 kJ/mol.

- For the transesterification process, the optimal process conditions were obtained as, Methanol to esterified poppy oil molar ratio 6.515M:1M, KOH catalyst content 1.0 % wt. of the esterified oil, reaction temperature 60 °C and of reaction period 120 minutes in a batch reactor system; for which the optimal yield could be achieved as 98.2624% with a 95% confidence interval (97.994, 98.531). The experimental yield was obtained as 98.34% for 6.5M methanol, 1% KOH, 60 °C and 120 minutes reaction conditions.
- The kinetic model for the transesterification process were as follows:

(i)
$$r = -\frac{dC_B}{dt} = k_1 C_B = A_f e^{\left[-\frac{Ea}{RT}\right]} C_B = 5.01 \times 10^{11} e^{\left[-\frac{83.09012 \ k_1}{RT}\right]} C_B$$
 when the

transesterification process is considered to be a pseudo-first order irreversible process.

(ii)
$$r = kC_B^n = A_f e^{\left[-\frac{Ea}{RT}\right]} [C_B^n] = 4.93 \times 10^{20} e^{\left[-\frac{137.887 \, kJ}{mol}\right]} C_A^{1.0998}$$
 for pseudo-homogeneous irreversible process with reaction order of 1.0998.

Due to difference in chemical reaction order, these two pseudo-homogenous processes have different activation energies and frequency factors.

 Based on the yield efficiency from the esterification process and the transesterification process, the overall process conversion efficiency can be obtained by multiplying the optimal conversion rates obtained from both the processes, which is 98.14% based on the experimental maximum yields of the respective processes.

This study has comprised an overall experimental and analytical procedure to investigate the biodiesel production from inedible poppy seed oil. Further studies on this reaction kinetics will help determining the accurate reaction process kinetics for the other biodiesel production processes.

5.5 Summary of the Sunflower Oil Biodiesel (SB) Production Optimisation and Kinetic Modelling

The sunflower oil used in this study is a highly refined and edible feedstock for the Australian retail market consumers. The free fatty acid content was within the favourable limit to decide the conversion process to be a single stage alkali-transesterification process. A strong alkali homogeneous catalyst KOH was used. The main objective of the study were to investigate the optimal reaction parameters for transesterification in a conventional reactor. The parameters were methanol to oil molar ratio, catalyst weighing as % (w/w) of the oil feedstock, reaction temperature and reaction period. Optimisation was performed by RSM analyses to determine the best possible parametric quantity within the considered range of operating parameters. Box-Behnken algorithm was used to design the required number of experiments based on 4 factors and 3 levels for each factor. Total of 27 reactions were designed according to this algorithm and all the results were imported to the statistical software Minitab 18.0. Then the transesterification process was analysed with response surface methodology (RSM) to determine both data fits and the optimal process parameters. Also, multivariable type ANOVA analysis was performed to check the effectiveness of parameters in the regression model. Once the optimisation was performed and mutual effectiveness of these parameters to the respective process outputs were analysed, these optimised parameters were considered to determine the respective process reaction kinetics (i.e. reaction rate constants, reaction order and activation energy, etc.). The models used for this case has been described properly. It is expected that the detail process optimisation and the reaction kinetics of this feedstock to biodiesel production may contribute to conduct further comparative analyses with other available biodiesel conversion processes to adopt the most economic and less energy extensive processes.

The results obtained in this analysis can be summarised as follows:

 For the transesterification process, the optimal process conditions were obtained as, Methanol to sunflower oil molar ratio 6.76768M:1M, KOH catalyst content 0.994949
%wt. of the sunflower oil, reaction temperature 60 °C and of reaction period 120 minutes in a batch reactor system; for which the optimal yield could be achieved as 98.7108% with a 95% confidence interval (97.994, 98.531). The experimental yield was obtained as 99.1% for 6.8M methanol, 1% KOH, 60 0 C and 120 minutes reaction conditions.

• The kinetic model for the transesterification process were as follows:

(i)
$$r = -\frac{dC_{TG}}{dt} = k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG} = 4.9 \times 10^{08} e^{\left[-\frac{O(RTG)}{RT}\right]} C_{TG}$$
 when the transesterification process is considered to be a pseudo-first order irreversible process. The activation energy of the process was found to be 64.2148 kJ/mol.

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(ii) $r = kC_{TG}^n = A_f e^{\left[-\frac{Ea}{RT}\right]} [C_{TG}^n] = 5.3 \times 10^{08} e^{\left[-\frac{51.86 \ kJ}{RT}\right]} C_{TG}^{1.11}$ for pseudo-homogeneous irreversible process with reaction order of 1.11 and activation energy of 51.86 kJ/mol.

Due to difference in chemical reaction order, these two pseudo-homogenous processes have different activation energies and frequency factors.

This study has comprised an overall experimental and analytical procedure to investigate the biodiesel production from sunflower oil, which is one of most consumable feedstocks for biodiesel production. The optimisation study and the kinetic determination may help determine the economic impact for progressing the biodiesel production business.

5.6 Summary of the Canola Oil Biodiesel (CB) Production Optimisation and Kinetic Modelling

The canola oil used in this study is a highly refined and edible feedstock for Australian retail market consumers. The free fatty acid content was within the favourable limit to conduct single stage alkali-transesterification process. A strong alkali homogeneous catalyst KOH was used. The main objectives of the study were to investigate the optimal reaction parameters for transesterification in a conventional reactor and develop the reaction kinetics. The parameters were methanol to oil molar ratio, catalyst weighing as % (w/w) of the oil feedstock, and reaction temperature. The reaction period was kept constant for each of the sampling transesterification reactions. Optimisation was performed by RSM analyses to determine the best possible parametric quantity within the considered range of operating parameters. Box-Behnken algorithm was used to design the required number of experiments based on 3 factors and 3 levels for each factor. Total of 15 reactions were designed according to this algorithm and all

the results were imported to the statistical software Minitab 18.0. Then the transesterification process was analysed with response surface methodology (RSM) to determine both data fits and the optimal process parameters. Also, multivariable type ANOVA analysis was performed to check the effectiveness of parameters in the regression model. Once the optimisation was performed and mutual effectiveness of these parameters to the respective process outputs were analysed, these optimised parameters were considered to determine the respective process reaction kinetics (i.e. reaction rate constants, reaction order and activation energy, etc.). The models used for this case has been described properly. It is expected that the detail process optimisation and the reaction kinetics of this feedstock to biodiesel production may contribute to conduct further comparative analyses with other available biodiesel conversion processes to adopt the most economic and less energy extensive processes.

The results obtained in this analysis can be summarised as follows:

- For the transesterification process, the optimal process conditions were obtained as, Methanol to canola oil molar ratio 5.88772M:1M, KOH catalyst content 0.5 % wt. of the canola oil, and reaction temperature 60 °C for the reaction period of 120 minutes in a batch reactor system. With these parameters, the optimal yield was predicted as 99.514% with a 95% confidence interval (99.077, 99.952). The experimental yield was obtained as 99.61% for 5.9M methanol, 0.5% KOH, 60 °C and 120 minutes reaction conditions.
- The kinetic model for the transesterification process were as follows:

(i)
$$r = -\frac{dC_{TG}}{dt} = k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG} = 3.05 \times 10^{10} e^{\left[-\frac{75.37 \text{ kJ}}{RT}\right]} C_{TG}$$
 when the

transesterification process is considered to be a pseudo-first order irreversible process. The activation energy of the process was found to be 75.37 kJ/mol.

(ii) $r = kC_{TG}^n = A_f e^{\left[-\frac{Ea}{RT}\right]} [C_{TG}^n] = 2.77 \times 10^{10} e^{\left[-\frac{62.577 \, kJ}{mol}\right]} C_{TG}^{1.175}$ for pseudo-homogeneous irreversible process with reaction order of 1.175 and activation energy of 62.577 kJ/mol.

Due to difference in chemical reaction order, these two pseudo-homogenous processes have different activation energies and frequency factors.

This study has comprised an overall experimental and analytical procedure to investigate the biodiesel production from canola oil, which is one of mostly used feedstocks for biodiesel production. The optimisation study and the kinetic determination may help determine the economic impact for progressing the biodiesel production business.

5.7 Properties of the Biodiesel Fuels

Feedstocks used for biodiesel production were, (i) Beef Tallow, (ii) Waste cooking oil, (iii) Castor oil, (iv) Poppy seed oil, (v) Sunflower oil and (vi) Canola oil. All but sunflower and canola oil feedstocks were processed with 2 stage biodiesel production process (esterification and transesterification) in a batch reactor. Waste cooking oil biodiesel (WCB) was blended with both beef tallow biodiesel (WTB) and poppy oil biodiesel (PB) respectively to produce, (i) Waste tallow (70%) + waste cooking oil (30%) binary blend (WTC) and (ii) Poppy oil biodiesel (70%) + waste cooking oil (30%) binary blend (PWC). Also, beef tallow biodiesel (WTB) was blended with poppy oil biodiesel (PB) to prepare binary biodiesel blend of waste tallow poppy (WTP) fuel. The fatty acid methyl ester compositions of these fuels are presented in the Table 5-19.

Key fuel properties along with fatty acid methyl ester (FAME) compositions were measured (Table 5-20) for these fuels by following relevant standards and experimental procedures. The relevant uncertainty analysis is presented in the Appendix A5 (Table A5-1). Table 5-20 shows that due to optimisation on esterification process, the acid values were very low. It is mostly desirable to have such low FFA in the feedstock before processing through transesterification process to produce biodiesel. The oxidation stabilities varied for the fuel in the order CaB>PB>CB>PWC>WTP>WCB>SB>WTC>WTB. Only, CaB, PB, CB and PWC could naturally meet the current European biodiesel standard for oxidation stabilities. Also, castor biodiesel (CaB) possess the highest of the viscosities, which limits its direct application as fuel. Rather this fuel could be used mixing with other less viscous and less oxidation stable fuel by meeting the acceptable biodiesel standard. Among three blends of the biodiesels used in this study, the PWC has good oxidative stability. All these fuels meet the ASTM standards. Among the cold flow properties of the fuels, the CFPP values of the fuels varied in the order WTB>WTC>WTP>WCB>SB>PWC>CB>PB>CaB. Since WTB and its binary blends with WCB and PB show higher CFPP, more options could be observed with further research works to naturally reduce their CFPP values where tallow biodiesel is a prominent source of alternative fuels.

Table 5-19 Fatty acid methyl ester (FAME) composition of the produced biodiesels, (i) Beef Tallow (WTB), (ii) Waste cooking oil (WCB), (iii) Castor oil (CaB), (iv) Poppy seed oil (PB), (v) Sunflower oil (SB) (vi) Canola oil (CB), (vii) WTC (70%WTB+30%WCB), (viii) WTP (70%WTB+30%PB) and (ix) PWC (70%PB+30%WCB)

FAME Group	Linear Structure	WTB	WCB	CaB	РВ	SB	СВ	WTC	WTP	PWC
C8:0	CH ₃ (CH ₂) ₆ COOCH ₃ (Methyl caprylate)						0.19			
C10:0	CH ₃ (CH ₂) ₈ COOCH ₃ (Methyl caprate)						0.1			
C12:0	CH ₃ (CH ₂) ₁₀ COOCH ₃ (Methyl laurate)						0.1			
C14:0	CH ₃ (CH ₂) ₁₂ COOCH ₃ (Methyl myristate)	4.03	4.8				0.1	4.28	2.74	1.49
C15:0	CH ₃ (CH ₂) ₁₃ COOCH ₃ (Methyl pentadecanoate)	1.03						0.72	0.71	
C16:0	CH ₃ (CH ₂) ₁₄ COOCH ₃ (Methyl palmitate)	23.5	16.5	0.74	9.2	12.15	6.35	21.26	18.93	11.46
C16:1	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl palmitoleate)	3.82	1.9		0.22			3.21	2.65	0.74
C17:0	CH ₃ (CH ₂) ₁₅ COOCH ₃ (Methyl heptadecanoate)	3.08						2.09	2.11	
C18:0	CH ₃ (CH ₂) ₁₆ COOCH ₃ (Methyl stearate)	28.19	4.1	0.55	2.7	3.83	5.65	20.48	20.03	3.13
C18:1	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl oleate)	33.21	44.1	3.85	15.3	26.77	42.47	36.69	27.51	24.21
C18:2	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl linoleate)	1.48	23.5	5.58	71.9	54.15	16.65	8.53	24.01	56.91
C18:3	CH ₃ CH ₂ CH=CHCH ₂ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl linolenate)	1.67	3.99	0.46	0.69		27.85	2.41	1.36	1.72
C18:1(OH)	CH ₃ (CH ₂) ₅ CH(OH)CH ₂ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl ricinoleate)			88.53						
C20:0	CH ₃ (CH ₂) ₁₈ COOCH ₃ (Methyl arachidate/ Archidic acid)		0.41	0.31		3.09	0.2	0.13		0.13
C22:0	CH ₃ (CH ₂) ₂₀ COO CH ₃ (Methyl behenate/hydroflo acid)		0.69				0.2	0.22		0.21
C22:1	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₁₁ COOCH ₃ (Methyl erucate/ Heneicosanoic acid.)						0.14			
SFAME	Total Saturated FAME	59.83	26.5	1.6	11.9	19.07	12.89	49.18	44.52	16.42
MUFAME	Total Monounsaturated FAME	37.03	46	92.38	15.52	26.77	42.61	39.9	30.16	24.95
PUFAME	Total Poly Unsaturated FAME	3.15	27.49	6.04	72.59	54.15	44.5	10.94	25.37	58.63

Properties	WTB	WCB	CaB	PB	SB	СВ	WTC	WTP	PWC	Diesel	Relative uncertainty
Kinematic Viscosity (mm ² /s, at 40 °C)	4.96	5.31	14.8	4.16	4.42	4.56	5.15	4.77	5.01	3.34	±0.35
Density (g/cm ³ , at 15 °C)	0.883	0.889	0.909	0.887	0.869	0.883	0.885	0.884	0.886	0.833	±0.005
Higher Heating Value (MJ/kg, HHV)	41.4	40.16	40.65	40.59	40.52	40.99	41.1	41.12	40.32	45.67	±0.1%
Lower Heating Value (MJ/kg, LHV)	39.40	39.51	39.23	39.77	39.67	39.61	39.42	39.48	39.59	42.30	±0.1%
Oxidation Stability (hours, at 110 °C)	4.02	5.88	23.21	12.31	4.87	10.42	4.45	7.8	10.7	39.5	±0.01 h
Flash Point (°C)	161	172.1	197	171.82	180.2	170.2	170.3	168.95	171.95	69	±0.1 °C
Pour Point (°C)	8.1	-3.2	-21	-13.16	-5.8	-8	6.2	-1.5	-9.4	0	±0.1 °C
Cloud Point (°C)	11.5	3.5	-16	-5.21	2.4	-1.8	9.8	4.4	-2.5	8	±0.1 °C
Cold filter plugging point (°C, CFPP)	10	-1.3	-14	-8.78	-1.5	-7.9	7.1	2.6	-6.5	5	±0.1 °C
Cetane Number (CN)	62.22	57.98	51.1	58.96	56.25	58.32	60.92	61.35	58.36	48	±0.13
Iodine Value (IV, g I ₂ /100g oil)	68.95	91.11	50.2	135.25	115.05	126.1	76	90	120	NA	±3.5
Saponification Value (SV, mg KOH/ g oil)	205.98	204.12	198.1	202.19	200.15	201.15	206	205	202.151	NA	±2.9
Acid Value (AV, mg KOH/g oil)	0.199	0.24	1.11	0.09	0.62	1.45	0.21	0.17	0.16	0.06	±0.001

Table 5-20 Physico-chemical properties of the biodiesel fuels, (i) Beef Tallow (WTB), (ii) Waste cooking oil (WCB), (iii) Castor oil (CaB), (iv) Poppy seed oil (PB), (v) Sunflower oil (SB) (vi) Canola oil (CB), (vii) WTC (70% WTB+30WCB) and (viii) PWC (70% PB+30% WCB)

5.8 Concluding Remarks

Altogether 6 feedstocks were processed to produce biodiesel and optimise their process operating parameters. The optimisation processes were analysed with response surface methodology (RSM) with statistical software Minitab 18.0 along with analysis of variance (ANOVA) to detect the significance of the models developed. Based on the experimental results and the relevant RSM-ANOVA analyses, the optimal process parameters for each of the processes are listed in the Table 5-21. For each of the feedstocks, the variation of FFA, oilto-methanol molar ratio, and the reaction conditions (i.e. time and temperature) can influenced the optimal amount of acid catalyst required for the esterification process. Similarly, the amount of base catalyst also differed based on the FFA content (within the maximum limit of FFA for transesterification process), moisture content, the oil-to-methanol molar ratio, temperature, and time for reaction processes. Also, the reaction kinetics obtained for different reaction process types of the esterification and transesterification processes of the biodiesel feedstocks are briefly tabulated in the Table 5-22. Since there is no universal kinetics available for the esterification and transesterification processes, the kinetics were developed based on most available and adopted reaction kinetic models for various biodiesel production methods. While determining the reaction kinetics, the assumptions caused the variation of activation energies, frequency factors and reaction orders for the same fuel. Fatty acid methyl ester compositions and a few of the key chemical properties were determined for the studied fuels.

	Optimal values of the esterification process parameters								
Oil/Feedstocks	Methanol to Oil Molar ratio	Acid catalyst content (% w/v of oil)	Reaction Temperature (⁰ C)	Reaction duration (minutes)	Acidity (FFA) removed (% of initial quantity)				
Tallow	12:1	1.89	59.75	108.49	98.34				
WCB	8.12:1	1.9	60	90	98.62				
CaB	12:1	2	64	120	96.18				
PB	11.65:1	1.5	62.8	105	99.23				
SB									
СВ									
	Optimal values of the transesterification process parameters								
Oil/Feedstocks	Methanol to Oil Molar ratio	Alkali catalyst content (% w/v of oil)	Reaction Temperature (⁰ C)	Reaction duration (minutes)	Biodiesel (FAME) yield efficiency (%)				

Table 5-21 Esterification and transesterification process optimisation parameters for various biodiesel feedstocks

Tallow	6.20:1	1.89	60.35	120	99.8
WCB	6.1:1	1.2	60	110	98.81
CaB	6.3:1	1	59.72	120	98.95
PB	6.52:1	1	60	120	98.26
SB	6.8:1	1	60	120	99.1
СВ	5.9:1	0.5	60	120	99.61

Table 5-22 Kinetic models of esterification and transesterification processes for various biodiesel feedstocks

Feedstock	Reaction process type	Kinetic Model
Tallow Esterification	Irreversible pseudo- homogeneous	$r_A = 3.16 \times 10^{10} e^{\left[-\frac{72.86 kJ/mol}{RT}\right]} [C_A]^{1.02}$
	Pseudo-homogenous reversible	$\frac{d[A]}{dt} = \frac{dE}{dt} = K_1(A_0 - E) - K_2 E^2 = 1.68 \times 10^{17} \cdot e^{\left[-\frac{119.62183}{RT}\frac{kJ}{mol}\right]} (A_0 - E) - 2.98 \times 10^6 \cdot e^{\left[-\frac{54.7693kJ/mol}{RT}\right]} E^2$
Tallow Trans- esterification	Pseudo-first order	$\begin{split} r &= -\frac{dC_{TG}}{dt} = k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG} = 1.252 \times \\ 10^{14} e^{\left[-\frac{98.712 \frac{kJ}{mol}}{RT}\right]} C_{TG} \end{split}$
WCB Esterification	Irreversible pseudo- homogeneous	$r_A = 2.38 \times 10^{19} e^{\left[-\frac{\frac{130.2471kJ}{mol}}{RT}\right]} [C_A]^{1.151}$
	Irreversible pseudo- homogenous first order	$r = -\frac{dC_A}{dt} = k_1 C_A = A_f e^{\left[-\frac{Ea}{RT}\right]} C_A = 4.73 \times 10^7 e^{\left[-\frac{57.369}{RT}\frac{kJ}{mol}\right]} C_A$
WCB Trans- esterification	Pseudo-first order irreversible	$r = -\frac{dC_{TG}}{dt} = k_1 C_B = A_f e^{\left[-\frac{Ea}{RT}\right]} C_B = 1.96 \times 10^8 e^{\left[-\frac{61.903 \text{ kJ}}{RT}\right]} C_B$
	Pseudo-homogeneous irreversible	$r = kC_A^n = A_f e^{\left[-\frac{Ea}{RT}\right]} [C_A^n] = 1.43 \times 10^{11} e^{\left[-\frac{79.13348 kJ}{RT}\right]} C_A^{1.088133}$

CaB	Pseudo-homogenous	$\left[\begin{array}{c} \frac{110.35k}{mal} \end{array}\right]$
Esterification	irreversible	$r_A = 5.71 \times 10^{15} \ e^{\left[\frac{-m_A}{RT}\right]} [C_A]^{1.013}$
CaB Trans- esterification	Pseudo-first order irreversible	$\begin{split} r &= -\frac{dC_B}{dt} = k_1 C_B = A_f e^{\left[-\frac{Ea}{RT}\right]} C_B = 1.1208 \times \\ 10^{17} e^{\left[-\frac{118.998282 \frac{kJ}{MOl}}{RT}\right]} C_B \end{split}$
	Pseudo-homogeneous irreversible	$r = kC_B^n = A_f e^{\left[-\frac{Ea}{RT}\right]} [C_B^n] = 7.45 \times 10^{14} e^{\left[-\frac{92.426738 kJ}{RT}\right]} C_A^{1.033167}$
PB Esterification	Pseudo-homogeneous irreversible	$r_A = 8.56 \times 10^{16} e^{\left[-\frac{117.2773kJ}{mol}\right]} [C_A]^{1.035}$
	First order pseudo- homogeneous irreversible	$r = 4.17 \times 10^{12} e^{\left[-\frac{\frac{90.0905 \text{ kJ}}{\text{mol}}}{\text{RT}}\right]} C_{\text{A}}$
PB Trans- esterification	Pseudo-first order irreversible	$\begin{split} r &= -\frac{dC_{B}}{dt} = k_{1}C_{B} = A_{f}e^{\left[-\frac{Ea}{RT}\right]}C_{B} = 5.01 \times \\ 10^{11}e^{\left[-\frac{83.09012 \ kJ}{RT}\right]}C_{B} \end{split}$
	Pseudo-homogeneous irreversible	$r = kC_B^n = A_f e^{\left[-\frac{Ea}{RT}\right]} [C_B^n] = 4.93 \times 10^{20} e^{\left[-\frac{\frac{137.887}{MOL}}{RT}\right]} C_A^{1.0998}$
SB Trans- esterification	Pseudo-first order irreversible	$r = -\frac{dC_{TG}}{dt} = k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG} = 4.9 \times 10^{08} e^{\left[-\frac{64.2148 kJ}{mOl}\right]} C_{TG}$
	Pseudo-homogeneous irreversible	$r = kC_{TG}^{n} = A_{f}e^{\left[-\frac{Ea}{RT}\right]}[C_{TG}^{n}] = 5.3 \times 10^{08}e^{\left[-\frac{51.86 \ kJ}{RT}\right]}C_{TG}^{1.11}$
CB Trans- esterification	Pseudo-first order irreversible	$r = -\frac{dC_{TG}}{dt} = k_1 C_{TG} = A_f e^{\left[-\frac{Ea}{RT}\right]} C_{TG} = 3.05 \times 10^{10} e^{\left[-\frac{75.37 \text{ kJ}}{RT}\right]} C_{TG}$
	Pseudo-homogeneous irreversible	$r = kC_{TG}^{n} = A_{f}e^{\left[-\frac{Ea}{RT}\right]}[C_{TG}^{n}] = 2.77 \times 10^{10}e^{\left[-\frac{62.577 kJ}{RT}\right]}C_{TG}^{1.175}$

Chapter 6

EXPERIMENTAL INVESTIGATION OF PLASTICS DISSOLUTION IN BIODIESEL

6.0 Introduction

This chapter presents the detail for the experimental investigations of the dissolution of plastics (PE, PP and PS) into various studied Biosolvents. All the nine biodiesel fuels are treated as biosolvents in this study. Dissolution profile (temperature vs dissolution time) for plastics into biodiesel solvents, variation of solution viscosities and reaction kinetic models for dissolution processes are also discussed.

6.1 Experimental Methodology of Plastics Dissolution in Biodiesel

The dissolution process was carried out in a chemical batch reactor. A general workflow chart that was followed in this study to investigate the dissolution profile of the plastics in the biodiesel solvents and a simplified experimental set up are presented as in the Figure 6-1(a-b).



Figure 6-1 (a) Schematic diagram of dissolving the plastics in biodiesel, (b) Simplified experimental set up for PS dissolution in biodiesel

This dissolution reactor was comprised of a stirring facility, heating system through temperature control system, condensing chamber and feeding unit. The feedback control system ascertained the efficient control of reaction temperatures. The stirring speed was also controlled by the integrated control system within reactor heating system and the stirrer inside the reactor was magnetically controlled. The temperature was raised gradually and the dissolution process was inspected. After visual inspection of completion of dissolution process, the dissolved solution was filtered to remove any undissolved plastic particle to avoid any risk of clogging in the engine fuel injection system. Prior to the mixing of the polymers in the solvent (i.e. biodiesel), it is highly recommended that the plastics should be cleaned and dried completely to avoid the presence of unwanted substances in the system that may require stricter filtration system after the polymers were dissolved. In this study, the plastic polymers were of granular sizes. Chopping or granulating the polymers increased surface areas for efficient heat transfer. Thus, dissolution was accelerated due to the increased number of polymer-solvent interactions.

The dissolution chamber (glass beaker) contained preheated (50-80 $^{\circ}$ C) biodiesel solvents, which were produced from various sources. The heating rate was varied from 5 $^{\circ}$ C/min to10 $^{\circ}$ C/min with the variable temperature controller of the hot plate, so that the solubility rate could be observed. Also, the maximum temperature of this process was selected as per the highest melting point of PIC1-6 plastics. Gradual increase of temperature and suitable stirring speed (500-800 rpm) improved the solubility of the solutes. The maximum amount of solute to be dissolved in the solvent was limited to 15% (w/v).

In spite of a visual inspection of completion of the dissolution process, there could be a trace amount of undissolved solid in the solvent. That is why, the solution was filtered through a fine grade filtration process after the solution temperature dropped to room temperature. For this study purpose, the dissolution experiments were performed with only polyethylene (LDPE), polypropylene (PP) and polystyrene (PS). However, about 9 types of biodiesel fuel-based solvents (i.e. biosolvents) were used for each of the solutes.

6.2 Dissolution Rate Constant Determination

In general, both the liquid solvent and the solid solute are distinctly bonded by their own inter-molecular bonding energies. So, if a solute is dissolving in a solvent, there is an obvious change of energy to break the particle bonding within solute and solvents. Energy input is required if the solvent's inter-molecular bonds are not attracted by those of the solute. While breaking their individual bonding, a new bonding is developed causing dissolution. The dissolution behaviour of a solute in the solvent has been briefly discussed in the section 3.1 and section 3.2.

A dissolution process can be either endothermic or exothermic. If the dissolution process needs external energy input to build the mutual bonding between solute and solvent, it is known as an endothermic reaction process. On the other hand, if there is release of energy during the dissolution process to construct the mutual bonding between solute and solvent the process is called exothermic reaction. During polymer dissolution the stress relaxation, change of viscoelasticity, chain disentanglement, chain reptation phenomena and various transport phenomena of the solvent occurs. Further details of the dissolution kinetics of various types of polymers (i.e. amorphous, crystalline, and semi-crystalline) are also presented in various publications **[185, 187, 190]**.

In this thesis, a gravimetric procedure was adopted to determine the dissolution rate constant for polymers in biodiesel solvents. Due to an excess amount of solvent within a batch reactor the dissolution process was considered as a pseudo first order chemical reaction process, similar to the reaction kinetics of the biodiesel esterification process for pseudo-homogeneous first order irreversible reaction process [314]. The reaction rate equation can be expressed as follows:

$$\ln\left(\frac{c_{po}}{c_p}\right) = k_{diss}t \quad \dots \quad (Eq. \ 6.1)$$

Here, C_{p0} is the initial concentration of polymer (which is completely dissolved in this process) at time t=0 and C_p is the concentration undissolved polymer after time t=t. Also, k_{diss} is the dissolution rate constant which can be derived from the $ln\left(\frac{C_{p0}}{C_p}\right)$ vs. t graph developed from the gravimetric analysis.

The activation energy for the dissolution process can be thus determined by following Arrhenius equation for rate constant as used for a similar purpose by Zhang at el. [347].

$$k_{diss} = Ae^{-\frac{E_a}{RT}}$$
 ------ (Eq. 6.1a)

With the known value of k_{diss} from equation 3.31 and T from the experimental conditions the Eq. 6.1a can be used to determine the activation energy for the dissolution of polymers in a solvent.

Analytically, the phenomenon of dissolution kinetics of polymer solute (solid substance) in a solvent can be explained by the combination [348] of Fick's first law of diffusion (states as, "the molar flux due to diffusion is proportional to the concentration gradient" [349]) and Noyes-Whitney equation [350-352].

Fick's first law can be expressed as follows:

$$\frac{dm}{dt} = -DA_s \frac{dC}{dh} - \dots - \dots - (Eq. \ 6.1b)$$

Here, $\frac{dm}{dt}$ is the rate of amount change with respect to time (i.e. the molar flux, mol/sec), D is the diffusion coefficient (m/s), A_s is the total surface area (phase interface) of the dissolved polymer, and $\frac{dC}{dh}$ (concentration gradient) is the change of concentration with respect to the diffusion layer thickness (h).

The diffusion coefficient (D) of the solute in solution can be determined by following Stokes-Einstein equation [353] as follows:

$$D = \frac{kT}{6\pi\eta r} - \dots - (\text{Eq. 6.1c})$$

Here, k is the Boltzmann constant (1.38064852×10⁻²³ m²kgs⁻²K⁻¹), T is the temperature in kelvin, η is the viscosity of solvent, and r is the radius of solute molecules.

In case of an efficient dissolution process, the tiny diffusion layer thickness can convert the differential version of the concentration gradient into a linear function as follows:

$$\frac{dc}{dh} = \frac{C_p - C_{p0}}{h}$$
 (Eq. 6.1d)
And $dm = VdC$ ------(Eq. 6.1e)

Here, V is the volume of the solution. C_{P0} and C_P are the total amount of solute to be dissolved and amount of dissolved substance in the solvent at time t, respectively.

Thus, transferring the relations of Eq. 6.1d and Eq. 6.1e into the Eq. 6.1b, the Noyes-Whitney equation [**353**, **354**] can be expressed as follows:

$$\frac{dC}{dt} = \frac{DA_s}{Vh} \times (C_{p0} - C_p) = k_{diss} (C_{p0} - C_p) - \dots - \dots - (Eq. \ 6.1f)$$

Here, k_{diss} is the constant of proportionality or rate constant of the process.

In terms of mass rate of dissolution, the Eq. 6.1f can be also expressed as follows:

$$\frac{dm}{dt} = \frac{DA_s}{h} \times (C_{p0} - C_p) = k_{diss} (C_{p0} - C_p) - \dots - \dots - (Eq. \ 6.1g)$$

Integrating the Eq. 6.1f for time t (o to t), Eq. 6.1f gives [351]:

$$\ln C_{p0} - \ln (C_{p0} - C_p) = k_{diss}t$$
 (Eq. 6.1h)

Here, Eq. 6.1h is an obvious form of first-order reaction rate. The rate constant can be obtained as in Eq. 6.1i or Eq. 6.1j.

Eq. 6.1j indicates that the dissolution time and dissolution rate constants are inversely related, i.e. the increase in the dissolution period will reduce the rate constant value. Hence, when there is increase in quantity of solute there will be an increase dissolution period and it will reduce the dissolution rate constant.

Taking logarithm in each side, the Eq. 6.1a, the following expression can be obtained:

$$\ln k_{diss} = \ln A + \left(-\frac{E_a}{R}\right) \cdot \frac{1}{T} - \dots - (\text{ Eq. 6.1k})$$

Now, a curve between $\ln k_{diss}$ and $\frac{1}{T}$ will provide the activation energy of the dissolution process, where A is the frequency factor of the dissolution process and R = 8.3145 Jmol⁻¹K⁻¹.

6.3 Dissolution Profile and Reaction Kinetic Modelling of Polymer in Biodiesel

6.3.1 Solubility Profile of Polyethylene (PE) in Various Biosolvents

Figure 6-2 (a-i) demonstrates the solubility profile of polyethylene (PE) in various solvents, (a) Ca100, (b) WCO100, (c) PWC100, (d) C100, (e) PB100, (f) WTP100, (g) WTB100 and (i) SF100. After theoretical analysis of solubility of PE at 25 °C in these solvents in the 6.2, the experimental analysis was performed at higher temperatures. The tests were performed at 85 °C, 100 °C, 120 °C, 135 °C and 145 °C for solvents mentioned in the Figure 6-1(b-h). But for Ca100, the dissolution temperatures were, 85 °C, 100 °C, 120 °C, 135 °C and 150 °C. Whereas for SF100, the dissolution temperatures were, 85 °C, 100 °C, 110 °C, 120 °C, and 135 °C. The reason for varying the temperatures of dissolution process observation is to investigate whether dissolution of PE is an exothermic or endothermic process. In all of these solvents, the increase in temperature indicates increased rate of dissolution. Polymers are made of large chains. So, it is essential to provide enough energy to break the chains of the solutes by the solvents and turn them into a polymer-biodiesel solution. The relevant energy changes of breaking the bonds and forming a new bond with the solvent to produce a solution has been identified as activation energy for the process.





Figure 6-2 Dissolution profile (dissolution duration and temperature relationship) of low density polyethylene (PE) in various biodiesel solvents: (a) Ca100, (b) WCO100, (c) PWC100, (d) C100, (e) PB100, (f) WTP100, (g) WTB100 and (i) SF100

Though the low-density polyethylene (LDPE), generally denoted as polyethylene (PE) in this study, forms a very good solution beyond 85 ^oC, the PE-biodiesel solutions turn cloudy when the temperature is reduced from that level. Once the PE was dissolved in any of these solvents, it turned into a gel like paste at room temperature. But, at higher temperatures, the solution was visually checked and a microfilter was used to check any undissolved portion of the PE solute.

6.3.1.1 Reaction Kinetics for Polyethylene (PE) Dissolution Process

To determine the reaction kinetics of the polymer dissolving in a certain biodiesel solvent, the experiments were designed to record the time requirements with weight fraction for each temperature and polymer contents. Due to the similarity in procedures, out of all the 9 solvents used for PE dissolution analyses, only the kinetic modelling of polyethylene (PE) dissolution in castor biodiesel (Ca100) will be explained in detail in this chapter. The dissolution experiments were performed with 5%, 10% and 15% (w/v) polyethylene at various temperatures, i.e. 85 °C, 100 °C, 120 °C, 135 °C, and 150 °C. To observe the time required to dissolve the PE solute in the Ca100 solvent, the total quantity of polymer to be dissolved was dividied into a few weight fractions. Once the solvent reached the desired temperture, the first weight fraction of PE (e.g. 20% of the total PE to be dissolved) was put in the solvent and inspected for the dissolution visually. When the dissolution of that certain amount of solute was confirmed through the visual inspection, then the next portion was fed in the the reactor and the duration of the dissolution was recorded.

The experimental conditions were as follows:

Quantity of solvent: 500 ml of Ca100 (100% (v/v) Castor oil biodiesel)

Quantity of solute: LDPE pellets (1) 15% (w/v) of solvent = 75 gm, (2) 10% (w/v) of solvent = 50 gm, (3) 5% (w/v) of solvent = 25 gm

The dissolution profile of LDPE in Ca100 has been shown in the Figure 6-3(a, c, and e) for 15%(w/v), 10%(w/v) and 5%(w/v) LDPE respectively at temperatures, 85 °C, 100 °C, 120 °C, 135 °C and 145 °C. These figures were used to determine the $\ln\left(\frac{c_{p0}}{c_{p0}-c_p}\right)$ vs t graphs for each of the temperatures at which the plastic was dissolved in the solvent. The details of this relationship have been explained in the section 6.2. As per the Eq. 6.1h, the slopes of these relationship are the dissolution rate constants (k_{diss}) at that respective temperature. In the

Figure 6-3(b, d, f), the relationships solute $\left(\ln\left(\frac{c_{p0}}{c_{p0}-c_p}\right)vs t\right)$ for LDPE solute are presented accordingly for 15%(w/v), 10%(w/v) and 5%(w/v). So, by using these three figures (Figure 6-3(b, d, f)) the dissolution rate constants were determined for the dissolution profiles given in the Figure 6-1(a, c, e). Due to assumption of pseudo first order reaction mechanism for the dissolution process, the initial point and the end point of the logarithmic components were impractical to measure.

Based on the temperature and the respective slopes, a relationship between $\ln k_{diss}$ and $\frac{1}{T}$ could be constructed to determine the activation energy of the dissolution process (Figure 6-3(g, h, i) and Table 6-1), where A is the frequency factor of the dissolution process and R = 8.3145 Jmol⁻¹K⁻¹. Thus, following the information from the Figure 6-3(b, d, and f), the Arrhenius equation plots were obtained for each of the weight categories of polymer dissolution in the Ca100 solvent. Here, Figure 6-2(g, h, and i) are the respective $\ln k_{diss}$ vs $\frac{1}{\tau}$ relationships respectively for 15%PE, 10%PE and 5%PE. As per the Eq. 6.1j, the slopes of these figures were used to determine the activation energies of the respective dissolution processes and the intercept of the ordinate was the reaction frequency factor. Table 6-1 presents the activation energies derived from the dissolution process of various quantities of LDPE in the Ca100 biodiesel solvent. Figure 6-3(j) presents the graphical relationship between the activation energy and the percentage weight of LDPE dissolved in the solvent to show how the activation energy varies with the variation of weights of solutes in the biodiesel solvent. It shows that the activation energy reduced with the increase in percentage weight of solute in the solvent. This feature can be explained as the increased number of intermolecular collisions during a given amount of heat energy to dissolve the polymers. As the solvent volume was constant for each of the temperature cases, the number of solute molecules increased the collisions among them, which increased the solubility.

LDPE quantity in Ca100 solvent (%w/v)	From graphs the slope: $-\frac{E_a}{R}$	From graphs the slope: $\frac{E_a}{R}$	R (Jmol ⁻¹ K ⁻¹)	Activation energy for the respective dissolution processes, Ea (kJ/mol)	Frequency factor, A
15	-2202.7	2202.7	8.3145	18.31	0.4488
10	-2358.8	2358.8	8.3145	19.61	0.9984
5	-2573.9	2573.9	8.3145	21.40	5.929

Table 6-1 Determination of activation energies of dissolution process of various weights of LDPE in Ca100 solvent

In order to determine the reaction kinetics of the dissolution profile, i.e. dissolution of PE in the Ca100, the required graphical information and calculations are presented in the Figure 6-3(a-j).







Figure 6-3(a-j) Reaction kinetics determination of 15% (a,b,g), 10% (c, d, h), and 5% (e, f,i) PE dissolving in Ca100 solvent, and the variation of activation energies during dissolution of PE while varying %wt in the solvent (j)



Figure 6-4 Activation energies due to variation of LDPE in various biodiesel solvents at given temperatures

The dissolution experimental investigation of LDPE was performed with 9 different solvents (i.e. Ca100, WCO100, PWC100, C100, PB100, WTP100, WTB100, WTC100 and SF100). All the reaction kinetic models were determined by following the steps for LDPE (or generally indicated as PE) dissolution kinetic model with Ca100 solvent. Figure 6-4 shows the variation of activation energies of the dissolution processes of PE in these solvents. The figure shows that the activation energies are positive, indicating endothermic effects during dissolution of the PE at given temperatures and quantities. The activation energy for 15% (w/v) PE varied from 18.31 kJ/mol to 30.01 kJ/mol, averaging 21.14 kJ/mol. The activation energy for 10% (w/v) PE varied from 17.68 kJ/mol to 30.50 kJ/mol averaging 22.94 kJ/mol. Similarly, the activation for the 5% (w/v) PE varied between 19.03 kJ/mol and 35.83 kJ/mol, averaging 24.35 kJ/mol. During the experiment, the volumes of the solvents were kept constant for the variable quantities of the PE solute. In Figure 6-2(a-i), it has been observed that the increase in dissolution process temperature increased the solubility rate of the PE for the given solvents. This temperature effect indicates that the chains require more energy to break down from their polymer states. The endothermic activation energies indicate that heat was absorbed while the dissolution process broke the polymers and dissolved them to form polymer-biodiesel solutions as per the Le Chatelier's principle [355]. Figure 6-4 also shows that activation energies for the dissolution process of the lower amount of PE in the given biodiesel solvents are mostly higher than that of the highest amount of PE dissolved except in case of WCO100. One of the reasons could be due to the presence of more solvent and less solutes within a given situation. Due to a lesser amount of solute in the solvent, the particles are mostly dealt by the solvent. But with more particles in the system, there could be mutual interactions of the particles while stirring. Fraction of bond dissociation energies for polymer bond breaking could be supplied from these interactions.

6.3.2 Solubility Profile of Polypropylene (PP) in Various Biosolvents

In the Figure 6-5(a-i), the dissolution profile of the polypropylene (PP) solute in various biodiesels (referred as bio-solvents), namely: (a) Ca100, (b) WCO100, (c) PWC100, (d) C100, (e) PB100, (f) WTP100, (g) WTB100 and (i) SF100, are shown at various temperatures. The figure also gives information about the variation of total dissolution duration of the amount of PP, i.e. 15% (w/v), 10% (w/v) and 5% (w/v) of the solvents. The dissolution processes of PP in various solvents were performed at various temperatures, i.e. at 100 $^{\circ}$ C, 120 $^{\circ}$ C, 135 $^{\circ}$ C, 145 $^{\circ}$ C and 155 $^{\circ}$ C respectively for each of the weight portions.

These dissolution profiles are indicating that, with the increasing temperature of the dissolution processes the total dissolution period reduced by a few hundred minutes. It explains that the solubility increases with the increase in heating rates in terms of higher temperatures. The lower the temperature, the higher time period is required to dissolve the given amount of solute. While observing the dissolution processes, it was found that, though the solution was very clear at any temperatures beyond 100 ^OC all of these PP-biodiesel solutions turned into cloudy solutions below this temperature level. Obviously, the lower amount of PP required lesser duration to be dissolved completely. But the dissolution profile indicates that the higher temperatures do not require more time to dissolve the increased quantity of the PP in the solvents as it occurred at lower temperatures. The relationships of polymer quantity, temperature increase and the dissolution periods are well described in the Figures 6-6 (a, c and e), which were used to determine the process kinetics in terms of solubility rate constants and the activation energies of the processes.





(a)

(g)







Temperature (^oC)







(b)

800

(minutes) 400 200

0

(d)

100 C

120 C

PP Dissolution Profile with WCO100 as Solvent WCO100PP5 WCO100PP10 WCO100PP15 0 100 C 120 C 135 C 145 C 155 C Temperature (°C)

PP Dissolution Profile with C100 as Solvent

135 C

Temperature (°C)

-C100PP15

145 C

155 C

*C100PP5



Figure 6-5 Dissolution profile (dissolution duration and temperature relationship) of polypropylene (PP) in various biodiesel solvents: (a) Ca100, (b) WCO100, (c) PWC100, (d) C100, (e) PB100, (f) WTP100, (g) WTB100 and (i) SF100

6.3.2.1 Reaction Kinetics for Polypropylene (PP) Dissolution Process

To investigate the dissolution kinetics of the PP solubility in the biodiesel solvents, the volumes of the solvents was kept constant at 500ml. While considering the dissolution process as a pseudo-first order reaction process as described in the section 6.2, the duration of % wt. of dissolution of the solute at given temperature was recorded. A brief presentation of the combination of various established relationships on solubility rate determination has been presented in this section. Figure 6-6(a, c, and e) presents the % wt. of PP dissolution amount vs time of dissolving that quantity of polymer in the given solvent, Ca100. Similar graphs were also obtained for the rest of the experiments. Due to similar calculation procedures used for the kinetic reaction modelling of PP in all the solvents used in this study, only one set of graphical calculations are shown here in the Figure 6-6 (a-j). To determine the dissolution rate constants, the graphs of $\ln(C_{P0}/(C_{P0}-C_P))$ vs time were determined and presented in the Figure 6-5(b, d, and f) for the 15%, 10% and 5% PP dissolution processes respectively. The linear trend lines of the relationships gave the slopes as the rate constant for dissolution (k_d) for the respective conditions.

Once the rate constants were determined with acceptable regression fits, the lnk_d vs 1/T graphs were applied to the Arrhenius equation, to determine the activation energies for each of the weight categories of the polymer dissolving in the Ca100 solvent. Here, the activation energies for 15%, 10% and 5% PP in the Ca100 solvent were obtained as 24.77 kJ/mol, 21.24 kJ/mol and 28.48 kJ/mol, respectively.







Figure 6-6(a-j) Reaction kinetics determination of 15% (a,b,g), 10% (c, d, h), and 5% (e, f,i) PP dissolving in Ca100 solvent, and the variation of activation energies during dissolution of PP while varying %wt in the solvent (j).



Figure 6-7 Variation of activation energies (Ea) of dissolution for % wt. variation of PP in various biodiesel solvents at given temperatures

All the obtained activation energy values are shown in Figure 6-7 for the PP-biodiesel solvents system. It was observed from Figure 6-7, that the average activation energy for PP dissolution in these given 9 biodiesel solvents were 27.94 kJ/mol, 25.99 kJ/mol and 25.31 kJ/mol for the 15%(w/v), 10%(w/v) and 5%(w/v) PP solute respectively. For 15%PP, the activation energy varied from 21.87 kJ/mol (for PWC100) to 32.70 kJ/mol (for SF100). Similarly, for the 10% and 5% PP the minimum values of activation energy were 18.93 kJ/mol (for WCO100) and 20.65 kJ/mol (for WTB100) respectively. Whereas the maximum values for activation energy were 29.26 kJ/mol (for WTC100) and 30.67 kJ/mol (for WCO100) respectively. The positive values of the activation energy indicate that the processes were endothermic, as heat was required to break the polymer bonds by the solvent to penetrate in the solution system.

6.3.3 Solubility Profile of Polystyrene (PS) in Various Biosolvents

Polystyrene (PS) solubility profiles in various biodiesel solvents at given temperatures are shown in the Figures 6-8(a-i). The solvents were (a) Ca100, (b) WCO100, (c) PWC100, (d) C100, (e) PB100, (f) WTP100, (g) WTB100 and (i) SF100, respectively. Though all the observations of dissolution processes were started from 60 ^oC, the other temperatures were selected from various small-scale tests from a wide range of temperature tests. All these graphs show that the time difference between 5% and 15% polymer content at temperatures beyond
80 ^oC did not have that much time gaps as observed at the lower temperature zones from 60-80 ^oC. The total duration for dissolving the PS in the solvent required the lowest amount of time, in comparison to the time required for both PP and PE in the same solvent. Also, both PE and PP required higher temperatures to maintain their solubility. But once the PS was dissolved in a solvent, it did not revert back to the solid or gel type paste conditions at room temperature. Both the visual inspection and the filtration tests confirmed the solubility of the PS in these solvents, after cooling down the solution to room temperature.





Figure 6-8 Dissolution profile (dissolution duration and temperature relationship) of polystyrenee (PS) in various biodiesel solvents: (a) Ca100, (b) WCO100, (c) PWC100, (d) C100, (e) PB100, (f) WTP100, (g) WTB100 and (i) SF100

6.3.3.1 Reaction Kinetics for Polystyrene (PS) Dissolution Process

To determine the dissolution kinetics of the PS dissolution process in the various biodiesel solvents, the same process was followed as described for both PP and PE. Only the temperatures were different in all cases. Since the process of determining the rate constants and the activation energies requires number of figures and tables, only one sample calculation for PS dissolution in the Ca100 solvent is shown in Figure 6-9(a-i). The Figure 6-9(j) shows the trend of how the activation energies varied with the variation of the quantity of PS in the solvent Ca100. It can be seen from the results that the 10% (w/v) PS in the Ca100 solvent has the lowest activation energy to turn into a solution. However, the Figure 6-10 shows the variation of activation energy of PS in various solvents, namely, Ca100, WCO100, PWC100, C100, PB100, WTP100, WTB100 and SF100. The figure shows that the minimum activation energy (Ea) for 15%, 10% and 5% PS in the solvents was 17.5 kJ/mol in WCO100, 19.07 kJ/mol in Ca100 and 23.44 kJ/mol in C100, respectively. Whereas the highest level of Ea for these PS samples was 34.71 kJ/mol in PB100, 35.12 kJ/mol in WTB100 and 37.24 kJ/mol in PB100, respectively.







Figure 6-9(a-j) Reaction kinetics determination of 15% (a,b,g), 10% (c, d, h), and 5% (e, f,i) PS dissolving in Ca100 solvent, and the variation of activation energies during dissolution of PS while varying %wt in the solvent (j)

Table 6-2 Variation of viscosity of the PS-biodiesel solutions

Kinematic Viscosity (mm ² /s, at 40 °C)	WTB	WCB	CaB	PB	SB	СВ	WTC	WTP	PWC	Relative uncertainty
Pure biodiesel	4.96	4.89	14.8	4.16	4.42	4.56	4.91	4.39	4.55	±0.35
Biodiesel with 5% (w/v) PS	50.99	50.27	152.14	42.76	45.44	46.87	50.47	45.13	46.77	±0.35
Biodiesel with 10% (w/v) PS	140.71	138.72	419.86	118.02	125.39	129.36	139.29	124.54	129.08	±0.35
Biodiesel with 15% (w/v) PS	494.94	487.95	1476.83	415.11	441.05	455.02	489.95	438.06	454.02	±0.35



Figure 6-10 Variation of activation energies for dissolution of PS in various biodiesel solvents

6.4 Variation of viscosity of the polymer-biodiesel solutions

The viscosity of the polymer-biodiesel solutions was measured at 40 $^{\circ}$ C. While investigating the solubility of both PE and PP in the studied biodiesel solvents, these polymers turned into gel or pastes below certain temperatures (85 $^{\circ}$ C and 95 $^{\circ}$ C for PE and PP respectively) after being dissolved at elevated temperatures. Only the PS-biodiesel solutions remained at pure solution state at 40 $^{\circ}$ C. So, only the viscosity of PS-biodiesel solutions was measured. Table 6-2 shows the variation of kinematic viscosities of 5%(w/v) PS, 10%(w/v) PS, and 15%(w/v) PS solutions in the solvents: WTB, CaB, WCB, PB, SB, CB, WTC, PWC and WTP. The higher range of viscosities of the solutions obviously restricted the direct applications of the PS-biodiesel solutions in the diesel engines (e.g. acceptable limit $\leq 6 \text{ mm}^2/\text{s}}$ as per the biodiesel standards [194]). Similar higher viscosity trends were observed for PS with various solvents in the article published by Jarusuwannapoom *et al.* (Table 2 of [356]). Also, the variation of CN, density, kinematic viscosity, and lower heating values (LHVs) of dieselbiodiesel-polymer and diesel-biodiesel fuel blends are shown in Figure A1-3 to Figure A1-6 respectively in **Appendix A1**.

6.5 Concluding Remarks

Temperature rise showed positive effect on solubility increase of PE, PP and PS in biodiesel solvents. Though the experimental investigations showed better solubility at higher temperatures, both the PE and PP turned into gel or pastes when the solution temperature dropped below 85 °C and 95 °C, respectively, i.e. both the PE and PP almost separated from the solvents at room temperature This phenomenon could be easily employed for efficient material recovery as well as recursive use of solvents. The temperature was not increased beyond 155 °C to avoid accelerated thermal oxidation of the biodiesel solvents due to possible use of these fuels in the diesel engines. But the experimental dissolution tests of PS in these biodiesel solvents demonstrated that the PS-biodiesel solutions remain good solution when the temperature was cooled down after the solute was dissolved. When the heat was applied to accelerate the solubility of the polymers (PE, PP and PS), the increase in temperature provided sufficient energy to weaken the chemical bonds of the long polymer chains of the solutes to be mixed with the solvents. The endothermic activation energies demonstrate the intensity effect of temperature on solubility characteristics of these polymers. The experimental uncertainty for the acquired data of the dissolution profiles and that of the properties of the PS-biodieseldiesel fuel blends are presented in the Appendix A5 (Table A5-2 to Table A5-).

This chapter has also demonstrated the chemical recycling process of waste plastics feedstock recovery by minimal consumption of energy. Once the solutes were dissolved, cooling down the system could separate the PE and PP without use of any non-solvent agents. Though various colours of the same polymers make the recycling process and other catalytic processes very complex, this dissolution process can overcome colour existence issues. Once the polymer pastes are removed by general filtration process, the decolourisation of solvents can be performed to reuse the solvents. In case of PS-biodiesel solutions, use of non-solvent agents can separate the solute at room temperature as well.

Since the PS plastic remains dissolved at room temperature in the biodiesel, the various %wt. combination of PS-biodiesel fuel will be considered to conduct diesel engine performance analyses. The results will be then compared with those of the diesel fuel.

Chapter 7

ANALYTICAL INVESTIGATION OF PLASTICS DISSOLUTION IN BIODIESEL

7.0 Introduction

This chapter presents the analytical assessment of solubility of a polymer in a desired solvent. With this investigation, the solubility parameters of the individual solute and solvents are determined. Then the solubility criteria are assessed to check the compatibility between a solute and a solvent if they are miscible to make a solution. In general, all the methodologies developed for analysis of solubility are based on room temperature, i.e. 25 ^oC.

7.1 Selection of Proper Waste Plastics to be used as Additives to the Biodiesel

Based on the literature survey from Chapter 2, that the following summary could be drawn to select the effective categories of waste plastics for the waste-to-energy conversion processes.

About 78.32% of the total plastic production share goes to thermoplastics recognised under the PIC 1 to PIC 6. Their energy value contents are also very much comparable to the other available fuels as these are also produced from the petrochemical crudes, gases, or coals. According to the target waste selection criteria, the PE, PP and PS are the most favourable thermoplastics which can be used as fuel additives to the biodiesel. The PVC and PET are dissolvable in certain extent, but they have halogenated compounds and excess oxygen, respectively. Halogens can be corrosive to the engine materials and the excess oxygen may cause loss of heating values. Therefore, further treatment of removing halogen molecules needs to be assured to avoid formation of unwanted acidic substance like hydrochloric (HCl) acid during combustion. On the other hand, the fuel derived from PET could be used with some loss of heating value. The amount of waste PET in the world is significant. So, converting that plastic into fuel could be effective in terms of recycling investment.

7.2 Solubility Parameter and Analysis of Solubility of Plastics in Biodiesel

7.2.1 Solubility Parameter of Thermoplastics

Several methodologies have been used in this study to analytically determine the solubility parameters of the thermoplastics. Based on the fundamental relationship between solubility parameters and cohesive energy densities as presented in the Eq. 3.3 and Eq. 3.4 in the Chapter

3, the Hildebrand solubility parameters of the thermoplastics were determined (Table 7-1) from the available cohesive energy and the molar volume of the polymers as reported by several researchers (Table A2-1 in Appendix A2). Group contribution theory has been used to determine the solubility parameters of the thermoplastics (PIC-1 to PIC-6 types) by using Fedors' (Table A2-2 in Appendix A2), Hoy's (Table A2-3 in Appendix A2) and van Krevelen-Hoftyzer (Table A2-4 in Appendix A2) methodologies. Table 7-2 summarises the solubility parameters derived in Table A2-2 to Table A2-4 (in Appendix A2) according to group contribution method and their average solubility parameter. The averaging of these three methods were done by considering an extension of van Krevelen's [196] proposition of averaging the van Krevelen-Hoftyzer and Hoy methods for reliable analytical output on solubility parameters of the substances. The average values of solubility parameters thus increase the reliability of the calculated values by being depending on the molar attraction constants, molecular density, and the assumptions of the Hansen solubility parameter components in the group contribution method. Fedor's and Hoy's methodologies developed methodologies for Hildebrand solubility parameters by the cohesive energy theory-based calculation, where the Hoy's method also considered the molecular density of the substance. On the other hand, the Hoftyzer-van Krevelen methodology can be employed to determine the Hansen solubility parameter components of the PIC 1 to PIC 6 type plastics by using the group contribution method Comparing both the Table 7-1 and Table 7-2, the average solubility parameters in the Table 7-2 are higher than those in the Table 7-1. But these values are satisfying the ranges mentioned in the Table 7-1.

Polymer	δ range (J/cm ³) ^{1/2}	Methods us	sed to determ	ine the solubi	lity paramete	er, $\delta = \left[\frac{E_{coh}}{V_m}\right]^{C}$	$(J/cm^3)^{1/2}$
	or	Fedors	Small	Hoy	Hoftyzer -	Avg.	
	(MPa) ^{1/2}				van	solubility	
						Krevelen	parameter
Polyethylene	15.8~17.1	17.33	16.54	16.99	16.35	15.96	16.64
Polypropylene	16.8~18.8	16.32	15.63	17.13	15.24	17.04	16.27
Polystyrene	17.4~19.0	20.28	18.71	19.77	18.82	19.06	19.33
Polyvinyl	19.2~22.1	20.99	19.51	19.73	19.11	19.73	19.81
chloride							

Table 7-1 Calculation of Hildebrand solubility parameters of thermoplastics based on data given in the Table 7-2

Polyethylene	19.9~21.9	23.31	22.05	20.67	23.16	33.78	24.59
terephthalate							

Plastic polymers	Repeating units	Fedors, δ_t (MPa) ^{1/2}	Hoy, δ_t (MPa) ^{1/2}	Hoftyzer-van Krevelen, $\delta_t \ (MPa)^{1/2}$	Average solubility parameters, δ (MPa) ^{1/2}
LDPE	-(CH ₂ -CH ₂)-	17.52	17.68	16.77	17.32
HDPE	-(CH ₂ -CH ₂)-	17.52	18.25	16.77	17.51
PP	-[CH ₂ -CH(CH ₃)]-	16.41	16.00	15.84	16.08
PVC	+CH ₂ -CH+ I CI	22.57	19.50	25.04	22.37
PS	- [CH ₂ - CH] -	21.59	18.66	20.61	20.29
EPS	- [CH ₂ - CH] -	21.59	16.36	20.61	19.52
PET	-[0-(CH ₂) ₂ -0-C	∑ ° ° ° ° ° ° ° ° °	23.09	22.66	23.12

Table 7-2 Solubility parameters of the thermoplastics at 25 ^oC by Fedors, Hoy and Hoftyzervan Krevelen methods

7.2.2 Solubility Parameter of Biodiesels

Usually, biodiesel is a mixture of various distinct fatty acid methyl esters (FAMEs) which possess their own solubility parameters. Table 7-3 is briefly showing the solubility parameters of the biodiesel fuels considered in this study. In order to determine the solubility parameters of the biodiesel fuels, solubility parameter of the FAMEs was determined by using group contribution method based on Fedor's, Hoy's and Hoftyzer-van Krevelen methodologies.

Table 7-3 Solubility parameters of the biodiesels (at 25 ^OC) as per Fedors, Hoy and Hoftzyervan Krevelen methods

	Average	Fedors, δ	Hoy, δ	Hoftyzer-v	a ^{1/2}	Average, δ		
Biodiesel	molar volume, V _m (cm ³ /mol)	MPa ^{1/2}	MPa ^{1/2}	δ_d	δ_{p}	δ_{h}	δ_t	MPa ^{1/2}
WTB	327.91	17.65	18.42	16.1	3.83	11.73	20.97	19.01

WCB	328.67	17.66	18.49	16.01	3.7	11.4	20.65	18.93
CaB	330.79	19.83	19.76	16.39	3.04	11.78	20.94	20.17
PB	331.21	17.68	18.56	15.93	2.73	8.47	18.88	18.37
SB	332.62	17.67	18.52	16.1	3.83	11.73	20.97	19.05
CB	331.95	17.68	18.56	15.93	3.54	10.87	20.33	18.86
WTC	328.19	17.65	18.45	16.07	4.03	12.38	21.38	19.16
WTP	329.10	17.67	18.47	16.05	3.9	11.96	20.93	19.02
PWC	330.41	17.67	18.54	15.95	3.27	10.09	19.96	18.72

The Hildebrand solubility parameters of the most common FAMEs have been determined following Fedors' molar additive group contribution method for cohesive energy and molar volumes of the respective FAMEs and presented in the Table (Table A2-5 and Table A2-6 in Appendix A2). Here, Table A2-5 shows how information in the Table A1-2 was used to determine the cohesive energy and the molar volume using the group contribution method. Besides, Table A2-6 and Table A2-7 are showing the summarised values of the solubility parameters of the distinct FAME groups by Fedors', Hoy's and Hoftyzer-van Krevelen methodologies. These individual solubility parameters of the fatty acid methyl esters were used to derive the Hildebrand solubility parameters (Table A2-8 to A2-16 in Appendix A2) and Hansen solubility parameters (HSP) (Table A2-17 to Table A2-25 in Appendix A2) respectively for the studied biodiesels.

It has been found that the group contribution method was extensively used in the Hoftyzer -van Krevelen method, which can be used to determine the Hansen solubility parameter (HSP) components instead of using the Hansen's graphical method. Furthermore, from the results of Table 7-3, it can be inferred that, the average values of the three methodologies could be also used effectively as the average value contain all the considerations of the methodologies described altogether. with the increasing number of $-CH_2$ - groups in the fatty acid methyl esters, the dispersion component of the solubility parameter (δ_d) increases. The reason for this increment is the intermolecular van der Walls forces [231].

7.2.2.1 Alternate Calculation of Determining Hansen Solubility Parameters of Biodiesels by Hoftyzer-Van Krevelen Method

The methodology of group contribution to determine the Hansen solubility parameters (HSP) by the Hoftyzer-van Krevelen applied in the Table A2-17 to TableA2-25 could be performed in an alternate way. In this procedure, the HSPs of the fatty acid methyl esters

(FAMEs) of the respective biodiesel can be multiplied by the fraction amount of the FAMEs present in the studied biodiesel fuel. These results are presented in the Table A2-26 to Table A2-34 in the Appendix A2. The results are summarised in Table 7-4. While comparing the Table 7-3 and Table 7-4, the differences of hydrogen bonding contribution to the solubility parameters of the biodiesels can be distinctly observed. The values obtained for total solubility parameter by the van Krevelen method do not vary much with the other methods. That is why, this alternative method also can be considered to be acceptable to determine the solubility parameters of the biodiesel fuels.

Biodiesel	Fedors δ (MPa) ^{1/2}	Hoy δ (MPa) ^{1/2}	Hoftyzer	-van Kre	velen, δ (MPa) ^{1/2}	Average,
Diodieser		110 <i>y</i> , 0 (111 u)	δd	бр	δh	δt	$\delta (MPa)^{1/2}$
WTB	17.65	18.42	16.10	1.50	1.17	16.21	17.43
WCB	17.66	18.49	16.01	1.49	1.17	16.12	17.42
CaB	19.83	19.76	16.39	2.05	1.24	16.56	18.72
PB	17.68	18.56	15.93	1.48	1.16	16.04	17.43
SB	17.67	18.52	15.97	1.47	1.16	16.08	17.42
CB	17.68	18.56	15.93	1.48	1.16	16.04	17.42
WTC	17.65	18.45	16.07	1.50	1.17	16.19	17.43
WTP	17.67	18.47	16.05	1.49	1.17	16.16	17.43
PWC	17.67	18.54	15.95	1.48	1.16	16.06	17.42

Table 7-4 Hoftyzer-van Krevelen method used alternatively to determine the HSPs of bioidiesels

7.2.3 Determination of Solubility Criteria

Hansen [207] reported the FH-Hansen model using the optimal value proposed by Lindvig *et al.* [241] (derived in Eq. 3.19f in section 3.2.3) as follows:

$$\chi_1 = 0.6 \frac{V_{sol}}{RT} \left[\left(\delta_{pd} - \delta_{sd} \right)^2 + 0.25 \left(\delta_{pp} - \delta_{sp} \right)^2 + 0.25 \left(\delta_{ph} - \delta_{sh} \right)^2 \right] - \dots - (Eq. 7.1a)$$

Van Krevelen [208] has mentioned that the high molecular weight polymers will dissolve only if $\chi_1 \leq 0.5$, whereas, for a regular low molecular weight solute the mixing can be happened for $\chi_1 \leq 2.0$. Since the solubility criteria for a polymer-solvent solution system in terms of interaction parameter is $\chi_1 \leq 0.5$ the equation 3.19f can be used as a first point of analysis of polymer-solvent miscibility if Hansen solubility parameters are available. The following criteria for solubility assessment has been proposed by van Krevelen [196, 219], when the HSP components are known for both the solute and solvent in the system.

Considering the volume of the solution be, $V_{sol} = 100$ ml, R= 8.314 J/mol.k, and T is 298K, then the Eq. 7.1a and Eq. 7.1b can be used to determine the interaction parameters (χ_1) and $\Delta\delta$ for solubility assessment of the plastics in biodiesel solvents. These criteria assessment results are presented in the Table 7-5 to Table 7-9 for LDPE/HDPE, PP, PVC, PS/EPS, and PET respectively in WTB, WCB, CaB, PB, SB, CB, WTC, WTP and PWC biodiesel solvents.

Moreover, as an alternative methodology of HSP components of the biodiesel solvents have been demonstrated, these solubility parameters were also used to investigate the solubility of the plastics in the biodiesel solvents. In order to investigate the solubility criteria, Greenhalgh criteria for solubility (Eq. 3.27) was also checked along with the FH-Hansen interaction parameter and van-Krevelen criterion. Table 7-10 shows the Greenhalgh criteria and Table 7-11 to Table 7-15 demonstrate the solubility criteria assessment of LDPE/HDPE, PP, PVC, PS/EPS and PET respectively in WTB, WCB, CaB, PB, SB, CB, WTC, WTP and PWC biodiesel solvents by using the solubility parameters obtained in the Table 7-4. All of these criteria were assessed based on the temperature of the solution system be 298K.

Biodiesel	HSP comp	onents by Ho	oftyzer-van Krev	velen meth	od		$\left(\delta_{pd}-\delta_{sd}\right)^2$	$\left(\delta_{pp}-\delta_{sp}\right)^2$	$\left(\delta_{ph}-\delta_{sh}\right)^2$	χ1	van Krevelen
(solvent)	Biodiesel s	olvents		LDPE/ H	IDPE (po	olymer)					criteria,
	δsd	δsp	δsh	δpd	брр	δph					$\Delta\delta < 5MPa^{\frac{1}{2}}$
WTB	16.1	3.83	11.73	16.77	0	0	12.36	14.67	137.59	0.93	12.36
WCB	16.01	3.7	11.4	16.77	0	0	12.01	13.69	129.96	0.88	12.01
CaB	16.39	3.04	11.78	16.77	0	0	12.17	9.24	138.77	0.90	12.17
PB	15.93	2.73	8.47	16.77	0	0	8.94	7.45	71.74	0.50	8.94
SB	16.1	3.83	11.73	16.77	0	0	12.36	14.67	137.59	0.93	12.36
CB	15.93	3.54	10.87	16.77	0	0	11.46	12.53	118.16	0.81	11.46
WTC	16.07	4.03	12.38	16.77	0	0	13.04	16.24	153.26	1.04	13.04
WTP	16.05	3.9	11.96	16.77	0	0	12.60	15.21	143.04	0.97	12.60
PWC	15.95	3.27	10.09	16.77	0	0	10.64	10.69	101.81	0.70	10.64

Table 7-5 Solubility criteria investigation for LDPE/ HDPE (polymer)-biodiesel system with FH-Hansen model for interaction parameter (χ_1) and van Krevelen criteria at 298 K

Table 7-6 Solubility criteria investigation for PP (polymer)-biodiesel system with FH-Hansen model for interaction parameter (χ_1) and van Krevelen criteria at 298 K

	HSP compor	nents by Hof	ftyzer-van Kre	velen metho	d			2			van Krevelen
Biodiesel (solvent)	Biodiesel sol	lvents		PP (polymer)			$\left(\delta_{pd}-\delta_{sd}\right)^2$	$\left(\delta_{pp}-\delta_{sp} ight)^2$	$\left(\delta_{ph}-\delta_{sh} ight)^2$	χ_1	criteria,
(50110110)	δsd	δsp	δsh	δpd	брр	δph					$\Delta\delta < 5MPa^{\overline{2}}$
WTB	16.1	3.83	11.73	15.84	0	0	0.07	14.67	137.59	0.92	12.34
WCB	16.01	3.7	11.4	15.84	0	0	0.03	13.69	129.96	0.87	11.99
CaB	16.39	3.04	11.78	15.84	0	0	0.30	9.24	138.77	0.90	12.18

РВ	15.93	2.73	8.47	15.84	0	0	0.01	7.45	71.74	0.48	8.90
SB	16.1	3.83	11.73	15.84	0	0	0.07	14.67	137.59	0.92	12.34
CB	15.93	3.54	10.87	15.84	0	0	0.01	12.53	118.16	0.79	11.43
WTC	16.07	4.03	12.38	15.84	0	0	0.05	16.24	153.26	1.03	13.02
WTP	16.05	3.9	11.96	15.84	0	0	0.04	15.21	143.04	0.96	12.58
PWC	15.95	3.27	10.09	15.84	0	0	0.01	10.69	101.81	0.68	10.61

Table 7-7 Solubility criteria investigation for PVC (polymer)-biodiesel system with FH-Hansen model for interaction parameter (χ_1) and van Krevelen criteria at 298 K

	HSP con	nponents b	y Hoftyze	er-van Kre	velen met	hod					van Krevelen criteria,
Biodiesel (solvent)	Biodiese	l solvents		PVC (po	lymer)		$\left(\delta_{pd}-\delta_{sd}\right)^2$	$\left(\delta_{pp}-\delta_{sp} ight)^2$	$\left(\delta_{ph}-\delta_{sh} ight)^2$	χ_1	$\Delta\delta < 5MPa^{\frac{1}{2}}$
(sorvent)	δsd	δsp	δsh	δpd	брр	δph					
WTB	16.1	3.83	11.73	20.46	14.07	3.19	19.01	104.86	72.93	1.54	14.03
WCB	16.01	3.7	11.4	20.46	14.07	3.19	19.80	107.54	67.40	1.54	13.96
CaB	16.39	3.04	11.78	20.46	14.07	3.19	16.39	3.04	11.78	0.49	5.59
PB	15.93	2.73	8.47	20.46	14.07	3.19	20.52	128.60	27.88	1.44	13.30
SB	16.1	3.83	11.73	20.46	14.07	3.19	19.01	104.86	72.93	1.54	14.03
CB	15.93	3.54	10.87	20.46	14.07	3.19	20.52	110.88	58.98	1.53	13.80
WTC	16.07	4.03	12.38	20.46	14.07	3.19	19.27	100.80	84.46	1.59	14.30
WTP	16.05	3.9	11.96	20.46	14.07	3.19	19.45	103.43	76.91	1.56	14.13
PWC	15.95	3.27	10.09	20.46	14.07	3.19	20.34	116.64	47.61	1.49	13.59

Biodiesel	HSP con	nponents	by Hoftyzer-va	n Krevelen n	nethod						van Krevelen
(solvent)	Biodies	el solvents			1		$\left(\delta_{pd}-\delta_{sd}\right)^2$	$\left(\delta_{pp}-\delta_{sp} ight)^2$	$\left(\delta_{ph}-\delta_{sh} ight)^2$	χ_1	criteria,
				PS/EPS (po	olymer)						$\Delta\delta < 5MPa^{\frac{1}{2}}$
	δsd	δsp	δsh	δpd	брр	δph					
WTB	16.1	3.83	11.73	20.57	1.27	0	19.98	6.55	137.59	1.36	12.81
WCB	16.01	3.7	11.4	20.57	1.27	0	20.79	5.90	129.96	1.33	12.52
CaB	16.39	3.04	11.78	20.57	1.27	0	17.47	3.13	138.77	1.28	12.62
PB	15.93	2.73	8.47	20.57	1.27	0	21.53	2.13	71.74	0.97	9.77
SB	16.1	3.83	11.73	20.57	1.27	0	19.98	6.55	137.59	1.36	12.81
CB	15.93	3.54	10.87	20.57	1.27	0	21.53	5.15	118.16	1.27	12.03
WTC	16.07	4.03	12.38	20.57	1.27	0	20.25	7.62	153.26	1.46	13.46
WTP	16.05	3.9	11.96	20.57	1.27	0	20.43	6.92	143.04	1.40	13.05
PWC	15.95	3.27	10.09	20.57	1.27	0	21.34	4.00	101.81	1.16	11.28

Table 7-8 Solubility criteria investigation for PS/EPS (polymer)-biodiesel system with FH-Hansen model for interaction parameter (χ_1) and van Krevelen criteria at 298 K

Table 7-9 Solubility criteria investigation for PET (polymer)-biodiesel system with FH-Hansen model for interaction parameter (χ_1) and van Krevelen criteria at 298 K

Biodiesel	HSP compor	nents by Hof	tyzer-van Kre	velen m	ethod		$(2 2)^2$	$(2 2)^2$	$(2 \qquad 2)^2$		van Krevelen criteria,
(solvent)	Biodiesel sol	lvents		PET (j	polymer)	$(\delta_{pd} - \delta_{sd})$	$(\delta_{pp} - \delta_{sp})$	$\left(\delta_{ph}-\delta_{sh}\right)$	χ_1	$\Delta\delta < 5MPa^{\frac{1}{2}}$
	δsd	δsp	δsh	δpd	брр	δph					
WTB	16.1	3.83	11.73	19.7	5.02	10.01	12.96	1.42	2.96	0.34	4.16
WCB	16.01	3.7	11.4	19.7	5.02	10.01	13.62	1.74	1.93	0.35	4.16

CaB	16.39	3.04	11.78	19.7	5.02	10.01	10.96	3.92	3.13	0.31	4.24
PB	15.93	2.73	8.47	19.7	5.02	10.01	14.21	5.24	2.37	0.39	4.67
SB	16.1	3.83	11.73	19.7	5.02	10.01	12.96	1.42	2.96	0.34	4.16
CB	15.93	3.54	10.87	19.7	5.02	10.01	14.21	2.19	0.74	0.36	4.14
WTC	16.07	4.03	12.38	19.7	5.02	10.01	13.18	0.98	5.62	0.36	4.45
WTP	16.05	3.9	11.96	19.7	5.02	10.01	13.32	1.25	3.80	0.35	4.29
PWC	15.95	3.27	10.09	19.7	5.02	10.01	14.06	3.06	0.01	0.36	4.14

Table 7-10 Greenhalgh Solubility criteria, $\Delta \delta_t = \left[\left(\delta_{t, solute} - \delta_{t, solvent} \right)^2 \right]^{0.5} < 7MPa^{\frac{1}{2}}$ assessment for biodiesel-plastic dissolution system

Biodiesel (solvent)	$\delta t_{solvent}$	LDPE/ HDPE	$\Delta \delta_t < 7 M P a^{\frac{1}{2}}$	PP	$\Delta \delta_t < 7 M P a^{\frac{1}{2}}$	PVC	$\Delta \delta_t < 7 M P a^{\frac{1}{2}}$	PS/ EPS	$\Delta \delta_t < 7 M P a^{\frac{1}{2}}$	PET	$\Delta \delta_t < 7 M P a^{\frac{1}{2}}$
WTB	16.21	16.77	0.56	15.84	0.37	25.04	8.83	20.61	4.40	22.66	6.45
WCB	16.12	16.77	0.65	15.84	0.28	25.04	8.92	20.61	4.49	22.66	6.54
CaB	16.56	16.77	0.21	15.84	0.72	25.04	8.48	20.61	4.05	22.66	6.10
PB	16.04	16.77	0.73	15.84	0.20	25.04	9.00	20.61	4.57	22.66	6.62
SB	16.08	16.77	0.69	15.84	0.24	25.04	8.96	20.61	4.53	22.66	6.58
CB	16.04	16.77	0.73	15.84	0.20	25.04	9.00	20.61	4.57	22.66	6.62
WTC	16.19	16.77	0.58	15.84	0.35	25.04	8.85	20.61	4.42	22.66	6.47
WTP	16.16	16.77	0.61	15.84	0.32	25.04	8.88	20.61	4.45	22.66	6.50
PWC	16.06	16.77	0.71	15.84	0.22	25.04	8.98	20.61	4.55	22.66	6.60

Biodiesel	HSP compo	nents by Hof	tyzer-van Kre	velen metho	d						van Krevelen
(solvent)	Biodiesel so	lvents		LDPE/ HI	OPE (poly	/mer)	$\left(\delta_{pd}-\delta_{sd}\right)^2$	$\left(\delta_{pp}-\delta_{sp} ight)^2$	$\left(\delta_{ph}-\delta_{sh} ight)^2$	χ_1	criteria,
	δsd	δsp	δsh	δpd	брр	δph					$\Delta 0 < 5 MPa^2$
WTB	16.10	1.50	1.17	16.77	0	0	0.45	2.25	1.36	0.03	2.01
WCB	16.01	1.49	1.17	16.77	0	0	0.58	2.23	1.36	0.04	2.04
CaB	16.39	2.05	1.24	16.77	0	0	0.15	4.18	1.53	0.04	2.42
PB	15.93	1.48	1.16	16.77	0	0	0.71	2.19	1.36	0.04	2.06
SB	15.97	1.47	1.16	16.77	0	0	0.65	2.17	1.36	0.04	2.04
CB	15.93	1.48	1.16	16.77	0	0	0.71	2.19	1.36	0.04	2.06
WTC	16.07	1.50	1.17	16.77	0	0	0.48	2.24	1.36	0.03	2.02
WTP	16.05	1.49	1.17	16.77	0	0	0.52	2.23	1.36	0.03	2.03
PWC	15.95	1.48	1.16	16.77	0	0	0.67	2.20	1.36	0.04	2.06

Table 7-11 Solublity criteria check for LDPE/HDPE-biodiesel dissolution at 298K when alternative van Krevelen method is used

Table 7-12 Solublity criteria check for PP-biodiesel dissolution at 298K when alternative van Krevelen method is used

Biodiesel	HSP compo	nents by Hof	tyzer-van Krev	velen metho	od						van Krevelen
(solvent)	Biodiesel so	lvents		PP (polyn	ner)		$\left(\delta_{pd}-\delta_{sd}\right)^2$	$\left(\delta_{pp}-\delta_{sp} ight)^2$	$\left(\delta_{ph}-\delta_{sh} ight)^2$	χ_1	criteria, $\frac{1}{2}$
	δsd	δsp	δsh	δpd	брр	δph					$\Delta \delta < 5 MPa^2$
WTB	16.10	1.50	1.17	15.84	0	0	0.07	2.25	1.36	0.02	1.92
WCB	16.01	1.49	1.17	15.84	0	0	0.03	2.23	1.36	0.02	1.90
CaB	16.39	2.05	1.24	15.84	0	0	0.30	4.18	1.53	0.04	2.45
PB	15.93	1.48	1.16	15.84	0	0	0.01	2.19	1.36	0.02	1.89
SB	15.97	1.47	1.16	15.84	0	0	0.02	2.17	1.36	0.02	1.88

СВ	15.93	1.48	1.16	15.84	0	0	0.01	2.19	1.36	0.02	1.88
WTC	16.07	1.50	1.17	15.84	0	0	0.05	2.24	1.36	0.02	1.91
WTP	16.05	1.49	1.17	15.84	0	0	0.05	2.23	1.36	0.02	1.91
PWC	15.95	1.48	1.16	15.84	0	0	0.01	2.20	1.36	0.02	1.89

Table 7-13 Solublity criteria check for PVC-biodiesel dissolution at 298K when alternative van Krevelen method is used

Biodiesel	HSP comp	onents by H	oftyzer-van Kre	velen metho	bd						van Krevelen
(solvent)	Biodiesel s	olvents		PVC (pol	ymer)		$\left(\delta_{pd}-\delta_{sd} ight)^2$	$\left(\delta_{pp}-\delta_{sp} ight)^2$	$\left(\delta_{ph}-\delta_{sh} ight)^2$	χ_1	criteria,
	δsd	δsp	δsh	δpd	брр	δph					$\Delta\delta < 5MPa^{\frac{1}{2}}$
WTB	16.10	1.50	1.17	20.46	14.07	3.19	18.99	158.03	4.10	1.44	13.46
WCB	16.01	1.49	1.17	20.46	14.07	3.19	19.84	158.14	4.10	1.46	13.49
CaB	16.39	2.05	1.24	20.46	14.07	3.19	16.58	144.60	3.81	1.30	12.85
PB	15.93	1.48	1.16	20.46	14.07	3.19	20.57	158.50	4.10	1.48	13.53
SB	15.97	1.47	1.16	20.46	14.07	3.19	20.19	158.65	4.10	1.47	13.53
CB	15.93	1.48	1.16	20.46	14.07	3.19	20.54	158.54	4.10	1.48	13.53
WTC	16.07	1.50	1.17	20.46	14.07	3.19	19.23	158.06	4.10	1.45	13.47
WTP	16.05	1.49	1.17	20.46	14.07	3.19	19.43	158.16	4.10	1.45	13.48
PWC	15.95	1.48	1.16	20.46	14.07	3.19	20.34	158.39	4.10	1.48	13.52

Biodiesel	HSP compo	onents by Ho	ftyzer-van Kre	velen metho	od						van Krevelen
(solvent)	Biodiesel so	olvents		PS/EPS (p	polymer)		$\left(\delta_{pd}-\delta_{sd} ight)^2$	$\left(\delta_{pp}-\delta_{sp} ight)^2$	$\left(\delta_{ph}-\delta_{sh}\right)^2$	χ_1	criteria,
	δsd	δsp	δsh	δpd	брр	δph					$\Delta 0 < 5 MP a^2$
WTB	16.10	1.50	1.17	20.57	1.27	0	19.96	0.05	1.36	0.49	4.62
WCB	16.01	1.49	1.17	20.57	1.27	0	20.83	0.05	1.36	0.51	4.72
CaB	16.39	2.05	1.24	20.57	1.27	0	17.49	0.60	1.53	0.44	4.43
PB	15.93	1.48	1.16	20.57	1.27	0	21.58	0.04	1.36	0.53	4.79
SB	15.97	1.47	1.16	20.57	1.27	0	21.19	0.04	1.36	0.52	4.75
CB	15.93	1.48	1.16	20.57	1.27	0	21.55	0.04	1.36	0.53	4.79
WTC	16.07	1.50	1.17	20.57	1.27	0	20.21	0.05	1.36	0.50	4.65
WTP	16.05	1.49	1.17	20.57	1.27	0	20.41	0.05	1.36	0.50	4.67
PWC	15.95	1.48	1.16	20.57	1.27	0	21.35	0.05	1.36	0.53	4.77

Table 7-14 Solublity criteria check for PS/EPS-biodiesel dissolution at 298K when alternative van Krevelen method is used

Table 7-15 Solublity criteria check for PET-biodiesel dissolution at 298K when alternative van Krevelen method is used

Biodiesel	HSP compo	nents by Hof	tyzer-van Krev	velen metho	od						van Krevelen
(solvent)	Biodiesel so	lvents		PET (poly	/mer)		$\left(\delta_{pd}-\delta_{sd}\right)^2$	$\left(\delta_{pp}-\delta_{sp} ight)^2$	$\left(\delta_{ph}-\delta_{sh} ight)^2$	χ_1	criteria,
	δsd	δsp	δsh	δpd	брр	δph					$\Delta 0 < 5 MP a^2$
WTB	16.10	1.50	1.17	19.7	5.02	10.01	12.94	12.40	78.22	0.86	10.18
WCB	16.01	1.49	1.17	19.7	5.02	10.01	13.65	12.43	78.23	0.88	10.21
CaB	16.39	2.05	1.24	19.7	5.02	10.01	10.97	8.85	76.96	0.79	9.84
PB	15.93	1.48	1.16	19.7	5.02	10.01	14.25	12.53	78.24	0.89	10.25
SB	15.97	1.47	1.16	19.7	5.02	10.01	13.94	12.57	78.24	0.89	10.23

СВ	15.93	1.48	1.16	19.7	5.02	10.01	14.23	12.54	78.24	0.89	10.25
WTC	16.07	1.50	1.17	19.7	5.02	10.01	13.15	12.41	78.22	0.87	10.19
WTP	16.05	1.49	1.17	19.7	5.02	10.01	13.31	12.44	78.22	0.87	10.20
PWC	15.95	1.48	1.16	19.7	5.02	10.01	14.07	12.50	78.23	0.89	10.24

7.3 Discussion on Solubility Criteria Assessment

While comparing the solubility criteria values between Table 7-5 and Table 7-11, Table 7-6 and Table 7-12, Table 7-7 and Table 7-13, Table 7-8 and Table 7-14, as well as Table 7-9 and Table 7-15, for the solubility assessment of LDPE/HDPE, PP, PVC, PS/EPS and PET polymers respectively in biodiesel solvents, it could be observed that there is a massive difference in the criteria values determined by using Eq. 7.1a and Eq. 7.1b.

Table 7-5 to Table 7-9 are showing that the FH-Hansen model for interaction parameter based solubility criteria, i.e. $\chi_1 \leq 0.5$, is followed by only LDPE/HDPE-PB ($\chi_1 = 0.5$), PVC-CaB ($\chi_1 = 0.49$), PET-WTB ($\chi_1 = 0.34$), PET-WCB ($\chi_1 = 0.35$), PET-CaB ($\chi_1 = 0.31$), PET-PB ($\chi_1 = 0.39$), PET-SB ($\chi_1 = 0.34$), PET-CB ($\chi_1 = 0.36$), PET-WTC ($\chi_1 = 0.36$), PET-WT ($\chi_1 = 0.35$), and PET-PWC ($\chi_1 = 0.36$) systems. Also, Table 7-5 to Table 7-9 show that the van Krevelen solubility criteria (i.e. $\Delta\delta < 5MPa^{\frac{1}{2}}$) was met by the PET-WTB ($\Delta\delta = 4.16$), PET-WCB ($\Delta\delta = 4.16$), PET-CaB ($\Delta\delta = 4.24$), PET-PB ($\Delta\delta = 4.67$), PET-SB ($\Delta\delta = 4.16$), PET-CB ($\Delta\delta = 4.14$), PET-WTC ($\Delta\delta = 4.45$), PET-WT ($\Delta\delta = 4.29$), and PET-PWC ($\Delta\delta = 4.14$) systems only. So, both the LDPE/HDPE-PB ($\Delta\delta = 8.94$) and PVC-CaB ($\Delta\delta = 5.59$) could not pass over the van Krevelen's criteria in spite of these systems conformed the FH-Hansen interaction parameter criteria for solubility at 298K temperature.

On the other hand, while observing the Tables 7-11 to Table 7-15, only LDPE/HDPE, PP, PS/EPS showed better solubility criteria with all of the considered biodiesel solvents for this analytical study. The solvent system in this study was a complex one due to inherently existing different types of FAMEs within the biodiesels. So, the methodology used to calculate the solubility parameters for a mixed solvent needs to be investigated well to apply the solubility criteria. Again, the Table 7-10 shows that the Greenhalgh solubility criteria [249] was maintained by the PET, PS/EPS, PP and LDPE/HDPE. But the criteria values are very close to the maximum acceptable limit for solubility at 298K temperature, that indicates further energy input could make the solute to be dissolved. Though PE and PP met the solubility criteria at 298K, in actual case, putting PE and PP in biodiesel solvents for up to one week at 298K temperature did not show much swelling. It infers that, though these solubility criteria roughly assist selecting the suitable solvent for a solute at 298K temperature, these are unable to indicate any dissolution period. On the other hand, a dissolution kinetic model gives the information about temperature, time and activation energy for the dissolution that takes place.

Though at 298K the plastic polymers exhibited limited solubility for all the systems, higher temperature based experimental conditions may show different results. Increasing the temperature of the solution system can increase the miscibility of the solute of higher molecular weight numbers with the solvent. Zhang *et al.* [21], investigated this issue of increasing temperature to obtain complete miscibility of the plastic polymers (e.g. PS and LDPE of higher molecular weight numbers). Due to very closeness of difference between the total solubility parameter of the biodiesel and PS/EPS, they are more soluble in biodiesel. But they need more temperature when the molecular weight number is increased. The researchers analysed the solubility with a molecular modelling and gravimetric analysis. It was also concluded that the molecules having larger surface area show good solubility due to higher porosity. Increasing temperature for a particular solute near to its melting point may increase the solubility of the substance.

7.4 Concluding Remarks

The analytical investigation of thermoplastics dissolution in various biodiesel solvents has shown limited solubility at 25 °C as per established solubility criteria. Even though several solutes fail to meet the solubility criteria within a marginal limit at this temperature, the analysis did not investigate the effect of temperature rise on solubility characteristics. But the experimental investigation extensively observed temperature effect and change of kinetic rate constants of the dissolution processes. According to the FH-Hansen model, the solvent rank, CaB>WTB>WTC>WTP>WCB>SB>PWC>CB>PB, could be observed to dissolve the PS/EPS plastics which shows that the chemical composition and the characteristics have effect on dissolving the Plastics at a given condition. However, van Krevelen's criteria also showed the same rank for the solvents as per respective dissolution criteria.

This analytical assessment helped determining the solvent capacity of the biodiesel fuels to the thermoplastics. The limitation of solubility of the thermoplastics could be resolved with the additional heating energy as described in the previous chapter. Among various thermoplastics-biodiesel solutions the PS/EPS-biodiesel solutions were found as good solution at room temperature. Therefore, various blends of PS-biodiesel-diesel fuels (Section 8.1.1) were prepared to conduct the fuel combustion, emission and performance tests in an unmodified diesel engine and the results were compared with the diesel, and diesel-biodiesel fuel blends, respectively. Chapter 8 and chapter 9 present the emission, performance, and combustion assessment results of the fuel blends, respectively.

Chapter 8

ASSESSMENT OF EMISSION CHARACTERISTICS OF POLYMER ADDITIVE-BASED DIESEL-BIODIESEL BLENDS IN THE DIESEL ENGINE

8.0 Introduction

The chapter presents the experimental investigation of the fuel emission characteristics in diesel engine. Ultra-low sulphur diesel (ULSD) which has been only named as diesel in this study was used as reference fuel in the diesel engine. The diesel fuel was blended with various biodiesel fuels and biodiesel-polystyrene fuels at various blend ratios. The experimental results of these blends and diesel are presented in this chapter.

8.1 Materials and methods

8.1.1 Fuel Selection

Diesel fuel (ULSD) was the base fuel to investigate the combustion, emission, and performance parameters with various fuel blends in the same diesel engine set up. In this study, four inedible biodiesel fuels were chosen, namely, waste tallow biodiesel (WTB), castor oil biodiesel (CaB), waste tallow (70%) + waste cooking oil (30%) binary biodiesel blend (WTC) and poppy oil biodiesel (70%) + waste cooking oil (30%) binary biodiesel blend (PWC). Based on the analytical investigations of solubility of PS in the biodiesel solvents, CaB and WTB were found to be the most suitable solvents for PS. Also, binary biodiesels, WTC and PWC, were considered to investigate the effect of binary biodiesel fuels in the engine performance assessment purpose. To conduct the experiments with biodiesel fuels, these fuels were distinctly blended with diesel fuel at a ratio of 5%, 10%, and 15% (v/v). The diesel-WTB biodiesel blends are designated as WTB5, WTB10 and WTB15 for mixing at blending ratios, respectively. Similarly, diesel-CaB biodiesel blends are CaB5, CaB10, CaB15; diesel-WTC biodiesel blends are WTC5, WTC10, WTC15; and diesel-PWC biodiesel blends are PWC5, PWC10, PWC15, respectively. Besides, each of these biodiesels were used as solvent for PS dissolution at a rate of 5% (w/v), 10% (w/v), and 15% (w/v) ratios to make ternary (i.e. dieselbiodiesel-PS) and quaternary (i.e. diesel-binary biodiesel-PS) fuel blends. For instance, WTB5PS5 is a blend of diesel and 5% (v/v) WTB with 5% (w/v) PS dissolved, WTB5PS10 is a blend of diesel and 5% (v/v)WTB with 10% (w/v) PS dissolved and WTB5PS15 is a blend of diesel and 5% (v/v) WTB with 15% (w/v) PS dissolved. Table 8-1 shows the complete list of the fuels used for experimental investigation in this study in order to assess the fuel performances, emission, and combustion characteristics in a diesel engine. Engine operating conditions, i.e. the engine speeds and load conditions were varied in this study. Each of the fuel samples were tested at 3 load conditions, namely, full (100%) load, part (50%) load and idle crank load. And the engine speeds ranged between 1200 rpm and 2400 rpm.

Base fuel	Biodiesel	Diesel-Biodiesel blends	Diesel-Biodiesel-PS blends
		WTB5	WTB5PS5, WTB5PS10, WTB5PS15
Diesel	WTB	WTB10	WTB10PS5, WTB10PS10, WTB10PS15
		WTB15	WTB15PS5, WTB15PS10, WTB15PS15
		CaB5	CaB5PS5, CaB5PS10, CaB5PS15
Diesel	CaB	CaB10	CaB10PS5, CaB10PS10, CaB10PS15
		CaB15	CaB15PS5, CaB15PS10, CaB15PS15
		WTC5	WTC5PS5, WTC5PS10, WTC5PS15
Diesel	WTC	WTC10	WTC10PS5, WTC10PS10, WTC10PS15
		WTC15	WTC15PS5, WTC15PS10, WTC15PS15
		PWC5	PWC5PS5, PWC5PS10, PWC5PS15
Diesel	PWC	PWC10	PWC10PS5, PWC10PS10, PWC10PS15
		PWC15	PWC15PS5, PWC15PS10, PWC15PS15

Table 8-1 Types of fuel samples used in the experiment

8.1.2 Engine Test Bed

For the test purpose, the diesel engine test bed (Figure 8-1) installed in the Thermodynamics Laboratory of the School of Engineering and Technology at the CQUniversity Rockhampton campus was used. Detail engine specifications are shown in the Table 8-2. The engine is coupled with an eddy current dynamometer. Though liquid cooled system is used to cool down both the engine and dynamometer, a well-designed forced air circulation system was maintained to remove the heat from radiator, engine's other hot surfaces and that of the dynamometer. A pneumatic throttle positioning system was used to control the applied load variations to the engine operation system, i.e. to control the charge intake (i.e. amount of air and fuel intake) in the engine to produce desired outputs in terms of power and torque. An engine combustion analyser (Figure 8-2) was used to detect real time pressure changes inside the combustion chamber with the variation of crank angle and cylinder volume during a full working cycle. It uses a pressure transducer (H32218-GPA, Optrand, MI, USA) and a crank angle sensor to read the in-cylinder pressure and volume change at a continuous mode with the variation of crank angles. These P and V were measured and analysed with the help of TFX Engine Technology's Combustion Pressure Analyser [357]. The eddy current dynamometer measures the engine output torque and power, which are recorded by an engine performance analyser. This engine performance analyser also keeps records of exhaust gas temperature (EGT), inlet air temperature and pressure, engine oil temperature, coolant inlet and outlet temperatures, and load variations corresponding to the engine speed and desired outputs (i.e. power and torque). To investigate the engine exhaust emissions, there are exhaust gas analyser (CODA 5 exhaust gas analyser) connected to the exhaust pipe to determine the emission contents of NOx, CO, CO₂, HC, and excess O₂ emissions after the combustion takes place. Moreover, the particulate matter emission was measured with a particulate matter (PM) emission analyser (MAHA MPM-4M) which is also connected with designed sampling line from the exhaust pipe. The equipment used to analyse the mass density of the PM emission due to fuel combustion can detect particles from as big as $>10\mu$ m to as low as <100nm. Both the emission analyser and the PM analyser are connected to computers to record data as per the experimental designs. There is an engine control system to follow some safe steps to start and shut down the engine to avoid any damage to the system and the equipment.

Fuelling to the engine has been arranged in two different ways. A diesel fuel tank line is connected with the fuel metering system followed by a fuel filter to run the engine with diesel fuel only. But a portable fuel tank was installed to supply fuels in the engine with biodiesel-diesel fuel blends and diesel-biodiesel-polymer fuel blends. Standard fuel line adapters were used to change the fuel flow supply from diesel fuel to the other fuel blends to avoid any air trapping in the fuel line. To avoid any issues with the other fuel blends to the engine components, it was operated with diesel fuel only before and after the tests were performed with various fuel blends for certain time.

Items	Units	Specifications
Model		Kubota V3300
Туре		Vertical
No. of Cylinders		4
Bore x Stroke	mm (in)	98.0 × 110.0 (3.86 × 4.33)
Displacement	L (cu.in.)	3.318 (202.53) or 3318 cm ³
Combustion System		E-TVCS (Three vortex combustion system)
Intake System		Natural aspirated
Cooling System		Radiator cooling (liquid cooling system)
Starter Capacity	V-A	12-2.5
Alternator Capacity	V-A	Dec-60
Dry Weight with SAE Flywheel & Housing	kg (lbs)	272 (600.0)
No Load High Idling Speed	rpm	2800
No Load Low Idling Speed	rpm	700-750
Direction of Rotation		Counterclockwise (from flywheel side)
Governing		Centrifugal flyweight high speed governor
Intake valve opening and closing		17 ^o (BTDC) and 63 ^o (ABDC)
Exhaust valve opening and closing		51 ^o (BBDC) and 28 ^o (ATDC)
Fuel		Diesel fuel No. 2-D (ASTM D975)
Emission standard		Tier 2
Compression ratio		22.6
Gross Intermittent Power	kW (HP)/rpm	54.5/2600 (68.0/2600)
Rated (Net) Power Output	kW (HP)/rpm	50.7/2600 (59.1/2600)
Net Continuous Power Output	kW (HP)/rpm	26.3/1500 (35.3/1500) and 44.1/2600
Rated Torque	(Nm/rpm)	230/1400

Table 8-2 Diesel engine specification of the engine test bed [358]



Figure 8-1 Kubota V3300 Engine test bed and dynamometer



Figure 8-2 Schematic of diesel engine test bed along with various diagnostic arrangement

Moreover, in order to avoid any cold start effect during the initial data collection, the engine was warmed up until the engine oil temperature rises beyond 80 ^oC. Usually, this warming up was done by running the engine with diesel fuel only and then the engine was switched off to quickly change the fuel connectors for other fuel blends. The tests were conducted within the range between 1200 rpm and 2400 rpm.

8.2 Emissions Characteristics

Among the various emission contents of the diesel engine emissions, the following emission contents were investigated for the fuels used in this study.

8.2.1 Carbon Monoxide (CO) Emission

Carbon monoxide (CO) emission from fuel combustion is the indication of improper combustion of the fuel injected in the combustion chamber. The higher the emission of CO, the lesser is the combustion efficiency. Researchers (e.g. **[359-362]**) have been reviewing existing results and conducting further experiments to determine the reasons for variation of

CO emission by the diesel-biodiesel fuel blends in comparison to that of diesel fuel. The most common issues mentioned by these authors **[359-362]** are: more oxygenated fuels (i.e. higher blend ratios of biodiesel with diesel), in-cylinder temperature, carbon-hydrogen ratio (C/H) in the fuel, unsaturation level, load variations, higher cetane number that leads to better combustion efficiency, advanced fuel injection timing, higher amount of long chain hydrocarbons, viscosity and acid values and oxidised fuel may effectively contribute in reducing the CO emissions.

CO is categorised as a toxic compound and people seldom can trace this gas in the air as it is odourless gas. Due to higher viscosity, increased blend ratio of biodiesel in the dieselbiodiesel blends is somewhat restricted in an unmodified diesel engine, though modified fuel injection systems may help by providing better spray and atomisation characteristics of the fuel. So, additives can be used to supply more oxygen within the fuel to reduce the emission of CO at variable load conditions during combustion.

Due to fluctuations in load and speeds of vehicles on the road, there is always a chance of occurring incomplete combustion within the engines. So, mixing of oxygenated ingredients with the fuel can lead to increased amount of complete combustion and produce more CO₂. Another reason for CO formation within the combustion chamber is the low temperature combustion which leads to quick temperature fall of the combustion chamber and catalyse the pollutant to be formed [363]. Biodiesel fuels are oxygenated fuels, so combustion of biodieseldiesel fuel blends can reduce the CO formation quantity. At lower engine loads, the CO emission is higher than that of diesel fuel. But at higher engine loads, the higher cetane number of the fuel influences fuel-rich-zone formation to reduce the CO formation in comparison to that of diesel fuel [364, 365]. But, due to higher quantity of fuel injected, the trend of biodiesel fuel combustion-based CO emission is increased with the load increase. Abed et al. [366] observed various blends of waste cooking oil based fuel combustion and reported that the CO emission by the blends of biodiesels are lesser than that of diesel fuel at any load condition but the emission quantity trend of individual fuel blend keeps increasing with the load increment. Kumar et al. [367] have reviewed many of such research works and compiled that the additives like Al-Mg, cobalt oxide, ethyl hexyl nitrate (EHN), BHA, BHT, Mg and Mn based compounds, diethyl ether (DEE), and dimethyl carbonate (DMC), etc are very effective in reducing the CO emission from combustion of biodiesel fuel blends (particularly 20% biodiesel - 80% diesel fuel blends).

In this study, biodiesel fuels of various types of FAME composition, level of viscosity and CN were tested. While operating the engine at various loading conditions, i.e. full load condition, part load condition and idle crank load condition, the CO emission quantities were recorded for various engine speeds. The CO emission from the combustion at full load condition of all the fuels are presented in the Figure 8-3(a-d) for speed conditions of high torque, higher efficiency and higher speed ratings considered for this study, respectively. Similarly, Figure A3-1(a-d) and Figure A3-2(a-d) delineate the variation of CO emission for the other studied fuels at part (50%) load and idle crank load conditions, respectively.

8.2.1.1 Full Load Condition

While investigating the CO emissions (Figure 8-3) by the diesel-biodiesel and dieselbiodiesel-PS fuel blends, it was observed that the CO emission reduced with these fuels at full load condition. When the engine speed increased, the overall CO emission reduced remarkably. At full load condition of engine operation by diesel-WTB and diesel-WTB-PS fuel blends, it was found that the most reduction of CO occurred at 1500 rpm in comparison to that of diesel fuel. In all cases, the CO emission by only diesel-biodiesel blends, i.e. WTB5 (-38.8%), WTB10 (-40.8%) and WTB15 (-45%) were lower than those of the diesel-WTB-PS based ternary blends. The highest CO reduction occurred for WTB15PS15 ternary blend (-72.4%), followed by other significant reductions by WTB10PS15 (-70.6%), WTB15PS10 (-69.1%), WTB110PS10 (-67.0%), and WTB5PS15 (-59.4%), etc. Due to increased amount of biodiesel blend ratio for combustion of fuels, obviously there was increased amount of oxygen supply in the combustion chamber from both the biodiesel and atmospheric air drawn by the system to conduct the combustion. Besides, the increased viscosity influenced fuel flow variation in the combustion chamber in comparison to those of diesel fuel combustions only with the same injector setting. So, there is an indication of more efficient combustion due to available oxygen. On the other hand, when the quantity of PS was increased within the same diesel-biodiesel fuel composition, i.e. WTB5, WTB5PS5, WTBPS10, WTB5PS15, etc. then the percentile reduction of CO emission rate was increasing. When there is a supply of oxygen within the fuel itself along with cleaner hydrocarbons, there is more opportunity of combustion of the fuel within the system. Good atomisation of fuel could be one of the best reasons, once the fuel was injected in the combustion chamber, for which the CO emission reduced. So, addition of biodiesel and PS with the diesel fuel was beneficial to ensure better combustion as the CO emission reduced remarkably with these fuel blends at same operating conditions of the engine control system.







(c) CO emission by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) CO emission by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 8-3 Carbon monoxide (CO) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

In case of CO emission by the combustion of diesel, diesel-CaB and diesel-CaB-PS fuel blends at full load condition (Figure 8-3(b)), most significant amount of reduction of CO occurred at 2400 rpm in comparison to diesel fuel. Besides, it can be identified that these fuels reduced CO emission at higher level when the engine speed increased. Castor, being naturally oxygen rich due to major portion of methyl ricinoleate $(CH_3-CH(OH)-(CH_2)_{15}-COOH)$, is usually a highly viscous fuel than the other biodiesel fuels. It also supplies more oxygen as a part of long chain poly unsaturated hydrocarbons to allow better fuel atomisation and combustion. While comparing with the diesel fuel, highest reduction of CO emission occurred by the CaB15PS15 (-69.38%) in comparison to that of diesel fuel. Such significant trends of reductions were also demonstrated by combustion of CaB15PS10 (-63.82%), CaB10PS15 (-61.24%), CaB5PS15 (-58.8%), CaB5PS10 (-54.84%) and CaB10PS10 (-54.2%), etc. at higher speed operation condition. Also, these fuels show very good reduction of CO emission at 2400 rpm, e.g. CaB15PS15 (-67.71%) and CaB15PS1 (-63.82%), with comparison to the diesel fuel. Among the diesel-CaB blends, highest CO emission occurred for CaB15 (-26.94%) at 2400 rpm, followed by CaB10 (-7.52%) and CaB5 (-1.3%) at the same speed. For higher speeds, these diesel-CaB blends could not reduce much like the lower speed operation condition at full load. The reason could be shorter combustion duration of the fuels at higher speeds. But as the fuel hydrocarbon content increased with the addition of PS, the CO emission reduced remarkably at the higher speeds as well. It indicates that the additional hydrocarbons were more reactive to participate in combustion.

Figure 8-3(c-d) are the CO emission results of diesel, diesel-binary biodiesel (ternary blends) and diesel-binary biodiesel-PS (quaternary blends) fuels. WTC and PWC are the binary biodiesel fuels here in this study. It can be seen from Figure 8-3(c) that the ternary blends of diesel-WTC reduced the CO emission by 18.4%, 23.54% and 32.72% with WTC5, WTC10 and WTC15 blends respectively at 1500 rpm. Whereas, among the quaternary blends of diesel-WTC-PS fuels reduced CO emission by 65.73% (WTC15PS15), 62.34% (WTC10PS15), (WTC15PS10), 57.79% (WTC10PS10), 46.28% 61.59% (WTC15PS5), 45.85% (WTC5PS15), 40.97% (WTC10PS5), and 40.64% (WTC5PS10), etc. With the highest amount of oxygen supplied by the WTC15 fuel blend, and more hydrocarbon supply by WTC15PS15 along with oxygen the highest amount of CO emission reduction was found to be 65.73% in comparison to diesel fuel only. On the other hand, the ternary blends of diesel-PWC showed reduction of CO emission as PWC5 (-36%), PWC10 (-43.94%), and PWC15 (-48.98%) in comparison to that of diesel fuel. But the quaternary blends (i.e. diesel-PWC-PS fuel blends) showed better efficiency on reducing CO emission due to addition of PS. The highest reduction of CO emission was seen to be PWC15PS15 (-78.66%), PWC15PS10 (-76.09%), PWC10PS5 (-71.83%) PWC5PS15 (-73.29%), PWC5PS10 (-70.72%), and PWC5PS5 (-68%), quaternary blends respectively at 1800 rpm. In all cases, the amount of CO emission reduction rate was observed to be more by the PS blended quaternary fuels.

Thus, at full load operating condition of diesel engine, the diesel-biodiesel blends showed reduction of CO emission at an order of PWC15(-48.98%)>WTB15(-44.99%)>PWC10(-43.94%)>WTB10(-40.82%)>WTB5(-38.8%)>PWC5(-36%)>WTC15(32.72%)>WTC10(23.54%)> CaB10(-20.02%)> WTC5(18.4%)> CaB5(-14%)> CaB15(-12.82%) significantly. Among the substantial contribution of various diesel-biodiesel-PS blends on CO emission reduction, the top 4 highest rank of CO emission reduction was found for PWC15PS15(-78.66%)> WTB15PS15(-72.4%)> CaB15PS15(-69.38%)> WTC15PS15(-69.38%)> WTC15PS15(-65.73%) fuels.

8.2.1.2 Part (50%) Load Condition

Figure A3-1(a-d) in the **Appendix A3** demonstrates the CO emission of diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS fuel blends when the diesel engine runs at part load condition. Only the CO emission variations of the fuels at higher

torque (1200 rpm), higher efficiency (1500 rpm) and highest speed for this study (2400 rpm) are shown for these fuels.

Figure A3-1(a) shows CO emission by diesel, diesel-WTB (binary blends), and diesel-WTB-PS fuel (ternary blends) samples. All the fuels demonstrated a reducing trend of CO emission with the increment of engine speed. Moreover, the increase of biodiesel portion within the binary blends show increased CO emission at the same speed. The effectiveness rank was, WTB15(-67.68%)>WTB10(-58.02%)>WTB5(-31.75%) for these diesel-WTB blends. The ternary blends (i.e. diesel-WTB-PS blends) also reduced the amount of CO emission with respect to their corresponding diesel-biodiesel blends with the increase in PS in the same type of diesel-WTB blend. The highest reduction was found for WTB15PS15(-69.80%). Besides, the other significant reductions of CO emission were seen for WTB15PS10(-64.47%), WTB15PS5(-61.96%), WTB10PS15(-60.78%), and WTB5PS15(-49.39%) blends in comparison to that of the diesel fuel at same operating condition.

The reduction of CO emission trends of other fuels like diesel-CaB, diesel-WTC and diesel-PWC along with their PS containing blends of various weight ranges showed good effectiveness on better combustion with the increased speed conditions. For both the full load and part load operation conditions, it was not only the amount of oxygen that increased the combustion of fuels but also the additional amount of hydrocarbon that enhanced atomisation quality that reduced CO emission. With diesel-CaB blends, the rank of CO emission reduction with comparison to that of the diesel fuel was, CaB15(-75.11%)> CaB10(-73.52%)>CaB5(-53.87%). Whereas, for the diesel-CaB-PS fuel blends, the rank of effectiveness of the blends CaB15PS15(-82.67%)>CaB10PS15(-80.97%)>CaB5PS15(found be were to 80.75%)>CaB15PS10(-79.61%).Similarly, the CO emission reduction efficiency by the diesel-WTC and diesel-PWC blends were ranked as, WTC15(-56.62%)> WTC10(-52.54%)> WTC5(-9%), and PWC15(-54.73%)> PWC10(-49.58%)> PWC5(-28.81%) respectively. Moreover, a few of the significant CO emissions by the diesel-WTC-PS quaternary blends were ranked as, WTC15PS15(-76.61%)> WTC10PS15(-73.57%)> WTC15PS10(-72.49%)> WTC15PS5(-70.54%)>WTC10PS10(-68.91%). Similarly, few of the highest CO emission reduction percentile by the diesel-PWC-PS quaternary blends in comparison to the diesel fuel was ranked as, PWC15PS15(-69.26%)> PWC15PS10(-63.83%)> PWC15PS5(-61.28%)> PWC10PS15(-61.09%).

8.2.1.3 Idle Crank Load Condition

This idle crank load condition is the lowest amount of load required to achieve the desired engine speed of operations. The engine does almost zero useful work at this condition and may experience unusual trends of emission production. Beyond this load condition, the engine starts working on consuming the required amount of fuel to produce the brake power and torque to perform a given task. Figure A3-1(a-d) shows the carbon monoxide (CO) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition with the engine speed variation. Total list of fuels is given in the Table 8-1.

Figure A3-2(a) shows the CO emission by diesel, diesel-WTB blends (binary) and diesel-WTB-PS (ternary blends) fuels. While comparing both the full load and the part load operating conditions of the engine with the CO emission reduction trend of the binary and ternary fuels at idle crank load condition, the additional amount of oxygenated biodiesel fuels showed better results than those of the ternary blends. Due to inefficient combustion at the idle condition, the additional amount of hydrocarbon just increased the CO emission rather than it being advantageous on other load operating conditions. Similar trends were also observed with the other fuels in the Figure A3-3(b-d). At the idle crank load, the percentile reduction of CO emission by the diesel-WTB fuels with comparison to the diesel fuel were, WTB15(-54.95%)> WTB10(-50.90%)> WTB5(-43.08%). The ternary blends showed reduction by WTB5PS5(-46.83%)> WTB10PS5(-45.88%)> WTB15PS10 (-44.68%)> WTB5PS10 (-38.54%). On the other hand, the CO emission reduction rate rank by the diesel-CaB fuel blends were found to be, CaB5(-63.62%)> CaB15(-54.95%)> CaB10 (-50.9%). Besides, the ternary blends reduced the CO emission by the rank of CaBCaB5PS5(-81.81%)> CaB10PS5 (-81.16%)> CaB15PS5 (-80.74%)> CaB5PS10 (-78.97%)> CaB10PS10(-78.22%), with respect to that of the diesel fuel emission at those respective speeds and idle crank load.

Figure A3-4(c) shows better CO emission reduction by the ternary biodiesel blends (diesel-WTC) than those of the ternary biodiesel of diesel-PWC blends as in the Figure 8-5(d). While checking the percentile amount of CO emission reduction by these fuels at all the experimental range of speeds, it was found that the diesel-WTC blends reduced CO emission as per the rank of WTC15(-57.37%)> WTC10(-26.83%)> WTC5(-24.10%). Also, the highest reduction of CO emission was done by the quaternary blends of diesel-WTC-PS fuels as per the rank of

WTC5PS10(-86.39%) > WTC5PS15(-82.91%) > WTC5PS5(65.20%) > WTC10PS5(-63.95%) > WTC15PS5(-63.16%). Moreover, the CO emission was reduced by the PWC-diesel ternary fuel blends by PWC15(-54.95\%) > PWC10(-50.9\%) > PWC5(-43.86\%). But the better results were obtained with the quaternary blends of diesel-PWC-PS fuels. The rank of effectiveness was found to be PWC5PS5(-71.93\%) > PWC10PS5(-70.92\%) > PWC5PS10(-67.55\%) > PWC10PS10(-66.38\%) > PWC15PS10(-65.64\%) > PWC5PS15(-62.16\%).

Though the trend of CO emission reduction by the fuels at idle crank load at various engine speeds were a bit different than those of the full load and part load conditions, additional PS benefitted the combustion efficiency when mixed at a lower quantity. So, the addition of PS proved to be beneficial to improve the combustion quality and reduce the CO emissions in comparison to that of the diesel fuel.

8.2.2 Carbon dioxide (CO₂) Emission

A complete combustion of fuel obviously emits carbon dioxide (CO₂) gas as one of the key products of the combustion process other than water vapour and various other pollutants. Increasing amount of CO₂ indicates better combustion efficiency and the amount increases with the increase in engine speeds [**368-372**]. Fuel injection pressure variation, injection timing, chamber profile and viscosity of the fuels injected in the combustion chamber can effectively control the swirling of the air-fuel mixture for better atomisation, which results into better turbulent energy accumulation of the fuel in the richer combustion areas and consequently more combustion to produce more CO₂ [**372**, **373**].

Stoichiometrically, 1 mole of diesel fuel ($C_{12}H_{26}$, general formula for diesel fuel with density of 0.864 tonnes/m³) reacts with 18.5 moles of oxygen (O₂) and 69.56moles of nitrogen (N₂) to perform the combustion within a diesel engine [**374**]. The reactions produce 12 moles of CO₂, 13 moles H₂O, and 69.56 moles of N₂. So, ideally, 2.683 kg of CO₂ is produced for every single litre of diesel fuel burning/combustion. Whereas, in an ideal condition, biodiesels like soybean (density 0.878 tonnes/m³) and waste cooking oil (density 0.878 tonnes/m³) completely burn to produce 2.48 kg/L and 2.492 kg/L of CO₂ respectively [**374**]. Biodiesel fuels, being oxygen rich, can increase the rate of complete combustion efficiency of fuels in the diesel engines, thus produce more CO₂ in order to produce equivalent amount of energy of the diesel fuel. Since the feedstocks of biodiesel fuels are mainly resourced from the environment, the net contribution of CO₂ to the environment is reduced due to combustion of
biodiesel fuels. The emitted CO_2 can be consumed by photosynthesis process for plant or feedstock preparation and the use of biodiesel can reduce the total diesel fuel consumption. Therefore, the net CO_2 contribution to the atmosphere is 0.578 kg/L of biodiesel fuel combustion in comparison to that of 2.683 kg/L of diesel fuel combustion, which is about 78.48% reduction and the lower blend ratios just follow linear regression to quantify their contribution (e.g. 20% soybean blend can reduce about 15.66% of net CO_2 emission) [**375**].

In this study, the fuels used for the analysis have viscosity, density, and CN variations in comparison to those of the diesel fuel only. The fuel injection system was always constant for all the fuels (Table 8-1) used for the experimental investigation. Fuels were produced by blending various portion of WTB, CaB, WTC and PWC biodiesels along with diesel fuel. Besides, the addition of PS in these fuels at various weight percentages also influenced the variation of these physical properties. Since the injection system was always constant, the variation of fuel's physical properties influenced the amount of injected fuels in the combustion chamber resulting in total fuel flow rate variation of other fuels in comparison to that of diesel fuel only. Due to importance of CO_2 emission quantification in order to assess the combustion dioxide parameter (i.e. gram of CO_2 emission to produce one kWh energy). It is expected that this parametric expression may indicate a better understanding of the CO₂ emission due to combustion of the fuels in the combustion chamber. A brief description of the CO_2 emission due to combustion of fuels at various loads are presented in the following subsections.

8.2.2.1 Full Load Condition

Figure 8-4(a-d) presents the brake specific CO_2 emission (BSCO₂) at full load condition for the fuels at various engine speeds. While considering the load was constant, the BSCO₂ emission variations against the engine speeds were observed. For all the fuels, it could be seen that the higher speed conditions increased the BSCO₂ emissions except at 1500 rpm. So, it is obvious that the BSFC influenced the overall BSCO₂ emission quantification. Increase in brake specific CO₂ emission indicates lower CO emission for a fuelling system. So, these dieselbiodiesel fuels increased the BSCO₂ emission in comparison to the diesel fuel. Also, additional hydrocarbon contributed by the PS blend increased the overall combustion and increased the BSCO₂ emission rate.

In case of comparing the BSCO₂ emission of diesel-WTB blends and diesel-WTB-PS blends against that of diesel fuel, increase in BSCO₂ emission could be seen for all the speeds

and fuels except by WTB5PS10 (-0.52%) and WTB5PS15 (-0.16%) at 2400 rpm. The rank of percentile increase of BSCO₂ emission by the diesel-WTB blends can be seen as, WTB15(11.39%)> WTB10(8.63%)> WTB5(2.28%).





(b) CO₂ emission by diesel, diesel-CaB, and diesel-CaB-PS blends at full load









Though the increased blending ratio of diesel-WTB binary fuels showed increased trend of BSCO₂ emission in comparison to the diesel fuel, the polymer added fuels showed better increases. The rank of significant rise in BSCO₂ emission by the diesel-WTB-PS ternary fuel blends could be observed as, WTB15PS5(14.09% at 1200 rpm)> WTB10PS5(13.64%)> WTB15PS15(12.81%)> WTB10PS15(10.49%)> WTB15PS10(9.75%)> WTB10PS10(9.1%)> WTB5PS5(8.35%)> WTB5PS15(3.45%)> WTB5PS10(3.08%). These were mostly observed at 1200 rpm. When hydrocarbon was added in the diesel-biodiesel blends, the additional hydrocarbons took part in combustion process due to presence of oxygen from the biodiesel. It can be easily comprehended from the comparison between diesel-WTB

blends and the diesel-WTB-PS blends that the higher blends of biodiesel contributed with higher amount of oxygen available to burn more than the hydrocarbons available within the system from diesel fuel only.

Figure 8-4(b) presents the BSCO₂ emission of diesel, diesel-CaB blends, and diesel-CaB-PS ternary blends. Unlike the other fuels presented in the Figure 8-6(a-d), this castor-based biodiesel and ternary fuel blends demonstrated mixed results of BSCO₂ emission variation. Only the CaB5 blend reduced the $BSCO_2$ emission at all speeds for the full load operation condition. The maximum reduction of BSCO₂ emission by the CaB5 blend was seen to be 9.28% at 1800 rpm. The other two blends, i.e. CaB10 (e.g. -9.28% at 1800rpm but +1.48% at 1500 rpm) and CaB15 CaB10 (e.g. -5.71% at 1800rpm but +4.69% at 1200 rpm) exhibited mixed results by decreasing and increasing of BSCO₂ emission at various speeds. The significant variation of BSCO₂ emission by the ternary blends were seen to be CaB5PS5(12.68%), CaB5PS10(7.22% and -9.4%), CaB5PS15(13.1% and -12.55%), CaB10PS5(16.53%), CaB10PS10(11.53% and -1.46%), CaB10PS15(4.12% and -8.1%), CaB15PS5(6.69% and -4.73%), CaB15PS10(3.35% and -8.36%) and CaB15PS15(4.97% and -7.63%), etc. Since the injection system was constant for each of these fuels, the variation of viscosity and the fuel-air mixing capacity to conduct better combustion were the key reasons to vary BSCO₂ emission for the same fuel at various speeds of the engine operations.

Figure 8-4(c) demonstrates the variation of $BSCO_2$ emission for diesel, diesel-WTC ternary blends and diesel-WTC-PS quaternary blends. At full load condition, the percentile increase in BSCO₂ emission by the ternary blends were obtained as WTC(12.45%), WTC10(9.83%) and WTC5(2.37%). Whereas, the significant variations by the quaternary blends were, WTC5PS5(-2.57% and 8.45%), WTC5PS10(3.18%), WTC5PS15(3.55%), WTC10PS5(10.71%), WTC10PS10(-5.45% 5.45%), WTC10PS15(9.13%), and WTC15PS5(11.92%), WTC15PS10(7.66%) and WTC15PS15(12.19%) in comparison to the diesel fuel.

Figure 8-4(d) shows the variation of BSCO₂ emission by diesel, diesel-PWC ternary blends and diesel-PWC-PS quaternary blends at 1200, 1500, and 2400 rpm for full load operation. The highest increase of BSCO₂ emission by ternary blends and quaternary blends of the fuels did not happen at the same engine speed, which indicates that the physical characteristics of the fuel affected the post injection combustion processes for each of the blends. Not only the viscosity, the amount of oxygen and the hydrocarbons during atomisation and combustion phases influenced the variation of BSCO₂ emission by the types of the fuels used in this experimental study. It was seen that the most increase of BSCO₂ emission occurred with the ternary fuel blends, e.g., PWC15(15.72%), PWC10(11.79%) and PWC5(2.97%) in comparison to diesel fuel. Whereas, few of the significant variations of BSCO₂ emission by the other quaternary blends were seen as, PWC5PS5(20.82%), PWC5PS10(18.03%), PWC5PS15 (25.02%), PWC10PS5(26.23%), PWC10PS10(21.18%), PWC10PS15(12.33%), PWC15PS5(17.93%), PWC15PS10(14.24%) and PWC15PS15(15.72%).

From these results, it was clear that when the oxygenated fuels were mixed with the diesel fuel, the available oxygen helped to burn the hydrocarbons of the fuel mixtures and still there were more oxygen to burn. So, additional hydrocarbons did the job of further combustion within the system. While adding the PS in various diesel-biodiesel blends, the lower the biodiesel quantity mixed with the diesel fuel and the higher the PS mixed in that diesel-biodiesel blend helped increasing the BSCO₂ emission, thus increasing the combustion efficacy.

8.2.2.2 Part (50%) Load Condition

Figure A3-3(a-d) show the brake specific carbon dioxide (CO₂) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition respectively. For each of the fuels in these figures, it is clearly observable that the additional biodiesel and PS with diesel fuel increased the fuel combustion efficiency remarkably.

While observing the variation of BSCO₂ emission with comparison to the diesel fuel at all the given speed conditions at part load operation, the diesel-WTB and diesel-WTB-PS blends showed very high level of increase of BSCO₂ emission. With diesel-WTB blends the highest BSCO₂ emission by these fuel blends could be ranked as, WTB15(20.69%), WTB10(20.70%) and WTB5(20.23%). Though the addition of PS in the diesel-biodiesel blends increased the BSCO₂ emission for full load condition in comparison to those of the diesel-WTB blends, the part load condition showed that the addition of PS did not help much. Few significant BSCO₂ emission increase by the ternary fuel blends were observed for WTB5PS5(20.23%), WTB5PS10(19.66%), WTB10PS5(14.92%), WTB15PS5(14.91%), WTB10PS10(14.8%), and WTB15PS10(14.79%) at 1200 rpm.

The part load condition of diesel-CaB blends and diesel-CaB-PS blends showed that the CaB blended fuels experienced only the increase in BSCO₂ emission with comparison to that of diesel fuel, which was very different in case of full condition for these fuels. Here, the increased blend ratio of diesel-CaB increased the BSCO₂ emission rate as the highest percentile increase of the fuels were observed for CaB10(12.42%), CaB5(10.59%) and CaB15(9.27%). Compared to the CaB-diesel fuel blends, the PS-CaB-diesel fuels showed lesser increment in BSCO₂ emission. Though these fuel blends increased the BSCO₂ emission in comparison to that of diesel fuel, the overall incremental trend reduced with the increase in engine speed while comparing with diesel fuel. For instance, the CaB10PS5 emitted about 12.38% more BSCO₂ at 1200 rpm, but it was about 4.98% higher at 2400 rpm at part load condition.

In case of diesel-WTC ternary blends and diesel-WTC-PS quaternary blends, the BSCO₂ emissions of the fuels are presented in the Figure A3-3(c). Among the ternary blends of WTCdiesel fuels, the rate of increasing of BSCO₂ emission increased for WTC5 and WTC10 blends at 1200 rpm while comparing with that of the diesel fuel, but the rate reduced with increased engine speeds. Also, the higher BSCO₂ by the WTC15 at 1500 rpm indicated better fuel efficiency related combustion and relevant emission increment due to lower calorific value of the WTC15 fuel. Whereas, among the quaternary blends of the WTC15-PS fuel had higher increment rate of BSCO₂ emission than those of the other quaternary blends. It mostly happened at 1500 rpm at which the highest combustion efficiency was achieved. Highest increase in BSCO₂ emission by the quaternary blends were noticed for, WTC5PS10(23.28%) and WTC5PS15(23.16%) at 2400 rpm, WTC15PS5(15.45%), WTC15PS10(15.31%), and WTC15PS15(15.20%).

The BSCO₂ emission by the diesel-PWC ternary blends, and diesel-PWC-PS quaternary blends are shown in the Figure A3-3(d). The variation of BSCO₂ emission by these ternary and quaternary blends are seen to be very high compared to other diesel-biodiesel and diesel-biodiesel-PS fuel blends at part (50%) load condition. Among all the diesel-biodiesel fuel blends, the PWC15 and PWC10 showed higher increment by BSCO₂ emission than that of diesel fuel. Whereas, the PWC10PS5 has the highest increase in BSCO₂ emission in among all the diesel-biodiesel-PS fuel blends while comparing with the BSCO₂ emission of diesel at their respective engine speed and part load operation condition.

8.2.2.3 Idle Crank Load

The quantity of BSCO₂ emission at idle crank load condition of all the studied fuels are shown in the Figure A3-4(a-d), which are grouped as BSCO₂ emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition. In this load operation condition, most of the fuels emitted more BSCO₂ at the lower speeds than usual trends observed for full load and part load operations for these fuels.

With diesel, diesel-WTB binary blends and diesel-WTB-PS ternary blends, change of BSCO₂ emission in comparison to that of diesel fuel can be observed. The highest increment of BSCO₂ emission by these fuels occurred between 1200 and 1500 rpm. Highest BSCO₂ emission was observed for WTB15 fuel at 1500 rpm. When PS fuels were added with WTB5/WTB10-diesel fuel blends, the BSCO₂ emission increased in comparison to diesel-biodiesel fuel only. But the rate of increment reduced with WTB15-PS ternary blends in comparison to the WTB15 fuels.

While comparing the CO₂ emission of the diesel-CaB and diesel-CaB-PS fuel blends with that of the diesel fuel, it could be observed that these fuels reduced the CO₂ emission for all speeds except at 2400 rpm during idle crank load. Here, the maximum reduction of BSCO₂ emission by the diesel-CaB blends occurred due to CaB5 blend (-49.64%) followed by the CaB10(-48.86%) and CaB15(-43.01%) respectively at 1500rpm. While adding PS in these binary fuels, all the fuels showed increase in BSCO₂ emission at higher engine speed (2400 rpm), The highest increase in BSCO₂ emission occurred by the CaB15(20.85%) followed by CaB10PS5(15.73%), CaB15PS5(15.73%), CaB15PS10(14.25%) and CaB10PS10(14.25%).

As per Figure A3-4(c), BSCO₂ emission increased by the diesel-WTC ternary fuel blends, the polymer added fuels reduced the CO₂ emission in comparison to that of diesel fuel. experienced mixed trends within the test limits. The rank of highest BSCO₂ emission increase in comparison to the diesel fuel was WTC15(20.97%), WTC10(13.15%), and WTC5(8.92%) at various speeds. Whereas the BSCO₂ emission reduced by 16.87%, 15.97% and 15.59% with the quaternary blends of WTC5PS15, WTC10PS15 and WTC15PS15 fuels, respectively.

Moreover, the Figure A3-4(d) shows mixed nature of changing BSCO₂ emission with the variation of engine speeds and fuel types by the diesel-PWC ternary blends and diesel-PWC-

PS quaternary blends with comparison to the diesel fuel. Though at 1500 rpm, the BSCO₂ emission reduced by all of these fuel blends by almost half of that emitted by the diesel fuel, the BSCO₂ emission increased at 2400 rpm. The highest increase in BSCO₂ emission occurred by the PWC15PS5 (30.03% at 2400 rpm) in comparison to that of the diesel fuel. Though extra oxygen and hydrocarbons were available, the reason for variation of BSCO₂ emission could be the quality of atomisation within the combustion chamber and the mixing residence time due to viscosity variation of the atomised fuels within the chamber with the variation of engine speeds and thermal conditions.

8.2.3 Nitrogen Oxides (NO_x) Emission

Biodiesel fuels generally possess higher viscosity than the diesel fuel. As a result, the diesel-biodiesel fuel mixture experiences viscosity increments with the increased quantity of biodiesel in diesel. Oxides of Nitrogen (NO_x) are formed due to physical properties of the fuel (i.e. higher viscosity), injection pressure and injection timing, higher temperature within the combustion chamber, equivalence ratio, longer duration of fuel combustion, adiabatic flame temperature, higher amount of available oxygen within the combustion chamber that can react with nitrogen from air at higher EGT [179, 360, 361, 368, 373, 376-380]. Diesel engines generally operate on higher temperatures, which is also supported by the oxygenated viscous biodiesel blends to produce NOx more than that formed with diesel fuel combustion only. The higher load and advanced start of combustion causes higher temperature of the in-cylinder gases to rise. As a result, the NO formation is increased in the NOx composition. The trend of NOx emission rise starts from the middle load to the higher load of the engine operation. Using amine type antioxidant additives with the biodiesel can improve its stability as well as the reduction of NOx emission [364]. Elshahib et al. [381] delayed the injection period by 5 ^oCA and observed reduced NOx emission for waste cooking oil methyl esters than that by diesel fuel only. Besides, the authors mentioned that the increased injection pressure along with 17% exhaust recirculation can effectively reduce NOx emissions. Among various mechanisms of forming NOx, the thermal NOx formation (Zeldovich) mechanism, the fuel NOx formation mechanism, and the prompt NOx formation (the Fenimore) mechanism are mostly mentioned to describe the NOx emission from the diesel engines [373, 377, 379, 382, 383].

In this study, the fuels mentioned in the Table 8-1 were tested for NOx emission comparison with diesel fuel at full load, part (50%) load and idle crank load at various engine speeds. Figure 8-5(a-d) presents the NO_x emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b)

diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition respectively. Whereas the Figure A3-5(a-d) and Figure A3-6(a-d) present NOx emission trends at part load and idle crank load conditions respectively by these fuels.

At full load condition, the binary (i.e. WTB5, WTB10, WTB15, CaB5, CaB10 and CaB15 blends) and ternary (i.e. WTC5, WTC10, and WTC15) blends showed increase in NOx emission when the biodiesel content increased in the diesel fuel (Figure 8-5(a-c)). Whereas PWC5, PWC10 and PWC15 ternary blends emitted lesser NOx than that of the diesel fuel at given speeds (Figure 8-5(d)) with the most reduction for PWC5 ternary blend. It could be observed that the highest increases of NOx emission by the binary and ternary biodiesel fuel blends were, WTB15(68.83%), WTB10(45.54%), CaB15(42.9%), WTC15(32.25%), WTC10(26.56%), WTB5(25.47%), CaB10(23.19%), WTC5(9.6%), and CaB5(6.2%), respectively. On the other hand, with the addition of PS in all of the diesel-biodiesel blends reduced the NOx emission remarkably. Among the PS added fuels, few of the significant amount of reduction of NOx emission in comparison to diesel fuel could be found for, WTB5PS15(-20.97%), WTB10PS15(-29.70%), and WTB15PS15(-34.13%), CaB5PS15(-CaB10PS15(-19.84%), and CaB15PS15(-16.63%), WTC5PS15(-28.8%), 12.74%). WTC10PS15(-36.66%) and WTC15PS15(-40.65%), PWC5PS15(-35.75%), PWC10PS15(-42.06%) and PWC15PS15(-36.06%).

It was also observed from Figure 8-5(a-d) that the increasing engine speeds reduced the NOx emission for all the biodiesel-diesel fuels. The diesel-biodiesel fuels are mostly being viscous and oxygen rich, so the available nitrogen is attracted to form NOx. But the additional hydrocarbons though addition of PS confirms better combustion by using this available fuel oxygen. As a result, the NOx formation is interrupted due to oxygen unavailability.







(c) NO_x emission by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



Figure 8-5 Nitrogen Oxides (NO_x) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

On the other hand, the part (50%) load condition of NOx emission by the fuels show mix trends of variation in comparison to the diesel fuel (Figure A3-5(a-d)). During part load operations, the engine produced more NOx at lower speeds and higher biodiesel blends for the fuels like WTB and WTC. The CaB biodiesel showed reduction of NOx emission at lower speeds but increase in the higher speeds with comparison to the diesel fuel. The PWC fuel blends show reduction of NOx emission in comparison to the diesel fuel for all of its fuel blends at all the speed conditions.

The comparative quantification of variation of NOx emission by all the studied fuels at part load condition distinctly showed that there are few fuels which showed both increase and decrease of NOx emission in comparison to that of the diesel fuel while increasing the engine speed. This demonstrates that it is not only the fuel compositions that need to be modified to reduce the NOx emission from the fuel combustion. Rather, modification of engine operation procedures along with the fuel's physical properties are required to obtain least NOx emission. Part load operation has more variation of NOx emission by the fuels than those at full load condition. In a real situation of vehicle operations, the engine may experience more of the part load operations than that of full load, which requires efficient engine control monitoring to reduce the NOx emission. Maximum variation of NOx emission by the diesel-biodiesel blends could be observed byWTB15(31.37%), WTB10(23.31%), WT5(19.5%), CaB5(11.21% and -9.15%), CaB10(13.32% and -5.52%), CaB15(20.12% and -1.74%), WTC5(6.7%),

WTC10(9.58%), WTC15(18.35%), PWC5(-37.30%), PWC10(-34.8%) and PWC15(-32.19%) respectively in comparison to that of the diesel fuel at respective engine speeds.

The effectiveness of addition of PS in the diesel-biodiesel fuel blends could be seen very much beneficial. In this study, the PS content was varied from 5-15% for each of the dieselbiodiesel blending composition. The addition of PS as additional hydrocarbon sources in the fuel blends reduced the NOx emission. Few of the remarkable NOx emission reductions reported by these fuels are, WTB15PS10(-10.59%) and WTB15PS15(--11.39%) at 2400 rpm, CaB15PS15(-23.42%), CaB15PS10(-22.73%), WTC5PS15(-18.24%), WTC15PS15(-19.3%), PWC5PS15(-43.26%), PWC10PS15(-44.43%), and PWC15PS15(-47.15%) respectively at 1200 rpm. Higher amount of PS addition influenced higher amount of reduction of NOx emission in comparison to that of the diesel fuel. Though a few of the blends showed mixed results, the addition of hydrocarbons with the diesel-biodiesel seems beneficial.

The NOx emission at idle crank load condition by the fuels are presented in the Figure A3-6(a-d) for diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively.

Among the diesel-WTB and diesel-WTB-PS fuel blends, the increase in speeds reduced the overall NOx emission, but only, WTB5PS15, WTB10PS15 and WTB15PS15 emitted lower NOx than that of diesel fuel for the given conditions. At 1500 rpm, the NOx emission quantity increased than those at 1200 rpm, but the emission reduced for all these fuel blends at 2400 rpm. WTB10PS10 and WTB15PS10 also emitted lower NOx than that of diesel emission at 2400 rpm along with WTB5PS15, WTB10PS15 and WTB15PS15 blends.

While the NOx emission varied by the fuels at various speeds, the highest variation by the diesel-biodiesel fuel blends can be observed as, WTB5(28.8%), WTB10(32.02%), WTB15(36.26%), CaB5(41.76%), CaB10(34.83%), CaB15(58.68%), WTC5(15%), WTC10(17.99%), WTC15(20.94%), PWC5(-28.03%), PWC10(-24.79%) and PWC15(-21.4%) in comparison to the diesel fuel's NOx emission at those corresponding engine speeds. On the other hand, it needed higher biodiesel and PS to be blended (WTB10PS15 and WTB15PS15) to efficiently reduce the NOx emission. At 2400 rpm, these two fuels reduced NOx emission by 38.90% and 47.57% respectively in comparison to the diesel fuel.

In case of NOx emissions by diesel-CaB and diesel-CaB-PS fuel blends at idle crank loading condition, the emission content reduced with the increase in engine speeds. Only, CaB5, CaB5PS5, CaB5PS10, CaB10, CaB15 had higher NOx emission at 1500 and 2400 rpm in comparison to the diesel fuel. But, at 1200 rpm, all the fuels emitted lower NOx than the diesel fuel. Most efficient outputs were observed with the CaB5PS15, CaB10PS15 and CaB15PS15 fuel blends at all the engine speeds. Highest amount of reduction was seen to be - 43.45%, -44.24% and -46.93% by CaB5PS15, CaB10PS15 and CaB15PS15 fuel blends at all the engine with the diesel fuel. Among the diesel-WTC and diesel-WTC-PS fuel blends, the WTC5PS15, WTC10PS15 and WTC15PS15 fuels emitted lower NOx than the diesel fuel and reduced with the increase in engine speeds. But an opposite behaviour was observed for the diesel-PWC fuels, which increased the NOx emission with the increase in the engine speeds. At 2400 rpm, all the diesel-PWC blends emitted more NOx than the diesel fuel does. But diesel-PWC-PS demonstrated the effectiveness of reducing the NOx emission with the increase in speeds. The more the PS addition, the higher was the effectiveness.

8.2.4 Particulate Matters (PM) Emission

Diesel engine exhaust particles (DEP) are a complex mixture of non-volatile (or solid) and semi-volatile components [**384**]. The non-volatile component mainly consists of fractal-like carbonaceous agglomerates also known as the accumulation (soot) mode in the size range of 30–500 nm [**385**]. Soot particles are formed in locally fuel-rich regions of the combustion flame in the engine. The semi-volatile components are mainly composed of low- and semi-volatile organic and sulphuric acid (H₂SO₄) vapours that originate from the unburned fuel, lubricant oil, and partial combustion products [**386**, **387**]. Upon dilution and cooling in ambient air or during sampling, these vapours either condense on pre-existing soot particles or nucleate to form nucleation mode particles in the size range of 3–30 nm [**386**, **387**]. Also, the semi-volatile organics may condensate on the surfaces of the generated nucleation particles.

Mohankumar and Senthilkumar **[388]** reviewed the formation processes of PM and their control methodologies in the diesel engines. As per their article, the soot formation due to fuel combustion in the diesel engines may follow six steps (namely, pyrolysis/combustion, nucleation, growth of surfaces, coalescence, agglomeration and oxidation) as delineated in the Figure A4-1 in Appendix A4. In an experiment of biodiesel combustion and emission, both the 5% (RME5) and 10% (RME10) blends of rapeseed methyl ester (RME) can show reduction of

PM emissions by 4.5% and 9.1% respectively with compare to diesel fuel **[389]**. But the blends of RME20 and above show discordance with the lower blends of RME fuel. If the fuel possesses higher boiling point or lower volatility, almost nil amount of sulphur, higher oxygen content in the FAMEs reduces the PM emissions **[390]**.

Because of lower soot characteristics of biodiesel, the total number of particles from SMPS (Scanning mobility particle sizer)-data is found decreasing by about 10% when going from D100 (normal diesel fuel) to BD20 (blend of 20% Biodiesel). Currently, in the case of massbased PM regulation, biodiesel-diesel blended fuel has the advantage in terms of PM reduction. Nevertheless, systems like the advanced CDPF (catalysed diesel particulate filter) used for the reduction of PM need to reduce nanoparticles, which are believed to be more harmful to human health than larger particles [**391**]. Proper sampling and filtrations process may reduce the emission of nanoparticles, thus ensuring clean combustion technology of diesel and biodiesel fuelled engine combustion process.

Current regulations on PM emission may shift their focus from particle mass to particle size distribution. As the biodiesel percentage in diesel fuel is increased, the total PM number is decreased and the particle size distribution is displaced towards lower diameter values [**392**]. However, there have been only few studies on the number concentration and size distribution of particles emitted from diesel engines fuelled with biodiesel for various engine operating conditions. EGR is widely used to reduce NOx emission from diesel engines [**393**]. But EGR affects particle growth including surface growth, coagulation, and aggregation. Reportedly, BD20 combustion is more tolerant to EGR addition than is D100 combustion [**391**].

Here in this study, the experimental results of combustion of the fuels listed in the Table 8-1 are presented. The tests were performed between 1200 rpm and 2400 rpm at full load, part (50%) load and idle crank load conditions for all the fuels.

Here, Figure 8-6(a-d) present the PM emission at full load condition by the diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively.



(a) PM emission by diesel, diesel-WTB and diesel-WTB-PS blends at full load



(b) PM emission by diesel, diesel-CaB, and diesel-CaB-PS blends at full load



(c) PM emission by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) PM emission by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 8-6 Particulate matters (PM) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

At full load, diesel fuel emitted 99.72, 28.02, 11.89, 6.59 and 4.5 mg/m³ of particulate matters while running at full load condition for the speeds 1200, 1500, 1800, 2100, and 2400 rpm, respectively. At higher torque speed (1200 rpm), the engine produced very high amount of diesel PM. Then the PM emission rate reduced significantly with the increase in engine speeds. The diesel-WTB and diesel-WTB-PS fuel blends produced almost half of the PM at 1200 rpm and then followed the same track as of diesel fuel PM emission. The only exception occurred with the WTB15 fuel blend, which rose to a peak after the usual peak of PM emission by the other fuel blends and it kept same profile with a higher level of PM emission than all. The diesel-CaB and diesel-CaB-PS fuels blends also generated lesser PM at 1200 rpm except few samples. Almost similar quantity of PM emission was observed for the diesel-WTC and diesel-WTC-PS fuel blends except WTC15 and WTC10. Also, in case of the diesel-PWC and diesel-PWC-PS fuels, greater PM emissions were observed for the PS added fuels. All these blends produced higher PM than that of the diesel fuel at every engine speed.

From Figure 8-6(a), only WTB5 emitted lower (highest reduction was -74.47%) PM emission than the diesel fuel for all the engine speeds. The other fuels showed mixed variation (increase and reduction) of PM emission while comparing the PM emission by the diesel fuel at those respective speeds. Through addition of oxygenated biodiesel fuel reduced the PM emission, the lower blend was more effective than higher blends. On the other hand, the additional PS in the diesel-biodiesel blends showed increasing rate of PM emission than those

by the original diesel-biodiesel blends. For instance, the highest reduction by the WTB5PS15, WTB5PS10 and WTB5PS15 were -69.1%, -67.56% and -67.24% respectively, which indicate the higher PM emission by the polymer added fuels than the WTB5 only. Among the higher blends of diesel-WTB fuels, the WTB15 emitted about 217.23% more PM than that of diesel fuel at 2400 rpm, though it reduced PM emission at 1200 rpm by -55.84%. The advantage of adding PS hydrocarbons in the biodiesel blends can be effectively observed with WTB15 fuel. When the PS amounts were increasing in the WTB15 fuel, the amount of PM emission increasing rate reduced remarkably than that of WTB15 fuel only. Highest PM emission increase by the WTB15PS5, WTB15PS10 and WTB15PS15 were 32.08%, 38.69% and 41.32% respectively in while comparing with diesel fuel PM emission for 2400 rpm engine speed. PM emissions also reduced for wider range of engine speed regions than that of WTB15. It indicates that the additional hydrocarbons react with the oxygens and reduce reactions with the available impure elements which are threat to the human health if emitted.

Similarly, the full load condition operation of the other fuels can be observed from the Figure 8-6(b-d). Figure 8-6(b) shows that highly viscous and oxygenated diesel-CaB fuel blends emitted very high amount of PM than those by the diesel fuel at respective engine speeds. Both low speed and higher speed operations produced higher PM emission by these fuels, which indicate that the fuel composition of castor biodiesel provoked formation of particles during the combustion and exhaust transport phases from the engine exhaust manifold to the atmosphere. Interestingly, though CaB15 fuel blend produced 579.38% more PM at 1500 rpm, the addition of PS, i.e. the PM emission by the CaB15PS5, CaB15PS10 and CaB15PS15 were just 48.29%, 55.71% and 58.67% higher at that speed. But the opposite results were also found at both higher and lower speeds by these three fuels. For instance, the PM emission by the CaB15, CaB15PS5, CaB15PS10 and CaB15PS15 at 2400 rpm were 293.03%, 353.61%, 376.29%, 385.34% higher than that of diesel fuel at the same speed, respectively.

In case of PM emission by the diesel-WTC blends and diesel-WTC-PS blends, the PM emission by the WTC10, WTC10-PS, WTC15, and WTC15-PS blends showed mixed variations with the change of speeds. But for the emission at 1500 rpm, the increased rate of PM emission by the WTC10(105.43%), and WTC15(84.88%) than the diesel fuel are reduced remarkably by the WTC10PS5(-30.26%), WTC10PS10(-26.77%), WTC10PS15(-25.38%), WTC15PS5(-28.17%), WTC15PS10(-24.57%), and WTC15PS15(-23.14%) at the same speed WTC fuel is a mixture of two different profile of FAME compositions from WTB and WCB

fuels. So, the amount of total saturated FAME and polyunsaturated FAME content varied than their parent biodiesels. Increased saturated FAME content produced lower PM emission while comparing the PM emissions by the WTC and WTB fuel blends for these PM emissions.

Figure 8-6(d) shows the PM emission by the diesel-PWC blends and diesel-PWC-PS blends of the fuels used in this study. Most of the fuels increased the PM emission in comparison to the diesel fuel, though followed almost similar profile of varying this emission content. In spite of showing reduction of PM emission at 1500 rpm by the PWC5(-4.9%), PWC15PS5(-19.17%). PWC5PS10(-15.12%), PWC5PS15(-13.17%), PWC10PS5(-14.31%), PWC10PS10(-10.03%), PWC10PS15(-8.32%), and PWC15PS5(-3.95%) in comparison to that by diesel fuel, all the fuels showed increased trend of PM with the increase in engine speeds. Among all these PWC and PWC-PS fuels, the few of the highest increase of PM emission were, PWC15PS(563.83%), PWC15PS10(551.45%), PWC15PS5(520.43%), PWC15(423.17%) at 2400 rpm in comparison to the diesel fuel PM emission at the same condition. While checking the overall polyunsaturated FAME content of the PWC fuel, the amount was more than other three fuels studies in this chapter, whereas the CaB had highest portion of the monounsaturated FAMEs. The existence of the polyunsaturated and monounsaturated FAMEs is found to the responsible to increase the PM emission along with the other criteria of excessive oxygen and higher viscosities of the respective fuels.

The part (50%) load condition PM emission by the fuels are presented in the Figure A3-7(a-d) for diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively. Overall, the diesel fuel emitted more PM than all the WTB-based fuels for all the engine speeds. Except the diesel-PWC and diesel-PWC-PS fuel blends, all other fuels had emitted lower PM at 1200 rpm, then started following reducing trends as demonstrated by the diesel fuel only. With the diesel-WTC and diesel-WTC-PS fuel blends, all the fuels emitted lesser PM than the diesel fuel at all engine speeds, specially, at 1500 and 2400 rpm. The rate of reduction of PM increased with the engine speeds for a same fuel blend. Obviously, addition of PS will increase chance of emitting more carbonaceous soots and in this study, the PS added fuel blends though reduced the PM emission in comparison to the diesel fuel but they are less efficient than the diesel-biodiesel blends. Moreover, the diesel-PWC blends and the diesel-PWC-PS fuel blends showed increase in PM emission at the lower speeds and then dropped at 1500 rpm, but again increased beyond that speed. It was observed that the addition of 5% PS with the diesel-PWC ternary fuels increased the PM emission by almost 3 times than those by the ternary fuel only at the lower engine speed. But all the fuels have almost 500% -600% extra PM emission than that of diesel fuel. Since the operating control was same for all the fuels for the part load condition, the type of FAME composition and their physical properties affected the PM emission quantity.

While operating the engine at idle crank load condition, the PM emission by the fuels mentioned in the Table 8-1 are pretty much comparable with these fuels except the PWC-based fuels as shown in the Figure A3-8(a-d). As the engine speed of 1200 rpm, the rate of reductions of PM emission were significant by all the fuels. But, with the increasing engine speeds, the PM emission also increased for fuels made of diesel-CaB, diesel-CaB-PS blends and diesel-PWC, diesel-PWC-PS fuel blends after 1500 rpm. Lowest PM emissions were recorded for the diesel-WTB and diesel-WTB-PS fuel blends at all speeds. For the diesel-WTC and diesel-WTC-PS fuel blends, there is not much difference in emission quantity though the PM emissions reduced with the fuels than that of diesel fuel.

Similar to the WTB, the WTC binary biodiesel demonstrated better PM emission reduction features while blending with diesel and PS. The detail variation of the PM emission by the fuels in comparison to the diesel fuel can be observed in Figure A3-8(c). The rate of reduction of PM emission increased with the increase in WTC blend ratio in diesel fuel. Though the lower speed operation at the idle crank load condition showed that the addition of PS in diesel-PWC fuel increased the rate of reduction of PM emission, the increased engine speeds reduced the amount and at the end (i.e. at 2400 rpm) the PM emission increased with comparison to the diesel fuel.

Moreover, the PM emission by the diesel-PWC blends and the diesel-PWC-PS fuel blends are observed to be reducing from 1200 rpm to 1500 rpm, and then start rising abruptly with the increased engine speeds. With these highly polyunsaturated containing fuels, the additional PS facilitated the better reduction of PM emission at the speed of maximum efficiency (1500 rpm) by the fuels.

8.2.5 Unburnt Hydrocarbons (HC) Emission

One of the key indications of increased unburnt hydrocarbons (HC) emission is the reduction of combustion efficiency. Few of the key reasons for emitting the HC contents are, increased fuel viscosity and density, poor atomisation of fuel, larger droplet diameter of the

atomised fuel, lesser reaction time, lesser amount of oxygen than the requirement for complete combustion of fuel, longer chain length of the FAME hydrocarbons, etc. **[360, 368, 394, 395]**. Though HC emission could not be totally eliminated, it can be controlled at a desired level by controlling few combustion parameters (e.g. higher air-fuel ratio, sacrificing BTE, and reducing turbulence, reducing ignition delay, etc), but reduction of HC will increase the emission of NOx contents **[396]**.

At lower engine loads (lean air-fuel mixture, poor fuel distribution), the emission of HC also increases for diesel fuel. But due to more oxygen enrichment in the biodiesel blends, the emission of HC decreases at all loads. The increased cetane number of the biodiesel blends reduce the delaying in combustion, which result in reduced HC emission [365, 389]. Higher fuel viscosity by the biodiesel fuel blends help better atomisation of the fuel molecules during injection of fuel in the combustion chamber, which facilitate the better mixing of air and fuel. Consequently, the combustion efficiency is increased [363]. Usually, the HC emission increases with the increase of load and biodiesel fuels exhibit lower HC emission than that of diesel fuel. Abed *et al.* [366] observed such trends very well with the blends of waste cooking oil biodiesels. Biodiesel fuel blends produce very low quantity of HC at lower part load conditions but increases with load increased. Various biodiesel feedstocks also produce variable amount of HC. Abed et al. [397] also observed that, 10% blends of Jatropha (J10), Palm (P10), Algae (A10), and Waste cooking oil (W10) fuels emits lower HC than diesel fuel at any load conditions but their mutual quantity at zero load and full load are P10>J10>W10>A10 and P10=J10=W10>A10 respectively. The authors mentioned that short ignition period and high cetane number affected the HC emission quantity of these fuels.

In this study, unburnt hydrocarbon emissions for the fuels mentioned in the Table 8-1 were investigated. Figure 8-7 presents the unburnt hydrocarbons (HC) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS fuel blends at full load condition respectively. From this figure, it can be observed that for the diesel-WTB and the diesel-WTC blends, the HC emission reduced with the lower biodiesel blends in comparison to that of diesel fuel. With the increase of these fuel blend quantity, the HC emission increased. But for the diesel-CaB and diesel-PWC blends, the lower biodiesel blends increased the HC emissions at lower engine speeds. Though diesel-biodiesel fuel blends increased the HC emissions, the addition of PS reduced the HC emission significantly for the WTB and WTC-

based fuels. But at 2400 rpm, all the studied PS blended fuels except PWC15-PS blends reduced HC emission. On the other hand, it could be observed that though the diesel-CaB-PS5 reduced HC emission compared to the diesel-CaB fuel blends, the higher PS addition also increased the HC emission. Similar trends were also seen for the diesel-PWC-PS fuel blends. The overall HC emissions by the PWC15-PS blends were even higher than that of the diesel fuel though those emissions were lesser than that of PWC15 fuel.

While comparing with the diesel fuel, the highest HC emission reduction was done by the WTB5 among diesel-WTB fuels. All the diesel-WTB-PS blends effectively reduced the HC emission for all the speed conditions at full load. Here, CaB15 fuel increased the HC emission by a maximum 142.27% and CaB5 produced 17% more HC than that of diesel fuel emission. Though these fuels were highly oxygenated, their higher viscosity and lower CN were reasons for emitting more HC. With increased percentage weight of the PS addition with these diesel-CaB fuel blends the emission condition developed in comparison to their originating diesel-CaB blends. Except CaB5PS5, all other diesel-CaB-PS fuels lesser increase in HC emission. The full load condition indicates that the WTC5 blend can reduced the HC emission efficiently than other diesel-WTC blends. But the diesel-WTC-PS blended fuels always reduced more amount of HC emission than both the diesel and the WTC5 fuel. The HC emissions increased rapidly with the increase in PWC blend ratio in the diesel-PWC fuel blends. Whereas the PWC5PS5 fuel can efficiently reduce the HC emission to the diesel fuel does. All other polymer blended fuels increased HC emission in comparison to the diesel fuel but are lower than the corresponding diesel-PWC fuel blends.



(a) HC emission by diesel, diesel-WTB and diesel-WTB-PS blends at full load



(b) HC emission by diesel, diesel-CaB, and diesel-CaB-PS blends at full load



(c) HC emission by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



Figure 8-7 Unburnt hydrocarbons (HC) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

The part load condition effect on the HC emission by the fuels mentioned in the Table 8-1 are shown in the Figure A3-9(a-d) for diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively for three different engine speeds. Due to the part load, the results of the trends of HC emissions were found to be different than those of the full load operations.

The diesel-WTB-PS fuel blends could not reduce the HC emissions than the increased level of HC emission experienced by the diesel-WTB blends, which is contrary to the full load condition. Insufficient quantity of active oxygens for the combustion process could not help burning all of the hydrocarbons added from the PS. It could be also seen for the WTB-based fuels that the HC emissions increased with the increase of blend biodiesel blend ratio at the same speed. Besides, the overall HC emissions are higher at lower speeds. But, when the speed increases, the additional hydrocarbons might not get enough reaction time to be burnt and it resulted into higher HC emissions than those of the diesel-WTB fuels as well. In case of the diesel-CaB, diesel-WTC and diesel-PWC fuel blends, the increased amount of blend ratio for the same engine speed increased the amount of HC emission. On the other hand, the diesel-CaB-PS and diesel-WTC-PS fuel blends reduced the HC emissions significantly than those emitted by the diesel fuel. The HC emission reduction efficiency by the diesel-PWC-PS fuels could be compared with those of the respective diesel-PWC ternary blends only.

The idle crank load effect on the HC emission by the fuels mentioned in the Table 8-1 are presented in the Figure A3-10(a-d) for diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively at various engine speeds. While observing the overall impact on HC emission, it can be observed that the increased engine speeds reduced the HC emission indicating the better combustion at higher speeds. Also, the diesel-WTB blends and the diesel-WTB-PS blends always reduced the HC emissions. The higher the PS mixed with the respective diesel-WTB fuel; the better reduction of the HC emission was observed for these fuels. Similar trends were also observed for the diesel-CaB and diesel-CaB-PS fuel blends as shown in the Figure A3-10(b). Though the diesel-WTC blends reduced the HC emissions than the diesel fuel at any speeds of idle crank load operation, the diesel-WTC-PS fuels showed unusual trends of increasing HC emission. This is a clear indication that the PS addition could not be helpful for increasing combustion efficiency at idle crank load condition. Similarly, the diesel-PWC fuels also increased HC emission than the diesel fuel for 5% and 10% biodiesel blends. But the PWC15 fuel effectively reduced the HC emission than those by the PWC5 and PWC10 as it provided the sufficient oxygen for combustions. Addition of PS was useful to reduce the HC emission as well.

8.2.6 Excess Oxygen (O₂) Emission

Emission of excess oxygen (O_2) could be the result of excessive air intake in the combustion chamber at the beginning of the working cycle of the combustion system. From the Figure 8-8, Figure A3-11, and Figure A3-12, it was observed that the overall quantity of the O_2 emission decreased with the increase in load applied. Similar trends were also observed by Elkelawy *et al.* **[394]**. This study was performed in three different load conditions, namely, the full load (Figure 8-8(a-d)), part (50%) load (Figure A3-11(a-d)) and the idle crank load (Figure A3-12(a-d)). All the fuels mentioned in the Table 8-1 were tested at different engine speeds varying from 1200 to 2400 rpm, for which usually the maximum torque, efficiency and maximum operating speed conditions were obtained, respectively. O_2 emission is not considered as a harmful emission component, rather it is an indication of quality of the combustion based on types of fuel and the amount of air intake in the system. The equivalence ratio is another indicator of rich to leaner air-fuel mixture processed within the combustion system. In spite of drawing desired air in the combustion system, the poor fuel quality (i.e. highly viscous, lower CN, etc.) can affect the combustion efficiency. Besides air intake as source of oxygen for the combustion, part of active oxygen was supplied by the biodiesel fuel. In that case, the O_2 emission quantification may be beneficial to investigate. Since the fuels used in this study possessed different physical properties than those of the diesel fuel, the O_2 emission was inspected.

Figure 8-8(a-d) presents the Excess oxygen (O_2) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition respectively. In general, the O_2 emission increased for all the fuels at higher speeds. It could be identified that the diesel-WTB and diesel-PWC fuel blends emitted more O_2 than the diesel at the same speed conditions.





(a) O₂ emission by diesel, diesel-WTB and diesel-WTB-PS blends at full load

(b) O₂ emission by diesel, diesel-CaB, and diesel-CaB-PS blends at full load



(c) O₂ emission by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) O₂ emission by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 8-8 Excess oxygen (O₂) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

The diesel-CaB blends emitted lower O_2 than the diesel. Moreover, only the WTC5 had higher O_2 emission than the diesel among the diesel-WTC blends. When the PS was added to make diesel-biodiesel-PS fuel blends, then the increased amount of PS into the diesel-5% biodiesel blends caused excessive O_2 emission than the diesel for all the fuels. For the full load operation of the fuels emitted lesser oxygen than the diesel at lower speed condition. Higher biodiesel blends of CaB, WTC and PWC were able to emit lesser oxygen due to more fuel combustion using the available oxygen within the system. Although it was expected that the addition of hydrocarbon might reduce the oxygen emission, the lower amount of addition of PS with lower blend ratios of the biodiesel fuels led to increase in O_2 emission, and then the further addition of PS just reduced that oxygen emission content for all the fuels. Here, the viscosity increase of these fuels might failed to make the best use of all the hydrocarbons to come in contact with the oxygen to react well.

The part (50%) load observations of the O₂ emission are presented in the Figure A3-11(ad) for by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively at 1200 rpm, 1500 rpm and 2400 rpm speed conditions.

Among the diesel-WTB blends, WTB5 reduced the O_2 emission than the diesel at all the speeds and same occurred for the WTB5-PS blends with the increased amount of PS in the WTB5 fuel. Both the WTB10 and WTB15 increased the O_2 emission though their increasing addition of PS reduced O_2 emission indicating the overcome of viscous effect while contacting with the oxygen for further reaction of the fuel droplets. The higher speeds facilitated better O_2 emission reduction than diesel fuel and the best reduction was done by WTB15PS15 (-90.41%) at 1200 rpm. Variation of O_2 emission by diesel-CaB and diesel-CaB-PS fuels against the diesel fuel could be significant. The O_2 emission reduced by the CaB10-PS and CaB15-PS blends with increased PS addition. The fuels produced by diesel-WTC and diesel-WTC-PS blends showed better reduction of O_2 emission reduction, with highest reduction of O_2 emission performed by WTC15PS15(-92.68%) against diesel fuel. The PWC10 and PWC15 fuels just reduced the O_2 emission by reacting with the available oxygen at those given engine combustion environment.

The effect of idle crank load engine operation condition with the fuels mentioned in the Table 8-1 for the O_2 emission are presented in the Figure A3-12(a-d). For the diesel-WTB fuels, though O_2 emission increased for the WTB5, WTB10 and WTB15 fuels at lower speeds, these fuels could reduce O_2 emission at higher speeds due to better combustion efficiency. In all cases of the diesel-WTB-PS fuels, the increasing amount of PS addition decreased the overall O_2 emission as the hydrocarbon addition could burn well with the help of available oxygen in the system. For all other fuels, it could be observed that the low amount of PS addition could not help reducing O_2 emission rather increased, but the higher amount could reduce O_2 emission. At 2400 rpm the diesel-CaB fuels increased O_2 emission, the CaB5PS15, CaB10PS and CaB15PS15 fuels were effective to reduce O_2 emission efficiently. The diesel-WTC and

diesel-WTC-PS fuel blends reduced O_2 emission with the increase in engine speed. For the diesel-PWC and diesel-PWC-PS fuels, both the lowest and highest engine speeds showed efficient O_2 emission reduction with the increased biodiesel blend ratios as well as the increased PS contents in those biodiesel-diesel fuels. The maximum reduction O_2 emission occurred by PWC15PS15 (-81.62%) fuel blend.

8.3 Concluding Remarks

Fuels used in this study were produced from inedible graded feedstocks. Total of 4 biodiesel fuels were studied for fuel emission analyses purpose. Of them, both CaB and WTB were produced from single inedible feedstocks. But to produce binary biodiesel PWC and WTC, the parent biodiesels (poppy, waste cooking oil and waste tallow) were produced and then blended together at a desired blending ratio by stirring the fuel mixtures in a magnetic stirrer flask for half an hour. To conduct the fuel combustion, various diesel-biodiesel (i.e. diesel-WTC, diesel-CaB, diesel-WTB, and diesel-PWC) fuels were prepared by adding 5%, 10% and 15% (v/v) from each of the biodiesel fuels in diesel fuel. Based on the methodologies presented in the chapter, the diesel-biodiesel-PS fuel blends were prepared by adding 5% (w/v), 10% (w/v) and 15% (w/v) of PS in the solvent fuels.

Total of 49 fuel samples were studied at various engine speeds (ranging between 1200 and 2400 rpm) and engine loads (i.e. full load, part load and idle crank load). The test results gave characteristics of emission (CO, CO₂, PM, HC, and O₂) to achieve a detail comparison of any fuel against that of the diesel fuel. Along with the graphical demonstration of these characteristics, the comparative analyses have been presented in the referred tables in case of these parameters to assess the fuel performances. In addition, there was unavoidable experimental uncertainty due to instrumentation limitations and data acquisition. Therefore, overall uncertainty analysis has been conducted, which is presented in the Appendix A5 (Table A5-77 to Table A5-11). Addition of higher amount of PS showed better performances with the higher biodiesel blends on reducing CO, HC, and NOx emissions. PS has been observed to be a potential fuel additive to enhance quality of emissions of the diesel engines. Besides, use of PS as fuel additive will help reducing the non-biodegradable wastes to be reduced from the environment, thus establishing a circular economy.

Chapter 9

ASSESSMENT OF PERFORMANCE AND COMBUSTION CHARACTERISTICS OF POLYMER ADDITIVE-BASED DIESEL-BIODIESEL BLENDS IN DIESEL ENGINES

9.0 Introduction

This chapter presents the detail assessment of performance and combustion characteristics of PS polymer additive-based diesel-biodiesel fuel blends in the diesel engines. The fuels, experimental set-up and methodologies required to analyse these characteristic parameters have been presented in the Chapter 8 (Section 8.1). Thus, this chapter will only present the analyses of the engine performance and combustion characteristics accordingly.

9.1 Performance Characteristics

Diesel engine power output, torque, efficiency, specific fuel consumption, etc. are known as performance parameters for fuel combustion in a diesel engine [398]. Musthafa et al. [399] investigated the performance characteristics of 20% palm oil methyl esters (P20) with and without additive (cetane improving additive: Di-tert-butyl peroxide (DTBP)). The trends of performance parameters at all load conditions of the diesel engine, i.e. BTE (P20+DTBP>D>P20), BSEC (P20>D>P20+DTBP), EGT (P20>D>P20+DTBP) demonstrated that the addition of additives improve the combustion efficacy of the fuel blend. Addition of additive reduced BSEC about 15%, which is indication of cost effectiveness of the additive. Srinivasan et al. [361] conducted investigation on performance characteristics of waste beef tallow (WT) biodiesel, commercial ethyl oleate(EO), ethyl stearate (ES), and ethyl palmitate (EP) to compare with ULSD (D). Both density and kinematic viscosity of the WT were 11.78% and 27.78% higher than those of the D, respectively. At full load condition, WT20 produced 5.43% more EGT and a comparable amount higher with other fatty acid esters. Increased WT blend portion increased the BSFC and all these blend fuels had higher BSFC than the diesel fuel. WT10 blend produced almost equal BTE but WT30 had least thermal efficiency output. Also, ethyl palmitate showed negligible amount of decrease in BTE in comparison to the diesel fuel. Same happened to the WT blends for indicated thermal efficiency calculation. But, for other ethyl blends, only ethyl palmitate shows higher efficiency among these fatty acid ester blends. An inference can be developed from the investigations of comparison of various biodiesel-diesel blends with the diesel fuel that, if the heating value of the biodiesels can be increased, there will be less loss of thermal efficiency of the fuel. PS has higher heating value than most of the biodiesel fuels and it has potential to be used as diesel fuel additive. So, blends of diesel-biodiesel-PS (PBD) fuels may have greater potential to improve thermal efficiency of the diesel engines. A sustainable development on improving the alternative fuel's performance may be possible with PBD fuel blends.

In this study, performance characteristics of various PBD fuels were investigated. The relationship of exhaust gas temperature (EGT), brake power (BP), toque (T), brake specific fuel consumption (BSFC), brake thermal energy (BTE), brake specific energy consumption (BSEC), and brake mean effective pressure (BMEP) with the engine speeds and loads were investigated for fuel blends, which are described as follows:

9.1.1 Exhaust Gas Temperature (EGT)

Fuel qualities and the engine combustion conditions influence the exhaust gas temperature (EGT). Engine load, available % of oxygen in the fuel blends, higher biodiesel content in the diesel-biodiesel mixture, high temperature combustion, shorter ignition delay period and combustion period, higher viscosity governed fuel atomisation quality, etc. are the key reasons to for higher EGT [368, 400-403]. It is obvious that higher EGT than that of the diesel fuel is not expected with the alternative fuel blends to assure better combustion. Lowering the EGT will be beneficial for both NOx emission reduction and efficient combustion as compared to the diesel fuel [404]. Figure 9-1(a-d), Figure A3-13(a-d) and Figure A3-14(a-d) show that the increase in applied load to the engine operations increased the EGT.

The full load condition EGT variations are shown in the Figure 9-1(a-d)) for the fuels, diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively at various engine speeds. This figure showed that the increase in engine speed also increased the EGT for the fuels based on the load condition. For the diesel, diesel-WTB and diesel-WTB-PS fuels, it can be observed from Figure 9-1(a) that the EGT did not vary much than that of diesel fuel at any given engine speed. For WTB5, WTB5PS5, WTB5PS10 and WTB5PS15 fuels, the EGT were lower than the diesel fuel EGT at all engine speeds except 2400 rpm. Also, WTB10, and WTB10PS5 fuels lowered EGT multiple times within the tested

engine speed range. The maximum increase by these diesel-WTB and diesel-WTB-PS fuel blends was found to be 11.72% by the WTB15PS15 at 2400 rpm. Higher engine speed influenced the engine combustion cycle to be completed within very short time, so the EGT increased. The lowering of EGT indicated better fuel atomisation and combustion efficiency by the fuels. It was also observed that the addition of extra hydrocarbons in terms of PS blends mostly reduced the EGT than the respective diesel-WTB blends. This phenomenon indicates that the additional hydrocarbon facilitated more combustion and consumption of oxygen.

Figure 9-1(b) shows that EGT increases with the CaB5 and CaB10 when engine speeds were increased. But the CaB5PS5, CaB5PS10, CaB5PS15, CaB10PS5, CaB10PS10, and CaB10PS15 fuels changed the EGT variation in comparison to that of diesel, from increasing at lower speeds to the reduction of EGT at higher speeds. Comparatively, the higher blending ratio of CaB, i.e. CaB15 and CaB15PS5, CaB15PS10, and CaB15PS15 fuels reduced the EGT. While adding PS in CaB15 fuels, the increased amount of PS increased the viscosity and reduced the CN of the fuel as well. It caused the higher amount of EGT reduction by CaB15PS5 fuel than that of the CaB15PS15 fuel.

The lesser amount of PS added to the diesel-WTC fuel blends caused better reduction of EGT in comparison to that of the diesel fuel as shown in the Figure 9-1(c). These fuels showed better EGT reduction, i.e. efficient combustion for all the diesel-WTC and diesel-WTC-PS fuels than the diesel fuel at 1500 rpm. It is the result of the balance of fuel viscosity reduction, available reactive oxygen from fuel and hydrocarbons at lower speeds.

Moreover, the fuel blends of the diesel-PWC and diesel-PWC-PS fuels exhibited lowest EGT for PWC15 and PWC-PS fuel blends as shown in the Figure 9-1(d). In general, among all the fuels used in this study for the full load engine operation purpose, the PWC fuel blends exhibited higher overall EGT than those of the WTB fuels. But the other two categories of the fuels presented in the Figure 9-1(a-b) showed higher average EGT than the PWC fuels. At any engine speeds, the PWC15 and the PWC15-PS fuel blends showed about 17.42% EGT drop by the PWC15 fuel, then the PWC15PS5 fuel showed 27.07% drop of EGT in comparison to the diesel fuel. Contrarily, the PWC5 (2.1%) and PWC10(5.88%) fuels showed higher EGT than the diesel at higher engine speed (2400 rpm). But the PS addition with these two biodiesel fuels caused reduction of EGT. So, it is not only the one single property of the fuel or the engine operations that control the EGT variation. Since, lower EGT also indicated lower NOx

formation, and the PS addition to the biodiesel fuels proved this mutual effect through reducing NOx emission in addition to the EGT reduction.



(a) EGT characteristics by diesel, diesel-WTB and diesel-WTB-PS blends at full load







(c) EGT characteristics by diesel, diesel-WTC, and diesel-WTC-PS blends at full load





Figure 9-1 Exhaust gas temperature (EGT) characteristics by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

Figure A3-13(a-d) presents the EGT characteristics by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively at part (50%) load condition. In all cases, the increased engine speeds and the increased biodiesel content in the diesel fuel raised the EGT level in comparison to the diesel fuel. Lower biodiesel contents (5%) might balance the requirement of the oxygen for complete combustion of the available hydrocarbons, resulting in reduction of EGT for each of the fuels. With increased speed, the 15% blend of the diesel-biodiesel fuels had the highest EGT.

While reducing the EGT at 1200 rpm by the diesel-CaB blends, the higher efficiency speed (i.e. 1500 rpm) experienced continuous increase in EGT with the increase in biodiesel blend content and the PS contents in the respective blends. Lower biodiesel blends and their lower addition of PS contents reduced EGT, specially the CaB5PS5 showed reduction in EGT at 2400 rpm in spite of showing 7.76% increase in EGT at 1500 rpm in comparison to the diesel fuel. On the other hand, all the diesel-WTC-PS blends reduced the EGT than those of diesel-WTC fuel. Only with the increased engine speed, the WTC15, WTC15PS10 and WTC15PS15 showed some increase in EGT except the WTC15PS5 fuel blend. WTC15 had the highest increase of EGT by 14.85% at 1500 rpm. In case of the diesel-PWC and the diesel-PWC-PS fuel blends, all the fuels up to 10% composition reduced the EGT in comparison to the diesel fuel at 1200 rpm. When the PWC15 fuel and PWC15-PS fuel blends were used the excess hydrocarbon might not be fully utilised for the combustion process at lower engine speeds. As a result, the EGT rise was observed. But the high-speed operation of the fuels caused better reduction in EGT while comparing with both PWC15 and diesel fuel.

Figure A3-14(a-d) shows the variation of EGT for the diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively at idle crank load condition. In general observation, the EGT for the fuels at 2400 rpm got doubled from those observed at 1500 rpm in most of the cases. In case of diesel-WTB and diesel-WTB-PS fuel blends, the EGT increased with the increase in biodiesel fuel content and the PS in the respective fuels except the WTB15 fuel. WTB15 influenced the reduction of the EGT by 11%-21% within the engine speed range. Whereas the WTB15PS fuel behave almost reverse than the WTB15 fuel, causing increase of EGT with the increased engine speed. About 21.96% more EGT was observed for this fuel while comparing this fuel with the diesel fuel. Among the diesel-CaB and diesel-CaB-PS fuel blends, the fuels reduce the EGT profile for mostly at 1200 and 2400 rpm. Moreover, the EGT of the diesel-WTC and diesel-WTC-PS fuel blends showed better reduction with the increased WTC fuel and PS fuel addition with the diesel fuel. WTC15 reduced the EGT most effectively at all the engine speeds. On the other hand, the diesel-PWC fuels showed mixed effect on EGT characteristics at 2400 rpm. With the increased amount of PWC in the diesel fuel, the amount of reduction rate of EGT increased at the same speed. Though addition of PS with the diesel-PWC increased the EGT with the increased PS quantity, both at highest and the lowest tested speeds, the combustion of these fuels occurred efficiently even at this idle load condition.

9.1.2 Brake Power (BP)

The brake power (BP) is the final usable and available output power due to combustion of fuel and the subsequent losses of energy by the time the power is available to be used for other purposes. In an internal combustion engine, the BP is found to be increasing with the increase of engine speed and the fuel consumption until a rated highest speed, then the frictional energy losses increase rapidly and BP is reduced. This power vs speed relationship is due to volumetric efficiency **[382]**. Along with the volumetric efficiency, the higher viscosity and frictional losses, larger fuel droplets, poor fuel atomisation, lower heating value, higher biodiesel blend ratios, etc. can result into lower brake power for the same amount of diesel-biodiesel blends in comparison to that of diesel fuel **[368, 382, 403, 405, 406]**.

Figure 9-2(a-d) depict the relationship between brake power (BP) and engine speed for diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively at full load engine operating (i.e. the wide open throttle) condition. In general, the lower speed operation takes more time to complete a working cycle for the engine than the higher speed operations. So, the total fuel consumption increases with the increase in speed. In general, these fuels almost followed the same trend of brake power curve. These curves featured how much BP was obtained as final useful power from the fuels used in comparison to the diesel fuel. For the fuels produced from diesel-WTB and diesel-WTB-PS blends most of the fuels were seen to produce lower BP than the diesel fuel at every engine speed condition. The first category of the fuels not only provide cleaner hydrocarbon in the combustion chamber but also provide inherent oxygen to be mixed with the fuels before being injected in the system.

Also, the addition of PS with the diesel-WTB fuel blends increased the amount of combustion rate with cleaner hydrocarbons and fuel oxygen. Overall fuel lower heating values (lower heating values were considered here in this study to determine the performance parameters) of the fuels are shown to be varied in comparison to the diesel fuel, which are responsible to influence the BP variation. The heating values of the fuels reduced with the increased amount of biodiesel added with the diesel fuel, and the heating value increased. So, it was anticipated that the BP would change positively than the biodiesel blends with the addition of PS in the fuel. Among the WTB5, WTB10 and WTB15 fuels, the WTB5 reduced BP for all the speeds. But the WTB10 produced mixed results (increase and decrease at different engine speed), and the WTB15 fuel blend increased the BP for each of the working

speeds considered in this study. The diesel-WTB-PS fuel blends mostly reduced BP in comparison to that of diesel fuel except the WTB10, WTB15PS10 and WTB15PS15 fuel blends. Maximum reduction (5.4%) of BP occurred by the WTB5PS5, WTB5PS10 and WTB5PS15 fuels at lower speeds, but the rate of reduction of BP reduced by as low as 1.21% in comparison to diesel fuel.

With the diesel-CaB and diesel-CaB-PS fuel blends, Figure 9-2(b) shows the reduction of BP by all the diesel-CaB and diesel-CaB-PS blends. It is not only the higher viscosity of the fuel, but also the resultant injection quantity of fuel due to the higher viscosity which result into reduction of the BP output. The comparison of BSFC of CaB fuel blends with that of the diesel fuel operations may help understanding the effect of lower heating values in reducing the BP. Only at 2400 rpm, the CaB15PS5 (3.04%), CaB15PS10 (3.24%) and CaB15PS15 (3.55%) fuels showed increase in BP due to higher speed governed combustion efficiency of the fuel. Because these three fuels produced very low amount of BP at lower speeds as well.

The BP output of the diesel-WTC and diesel-WTC-PS fuels are shown in the Figure 9-2(c). It could be found that the PS added fuels of WTC5 showed higher reduction of BP than that of WTC5. Good level of increment of BP output could be obtained for WTC15 and its related PS fuels. Highest increment of BP was seen for the WTC15. On the other hand, the fuels like PWC5, PWC5PS5, PWC5PS10 and PWC5PS15 reduced BP than the diesel fuel. But the PWC10 and beyond designed fuels varied with reduction and increment of the BP with the change of engine speed. The highest reduction of BP was with the PWC5PS15, whereas the highest increase was 4.29% by PWC15PS15 at 2400 rpm. These results conform with the reasons presented at the beginning of the discussion for BP outputs in this section.


(a) BP vs engine speed by diesel, diesel-WTB and diesel-WTB-PS blends at full load



(b) BP vs engine speed by diesel, diesel-CaB, and diesel-CaB-PS blends at full load



(c) BP vs engine speed by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) BP vs engine speed by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 9-2 Relationship between brake power (BP) and engine speed by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

Though the BP variations with the fuels considered at the full load operations was not that much, the part (50%) load effect on the BP variations are observable due to higher bandwidth of their BP profile as shown in the Figure A3-15(a-d). General observation indicates that most of the fuels produced higher BP in comparison to that of diesel fuel at this operation condition. While comparing with the diesel fuel, the highest increase in BP was produced by the WTB15PS15 (21.06%) and the highest reduction was produced by WTB5PS5(-9.17%).

At part (50%) load condition, the diesel-CaB and diesel-CaB-PS fuels behave very different than those in the full load condition. In this case, all the fuels of this category except the CaB5, Ca5Ps5 and Ca10 increased the BP output at varying engine speeds. The highest increasing rate of BP was observed for the fuel CaB15PS15(20.74%), whereas the highest reduction was seen for CaB10(-8.66%). Though both the CaB5 and CaB10 produced lesser BP, their respective increasing PS blends kept increasing the BP outputs. Moreover, among the diesel-WTC and diesel-WTC-BP fuels, the WTC10 fuel showed reduction of BP at every engine speed. But the WTC5 and WTC15 increased the BP output, specially the WTC15 fuel could increase BP by 14% in comparison to the diesel fuel. The WTC5PS5, WTC5PS10, WTC5PS15, WTC10PS5 and WTC15PS5 fuels showed BP reductions for wider range of engine speeds as well. The part load condition of the diesel-PWC and diesel-PWC-PS fuels increased BP at higher rates than these fuels did at the full load condition. Except partially reducing BP with the PWC5 and PWC10 fuels, the other blends just increased the BP output

in comparison to the diesel fuel. The PWC15PS15 fuel blend showed higher rate of increment of BP among all the PWC category fuels.

In the Figure A-16(a-d), the BP variation of the fuels listed in the Table 8-1 are shown for idle crank load condition with the change of engine speeds. It could be observed that the BP variation band was not big, which indicated better fuel performance within acceptable limits. Among all the diesel-WTB and diesel-WTB-PS fuels, the WTB10PS15 fuel showed increasing rate of BP with the increase in engine speed as well. The highest increase was found to be 28.35% by the WTB10PS15 at 2400 rpm.

Moreover, as per the Figure A3-16(a-d), all the fuels are seen to be increasing at a positive rate from 1200 until 2400 rpm of the engine operations at idle crank load. Due to such profile of BP fluctuations by these fuels, all the fuels generated reduced rate of BP than the diesel at 2400 rpm speed for diesel-CaB and diesel-CaB-PS fuels. The highest reduction of BP was found for CaB5PS5(-50.8%), CaB10(-50.14%) and CaB15(-49.89%) at 2400 rpm. Whereas the highest increase was observed for the Ca15PS15(89%) at 1500 rpm. At this speed, all the other fuels also showed increased rate of BP profile. The highest rate of increase in BP was found for WTC15PS15 (56.19%) at 1500 rpm. Moreover, the diesel-PWC and diesel-PWC-PS fuels at idle load conditions, showed higher level of BP reduction at 2400 rpm, whereas the fuels showed better rate of increase in BP at high efficiency speed (1500 rpm) level. The highest increase was reported to be 99.46% by the PWC15PS15 at that speed, though this fuel also reduced BP by 33.57% at 2400 rpm.

9.1.3 *Torque* (*T*)

When the power output and the engine speeds are recorded, the performance parameter called toque (T) can be determined. It is the measure of capacity of the engine crankshaft of how much rotational force it can apply to rotate other coupled objects about an axis of rotation. Usually, torque increases until the engine reaches to the maximum efficiency level of operating speed, then starts reducing with the engine speed rise. But the reduction of the diesel engine torque is not as sharp as the petrol engines do. The rate of reduction is very low, for which the torque vs speed curves of the diesel engines are sometimes called as flat-curve torque graph **[407, 408]**. Here in the study, the diesel engine was used to study the performances of the fuels mentioned in the Table 8-1 at various loading conditions.



(a) T vs engine speed by diesel, diesel-WTB and diesel-WTB-PS blends at full load



(b) T vs engine speed by diesel, diesel-CaB, and diesel-CaB-PS blends at full load



(c) T vs engine speed by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) T vs engine speed by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 9-3 Relationship between Torque (T) and engine speed by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

Here, Figure 9-3(a-d) depicts the toque produced by the diesel engine due to combustion of various fuels: diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively at full load condition. The torque vs speed curves for all of these fuels increased from low speed to a peak value near higher efficiency speed of the engine operation and then start decreasing with the increase in engine speed. Due to brake power deviation the torque also deviated for these fuels. Else, the overall reduction could be considered smooth with the engine speed increasing after the maximum efficiency point. These figures also show that in most cases, the torque generated by the diesel fuel was higher than those produced by the other fuels at the respective conditions. Ong *et al.* [368] also supported with experimental investigation of torque produced by the biodiesel fuels that the higher viscosity and the lower calorific values are the reasons for lower torque generation by the biodiesel fuels that the higher lower torque generation by the biodiesel fuels that that of the diesel fuel.

The diesel-WTB and diesel-WTB-PS fuels produced lower torque than the diesel except the WTB15 fuel, which produced very little amount of higher torque than the diesel fuel. The reason could be sufficient oxygen supplied by the WTB15 fuel for the combustion to take place. The lowest amount of torque was generated at 2400 rpm by most of the fuels. While investigating the torque variations by the diesel-CaB and diesel-CaB-PS fuel blends with the variation of engine speeds at full load, it shows that only a few fuels just generated higher torque than diesel at higher speeds. But the lion portion of the results are lesser than that of the diesel fuel. At 1500 rpm, all the diesel-CaB and diesel-CaB-PS fuel blends experienced the highest reduction of torque production than the diesel fuel. On the other hand, the diesel-WTC and diesel-WTC-PS fuel blends showed very low amount of variation with the diesel fuel. The increased amount of addition of PS with PWC5 fuel increased the reduction rate of torque generation than the PWC5 does. With higher biodiesel blend of PWC15, the PS blends also showed increase in torque. Highest increase in torque production was observed for PWC15PS15 at 2400 rpm.

The torque vs engine speed curves in the Figure A3-17(a-d) are the variation of torque produced by the fuels mentioned in the Table 8-1 at part (50%) load condition. These figures are showing better flat-curve torque vs speed relationship. Besides, these curves are showing that most of the fuels produced higher torque than the diesel fuel at this loading condition. The reason behind could be the higher amount of fuel consumption than the diesel fuel by the engine in order to maintain the part load condition. Among the fuel of WTB blends, the WTB10PS10, WTB10PS15, WTB15, WTB15PS5, WTB15PS10 and WTB15PS15 fuels showed overall increase in torque production at the given speeds. Mostly, the torques were higher nearby the1200 and 1500 rpm engine speed conditions and the following reductions were not much sharp. The highest increase in torque was achieved by the WTB15PS15(21.06% at 1200 rpm and 19.24% at 1500 rpm). Also, the lower biodiesel blend and their respective PS blends produced reduced amount of torque than the diesel fuel. The highest amount of torque reduction was by WTB5PS5 (-9.17%) at 1800 rpm.

Moreover, only the CaB5 showed reduced amount of torque generation along with mixed reduction by the CaB5PS5, CaB10 and CaB15 fuel. The other diesel-CaB and diesel-CaB-PS fuels increased the torque at part load condition. The highest torque was generated by the CaB15PS15 (20.74% more than the diesel) at 1800 rpm. Addition of PS with the WTC fuels caused reduction of torque. This could be due to the increase in viscosity because of addition of PS. The highest increase of torque was seen for WTC15(14%) at 1800 rpm, whereas the highest reduction was shown by WTC5PS10(-12.69%) at 1200 rpm. In case of the diesel-PWC and diesel-PWC-PS fuel blends, the addition of PS indicated positive approach in case of torque increment. The highest torque was observed for the PWC15PS15 blend, which was 24.22% higher than that of diesel fuel at 1500 rpm.

The idle crank load effect on the engine torque production by the combustion of the fuels mentioned in the Table 8-1 are presented in the Figure A3-18(a-d). The curves are showing that the highest torque was generated for each of the fuels at lowest operating engine speed in this study. Then the torque generation dropped sharply around 1200 and 1500 rpm region. Then the torque started rising up very slowly. It could be also seen that very few diesel-biodiesel and diesel-biodiesel-PS blends produced lesser torque than the diesel fuel at this operating condition. From observation of Figure 9-3(a-d), Figure A3-17(a-d) and Figure A3-18(a-d), it could be understood that these fuels mostly generated higher torque than the diesel fuel at lower loading applications. Only few of the speed conditions of the WTB5, WTB5PS10 and WTB15PS5 fuels produced lesser torque than the diesel fuel. It also shows that the WTB5PS5 and WTB10PS5 fuels dropped the torque generation capacity of the WTB5 and WTB10 fuels severely due to addition of PS. Both the higher and lower speed operations influenced the reduction of torque than the diesel fuel for CaB-based fuels. The highest drop of toque occurred with the CaB5 (-52.23%) fuel at 2400 rpm. The increased addition of WTC fuels in the diesel fuel the rate of torque increased with the increase in blend ratio. The highest increment among the diesel-WTC blends were achieved by the WTC15 blend (45.96%) at 1500rpm. It could be also observed that the increasing amount of PS addition in the respective WTC-diesel blends also increased the torque than that by the diesel fuel at the same operating condition. For instance, at 1500 rpm, the % rate of increase of torque by the fuels were, WTC15PS15(37.24%)> WTC5(3.30%), WTC10PS15(45.96%)> WTC10(9.36%), WTC15PS15(56.19%)>WTC15(9.91%).

It could be found that each of the diesel-PWC and diesel-PWC-PS fuels have variation of impact on torque generation in comparison to the diesel fuel at the respective given conditions. The fuels generated lesser torque at 2400 rpm, whereas the fuels generated very higher rate of torque than the diesel fuel at 150 rpm. Not only the increase in blend ratio of PWC increased the torque but also the increasing amount of PS lead to increment of torque at the given condition in comparison to that of diesel fuel output. The percentile increase of torque by few of these fuels at 1500 rpm can be mentioned as, PWC5(41.52%)<PWC5PS15(76.06%), PWC10(49.83%)<PWC10PS15(85.54%), PWC15(50.58%)<PWC15PS15(99.46%) with respect to the diesel fuel at their given conditions.

9.1.4 Brake Specific Fuel Consumption (BSFC)

Along with the brake power (BP) produced by the engine it is essential to understand how much fuel the engine consuming to produce that reported brake power. Due to variation of fuel's rheological properties and calorific values, both the amount of fuel drawn in the combustion chamber as well as the power output differ in comparison to the diesel fuel only. The brake specific fuel consumption (BSFC) has been considered a reliable unit of expression (gm of fuel consumed to produce each kWh of energy) to understand the variation of fuel consumption by the engine while running with different fuels.

In this study, the fuels mentioned in the Table 8-1 were considered. Figure 9-4(a-d) is showing the BSFC relationship against varied engine speeds at full load condition. From 1200 rpm speed condition to 1500 rpm, the BSFC of the fuels reduced from a higher value to their lowest value to deliver the highest efficiency from the engine. After that, the BSFC started increasing with the increase in speed. Most of the fuels had higher BSFC than the diesel fuel within these given operation conditions. It could be found that at the full load condition all the fuels of diesel-WTB and diesel-WTB-PS blends have continuous increase in BSFC with the increase in blend content at a certain speed. Increase in BSFC could be due to higher viscosity, density, and the lower calorific value. The lowest BSFC from these fuels were shown by WTB5 (just 7.64% higher than that of diesel fuel) at higher efficiency speed (1500 rpm).

The CaB5 exhibited better BSFC among all the CaB-based fuels. At 1500 rpm, the lowest BSFC was 1.06% higher than that of diesel by the CaB5 fuel. For other speeds, the BSFC were lesser than the diesel fuel. If less fuel is consumed for a fuel having lower calorific value than diesel fuel, there will be loss of BP output. Obviously higher BSFC is unexpected for economic reasons, but other comparative benefits of the diesel-biodiesel and diesel-biodiesel-PS fuels need to be considered. Comparative information help choosing the optimal option among available options. Among the diesel-WTC and diesel-WTC-PS fuels, the WTC15PS10 and WTC15PS5 fuels had lower BSFC than the WTC15 at the given engine speeds. Though these fuels were having more BSFC, the addition of PS blends helped reducing the overall BSFC in comparison to those at 2100 rpm for the diesel-WTC and diesel-WTC-PS fuels at the full load condition. At full load condition, the BSFC increased with the increasing rate of biodiesel content as well as PS content in the respective fuels. But the PWC10PS15 fuel offered reduced BSFC than that of PWC10PS10. Comparatively, though higher than the diesel fuel,

the PWC5 fuel had the better BSFC values over the entire range of engine speeds among all the PWC fuels.



(a) BSFC vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at full load



(b) BSFC vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at full load



(c) BSFC vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) BSFC vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 9-4 Brake specific fuel consumption (BSFC) characteristics at various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

Figure A3-19(a-d) presents the BSFC relationship with the varying engine speeds at part (50%) load for various fuels mentioned in the Table 8-1. The BSFC profile for all the fuels are showing that, all the fuels had much higher level of BSFC than that of the diesel fuel at the respective conditions. While checking the BSFC variation from diesel fuel by the diesel-WTB and diesel-WTB-PS fuels at given speeds, it was seen that, among the WTB5, WTB10 and WTB15 fuels, there is not much difference in BSFC for both the WTB10 and WTB15 blends. These two fuel blends were consumed more than the WTB5 fuel in the diesel engine. Lower biodiesel content in the fuel helped reducing the BSFC increment in comparison to the diesel

fuel. But, among the WTB5-PS blends, 5% addition of PS reduced the fuel consumption than that required for the fuel WTB5. Similar patterns were seen for 5% PS addition to WTB10 and WTB15 fuels as well.

At lower speed, the CaB5 and CaB5PS5 had the lower BSFC than the diesel fuel at that condition. Obviously, the addition of PS helped reducing the BSFC level from those by CaB5 for the CaB5PS5, CaB5PS10 and CaB5PS15 at all engine speeds. The other PS blended CaB fuels also showed similar reduction than their respective CaB10 and CaB15 fuels. Also, the BSFC increased with the increasing biodiesel ratio of WTC in the diesel fuel, but the addition of PS with WTC-diesel blends reduced the BSFC. Though WTC-diesel blends showed reduction of BSFC increase in BSFC from the level at 2100 rpm.

Here, the polymer blended fuels were efficient in reducing the overall BSFC, so they showed less increment of BSFC in comparison to the diesel fuel. The fuels showed very high BSFC than they showed for full load condition. Both PWC10 and PWC15 were consumed about 30% more than the diesel does at the respective operation condition to produce one kWh of energy by the diesel engine. The part load condition is very much challenging for the engine governing system. A better control system for fuel injection system based on the fuel's viscosity, density, heating value and the CN may help controlling the uneven fuel demand during part load combustion of the fuels in the diesel engine. Using an unmodified fuel management and combustion system may not be economic while using alternative fuels due to fluctuating load condition.

Though both the full load and the part load operation showed the lowest BSFC for fuels at higher efficiency zones, the idle crank load operation of the fuels shows different trend of BSFC variation with the engine speed variation. Figure A3-20(a-d) shows the BSFC variation of the fuels. Usually, for all the fuels, the BSFC starts reducing from 1200 rpm like a flat-curve fall except the CaB and PWC fuels. From this figure (Figure A3-20(a-d)), it could be seen that the diesel fuel had lowest BSFC for the diesel-WTB and diesel-WTB-PS fuels showed higher BSFC than the diesel fuel at all cases. But the diesel-CaB, diesel-CaB-PS, diesel-PWC and diesel-PWC-PS fuels showed reduction of the BSFC for the fuels against the diesel fuel. At 2400 rpm, the diesel-CaB, diesel-CaB-PS fuels had higher BSFC than that of diesel fuel. In case of the diesel-WTC and diesel-WTC-PS fuels showed mixed results, i.e. few of the fuels had higher BSFC and few had lower BSFC than the diesel fuel at their respective conditions.

9.1.5 Brake Thermal Efficiency (BTE)

In general, the biodiesel fuels have lower calorific values. Whatever the amount of total fuel was injected in the combustion chamber, part of it was actually the fuel oxygen which helped in combustion process and extracted energy from the hydrocarbons rather than giving energy like the hydrocarbons [368]. Such detail is enough to realise that the power output at the shaft against the amount of fuel blends consumed should be lower than those for the diesel fuel. In this study, all the listed fuels in Table 8-1 were tested to investigate the brake thermal efficiency of the fuels at various engine speeds and load conditions. The tests were performed at full load (in Figure 9-5(a-d)), Part (50%) load (in Figure A3-21(a-d)) and at idle crank load (in Figure A3-22(a-d)) conditions.

At full load operation condition, Figure 9-5(a) shows the BTE variation of the diesel-WTB and diesel-WTB-PS fuels at various speeds between 1200 and 2400 rpm. Similarly, the BTE variations of the diesel-CaB and diesel-CaB-PS fuels, diesel-WTC, and diesel-WTC-PS fuels, and diesel-PWC and diesel-PWC-PS fuels are presented in the Figure 9-5(b-d) respectively. While observing, all the fuels showed wide range of variation of BTE than the diesel fuel. Comparatively, the BTE obtained from these fuels were lesser than that of diesel fuel. When the hydrocarbons were added in the form of PS, the overall calorific values of the fuels increased but their viscosities also increased. These two were contradictory to facilitate efficient atomisation, thus the brake output (BP) reduced. Consequently, the BTE reduced remarkably. Where WTB5 reduced BTE by 7.05% at 1500 rpm in comparison to the diesel fuel, the WTB15PS15 reduced the BTE by 15.36% in comparison to that of diesel fuel at the given operations condition. Though in most cases, the BTE reduced with the CaB-based fuels, the same fuel also experienced higher BTE in part of the operations. For instance, the CaB5, CaB10 and CaB15PS5 fuels showed higher BTE than the diesel fuel between 1800 and 2400 rpm engine speeds. Indeed, CaB5 fuel reduced BTE for only 1500 rpm, else it increased the BTE. Highest increment of BTE by the CaB5 fuel was 4.82% in comparison to the diesel fuel efficiency at 1800 rpm. Though rate of BTE reduction in comparison to the diesel fuel increased with the increase in CaB blend ratio in diesel fuel, PS addition just could not help producing higher efficiency in spite of facilitating better combustion with excess hydrocarbon. The diesel-WTC and diesel-WTC-PS fuels also reduced the BTE in overall. Increased WTC quantity in the diesel-WTC blends increased the rate of reduction of BTE. It was also seen that when 5%-10% PS was added with WTC10 and WTC15 fuels, the rate of reduction of BTE lessen than those by these biodiesel blends. Similarly, the BTE also reduced by the combustion of diesel-PWC and diesel-PWC-PS fuels at all the operating speeds. The amount of reduction rates was higher than those by other biodiesel fuels in this study. The highest amount of reduction of BTE occurred by the PWC5PS15 (-20.78%) in comparison to the diesel fuel.



(a) BTE vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at full load



(b) BTE vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at full load



(c) BTE vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) BTE vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 9-5 Brake thermal efficiency (BTE) characteristics at various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

The part (50%) load variation of the BTE by the considered fuels are shown in the Figure A3-21(a-b) for diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively. The BTE of these fuels increased up to engine speed of 1500 rpm and then started reducing with the increase in speeds due to increased frictional power losses. Highly viscous fuels caused more friction to overcome by the engine's dynamic components. While observing, all the fuels produced lesser BTE in comparison to their

effectiveness at full load operations. Also, the difference between the produced BTE by these diesel-biodiesel and diesel-biodiesel-PS fuels are highly visible from the Figure A3-21(a-d).

The idle crank load condition operation effect on BTE is different than the part load and full load engine operations. It can be observed from the Figure A3-22(a-d) for the diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS fuel blends respectively at various engine speeds. It could be seen that BTE dropped from higher level at 800 rpm to the lowest level at around 1200-1500 rpm region, then the BTE increased at a very slow rate of increment with the increase in engine speed. It could be observed that with the increase in loading in the engine operation, the higher BTE were observed from these fuels.

9.1.6 Brake Mean Effective Pressure (BMEP)

Brake mean effective pressure (BMEP) is directly related to the measured torque output of the engine system. BMEP is one of the important parameters to define how much the engine is capable to perform desired work regardless of how big the engine is, generally the maximum level of BMEP ranges between 700 and 900 kPa for naturally aspirated 4-stroke compression ignition engines [**382**].

In this study, various fuels listed in the Table 8-1 were tested at various engine speeds and loads. Figure 9-6(a-d) depicts the engine speed vs BMEP characteristics of diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively at full load condition. Similarly, the Figure A3-23(a-d) and Figure A3-24(a-d) are showing the BSFC variations against engine speeds for all the fuels at part (50%) load and idle crank load, respectively. While comparing the BMEP of the fuels with that of the diesel fuel at the given condition, the BMEP for a fuel was higher than the diesel only if the respective fuel's produced higher torque or higher brake power at that particular condition (i.e. throttle condition and engine speed). At the full load condition, all the fuels raised the BMEP with the increase in speed until maximum efficiency was achieved. Then the BMEP than that of the diesel fuel at the given is engine speeds. All these fuels almost exhibited lower BMEP than that of the diesel fuel at the fuel at the fuel load with few exceptions.



(a) BMEP vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at full load



(b) BMEP vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at full load



(c) BMEP vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) BMEP vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 9-6 Characteristics of Brake Mean Effective Pressure (BMEP) for various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

While observing the rate of variation of BMEP, it could be seen that, among the diesel-WTB and diesel-WTB-PS fuel blends, the higher WTB content in the diesel fuel increased the BMEP. For instance, the WTB15 showed higher BMEP than the diesel at every engine speed, whereas, the WTB5 blend had increasingly reduction rate of BMEP with the increase in engine speeds while comparing with the diesel fuel. In case of addition of PS in diesel-WTB blends, the rate of reduction of BMEP increased with the increased quantity of PS in the fuel. With the diesel-CaB and diesel-CaB-PS fuels, the increased quantity of CaB with the diesel fuel did not have much variation of BMEP at certain speed among CaB5, CaB10 and CaB15 fuels. While

comparing their respective PS blended fuels, the fuels produced lesser BMEP than the biodiesels. Since, the calorific value, viscosity, and CN of the fuel along with the engine's frictional power losses governed the brake power and torque outputs, the variation of BMEP obviously related to these factors as well. The fuels from diesel-WTC and diesel-WTC-PS blending systems are showing very close BMEP variation in comparison to the diesel fuel. The addition of higher WTC-diesel fuel blend increased the BMEP. WTC15PS15 could deliver about 2.28% and 2.64% increase in BMEP with respect to those of the diesel fuel. These fuels also showed reduction of BMEP at highest thermal efficiency region in comparison to the diesel at 1800 rpm). Higher PWC blend (PWC15) and their PS blended fuels also can produce higher BMEP than the diesel fuel for partial of the entire speed region in this study. PWC15PS produced 4.23% higher BMEP than the diesel fuel at 2400 rpm engine speed at full load operation condition. Diesel fuel BMEP varied between 829.57 kPa and 720 kPa for the engine speed ranging from 1200-2400 rpm at full load condition.

The part (50%) load effect on the engine speed vs BMEP characteristics for the fuels, diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively are shown in the Figure A3-23(a-d). Though, not so sharp variation like the full load condition, these fuels exhibited gradual increase in BMEP from low speed to their maximum at around high torque zone, then the BMEP of these fuels started falling down with the increase in engine speeds. It could be seen that the range of BMEP at part load condition are lower than that at full load condition, which implies that the fuel BMEP increased with the load increment. Unlike full load condition, most of these fuels had higher BMEP than the that by the diesel fuel at the given engine speed.

The WTB5 and WTB5PS5 had lower BMEP at all engine speeds but WTB15PS15 had very high level of BMEP than the diesel fuel. Diesel fuel BMEP varied between 447 kPa and 383 kPa, whereas the BMEP of WTB15PS15 varied between 526 and 430 kPa for the engine speed ranging from 1200-2400 rpm. In comparison, the rate of increase in BMEP by the WTB15PS15 varied between 12.2% and 21.06% in comparison to those of the diesel fuel at their respective conditions. Only the CaB5 and CaB10 fuels produced lower BMEP than the diesel fuel at all the engine speeds. With increasing bending content of CaB their capacity of BMEP production increased. CaB15 produced about 7.36% higher BMEP than the diesel fuel

at 1500 rpm. This table also shows that the addition of PS in the respective diesel-CaB fuel helped increasing the BMEP. For instance, CaB5PS15(13.78%), CaB10PS15(12.21%) and CaB15PS15(17.71%) produced higher BMEP than the diesel fuel at 1500 rpm. The rate of increment of BMEP has been shown in parenthesis here. With increasing blend content of WTC, the rate of increase of BMEP increased. For instance, the rank of rate of increment of BMEP by the WTC fuel blends is, WTC15(14%)> WTC10(6.55%)> WTC5(0.8%) at 1800 rpm. When PS was added with WTC-diesel fuel blends, the WTC5PS5, WTC5PS10, and WTC5PS15 showed BMEP increase among these three fuels. But they produced lower BMEP than the WTC5 fuel and rate of reduction of BMEP reduced with the increase in PS amount. Though WTC10PS5 fuel produced lesser BMEP than the diesel fuel at all the engine speeds, the WTC10PS10 and WTC10PS15 fuels had mixed trend. Same trend occurred with WTC15 and WTC15-PS fuels. Though WTC15 had very higher BMEP than the diesel fuel, the WTC15PS5 had lower BMPET than the diesel. The PWC15PS15, PWC10PS15 and PWC5PS15 fuels had the best increment of BMEP among the diesel-PWC and diesel-PWC-PS fuels. Diesel-PWC blends had increasing BMEP production trend with the increase in PWC quantity as well.

On the other hand, the Figure A3-24(a-d) shows the BMEP variation of all the fuels mentioned in the Table 8-1 at idle crank load condition and for various engine speeds. From the figure it could be observed that the BMEP of all the fuels were very low at 1200 rpm, and then increased narrowly with the increase in engine speeds. Diesel fuel produced BMEP of about 12.65 kPa at 1200 rpm and then raised up to 30.27 kPa at 2400 rpm. Addition of WTB fuel with the diesel fuel caused increase in BMEP. Also, these fuels (diesel-WTB blends) increased the BMEP with the increase in engine speeds. Though addition of PS5 in the WTBdiesel fuels caused the BMEP reduction, the higher quantity of PS addition with these WTBdiesel fuels led to increase in BMEP. WTB15PS15 and 20.45% higher BMEP than the diesel fuel at 1500 rpm. It can be observed that the diesel-CaB and diesel-CaB-PS fuels had mixed rate of variation of BMEP with the CaB and PS quantity increment. Only CaB5 fuel had lesser BMEP than the diesel fuel at all the engine speeds. Whereas all other fuels had very low level of BMEP than the diesel fuel at 2100 and 2400 rpm speeds. At 2400 rpm, the rate of BMEP reduction by these fuels were very high, e.g. CaB5 (-52.23%), CaB5PS5(-50.80%), CaB10(-50.14%), CaB10PS5(-48.64%0, CaB15(-49.89%), and CaB15PS5(-44.07%), etc. fuels had very low BMEP than the diesel fuel. Not only higher reduction rate, but these fuels also had good rate of BMEP increment than the diesel fuel at 1500 rpm. For instance, the CaB15PS had 89% higher BMEP than that of the diesel fuel at that condition. The diesel-WTC, and diesel-WTC-PS fuels had mostly increasing rate of BMEP variations at any given engine speed than that of diesel fuel except few exceptions. Not only the increased rate of addition of WTC with the diesel fuel increased the BMEP, the increased addition of PS with the respective diesel-WTC blends also led to increase in BMEP than that of diesel fuel at a given speed. Higher increase in BMEP were obtained for 1200 and 1500 rpm engine speeds. It was found that the BMEP reduced by the diesel-PWC and diesel-PWC-PS fuels at 2100 and 2400 rpm. Also, the BMEP increased at 1500 rpm by these fuels.

9.1.7 Brake Specific Energy Consumption (BSEC)

Brake specific energy consumption (BSEC) is another effective performance parameter in spite of traditionally available BSFC parameter to investigate how much power is obtained with the fuel injected in the engines. In case of multiple fuels, the BSEC could be a more sensible parameter to understand how much the fuels are efficient in producing the usable power due to their inherent physicochemical properties. The unit of BSEC is J/Wh (or, MJ/kWh). With this parameter, not only how much fuel is consumed by the engine to produce each unit of energy is known but also the effect of its calorific value could be understood [**394**, **409**, **410**]. Though it is expected that the BSEC should be as low as possible, to produce similar amount of brake power that is produced by diesel fuel the BSEC increased for the fuels possessing lower calorific values, higher boiling point and higher viscosities [**409**, **411**].

Figure 9-7(a-d) presents the BSEC for the fuels, diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends respectively for various engine speeds at full load condition. While comparing the BSEC for diesel with those of the other fuels, the lowest BSEC was observed for the diesel fuel. Though addition of higher amount of PS in these fuels raised the LHV, the viscosity had effect on increasing the BSEC as well. Similar to diesel fuel, all these fuels had higher BSEC at lower speed and then it started decreasing with the increase in BTE of the fuel and then increased with the engine speeds. The diesel-WTB and diesel-WTB-PS fuel blends mostly have higher BSEC between 1200 and 1500 rpm in comparison to the diesel fuel. The increase amount of PS in the respective diesel-WTB blends increased the BSEC. Similarly, the addition of increased amount of PS in the respective diesel-WTB blends also led to increment of BSEC against the diesel fuel. Highest increment of BSEC was found for WTB15PS15 (18.5% at 1200 rpm).



(a) BSEC vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at full load







(c) BSEC vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at full load



(d) BSEC vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at full load

Figure 9-7 Characteristics of Brake Specific Fuel Consumption (BSEC) for various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at full load condition

Moreover, the CaB5 exhibited lesser BSEC than the diesel fuel in almost every engine speed at full load except at 1500 rpm. Also, CaB10 and CaB15PS5 fuels showed lesser BSEC at higher engine speeds (1800-2400 rpm). With the diesel-CaB and diesel-CaB-PS fuels the increase in PS content in the respective diesel-CaB fuels showed that BSEC increased highly with comparison to their respective diesel-CaB blends. The highest increase in BSEC was found for the WTC15PS15(17.85%) at 1200 rpm in comparison to that of diesel fuel at full load condition. Among all the fuels tested in this study, diesel-PWC and diesel-PWC-PS fuels had mostly higher BSEC. The highest increment of BSEC was observed for PWC5PS15(32.12% higher than that of diesel fuel) at 1200 rpm in comparison to that of diesel fuel that of diesel fuel. With increasing rate of adding PS in PWC5 fuel, the BSEC increased at a higher rate than the other PS blends with WTC10 and WTC15 fuels. Also, the PWC10PS15, PWC15PS5 and PWC15PS10 fuels had lower BSEC than those of WTC10 and WTC15 fuels, respectively.

The part (50%) load operation effect on diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS fuel blends are presented in the Figure A3-25(a-d) against various engine speeds between 1200 rpm and 2400 rpm. Though all the fuels had higher BSEC at part load condition, the differences were highly visible against the diesel fuel than those observed at full load condition. Only the BSEC by diesel-WTC and diesel-WTC-PS fuels were very close to the those of the diesel fuel. The rate of increment of BSEC by diesel-WTB-PS fuels were mostly increasing with the increase in engine speeds. Whereas that by the diesel-WTB fuels reduced with the increased engine speeds. Addition of PS in diesel-WTB fuels reduced the rate of BSEC increment against the diesel fuel in many cases due to raising the calorific values of the blends. Though the overall increasing rate of BSEC by the diesel-CaB fuels were not much higher than the rate at full load condition, the PS added diesel-CaB fuels also experienced reduction in the rate of increment of BSEC than their respective diesel-CaB fuel blends. Similar trends were also observed for the diesel-WTC, diesel-WTC-PS fuels and diesel-PWC, diesel-PWC-PS fuels for part (50%) load condition.

An opposite trend was observed for BSEC by the fuels mentioned in the Table 8-1 at idle crank load condition as depicted in the Figure A3-26(a-d). The BSEC kept increasing for all the fuels up to a maximum level between 1200-1500 speed region, then started decreasing. These figures indicate that the diesel fuel had lower BSEC for diesel-WTB, diesel-WTB-PS fuels. But BSEC for diesel fuel was higher for most of the diesel-CaB, diesel-CaB-PS, diesel-PWC, and diesel-PWC-PS fuels. The diesel-WTC, diesel-WTC-PS fuels had mixed (few increased and few reduced) trends of BSEC in comparison to those of the diesel fuel. At idle crank load operation condition, less frictional energy has to overcome by the engine power output. Also, the injection of more pure oxygenated FAME and hydrocarbons provided more reliable combustion than diesel fuel which also contains other impurities to put in unnecessary reactions. Addition of PS with WTB15 fuel reduced the BSEC in comparison to the diesel fuel and the BSEC were much lower at other speeds in comparison to the WTB15 fuel. The diesel-CaB and diesel-CaB-PS fuels kept on increasing the rate of reduction of BSEC with the increased rate of CaB and PS contents in their respective blends. At 1500 rpm, these fuels achieved more than 40% reduction in BSEC in comparison to that by diesel fuel at the idle crank load condition. The BSEC increased for WTC5(6.33%), WTC10(7.5%) and WTC15(19.39%) at 1500 rpm in comparison to the diesel fuel. But with increased % of PS in diesel-WTC-PS fuels, the BSEC reduced with respect to the diesel fuel. WTC5PS15 and 16.87% lesser BSEC than the diesel fuel at 1500 rpm.

9.2 Combustion Analysis

In general, the biodiesel fuels have higher bulk modulus of compressibility for which the fuel injection timing is advanced and the rise in fuel injection pressure is observed due to increased amount of biodiesel content in the diesel-biodiesel fuel mixture [410, 412]. In this study, a direct injection naturally aspirated diesel engine test bed was used. The methodology of combustion system in this studied engine is called the E-TVCS (three vortex combustion system), in which the charge undergo three intensified swirling to obtain optimal air/fuel mixture, resulting in efficient combustion of the fuel and reduction of unwanted less efficient combustion related emissions [358]. To investigate the combustion characteristics of the fuels used in this study, three key parameters, namely, the in-cylinder pressure variation (CP), apparent heart release rate (HRR) and ignition delay (ID) period, were analysed. The incylinder pressure (CP) indicates how effectively air was mixed with the fuel to conduct the combustion. When the fuel's heating value (LHV) and mass flow rate are determined, the comparative picture of in-cylinder charge mixing can be understood. On the other hand, the variation of CP along with the fuel's qualities influence how much energy has been lost due to engine's design, fuel injection parameters and operating conditions. The pre-combustion quality of the fuels injected in the diesel engine combustion chamber can be determined from the ignition delay period (ID). All these three parameters of the tested fuels were compared against those of the diesel fuel.

9.2.1 In-Cylinder Pressure (CP)

Fuels having higher CN, viscosity, BSFC, amount of total oxygen within the combustion chamber, start of injection (SOI) of fuel, bulk modulus of the fuel, fuel compression ratio and the alternative fuel content with diesel fuel, etc. may have combined effect on variation of incylinder pressure **[413-415]**. Among the fuels listed in the Table 8-1, the in-cylinder pressure variation of diesel, diesel-WTC (i.e. WTC5, WTC10, WTC15) and diesel-WTC-PS blends (WTC5PS5, WTC5PS10, WTC5PS15, WTC10PS5, WTC10PS10, WTC10PS15, WTC15PS5, WTC15PS10 and WTC15PS15) fuel blends against crank angle variation are shown in the Figure 9-8(a-d), Figure A3-27(a-d) and Figure A3-28(a-d). Here, these results were inspected at various engine speeds and applied loading conditions (i.e. full load (Figure 9-8(a-d)), part (50%) load (Figure A3-27(a-d)) and idle crank load (Figure A3-28(a-d))) to investigate the variation of CP. Besides, the peak in-cylinder pressure for all the fuels are presented in the Table A4-1 to Table A4-4 in the **Appendix A4**.

In the Figure A4-2 (Appendix A4), it has been already mentioned that the combustion process in the diesel engines occur in few stages, namely, the ignition delay period, rate-controlled rapid or premixed combustion, mixing-controlled combustion and late combustion

stage. Several researchers **[416-418]** have explained the CP variation in terms of combustion of the fuel, which can be summarised as, the pressure profile with the variation of crank angle variation is the primary response of the fuel burning conditions. The CP actually attributes how efficiently the fuel mixed with the air to conduct the combustion. Mainly, the premixed and mixing controlled stages burn more than 90% of the fuel for the combustion cycle and show multiple high-pressure peaks for the pressure variations in each of these combustion stages. So, the higher pressures in the respective combustion stages indicate when most of the fuels were burnt for the particular operation condition.







Figure 9-8 In-Cylinder pressure (CP) variation with Crank Angle (CA) variation for diesel, diesel-WTC and diesel-WTC-PS fuel blends for Full load condition at, (a) 1200 rpm, (b) 1500 rpm, (c) 2100 rpm (d) 2400 rpm

Here, Figure 9-8(a-d) is showing CP profile with Crank Angle (CA) variation for diesel, diesel-WTC and diesel-WTC-PS fuel blends for Full load condition at (a) 1200 rpm (b) 1500 rpm (c) 2100 rpm (d) 2400 rpm respectively. At lower engine speed, the multiple pressure peaks for a single fuel are very close to each other. But with the increase in speeds, the pressure variations are very much observable with peaks of the various combustion stages. Similarly, the Figure A3-27(a-d) and Figure A3-28(a-d) are showing the CP vs CA profile at various speeds for part (50%) load and idle crank load conditions, respectively for the diesel, diesel-WTC and diesel-WTC-PS fuel blends. These results indicate that, the higher the load the longer were the combustion periods. It could be seen that the higher biodiesel blends of WTC in the diesel fuel caused higher cylinder pressure than the diesel fuel. Though the lower biodiesel blends had very close profile like the diesel fuel. The peak in-cylinder pressure profile for all fuels were almost similar, e.g. at full load condition, starting from being very high peak CP at 1200 rpm to lowering at around the 1500 rpm region and then increase towards 2100 rpm and start decreasing beyond that speed (Table A4-1). It could be also seen that the addition of PS

in the respective fuel blends caused higher cylinder pressure due to viscosity increment of the fuel in comparison to that of diesel fuel.

Table A4-2 shows the peak in-cylinder pressure (bar) changes due to combustion of diesel, diesel-WTB and diesel-WTB-PS fuel blends at various speeds (i.e. 1200, 1500, 1800, 2100, and 2400 rpm) and loads (i.e. full, partial and idle crank load). The differences in peak CP increased with the increase in engine speeds. Besides, both the WTB10 and WTB15 had higher peak CP than the diesel fuel at all conditions. Increased viscosity and CN caused the increment of CP. Similarly, when the increased PS amount (i.e. 5%, 10%, and 15%) were added to each of the diesel-WTB blends, then their higher viscosities, CN and LHV influenced their respective pressure profile. Mainly, the peak CP for each of the diesel-WTB-PS fuels showed gradual increment of CP with the increased addition of PS. Due to addition of actively pure hydrocarbons in oxygenated fuels (due to addition of biodiesel in diesel fuel) caused more combustion within the desired combustion stages. So, it caused higher peak CP than the diesel fuel in most of the operating conditions.

For the full load condition of the diesel-CaB fuel blends, the higher blends of CaB also demonstrated lesser peak CP than those of the diesel fuel at various speeds (Table A4-3). Also, the addition of higher amount of CaB in the diesel fuel reduced the peak CP. Moreover, it could be found that the increased amount of PS with CaB-diesel fuels caused reduction of pressure. On the other hand, PWC-diesel fuel blends also showed lower peak CP (Table A4-4). But the higher PS blends with the higher amount of PWC showed increase in peak CP.

While checking the variation of Peak CP of the fuels in comparison to that of diesel fuel, it could be observed that WTC15 had the highest (7.85%) increase in peak CP at idle load and 1500 rpm, but both the WTC5PS15 and WTC10PS15 fuels demonstrated highest increase in peak CP in most of the cases among the given load and speed conditions. These fuels had higher viscosities compared to the other fuels presented in that table. Due to viscosity effect the fuel flow rate was increased and it resulted in increase in CP. Also, the WTB10PS15 fuel exhibited highest rate of increment at all the given speeds and loads for the fuels presented in that table. Similarly, PWC10PS15 and CaB10PS15 fuels showed the most incremental rate of peak CP respectively in comparison to that of diesel fuel.

Though increased fuel viscosity with the increased amount of PS addition in the dieselbiodiesel fuels were observed, they demonstrated higher peak CP in most operating conditions. It is due to the availability of active oxygen and hydrocarbons for combustion to be occurred spontaneously in the premixed combustion stage. It is essential to see what ingredients in the fuel is causing viscosity variation. Due to addition of pure hydrocarbons in the oxygenated viscous fuels, the combustion performance increased as a synergistic effect of combination of both extra oxygen and hydrocarbons from the fuel. Such things may not be seen with increased biodiesel in diesel-biodiesel blends only as the LHV and poor atomisation of the diesel-biodiesel can cause pressure reduction along with early starting of combustion.

9.2.2 Apparent Heat Release Rate (HRR)

The apparent heat release rate (HRR) is a function of cylinder volume and in-cylinder pressure with the crank angle variation. Both the pressure differential and the volume differential in terms of the crank angle variation are also considered to determine the apparent heat release rate (HRR).

In a direct injection (DI) diesel engine, crevice flow effect can be neglected to calculate the heat rejection rate of the combustion of fuel within the combustion chamber. Then the first law of thermodynamics can be applied to the system to determine the heat transfer with respect to the crank angle change can be expressed as follows **[382]**:

$$\frac{dQ}{d\theta} - P\frac{dV}{d\theta} + m_f h_f = \frac{dU}{d\theta} \qquad \dots \dots \dots (Eq. 9.1a)$$

Here, dQ/dt is the heat release rate from the system, P(dV/dt) is the amount of work done due to combustion of fuel (i.e. output work), u is the sensible internal energy of the fuel in the chamber, m_f and h_f are the fuel mass flow rate and sensible enthalpy of the injected fuel respectively. Eq.9.1a can be used to determine both the heat release rate (fuel energy) and rate of mass burning of the fuel in the combustion chamber. Both these quantities are considered to be *apparently measured* due to intricacies involved in real measurements. The sensible enthalpy is usually considered to be negligible (it is less than 1% of the heating value of fuel) for the fuel as the temperature gradients, vaporisation of fuel was ignored. Hence, considering the fuel behaves like an ideal gas, the final form of equation for the heat rejection rate from the combustion can be obtained as follows **[382, 419]**:

$$\frac{dQ}{d\theta} = \frac{\gamma}{\gamma - 1} P \frac{dV}{d\theta} + \frac{1}{\gamma - 1} V \frac{dP}{d\theta} \qquad \dots \dots (Eq. 9.1b)$$

Where, $\gamma = C_p/C_v = \frac{\text{specific heat capacities at constant pressure}}{\text{pecific heat capacities at constant volume}}$

Here, range of γ is 1.3 to 1.35, and frequently γ =1.35 is considered.

This equation is known to determine the apparent net heat release rate (J/°CA) from the combustion reaction in the cylinder.

 $\frac{dv}{d\theta}$ can be obtained by differentiating the instantaneous cylinder volume with respect to the crank angle as follows:

$$V = V_c + \frac{\pi B^2}{4} \left[l + a - \left\{ a \cos \theta + \sqrt{(l^2 - a^2 \sin^2 \theta)} \right\} \right]$$
.....(Eq. 9.1c)

So, differentiating and converting radian into degree unit,

$$\frac{dV}{d\theta} = \left(\frac{\pi B^2}{4}\right) \times \left(\frac{\pi}{180}\right) a \left\{ \sin\left(\frac{\pi\theta}{180}\right) + \frac{R^2 \sin^2\left(\frac{\pi\theta}{180}\right)}{2 \times \sqrt{1 - R^2 \sin^2\left(\frac{\pi\theta}{180}\right)}} \right\} \qquad \dots \dots (Eq. 9.1d)$$

Where, R=l/a= ratio of connecting rod length to the crank radius. B is the cylinder diameter, a is the crank radius and l is the connecting rod length, which is half of the stroke length.

Besides, $\frac{dP}{d\theta}$ for ith crank angle can be determined from the experimental data set θ vs P as per the following forward order differentiation equation [420]:

$$\frac{dP}{d\theta} = \frac{\Delta P}{\Delta \theta} = \left(\frac{P_{i+1} - P_i}{\theta_{i+1} - \theta_i}\right) \tag{Eq. 9.1e}$$

A typical HRR diagram for diesel fuel combustion can be observed from the Figure A4-2 in the Appendix A4.

Similarly, instead of using the Eq. 9.1d, the experimental data set θ vs v can be used to determine the $\frac{dV}{d\theta}$ as per the regression equation used to determine $\frac{dP}{d\theta}$ (Eq. 9.1e).

Here in this study, the HRR analysis has been conducted for all the fuels mentioned in the Table 8-1 for three engine loading conditions (i.e. full load, part (50%) load and idle crank load conditions) at various engine speeds (i.e. 1200, 1500, 1800, 2100 and 2400 rpm). Figure 9-9(a-d), Figure A3-29(a-d) and Figure A3-30(a-d) are showing the HRR variation with crank

angle (CA) variation for diesel, diesel-WTC and diesel-WTC-PS fuel blends for full load, part (50%) load and idle crank load conditions respectively.

While observing these figures, it could be seen that the peak HRR points are going away from the top dead centre (TDC) of the combustion chamber with the increase in engine speeds at all loading conditions. Rapid increase in heat release rate is also observed for all of these cases which indicated the start of combustion (SOC). The first two peaks of the HRR profile after the rapid rise of HRR due to SOC are due to the premixed (rate-controlled) and mixed-controlled combustion stages, whereas the lower HRR peaks are due to late combustion stages. Ferguson and Kirkpatrick **[418]** explained these multiple peaks of the HRR profile for diesel and diesel blended fuels due to their multiple combustion stages. With increased biodiesel and PS blends in the diesel fuel for a certain speed and load condition of the fuel combustion, it could be found that both the SOC and HRR_{max} (maximum heat rejection rate) are approached towards the TDC.









Figure 9-9 Apparent heat release rate (HRR) variation with Crank Angle (CA) variation for diesel, diesel-WTC and diesel-WTC-PS fuel blends for Full load condition at, (a) 1200 rpm, (b) 1500 rpm, (c) 2100 rpm (d) 2400 rpm

Due to fuel injection process in the pre-combustion (ignition delay) period, the HRR was seen to be negative until the rapid rise of HRR was observed due to inception of complete combustion. When the fuel is injected in the combustion chamber, the difference of thermokinetic energies between the fuel molecules and the highly compressed air cause the heat to be absorbed (heat of evaporation) by the fuel molecules **[410, 418, 421]**. As a result, an adiabatic reaction process takes place at this stage until the fuel's kinetic energy surpasses its activation energy level to conduct the combustion reaction process for energy production. The higher HRR drop near 21 ^oCA before the TDC (as in Figure 9-9, Figure A3-29, and Figure A3-30) shows the quick heat rejection from the system to the fuel due to injection of fuels at that position. In this study, both the compression ratio and the fuel injection starting point were constant for all the fuels. So, the variation of fuel types and their corresponding physicochemical properties may influence the amount of heat it would consume just after the injection. All the figures presented in the Figure 9-9, Figure A3-29 and Figure A3-30 are showing variation of HRR in all the four stages of combustion process due to variation of fuel properties

as the combustion operation processes were same in the respective operations. In each of the loading conditions, the increase in speeds indicated the increased length of negative HRR profile of the fuels. The sudden rise of HRR indicates the start of combustion for the rate-controlled premixed (diffusion combustion) stage due to the rapid fuel burning. Besides, these figures show that the maximum level of HRR (HRR_{max}) increased with the increase of load for these fuels (i.e. diesel, diesel-WTC, and diesel-WTC-PS fuel blends). Table A4-5 to Table A4-8 (in Appendix A4) show the HRR_{max} values for the tested fuels.

At full load condition and 1500 rpm, diesel fuel had lower peak HRR than that of WTC5. But both the WTC10 and WTC15 had lower peak HRR against the diesel fuel. When PS was added with WTC5 fuel, the 5% PS addition caused drop of HRR than that of the WTC5 fuel. The other two blends, WTC5PS10 and WTC5PS15 had increased rate of HRR than that of the WTC5PS5 but still lower than that of WTC5 fuel only. The rank of peak HRR could be obtained as WTC5> WTC5PS15> WTC5PS10> WTC5PS5> diesel.

Similarly, the peak HRR for the PS added fuel of the WTC10 and WTC15 blends showed the rank as, WTC10PS15> WTC10PS10> WTC10PS5> WTC10> diesel, and WTC15PS15> WTC15PS10> WTC15PS5> WTC15> diesel, respectively. The reason of higher increasing heating rate due to addition of pure hydrocarbon is the availability of the more combustion reaction with the available fuel oxygen due to higher blends of WTC with the diesel. With lower biodiesel blends, the available oxygen quantity from the fuel is less than the amount of pure reactive hydrocarbons available in the fuel. Such behaviour indicates that the inherent fuel oxygen was more active than the oxygen from the air for more combustion to be occurred within the same cycle period of diesel fuel. Comparatively lower but similar trend of already described HRR peak values can be observed for part (50%) load operation (Figure A3-29).

But the idle load condition (Figure A3-30) indicates that all the diesel-WTC and diesel-WTC-PS fuels have higher peak HRR than the diesel fuel and the values increased with the increment of biodiesel content as well as the increment of PS content. Idle crank load demands the fuel to achieve the desired engine speed rather than focusing on torque production. So, lesser fuel was injected at this condition with apt opportunity to conduct burning of the fuels within a very short time. The higher amount of hydrocarbon and oxygenated fuels enhanced the amount of fuel burning rate and caused the increased HRR than that happed with the diesel fuel only.

The in-cylinder peak HRR (HRR_{max}) for diesel-WTB and diesel-WTB-PS at all the considered engine operating conditions are presented in the Table A4-6. In most of the cases the WTB5 fuel had the highest amount of HRR than those of the other fuels. Addition of PS blends with the WTB5 initially dropped severely though kept increasing with the increase of PS in WTC5 fuel blend. Both the WTB10 and WTB15 fuels had lower peak HRR at 2400 rpm but had increasing trend of higher HRR in other increasing speeds. Similar trends were observed for the PS blends of these respective biodiesel-diesel fuel blends. These WTB-diesel fuels showed lower peak HRR than the diesel fuel at part (50%) load at all speeds. But the addition of PS in the diesel-WTB fuels effectively increased the amount of HRR indicating more combustion due to oxygen and hydrocarbon availability. Except the WTB5 and the WTB5-PS blends, the other fuels released lower peak HRR at idle crank load condition.

In the Table A4-7, the peak HRR of the diesel, diesel-CaB and diesel-CaB-PS fuel blends at various speeds and loads are shown. Except the HRR at 2100 and 2400 rpm (full load), the CaB5, CaB10 and CaB15 fuels had higher peak HRR. But for the PS blends of CaB-diesel fuels had higher HRR than that of diesel except at 2400 rpm. The higher speeds and higher loads demanded more fuels that caused longer CA duration of negative HRR to start the combustion. More oxygenated and hydrocarbons caused more combustion instead of higher viscosity related combustion complexities for Castor biodiesels. Moreover, the HRR of diesel-PWC and diesel-PWC-PS fuel showed that the lower PWC blends in the diesel fuel can release more heat than the diesel fuel. The addition of increased amount of PS (i.e. 5-15%) in the PWC-diesel fuels were having higher viscosity, lower calorific values and caused lower HRR peaks than that of the diesel-PWC-PS fuel blends at various speeds and loads are shown in the Table A4-8. Overall, apart from PWC5 and CaB5, higher PS containing fuels like WTC5PS15, WTB10PS15, PWC10PS15, CaB10PS15 fuels demonstrated higher incremental rate of HRR than the diesel fuel.

9.2.3 Ignition Delay (ID)

Ignition delay period is the first stage combustion of fuel in the diesel engine. It is the crank angle distance between start of injection (SOI) of the fuel and that of the start of combustion (SOC). Brief analysis on diesel fuel ID has been presented as follows.

9.2.3.1 Brief Analysis on ID determination

Usually, ignition delay (ID) period ranges between start of injection to about 5% of the mass of fuel burnt in the combustion chamber [422]. Notably, chemical characteristics (i.e. fuel composition, viscosity, cetane number, oxygen content, etc), physical characteristics (e.g. inlet air temperature, inlet air pressure, air-fuel mixture, atomisation, fuel vaporisation, reducing the angle of the start of ignition, etc.), geometrical variation (e.g. combustion chamber and cylinder design parameters, injectors and injection parameters, compression ratio, MEP, etc.) and varying operation parameters (e.g. engine speed, coolant thermal condition, amount of excess air, sealing of combustion chamber, EGR ratio, etc.) have the most significant impact on the ignition delay for the self-ignition properties of the fuel [423].

In case of fuel composition chemistry [418], both the aromatic and alcoholic contents in the fuel lead to longer ignition delay due to complexities during cracking of these molecules; but the alkane contents in the fuel lead to shorter ID due to simplification of cracking. With increasing engine speed, the ID needs to be lowered to ensure steady combustion duration. Besides, the higher the peak in-cylinder pressure the longer the ignition delay. Longer ID can lead to unwanted accumulation of unburned fuel mass and richer air-fuel ratio. As a result, efficiency reduces along with increasing knocking combustion issues **[424]**. Abbaszadehmosayeb [420] has reviewed few articles related to diesel and biodiesel fuel-based ignition delay and noted that the other factors influenced by the ID are the premixed fraction of fuel mass burnt, HRR, noise/knocking, fuel viscosity, cetane index, in-cylinder pressure and temperature, etc. The author also reported that the biodiesel fuels usually exhibit shorter ID with compare to that of diesel fuel in a given condition. Lahane and Subramanian [410] mentioned specifically that the reason for shorter ID with the biodiesel combustion is due to their higher value of bulk modulus (i.e. ratio between the variation of applied pressure and the resulting change of fluid volume). Nevertheless, Heywood [382] mentioned that fuel spray characteristics (e.g. pressure, temperature, velocity), injection timing, injection quantity, injector geometry, temperature and pressure of intake air, engine speed, wall characteristics of
the combustion chamber, swirling rate at starting and at compression temperature, and oxygen concentration are related to the ID.

On the other hand, to determine the ignition delay graphically from the experimental results. The start of injection can be a fixed point with a fixed injection pressure set by the engine manufacturer. Alternately, the injection pressure could be determined by obtaining fuel injection pressure based on needle opening signal, which is the onset of fuel injection. A highly sensitive and efficient strain gage set on a rocker arm was used by Assanis et al. [425] to correlate the in cylinder pressure with injection pressure. Usually, an engine running at 800 rpm requires only 0.075 seconds (75 ms) to complete a full cycle, whereas that of engine running at 2400 rpm just spends 0.025 seconds (25ms). Both the fuel injection period and combustion period are fraction of these cycle periods. When the fuel injection starts, the fuel rate-of-pressure-rise within the combustion chamber decreases (Figure A4-3 in Appendix A4, corresponding point of A for the $\frac{dp}{d\theta}$) curve) in addition to reduction of in cylinder temperature [426]. Also, the ROI (rate-of-injection) meter was used by Rothamer and Murphy [427] to determine the start of injection (SOI) profile for different fuels. Bodisco et al.[428, 429] presented the Bayesian approach to determine the ignition delay. In this approach, the researchers used injection latency and statistical procedures to investigate the injection signal variations with the heat release rate signals so that the accurate SOI can be located in terms of crank angle variations. It was mentioned by the authors that the SOI point will be the crank angle point at which two points of heat release curve deviate.

The starting point of ignition or namely the start of combustion (SOC) is the final reference point for delay period of combustion process. Though it was mentioned earlier that up to 5% fuel mass fraction burning could be considered as the point of start of combustion (SOC), it can be varied up to 10% burning of the fuel mass as well **[430]**. Various graphical procedures can be used to obtain the SOC point of crank angle position on "Pressure vs Crank Angle curve", or "HRR vs Crank Angle curve" or from the "Mass of fuel burn vs Crank Angle graph. While the SOI demonstrates the lowering of temperature in the cylinder, the SOC indicates the sudden temperature rise and sharp change of pressure in it **[382, 426, 431]**. Besides, the HRR curve shows a sudden slope variation when the combustion begins **[426]**. On the other hand, when the mass fraction of the burned fuel vs crank angle curve is obtained, the crank angle against the 5%-10% quantities could be easily detected to determine the ID. The change of slopes of both the pressure and heat release rate have been adopted by many researchers to

detect the highly accurate crank angle position for SOC [426, 428, 431, 432]. When the combustion initiated, a sudden change of rate-of-change-of-pressure is observed, for which the first derivative $\left(\frac{dp}{d\theta}\right)$ of the pressure curve shows a point of inflection as a minimum point. Since the point is the minimum point of inflection for $\frac{dp}{d\theta}$ curve, the second derivative of the pressure curve $\left(\frac{d^2p}{d\theta^2}\right)$ shows intersection with zero line, (i.e. $\frac{d^2p}{d\theta^2} = 0$). In Figure A4-3, point B is the point at which the combustion starts. So, the difference of crank angle travel between point A and point B on the Figure A4-3 (in Appendix A4) is the ignition delay period.

However, the heat release rate equation (i.e. $\frac{dQ}{d\theta} = \frac{\gamma}{\gamma-1}P\frac{dV}{d\theta} + \frac{1}{\gamma-1}V\frac{dP}{d\theta}$) also shows a relationship with pressure derivative (i.e. $\frac{dQ}{d\theta} \propto \frac{dP}{d\theta}$). So, if the change of pressure derivate demonstrate the SOC, the sudden variation of heat release rate curve will also be capable of detecting the SOC. Katrašnik *et al.* [433] proposed that the second derivative of the HRR ($\frac{dQ}{d\theta}$) curve will be departing from a maximum point at a certain crank angle. As a result, the crank angle position for SOC in the HRR curve will show a maximum point for ($\frac{d^3Q}{d\theta^2}$). Thus, the third derivative of pressure curve can also indicate the SOC, though Checkel and Dale [434] demonstrated that the third derivative of pressure vs crank angle curve effectively help to detect the knocking in the engine.

9.2.3.2 Result Analyses of ID Characteristics

In this study, ID for all the fuels listed in the Table 8-1 were determined at various engine speeds and loading conditions. Among various methods, the graphical method seemed very effective to detect the SOI and SOC for the combustion of fuels. It is to be noted that the fuel injection timing was constant for all the tested fuels and the gradients of the pressure curves were investigated to locate the SOC in the HRR curve as the pressure derivative is a function of HRR. Both the SOI and SOC have been shown with a circle on the HRR curves presented in the Figure 9-9(a-d), Figure A3-29 and Figure A3-30. As an example of how the SOI and SOC were located from the pressure, HRR, first and second derivative of the pressure curves is shown in the Figure 9-10 for combustion of diesel fuel at 2400 rpm and at full load operation condition. Both the pressure and the HRR curves were scaled as per the secondary vertical axis against the crank angle variation on the horizontal axis. On the other hand, both the first derivative of pressure (dP/dCA) and second derivative of pressure (d²P/dCA²) were scaled as per primary vertical axis in the middle of the figure. While detecting the SOI, it could be seen

that the dP/dCA curve shows a sudden change of gradient and a peak at 21 ^oCA before TDC. The crank angle point at which the first derivative shows a peak, must make the second derivative to be zero. In the Figure 9-28, it is the 21 ^oCA before TDC on which the second derivative crosses the zero point. So, the fixed SOI point is obtained in the HRR curve. Again, at the end of the ignition delay period the fuel reaches in its start of combustion phase by acquiring energy from the highly compressed hot air. So, when the combustion starts, the first derivative will show a large gradient change and that of the second derivative will pass through the zero value. Due to rapid change of the pressure gradient, the HRR curve also shows a rapid rise of HRR. The CA point at which the second derivative of the pressure curve crosses with zero vertical axis value is the SOC. At the SOC point, both the pressure derivative and HRR showed rapid rise. Figure 9-28 is showing the SOC on the graph with a black circle that shows the beginning of rapid rise of the HRR for the fuel. So, the CA distance between the SOI and the SOC is the ignition delay period in terms of crank angle parameter.



Figure 9-10 Determination of ID (CA) by first and second derivative of pressure curve for diesel fuel at 2400 rpm and full load condition



Figure 9-11 Ignition delay (ms) variation with engine speed for diesel, diesel-WTC and diesel-WTC-PS fuel blends at Full Load, Part (50%) Load and Idle Crank Load condition

Figure 9-11, and Figure A3-31 to Figure A3-33 are showing the ignition delay for diesel, diesel-WTC and diesel-WTC-PS fuel blends, diesel-WTB and diesel-WTB-PS fuel blends, diesel-PWC and diesel-PWC-PS fuel blends and , diesel-CaB and diesel-CaB-PS fuel blends, respectively. Also, 3 different engine load conditions, i.e. full (100%) load, part (50%) load and idle crank load conditions, were applied at various engine speeds ranging between 1200 and 2400 rpm. Three key characteristics of the ID could be seen from these figures, firstly, the increase in load increased the ignition delay period due to increased amount of fuel injected to meet the load requirements. In each of the loading condition, the ID kept on decreasing with the increase in engine speeds. The third observation is, for a certain speed and loading condition, the diesel fuel had the maximum ignition delay period followed by the WTC-diesel blends and then the WTC-diesel-PS fuels. These were also supported from the published works of various researchers [431, 435]. One of the key reasons is the combustibility of the fuels injected in the system that accelerated the SOC and reduced the total ID period for the respective fuel. Due additional oxygenated fuels and pure hydrocarbon injected in the combustion chamber; the fuel blends earn better combustibility in spite of the viscosity increment in comparison to the diesel fuel. The variation of the injection pressure at the SOI point demonstrated the amount of negative heat rejection by the fuel, which also affected the quality of the fuel atomisation, reaction (combustion related) rates and combustion efficiency.

Due to shorter ID period, these fuels get more time to perform the combustion. Due to higher combustion duration, the HRR (J/^OCA) may reduce in spite of higher burning efficiency of the fuel. Lower overall HRR helped reducing the unwanted emission formation, e.g. CO and NOx emission, which were mostly seen to be lower for the PS blended diesel-biodiesel blends. The increased addition of biodiesel in the diesel fuel ID for the fuels prepared from diesel-WTC, diesel-WTC-PS fuels. While comparing with the diesel fuel ID, the CA duration increased with the increment of the engine speeds for each fuel at given loading condition. For a certain speed at full load, e.g. at 1800 rpm, the diesel fuel had the highest ID (CA). The rank of ID (CA) for the fuels (full load, 1800 rpm) could be stated as, Diesel>WTC5> WTC5PS15> WTC10PS15> WTC10PS15> WTC10PS15> WTC10PS15> WTC10PS15> WTC10PS15> WTC10PS15> WTC10PS15> WTC10PS15> WTC15PS10> WTC15PS10> WTC15PS15. The shorter CA length, i.e. shorter ID gave these PS blended fuels enough time to complete combustion in a wider CA region. Similar observations were also found for the other fuels like diesel-WTB, diesel-WTB-PS fuel blends, respectively.

9.3 Concluding Remarks

This chapter presented detail characteristic behaviour of performance parameters (EGT, BP, T, BSFC, BTE, BSEC, BMEP) and combustion parameters (In-cylinder pressure, apparent heat rejection rate, and ignition delay) for the fuels studied for the experimental analyses and conduct the assessment of the fuels in the diesel engines. Along with the graphical demonstration of these characteristics, the comparative analyses have been presented in the referred tables in case of these parameters to assess the fuel performances. Addition of higher amount of PS showed better performance with the higher biodiesel blends. PS has been observed to be a potential fuel additive to enhance quality of combustion and performances of the diesel engines. Use of PS as fuel additive will help reducing the non-biodegradable wastes to be reduced from the environment.

Overall engine test bed measurement system's relative uncertainty has been determined from the Table A5-12. Also sample uncertainty analyses for diesel, WTB5, WTB5PS5, WTB5PS10, and WTB5PS15 fuels are shown in the Appendix A5 (Table A5-7 to Table A5-11).

Chapter 10 CONCLUSION

10.0 Introduction

In this study, a comprehensive investigation has been conducted to convert waste plastics in fuel and high-quality recycled commodity in a least expensive way. The biodiesel used in this study was produced from the inedible and waste resources (known as second generation feedstocks for biodiesel production). Application of PS-biodiesel-diesel fuel blends in the diesel engine will not only reduce the liquid fuel supply chain vulnerability but also reduce non-biodegradable wastes from the environment. The use of cleaner fuels and reduction of nonbiodegradable plastic wastes will also potentially reduce the harmful environmental pollutants and contribute to establishing a sustainable environment and energy supply.

The key findings of this study are presented briefly in this chapter. The following sections will address how the findings have met the objectives set earlier in the Chapter 1.

10.1 Biodiesel Production, Process Optimisation and Reaction Kinetics Development

In this study, a total of 6 biodiesel fuels were produced through process optimisation of their respective fuel production stages. Also, 3 binary biodiesel fuels were produced by blending three chosen biodiesels from these 6 fuels. Optimisation of each of the processes were performed to increase fuel production efficiency from the adapted methodologies. The parameters for each of the processes were determined based on the Response Surface Methodology (RSM) for optimisation by using the Box-Behnken (BB) model. A number of required esterification and transesterification reactions were performed from the set of experimental conditions based on the BB model. A statistical software tool, Minitab, was used to determine the number of experiments and their operation parameters based on the BB model. The experimental results were then used as input to conduct the RSM optimisation and observe the effect of the parameters used to optimise the process with the help of ANOVA analyses. For both the esterification and transesterification processes, the kinetic models were developed based on the possible nearest to the optimal parametric conditions as obtained from the RSM-based optimisation.

It was found that the conventional batch reactor system could be effective with pertinent process parameters. It was obvious that the optimal efficiency of the esterification process significantly helped to get very high amount of fatty acid methyl ester yield from the optimal transesterification process for the inedible second-generation feedstocks. Tallow had the most efficient transesterification processes due to the effective esterification process output, i.e., higher amount of free fatty acids was removed. Also, attention was paid to conduct other relevant pre-treatment and post-treatment processes carefully.

No single universal kinetic model could be used or followed for esterification and transesterification processes for each of the biodiesel feedstocks. The reaction processes could be assumed either homogeneous or heterogeneous, reversible, or irreversible, zero, first or second order, and it could be considered as pseudo of all the options mentioned. Multiple assumptions were adapted to develop the reaction kinetics. Also, shunt reaction process kinetics was developed for the transesterification process instead of individually analysing all the reaction stages. Activation energies, reaction rate frequency factor and the reaction orders varied as per the respective processes considered to determine the kinetic model. Due to differences in the reaction processes, the activation energies varied significantly for the same feedstock. It is evident that the kinetic model will help to understand the energy requirement to achieve the efficient process accomplishment for better yield efficiency.

Biodiesel fuels produced based on optimal reaction conditions were used as solvent for the polymer-biodiesel solubility analyses to investigate the potential of waste-to-liquid fuel production. Besides, these fuels were used to prepare biodiesel-diesel as well as biodiesel-diesel-polymer fuel blends to conduct diesel engine combustion, performance and emission characterises in comparison to those of the diesel fuel.

The above satisfies the achievement of the first objective of this study.

10.2 Solubility of Plastics in Biodiesel and Development of Dissolution Kinetic Models

While investigating the solubility of plastics in mix of organic fatty acid methyl esters, multiple proposed methodologies were applied. Then the obtained results were averaged to increase the effectiveness of evaluation of solubility parameters to analyse the dissolution of polymers in FAME solvents. Values of functional groups were used to determine the solubility parameters of the solute and solvents by the group contribution method (GCM). The average solubility parameters (J/cm^3)^{1/2} or (MPa^{1/2}) of the thermoplastic polymers were determined for

PE, PP, PS, PVC, and PET as 16.64, 16.27, 19.33, 19.81 and 24.59 (J/cm³)^{1/2}, respectively. To determine the solubility parameters of the biodiesel fuels, a set of complex calculation was performed to determine their average molar volume and that of solubility parameters (following Fedors, Hoy and Hoftzyer-van Krevelen methods distinctly). The average solubility parameters (MPa^{1/2}) of the biodiesel fuels used for dissolution studies in this study were found to be 19.01, 18.93, 20.17, 18.37, 19.05, 18.86, 19.16, 19.02 and 18.72 for the WTB, WCB, CaB, PB, SB, CB, WTC, WTP, and PWC fuels, respectively. In Addition, an alternate group contribution method was used to determine the Hansen solubility parameters for the biodiesels. The alternate method gave the average solubility parameters (MPa^{1/2}) of 17.43, 17.42, 18.72, 17.43, 17.42, 17.43, 17.43, 17.42 for the WTB, WCB, CaB, PB, SB, CB, WTC, WTP, and PWC fuels, respectively.

The theoretical analysis of the solubility of these polymers in these biodiesel fuel solvents were limited to 298 K temperature, which showed limited solubility of these solutes in many cases to meet the solubility criteria. The temperature effect on the polymer miscibility with the biodiesel solvents supported the study of kinetic modelling of dissolution of plastics in the biodiesel. In order to determine the reaction kinetics, only PE, PP and PS were taken into consideration to investigate solubility in all the 9 biodiesels. It was obvious from the experimental results that the temperature increase, i.e. adding heat energy in these plasticbiodiesel systems increased the number of intermolecular interactions and overcome the required activation energy (Ea) to make the collisions effective enough to dissolve in the solvents. For PE (i.e. LDPE), the activation energies reduced with the increase in quantity of PE dissolved in these 9 biodiesel solvents. Also, it was observed that the activation energy for the PE in SF100 were the highest. In case of the PP, the highest Ea required were for the highest quantity of PS dissolution in PB100, WTP100, WTB100 and WTC100 fuels. On the other hand, the 5% PP in Ca100 required more activation energy than that of the 15% PP being dissolved in this solvent. In case of the PS being dissolved in the biodiesel, the highest Ea were recorded for the C100, WTP100, WTB100 fuels.

Investigations showed that both the PE and PP turned into gel like pastes under 85 ^oC and 95 ^oC respectively, but the PS-biodiesel mixture remained liquid. Cooling down the PE and PP solution can easily help separate the solvents and make them reusable. And the gel/paste commodities can be used as raw materials for new plastic component manufacturing. On the other hand, the PS-biodiesel solution can be potentially used as fuel in the diesel engines.

This is how the second objective of the study was achieved.

10.3 Polymer Wastes-to-Energy Production Processes

Among numerous polymer wastes generating plastics every day in the world, only the thermoplastics were considered for this particular study. The most preferable thermoplastic wastes which were identified as potential to be used as feedstocks for liquid hydrocarbon production purposes were PE, PP and PS. Also, the PVC and PET were found to be moderately preferred as these plastics need extra chemical treatment to remove some of the unfavourable ingredients to meet the liquid fuel application standards.

This study considered using sustainable solvent (biodiesel fuels) in order to produce fuel grade liquids. Since the biodiesel has been already accepted as diesel fuel alternative, the polymer-biodiesel solution can be potentially used in the diesel engines by blending with the diesel fuels. The biodiesel fuels used in this study have proved to be good solvents for these polymers at elevated temperatures. Both the PP and PE turned into gel like pastes when cooled down to room temperature, but the PS was found to be well dissolved with the biodiesel fuels. Both the PE and PP could be just removed by general filtration process and the solvent could be reused. So, the study of solubility of these plastics shows that the recycling clumsiness could be easily dealt with and some of the polymer could be directly used as fuel alternative.

That is how the third objective of the study was achieved.

10.4 Fuel Characterisation

Relevant standards (EN14214:2012 and ASTM D6751-12) were followed in order to determine and check the properties of the biodiesel, biodiesel-PS, and diesel-biodiesel-PS fuel blends. The fatty acid methyl ester (FAME) composition for the biodiesel fuels are presented in section 4.17, which shows the following rank of total FAME contents.

In case of the saturated fatty acid methyl esters (SFAME): waste tallow biodiesel (59.83%)> binary biodiesel of waste tallow and waste cooking oil (49.18%)> binary biodiesel of waste tallow and poppy (44.52%)> waste cooking oil biodiesel (26.5%)> sunflower biodiesel (19.07%)> binary biodiesel of poppy and waste cooking oil (16.42%)> canola biodiesel (12.89%)> poppy biodiesel (11.9%)> castor biodiesel (1.6%).

In case of the monounsaturated fatty acid methyl esters (MUFAME): castor biodiesel (92.38%)> waste cooking biodiesel (46%)> canola biodiesel (42.16%)> binary biodiesel of waste tallow and waste cooking oil (39.9%)> waste tallow biodiesel (37.03%)> binary biodiesel of waste tallow and poppy (30.16%)> sunflower biodiesel(26.77%)> binary biodiesel of poppy and waste cooking (24.95%)> poppy biodiesel (15.52%).

In case of the polyunsaturated fatty acid methyl esters (PUFAME): poppy biodiesel (72.59%)> binary biodiesel of poppy and waste cooking oil (58.63%)> sunflower biodiesel (54.15%)> canola biodiesel (44.5%)> waste cooking biodiesel (27.49%)> binary biodiesel of waste tallow and poppy (25.37%)> binary biodiesel of waste tallow and waste cooking oil (10.94%)> castor biodiesel (6.04%)> waste tallow biodiesel (3.15%).

The addition of PS in the biodiesel fuels increased the fuel viscosity. The same happened with the diesel-biodiesel-PS fuel blends. Figure A1-3 to Figure A1-6 show the variation of CN, density, kinematic viscosity, and lower heating values of the biodiesel-diesel fuels (5%-15% blends) and diesel-biodiesel (5%-15%)-PS (5%-15%) fuel blends respectively. These properties explain the variation of fuel performances in the diesel engine emissions, performance, and combustion analyses. The viscosity was a limiting factor on how much PS could be used with the biodiesel as fuel additive as well.

Results of these section thus cover the fourth objective of this study.

10.5 Fuel Performance Assessment in the Diesel Engine

To assess the fuel performance in the diesel engine, only four inedible biodiesels were chosen. These were, WTB, CaB, WTC and PWC. Both the WTC and PWC fuels were the binary inedible biodiesels. Detailed experimental set up, procedures and the results of the tests are presented in the Chapter 8. The experiments were performed with the fuels listed in the Table 8-1 at various engine speeds (i.e. 1200, 1500, 1800, 2100 and 2400 rpm) and load conditions (i.e. 100% load, 50% load, and idle crank load) in a diesel engine test bed.

These investigations complete the fifth and final objective of this study.

Fuel performances on emissions, performance and combustions are briefly described below.

10.5.1 Engine Emission Characteristics

The emission characteristics were investigated by measuring the CO, CO₂, NOx, PM, HC and O₂ emissions. Variations of emission quantity of these emission components were compared against those of the diesel fuel. CO emission by these fuels reduced remarkably at all load, but further reduction was seen for higher load conditions. When more complete combustion occurs, CO emission reduces but CO₂ emission increases. Likewise, the excess oxygen and excess hydrocarbons from the diesel-biodiesel-PS fuel blends caused more CO₂ emission by facilitating more fuel combustion than that by the diesel fuel. Part (50%) load condition caused more CO₂ emission than the full load condition for WTB and WTB-PS blends. Increased amount of PS in the diesel-CaB-PS fuels increased the rate of production of CO₂ than those by the respective diesel-CaB fuel blends. With the WTC, WTC-PS, PWC and PWC-PS fuel blends, the idle crank load conditions showed more reduction of CO₂ emissions with the addition of PS in the diesel-biodiesel fuel blends.

With biodiesel-diesel fuel blends, the NOx emission increased with the increase in engine speeds. The part (50%) load condition caused lower amount of NOx emission than those of the other loading operations. With the increase in biodiesel content in the diesel-biodiesel fuel blends, the amount of NOx emission increased due to increased quantity of reactive oxygens and higher combustion temperatures. When the PS hydrocarbon was added to any of the diesel-biodiesel blends, the rate of NOx emission reduced. At full load condition, the NOx emission reduced remarkably with increasing engine speeds for PWC fuels. The diesel-WTB-PS fuel blends reduced the NOx emission more effectively than those by other fuel blends.

Particulate matters (PM) emission increased for almost all the fuels at 1200 rpm and the rate of PM emission reduced with the increase in engine speeds. In case of part (50%) load condition, the PM emissions were found to be reducing significantly with the increase in engine speeds. In the idle crank load condition, the PM increased at a slower rate when the engine speeds increased beyond 1200 rpm. Overall, the diesel-biodiesel fuel blends reduced the PM emission in comparison to that of diesel fuel. Also, the addition of PS-based hydrocarbons reduced PM emission for diesel-WTB-PS and diesel-WTC-PS fuel blends. But the diesel-CaB-PS and diesel-PWC-PS fuels increased the PM emission in comparison to that by the diesel fuel.

Unburnt hydrocarbon (HC) emissions increased due to reduction of combustion efficiency of the fuels in the diesel engine. Higher fuel viscosity caused poor fuel atomisation and consequently the HC emissions increased. With the addition of PS hydrocarbons in the dieselbiodiesel fuel mixtures, the combustion efficiency improved significantly at all the engine speeds and loading conditions. As a result, the HC emission reduced with the diesel-biodiesel-PS fuel blends. Specially, the addition of lower amount of PS had the most significant effect with any of the diesel-biodiesel fuel blends to reduce the HC emission. Mostly, CaB-diesel and diesel-CaB-PS fuel blends emitted increased quantity of HC when engine load increased. In case of other fuels, the part load operations caused higher amount of HC emission.

Based on the emission characteristics of the studied fuels, it was found that the part (50%) load operations caused more CO_2 emission. In case of NOx, the addition of higher amount of PS, i.e. the PS15 blended with any of the biodiesel blends caused effective NOx emission reduction at any loading systems. The slight increase in the PM emissions could be tackled by the use of diesel particulate filters as the increment happened due to addition of more pure hydrocarbons. Better fuel mixing and low temperature combustion processes could be useful in decreasing the NOx and HC emission.

10.5.2 Engine Performance Characteristics

Exhaust gas temperature (EGT), Brake power (BP), Torque (T), Brake specific fuel consumption (BSFC), Brake thermal efficiency (BTE), Brake specific energy consumption (BSEC) and the Brake mean effective pressure (BMEP) were the performance parameters investigated and analysed in this study.

EGT could be increased due to inefficient conversion of the energy generated due to fuel combustion, higher temperature-based combustion reactions, shorter ID, and combustion duration. As a result, the increase in both the engine loading and engine speeds increased the EGT. Higher EGT can also results into higher NOx generation. Most of the fuels used in this study had significant effect on reducing the EGT at full load condition. About 3.1%, 15.9%, 9.9% and 19.1% reduction in EGT was observed with WTB5PS5, CaB15PS5, WTC10PS5, and PWC15PS5, respectively, at full load. During the part (50%) load condition, higher engine speed conditions caused the biodiesel fuels to produce higher EGT. Engine performances strongly related to the EGT characteristics. Addition of PS with the diesel-biodiesel fuel blends efficiently reduced the EGT by absorbing heat energy as the energy required to conduct further

reactions with the additional hydrocarbons. Engine efficiency also improved due to addition of PS-based hydrocarbons in comparison to that of biodiesel-diesel fuels.

Due to lower LHV of PS and that of the biodiesel fuels, the addition of biodiesel and PS caused lowering the BP in comparison to that of the diesel fuel. At full load condition, about 1.9%, 7%, 0.7% reduction in BP was found with WTB15PS15, CaB15PS15, and PWC15PS15 fuels, respectively. But almost similar (0.02% increase) BP was observed with WTC15PS15 fuel. At part (50%) load condition BP increased up to 24.2% and that of up to 99% at idle crank load condition with the increased amount of PS and biodiesel in the PS-biodiesel-diesel fuels. It happened due to availability of higher amount hydrocarbons along with extra oxygen in the fuel blends like WTB15PS15, CaB15PS15, PWC15PS15 and WTC15PS.

Higher viscosity and the lower calorific values of the biodiesel and PS fuels caused lowering the torque generated by the diesel blends. At full load, diesel-WTB and diesel-WTB-PS fuels produced lower torque than the diesel except the WTB15 fuel, which produced very little amount of higher torque than the diesel fuel. At 1500 rpm, all the diesel-CaB and diesel-CaB-PS fuel blends experienced the highest reduction of torque production than the diesel fuel. Though lower torque generated, the diesel-WTC and diesel-WTC-PS fuel blends did not show many variations of toque in comparison to that that of the diesel fuel. The PWC15-PS (5%-15%) blends showed higher torque than the diesel fuel. The part (50%) load torque variations of these fuels are wider than those observed in the full load condition. The torque variation for a fuel with the engine speeds had common trend (i.e. from higher at 1200 rpm to lower at higher engine speeds). But the idle crank load condition torque variations were of different trends than those in the full load and part load conditions. Indeed, lowest torque was found at 1200 rpm at which fuels showed better torque in other loading conditions. The idle crank load condition does not focus on torque generation rather achieving the desired speeds with minimum throttling possible. So is the reason of such torque profile than the part load and full load conditions.

At full load condition, all the diesel-biodiesel and diesel-biodiesel-PS fuel blends demonstrated higher BSFC than that of the diesel fuel. BSFC increased by 8.8%, 7.2%, 9.1%, 14.9%, and 7.9% with WTB5PS10, CaB15PS5, WTCPS5, and PWC15PS5 fuels, respectively. The obvious reasons were higher amount of fuel injected with the almost similar injection pressures and injector which was designed for diesel fuel injection only. All these fuels almost followed the BSFC profile as demonstrated by the diesel fuel, higher at lower engine speeds,

then reduced to the lowest at higher efficiency speeding condition and again kept increasing with the increase in engine speeds. Similar trend was also observed at part (50%) load condition. But the idle crank load showed different trend in fuel consumption. At part (50%) load, maximum increase of BSFC was found as 19.9% with PWC15PS5 fuels. At idle crank load condition, 49.9% reduction in BSFC was observed with CaB15PS15 and a minimum increase of 4.5% was found for WTB15PS15 fuel blends.

BTE reduced with the use of PS-biodiesel-diesel and biodiesel-diesel fuel blends at both full (100%) load and part (50%) conditions in comparison to that of the diesel fuel. Among all the PS-biodiesel-diesel fuels, reduction of BTE was found to be 7.9%, 5.8%, 8%, and 12% with WTB5PS10, CaB15PS5, WTC5PS10 and PWC15PS5 fuels, respectively, at full load condition. BTE reduced by 8.8%, 6.3%, 8.1%, and 12.7% with WTB5PS5, CaB5PS15, WTC5PS5 and PWC5PS15 fuel, respectively at part load condition. On the other hand, minimum reduction of BTE was 3.7% with WTB15PS15 and maximum increase of BTE was 100%, 81.4%, and 20.3% with CaB15PS15, PWC15PS5 and WTC5PS15 fuels, respectively at idle crank load.

BMEP is one of the important parameters to define how much the engine is capable of performing desired work regardless of how big the engine is, generally the maximum level of BMEP ranges between 700 and 900 kPa for the naturally aspirated 4-stroke compression ignition engines. In this study, Diesel fuel BMEP varied from 829.6-720 kPa, 383-461 kPa, and 12-30 kPa at full (100%) load, part (50%) load and idle crank load conditions, respectively for the engine speed ranging from 1200-2400 rpm. At full load condition, WTC15PS15 fuel blend had almost similar BMEP (0.04% less than the diesel). About 24.2% and 99.5% increase in BMEP were observed for PWC15PS15 at part (50%) load and idle crank load conditions, respectively in comparison to the diesel fuel. BMEP variation is regulated by the variation of the fuel's calorific value, viscosity, and CN along with the engine's frictional power losses governed the brake power and torque outputs.

10.5.3 Engine Combustion Characteristics

The combustion characteristics of the fuels were analysed using three key parameters, namely, the in-cylinder pressure variation (CP), apparent heart release rate (HRR) and ignition delay (ID) period.

With the increase in the engine speeds at a certain engine load condition, multiple peaks of the in-cylinder pressure was clearly observed. At lower engine load condition, the pressure curve had narrower range. In case of the biodiesel-diesel blended fuels, the increase in load also increases the peak in-cylinder pressure. When the PS was increased with a certain diesel-biodiesel fuel blend, the peak CP increased. Also, the PS blended fuels had higher peak CP at part (50%) load condition at various engine speeds. The peak CP was achieved near by the TDC and the cylinder pressure increases rapidly since the injection of fuel started.

While observing the HRR trends for the various fuels, it was found that the peak HRR points were going away from the TDC of the combustion chamber with the increase in engine speeds at all loading conditions. Rapid increase in the heat release rate was also observed for all of these cases which indicated the start of combustion (SOC). The peak HRR increased up to 1500 rpm from 1200 rpm and dropped from 1500 rpm up to 1800 rpm and then increased up to its peak at 2400 rpm. WTC15 showed higher peak HRR than that of diesel fuel until 2100 rpm at full load. At partial load operation, the WTC10 fuel had very high HRR with the increased engine speeds. This could be one of the reasons of emitting more NOx from the diesel-biodiesel combustion process. The addition of increased amount of PS in a biodiesel-diesel fuel system increased the overall peak HRR but not at the 2400 rpm speed. The moderate increment could be one of the factors of reducing the NOx emission due to the addition of the PS in the diesel-biodiesel fuel system.

This ignition delay and the variation of HRR needed to be occurred uniformly to avoid engine knocking. The SOI was fixed at 21 ^oCA before TDC and the SOC was observed to be varied with the change of fuels, engine speeds and loading conditions. ID (ms) increased with the increase in loading conditions and decreased with the increase in engine speeds. Obviously, at higher speeds the total cycle period (in time scale) is shorter and ID has to be shorter to conduct the combustion in an efficient manner.

10.6 Summary of Conclusions

This study identified that amongst PE, PP and PS, only PS was found to dissolve in biodiesel (solvents) at ambient conditions, and the diesel engine performed very well with the PS blended biodiesel-diesel fuels than those of the biodiesel-diesel blended fuels. It indicates that the PS could be considered as one of the effective fuel additives to improve the fuel performance in the diesel engine.

10.7 Future Line of Research

Several recommendations for future study can be made from this study. Some of them are listed below:

- By integrating the dechlorination process, PVC plastic can also be treated with the biodiesel solvent as a sustainable method of chemical recycling processes.
- Use of thermo-catalytic liquefaction standard catalysts could be used to investigate the catalytic effects on increasing the solubility of the PE and PP at lower temperatures.
- Repeatability of using the recovered biodiesel solvents could be checked to determine the number of times the same solvent could be used to recycle the plastics. It may reduce the biodiesel production process cost. Multi-coloured thermoplastics could be treated in this method, and the bleaching would be easier with the liquids above 85 ^oC. The PE was seen to turn into cloudy gels below that temperature but it behaves well as a liquid solution beyond that.
- No antioxidant was used in this study to improve the oxidation stability of the WTB and WTC fuels during combustion analyses. Application of antioxidants may have some other results on combustion, performance, and emissions from the combustion of those fuels.
- In this study, only the conventional batch reactor was used to produce biodiesel and determine their optimal production parameters as well as the reaction kinetics. Other available production methodologies (e.g. supercritical process, microwave process and ultrasound assisted process), their optimisation and kinetic studies may give a better comparative idea of choosing the best method that consume least energy.

REFERENCES

- 1. IEA, *Renewables 2019.* 2019, International Energy Agency (IEA): Paris. Available from: https://www.iea.org/reports/renewables-2019.
- 2. Syed, A., *Australian energy projections to 2049-50.* 2012, Bureau of Resources and Energy Economics (BREE): Canberra. C.o. Australia Available from: http://www.bree.gov.au/sites/bree.gov.au/files/files//publications/aep/australian-energy-projections-to-2050.pdf.
- Thomas, M., B. Stone, T. Beer, D. Lamb, L. Edye, P. Rogers, D. Batten, and G. Tegart, Biofuels for Transport: A Roadmap for Development in Australia, M. Thomas and J. Wright, Editors. 2008, The Australian Academy of Technological Sciences and Engineering (ATSE): Australia. Report Number: 187561897X. Available from: http://www.atse.org.au/Documents/Publications/Reports/Energy/ATSE%20Biofuels% 20for%20Transport%20Development%20in%20Australia%202008.pdf.
- 4. BREE, *Australian Petroleum Statistics*. 2014, Commonwealth of Australia: Canberra. p. 1-30. Report Number: aps-210-201401. Available from: http://www.bree.gov.au/sites/bree.gov.au/files/files//publications/aps/2014/aps-210-201401.pdf.
- 5. Blackburn, J., *Australia's Liquid Fuel Security (Part-2)*, in *A report for NRMA Motoring & Services*. 2014. Available from: http://www.mynrma.com.au/images/About-PDF/Fuel-Security-Report-Pt2.pdf.
- 6. Blackburn, J., *Australia's Liquid Fuel Security (Part-1)*, in *A Report for NRMA Motoring and Services*. 2013. Available from: http://www.mynrma.com.au/media/Fuel_Security_Report.pdf.
- 7. COA, *Australian Energy Update*. 2019, Department of the Environment and Energy in the Commonwealth of Australia (COA): Australia. C.o. Australia Available from: https://www.energy.gov.au/government-priorities/energy-data/australian-energy-statistics.
- 8. IEA. *IEA Stisitics Global energy data at your fingertips*. World Energy Balances 2019, 2019, Available from: https://www.iea.org/statistics/.
- 9. IEA, *Energy Policies of IEA Countries Australia 2018 Review*. 2018, International Energy Agency (IEA). OECD/IEA Available from: https://www.iea.org/publications/freepublications/publication/EnergyPoliciesofIEACo untriesAustralia2018Review.pdf.
- Aro, E.-M., *From first generation biofuels to advanced solar biofuels*. Ambio, 2016.
 45 Suppl 1(Suppl 1): p. S24-S31.DOI: 10.1007/s13280-015-0730-0.
- 11. Ashwath, N., *Evaluating Biodiesel Potential of Australian Native and Naturalised Plant Species.* 2010, Rural Industries Research and Development Corporation. p. 1-113.
- 12. OECD, Improving Markets for Recycled Plastics: Trends, Prospects and Policy Responses. doi:https://doi.org/10.1787/9789264301016-en2018: OECD Publishing. ISBN: 9789264301016.
- 13. Geyer, R., J.R. Jambeck, and K.L. Law, *Production, use, and fate of all plastics ever made.* Sci Adv, 2017. **3**(7): p. e1700782.DOI: 10.1126/sciadv.1700782.
- 14. O'Farrell, K., 2017-18 Australian Plastics Recycling Survey National Report. 2019, Deaprtment of the Environment and Energy of the Australian Government. Available from: https://www.environment.gov.au/protection/waste-resourcerecovery/publications/australian-plastics-recycling-survey-report-2017-18.

- 15. Schanssema, A., *Resource efficiency: Best Practices for the recovery of plastics waste in Europe*. 2007, PlasticsEurope.
- 16. Bordynuik, J.W. Viable Production of Diesel From Non-Recyclable Waste Plastics. in Proceedings of the 21st Annual North American Waste-to-Energy Conference. 2013. Florida, USA, http://www.plastic2oil.com/files/NAWTECFinalBordynuik.pdf.
- 17. Holton, C., *Dissolving the plastics problem*, Environ Health Perspect, 1997. **105**(4): p. 388-390, http://www.ncbi.nlm.nih.gov/pmc/articles/PMC1469979/.
- Kannan, P., A.A. Shoaibi, and C. Srinivasakannan, Optimization of Waste Plastics Gasification Process Using Aspen-Plus, in Gasification for Practical Applications,11, Y. Yun, Editor. 2012, Intech. p. 279-295.DOI: http://dx.doi.org/10.5772/48754. ISBN: 978-953-51-0818-4.
- Harshal, P.R. and L.M. Shailendra, *Waste plastic Pyrolysis oil Alternative Fuel for CI* Engine – A Review. Research Journal of Engineering Sciences, 2013. 2(2): p. 26-30, http://www.isca.in/IJES/Archive/v2i2/6.ISCA-RJEngS-2013-001.pdf.
- Kuzhiyil, N. and S.-C. Kong, Energy Recovery from Waste Plastics by Using Blends of Biodiesel and Polystyrene in Diesel Engines. Energy Fuels, 2009. 23(6): p. 3246-3253.DOI: 10.1021/ef801110j.
- 21. Zhang, Y., S.K. Mallapragada, and B. Narasimhan, *Dissolution of Waste Plastics in Biodiesel*. Polym Eng Sci, 2009. **50**(5): p. 863-870.DOI: 10.1002/pen.21598.
- Azad, A., M. Rasul, M. Khan, S.C. Sharma, and M. Hazrat, *Prospect of Biofuels as an Alternative Transport Fuel in Australia*. Renewable Sustainable Energy Rev, 2015. 43: p. 331-351.
- 23. IEA, *IEA Bioenergy Countries' Report Update 2018 Bioenergy Policies and Status of Implementation*, L. Pelkmans, Editor. 2018, IEA Bioenergy. I. Bioenergy Available from: https://www.ieabioenergy.com/wp-content/uploads/2018/10/IEA-Bioenergy-Countries-Report-Update-2018-Bioenergy-policies-and-status-of-implementation.pdf.
- 24. WBA, *Wba Global Bioenergy Statistics 2018*. 2018, World Bioenergy Association (WBA). Available from: https://worldbioenergy.org/uploads/181203%20WBA%20GBS%202018 hq.pdf.
- 25. O'Hara, I.M., K. Robins, and B. Melssen, *Biofuels to bioproducts: a growth industry for Australia*. 2018, Queensland University of Technology: Australia. Available from: http://www.manildra.com.au/ebooks/biofuels/#p=10.
- 26. Latimer, C., *Biofuel the forgotten renewable energy, report says*, in *The Sydney Morning Herald*. 2018, The Sydney Morning Herald: Australia, https://www.smh.com.au/business/the-economy/biofuel-the-forgotten-renewableenergy-report-says-20180327-p4z6j6.html.
- 27. Sasongko, N.A., C. Thorns, I. Sankoff, S.T. Chew, and S. Bista, *Transitioning to sustainable use of biofuel in Australia*. Renewable Energy and Environmental Sustainability, 2017. **2**: p. 25.DOI: 10.1051/rees/2017034.
- Willett, K., J. Diamantopoulos, and A. Lobb, *Final Report Economic Assessment of Commonwealth and State Biofuel Policies*. 2018, ACIL Allen Consulting: Australia. M.a.L.A.L. (MLA) Available from: https://www.acilallen.com.au/uploads/files/projects/234/AcilAllen_BiofuelPolicies_2 018-1541038049.pdf.
- Young, D., Biodiesel Production for Rural Australia: An Initial Concept and Model. 2007, Australian Agricultural Crop Technologies Pty. Ltd.: Australia. Report Number: RIRDC Publication No 07/140 and RDC Project No ACO-1A. R.I.R.a.D.C. (RIRDC) Available from: https://www.agrifutures.com.au/wp-content/uploads/publications/07-140.pdf.

- 30. Haritos, V., *Rethinking biofuels in Australia*. 2019, Monash University: Australia. Available from: https://www.monash.edu/__data/assets/pdf_file/0003/1813458/Rethinking-Biofuels-Masterclass-Pres-Comb-Survey-Issue.pdf.
- 31. DEE, Australian Petroleum Statistics July 2019. 2019, Department of the Environment and Energy (DEE) Commonwealth of Australia: Australia. Available from: https://www.energy.gov.au/sites/default/files/australian_petroleum_statistics____issue_276_july_2019_1.pdf.
- 32. CSIRO *Biodiesel in Australia*. 2013. http://www.biofuelsassociation.com.au/biodiesel-in-australia.
- 33. DIS, 2015 Energy White Paper. 2015, Department of Industry and Science (DIS): Canberra, Australia. C.o. Australia Available from: http://www.industry.gov.au/EnergyWhitePaperataglance/files/Energy-White-Paper-2015.pdf.
- Bhuiya, M.M.K., M.G. Rasul, M.M.K. Khan, N. Ashwath, A.K. Azad, and M.A. Hazrat, *Prospects of 2nd generation biodiesel as a sustainable fuel Part 2: Properties, performance and emission characteristics.* Renewable Sustainable Energy Rev, 2016. 55: p. 1129-1146.DOI: http://dx.doi.org/10.1016/j.rser.2015.09.086.
- 35. Bhuiya, M.M.K., M.G. Rasul, M.M.K. Khan, N. Ashwath, and A.K. Azad, *Prospects* of 2nd generation biodiesel as a sustainable fuel—Part: 1 selection of feedstocks, oil extraction techniques and conversion technologies. Renewable Sustainable Energy Rev, 2016. **55**: p. 1109-1128.DOI: http://dx.doi.org/10.1016/j.rser.2015.04.163.
- 36. Azad, A.K., M.G. Rasul, M.M.K. Khan, S.C. Sharma, M. Mofijur, and M.M.K. Bhuiya, *Prospects, feedstocks and challenges of biodiesel production from beauty leaf oil and castor oil: A nonedible oil sources in Australia.* 2016. **61**: p. 302-318.DOI: 10.1016/j.rser.2016.04.013.
- 37. Bhuiya, M.M.K., M.G. Rasul, M.M.K. Khan, N. Ashwath, A.K. Azad, and M.A. Hazrat, Second Generation Biodiesel: Potential Alternative to-edible Oil-derived Biodiesel. Energy Procedia, 2014. 61: p. 1969-1972.DOI: http://dx.doi.org/10.1016/j.egypro.2014.12.054.
- 38. Azad, A.K., M.G. Rasul, M.M.K. Khan, A. Omri, M.M.K. Bhuiya, and M.A. Hazrat, *Modelling of Renewable Energy Economy in Australia*. Energy Procedia, 2014. **61**: p. 1902-1906.DOI: http://dx.doi.org/10.1016/j.egypro.2014.12.238.
- Azad, A.K., M.G. Rasul, M.M.K. Khan, S.C. Sharma, and M.A. Hazrat, *Prospect of biofuels as an alternative transport fuel in Australia*. Renewable Sustainable Energy Rev, 2015. 43: p. 331-351.DOI: http://dx.doi.org/10.1016/j.rser.2014.11.047.
- 40. Ritchie, M., *The state of waste in Australia a 2019 review*, in *InsideWaste*. 2019, Waste Management Resource Recovery Association of Australia: Australia, https://www.insidewaste.com.au/index.php/2019/08/14/a-review-of-the-state-of-waste-in-australia-in-2019/.
- 41. Australia, C.o., *National Waste Policy 2018 Less Waste, More Resources*. 2019: Australia. Available from: https://www.environment.gov.au/system/files/resources/d523f4e9-d958-466b-9fd1-3b7d6283f006/files/national-waste-policy-2018.pdf.
- 42. Locock, K.E., J. Deane, E. Kosior, H. Prabaharan, M. Skidmore, and O.E. Hutt, *The Recycled Plastics Market: Global Analysis and Trends*. 2017, CSIRO: Australia. Available from: https://www.csiro.au/en/Research/MF/Areas/Chemicals-and-fibres/plastic-recycling-analysis.
- 43. Dooley, B., *Emissions Comparison between 'Plastic Waste to Liquid' Fuel and Conventional Diesel.* 2019, Integrated Green Energy Solutions (IGESolutions).

IGES olutions Available from: https://www.igesolutions.org/wp-content/uploads/White-Paper-Emissions-Comparison.pdf.

- Zadgaonkar, A., Process and Equipment for Conversions of Wsate Plastics into Fuels, in Feedstock Recycling and Pyrolysis of Waste Plastics, J Scheirs, W Kaminsky (Eds) John Wiley & amp; Sons Ltd, Chichester, West Sussex, England (2006), ISBN: 0-470-02152-7,27, J. Scheirs and W. Kaminsky, Editors. 2007, John Wiley & Sons. p. 709-728.DOI: http://dx.doi.org/10.1016/j.jhazmat.2007.04.035. ISBN: 0-470-02152-7.
- 45. PlasticsEurope, *Plastics the Facts 2019.* 2019: Belgium. PlasticsEurope Available from: https://www.plasticseurope.org/en/resources/publications/1804-plastics-facts-2019.
- 46. Garside, M. *Global plastic production from 1950 to 2018* 2019, Includes thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coatings and sealants, and polypropylene-fibers. Does not include the following fibers: PET-, PA-, PP- and polyacryl-fibers. This statistic was assembled using several editions of the annual report.]. Available from: https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/.
- 47. CIEC, *Polymers*, in *The Essential Chemical Industry (ECI) Online*. 2013, Chemical Industry Education Centre (CIEC) Promoting Science: University of York, York, UK, http://www.essentialchemicalindustry.org/polymers.html.
- 48. Beckman, E., *The world of plastics, in numbers.* 2018, The Conversation: Australia, https://theconversation.com/the-world-of-plastics-in-numbers-100291.
- 49. Velis, C., Global Recycling Markets Plastic Waste: A story for one player China.
 2014, International Solid Waste ASsociation (ISWA): Vienna. p. 1-67. S.T.F.o.G.a.W.
 Management Available from: http://www.iswa.org/fileadmin/galleries/Task_Forces/TFGWM_Report_GRM_Plastic_China_LR.pdf.
- 50. Beckman, E., *The World's Plastic Problem in Numbers*, in *The Conversation*. 2018, The Conversation: Australia, https://theconversation.com/the-world-of-plastics-in-numbers-100291.
- 51. Hopewell, J., R. Dvorak, and E. Kosior, *Plastics recycling: challenges and opportunities.* Philos Trans R Soc Lond B Biol Sci, 2009. **364**(1526): p. 2115-2126.DOI: 10.1098/rstb.2008.0311.
- 52. Ritchie, H. and M. Roser, *Plastic Pollution*. 2018, OurWorldInData.org: UK, https://ourworldindata.org/plastic-pollution#.
- 53. Senet, S., *Plastic production on the rise worldwide but slowing in Europe*. Journal de l'Environnement, 2019. **Waste**, http://www.journaldelenvironnement.net/article/plus-de-plastique-dans-le-monde-mais-moins-en-europe,97858.
- Hazrat, M.A., M.G. Rasul, M.M.K. Khan, A.K. Azad, and M.M.K. Bhuiya, Utilization of Polymer Wastes as Transport Fuel Resources- a Recent Development. Energy Procedia, 2014. 61: p. 1681-1685.DOI: http://dx.doi.org/10.1016/j.egypro.2014.12.191.
- 55. Hazrat, M.A., M.G. Rasul, and M.M.K. Khan, A Study on Thermo-catalytic Degradation for Production of Clean Transport Fuel and Reducing Plastic Wastes. Procedia Eng, 2015. 105: p. 865-876.DOI: https://doi.org/10.1016/j.proeng.2015.05.108.
- 56. Themelis, N.J. and C. Mussche, 2014 Energy and Economic Value of Municipal Solid Waste (MSW), Including Non-Recycled Plastics (NRP), Currently Landfilled in the Fifty States. 2014, Columbia University: USA. p. 1-40. C. University Available from: http://www.americanchemistry.com/Policy/Energy/Energy-Recovery/2014-Update-

of-Potential-for-Energy-Recovery-from-Municipal-Solid-Waste-and-Non-Recycled-Plastics.pdf.

- 57. EPA, Advancing Sustainable Materials Management: 2016 and 2017 Tables and Figures. Assessing Trends in Material Generation, Recycling, Composting, Combustion with Energy Recovery and Landfilling in the United States 2019, United States Environmental Protection Agency (EPA): USA. EPA Available from: https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plasticsmaterial-specific-data.
- 58. Verma, R., K.S. Vinoda, M. Papireddy, and A.N.S. Gowda, *Toxic Pollutants from Plastic Waste- A Review.* Procedia Environ Sci, 2016. **35**: p. 701-708.DOI: https://doi.org/10.1016/j.proenv.2016.07.069.
- 59. Hahladakis, J.N., C.A. Velis, R. Weber, E. Iacovidou, and P. Purnell, *An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling.* J Hazard Mater, 2018. **344**: p. 179-199.DOI: https://doi.org/10.1016/j.jhazmat.2017.10.014.
- 60. Wang, Z., B. Peng, Y. Huang, and G. Sun, *Classification for plastic bottles recycling based on image recognition*. Waste Manage, 2019. **88**: p. 170-181.DOI: https://doi.org/10.1016/j.wasman.2019.03.032.
- 61. Eriksen, M.K., K. Pivnenko, M.E. Olsson, and T.F. Astrup, *Contamination in plastic recycling: Influence of metals on the quality of reprocessed plastic.* Waste Manage, 2018. **79**: p. 595-606.DOI: https://doi.org/10.1016/j.wasman.2018.08.007.
- 62. Eriksen, M.K. and T.F. Astrup, *Characterisation of source-separated, rigid plastic waste and evaluation of recycling initiatives: Effects of product design and source-separation system.* Waste Manage, 2019. **87**: p. 161-172.DOI: https://doi.org/10.1016/j.wasman.2019.02.006.
- 63. Ragaert, K., L. Delva, and K. Van Geem, *Mechanical and chemical recycling of solid plastic waste.* Waste Manage, 2017. **69**: p. 24-58.DOI: https://doi.org/10.1016/j.wasman.2017.07.044.
- 64. Faraca, G. and T. Astrup, *Plastic waste from recycling centres: Characterisation and evaluation of plastic recyclability.* Waste Manage, 2019. **95**: p. 388-398.DOI: https://doi.org/10.1016/j.wasman.2019.06.038.
- Jambeck, J.R., R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, R. Narayan, and K.L. Law, *Plastic waste inputs from land into the ocean*. Sci, 2015. 347(6223): p. 768.DOI: 10.1126/science.1260352.
- 66. Brooks, A.L., S. Wang, and J.R. Jambeck, *The Chinese import ban and its impact on global plastic waste trade.* Sci Adv, 2018. **4**(6): p. eaat0131.DOI: 10.1126/sciadv.aat0131.
- 67. Ebewele, R.O., *Polymer Science and Technology*. 2000, New York: CRC Press. 544. ISBN: 0-8493-8939-9.
- 68. Askeland, D.R. and P.P. Phulé, *The Science and Engineering of Materials*. 4th ed., http://books.google.com.au/books?id=fRbZslUtpBYC2005, USA: Nelson. 888. ISBN: 0-534-55396-6.
- 69. Chanda, M. and S.K. Roy, *Plastics Technology Handbook*. 4th ed. Plast Eng, ed. D.E. Hudgin. Vol. 72. 2006, New York: CRC Press Taylor & Francis Group.
- 70. Rodriguez, F. *Plastic*. 2019, Available from: https://www.britannica.com/science/plastic.
- 71. Rogers, T. *Everything You Need To Know About Polystyrene (PS).* 2015, Available from: https://www.creativemechanisms.com/blog/polystyrene-ps-plastic.

- 72. Staff, C.M. *Everything You Need To Know About PVC Plastic*. 2016, Available from: https://www.creativemechanisms.com/blog/everything-you-need-to-know-about-pvc-plastic.
- 73. SITA *Plastics Identification Code*. 2014. http://www.sita.com.au/commercial-solutions/resource-recovery-recycling/plastic-polystyrene/, 1.
- 74. A'Vard, D. and K. O'Farrell, 2011–12 National Plastics Recycling Survey. 2013, Plastics and Chemicals Industries Association (PACIA). Available from: http://www.pacia.org.au/Library/PageContentVersionAttachment/b32ecc28-36a3-4087-bd68-33a889cf9aef/r02_05_a10802_nprs_2011_12_report.pdf.
- 75. ASTM, Standard Practice for Coding Plastic Manufactured Articles for Resin Identification, in ASTM D7611 / D7611M-13e1. 2013, ASTM International: West Conshohocken, PA.DOI: 10.1520/D7611_D7611M-13E01.
- 76. PolymerProcessing.com. *Polymers*. 2000, Available from: http://www.polymerprocessing.com/polymers/class.html.
- 77. Allan, P., *Recycling market situation: Summary Review*. 2019, Sustainable Resource Use Pty Ltd Australia. D.o.E.a. Energy Available from: https://www.environment.gov.au/system/files/resources/12ab3fc8-7154-44e1-8691-cc05fd9d72bb/files/recycling-market-review-paper.pdf.
- 78. Bruno, E.A., *Automated Sorting of Plastics for Recycling*. 2000, North Carolina Department of Environment and natural resources Available from: http://infohouse.p2ric.org/ref/09/08620.pdf.
- 79. Battle, K.E., A.P. Moore, J.C. Lynch, and E.B. Nauman, *Plastics recycling by selective dissolution*, in *The DeWitt Conference*, U.S. Patent, Editor. 1992.
- 80. UNEP, *Convering Waste Plastics into a Resource Compendium of Technologies*. 2009, United Nations Environment Programme: Japan. UNEP.
- 81. Sekula, R. and S. Leszczynski, *Utilization of Scrap Thermosets Using Pyrolysis*. Energy Sources Part A, 2008. **31**(1): p. 76-85.DOI: 10.1080/15567030701468191.
- 82. Gharde, S. and B. Kandasubramanian, *Mechanothermal and chemical recycling methodologies for the Fibre Reinforced Plastic (FRP)*. Environ Technol Innovation, 2019. **14**: p. 100311.DOI: https://doi.org/10.1016/j.eti.2019.01.005.
- 83. EPA, *NSW Waste Avoidance and Resource Recovery Strategy 2014–21*. 2014, Environment Protection Authority (EPA): NSW. Report Number: EPA 2014/0876. E.P. Authority Available from: https://www.epa.nsw.gov.au/-/media/epa/corporatesite/resources/wastestrategy/140876-warr-strategy-14-21.pdf.
- 84. AA. *Euro Emissions Standards: Limits to Improve Air Quality and Health*. Fuels and the Environments 2017, Available from: https://www.theaa.com/driving-advice/fuels-environment/euro-emissions-standards#euro6. Access Date: 03 August 2018.
- Lingaiah, N., M. Azhar Uddin, A. Muto, Y. Sakata, T. Imai, and K. Murata, *Catalytic dechlorination of chloroorganic compounds from PVC-containing mixed plastic-derived oil*. Appl Catal, A, 2001. 207(1–2): p. 79-84.DOI: http://dx.doi.org/10.1016/S0926-860X(00)00656-6.
- 86. Li, C.-T., H.-K. Zhuang, L.-T. Hsieh, W.-J. Lee, and M.-C. Tsao, *PAH emission from the incineration of three plastic wastes*. Environ Int, 2001. **27**(1): p. 61-67.DOI: http://dx.doi.org/10.1016/S0160-4120(01)00056-3.
- 87. UNEP, Converting Waste Plastics into a Resource-Assessment Guidelines. 2009, United Nations Environment Programme (UNEP). Available from: http://www.unep.or.jp/Ietc/Publications/spc/WastePlasticsEST_AssessmentGuideline s.pdf.

- 88. Gao, F., PhD, *Pyrolysis of Waste Plastics into Fuels*, in *Chemical and Process Engineering*. 2010, University of Canterbury, Available from: http://ir.canterbury.ac.nz/bitstream/10092/4303/1/Thesis_fulltext.pdf.
- 89. Thahir, R., A. Altway, S.R. Juliastuti, and Susianto, *Production of liquid fuel from plastic waste using integrated pyrolysis method with refinery distillation bubble cap plate column*. Energy Rep, 2019. **5**: p. 70-77.DOI: https://doi.org/10.1016/j.egyr.2018.11.004.
- 90. Tang, C., Y.-Z. Wang, Q. Zhou, and L. Zheng, *Catalytic effect of Al–Zn composite catalyst on the degradation of PVC-containing polymer mixtures into pyrolysis oil.* Polym Degradation Stab, 2003. 81(1): p. 89-94.DOI: http://dx.doi.org/10.1016/S0141-3910(03)00066-1.
- 91. Sarker, M. and M.M. Rashid, *Hydrocarbon Compounds Fuel Recover from LDPE/HDPE/PP/PS Waste Plastics Mixture Using Zinc Oxide Catalyst*. International Journal of Sustainable Energy and Environment, 2013. **1**(2): p. 14-24, http://www.ijsee.com/IJSEE_Vol.%201,%20No.%202,%20March%202013/Hydrocar bon%20Compounds%20Fuel%20%20Recover.pdf.
- 92. Kodera, Y., Y. Ishihara, and T. Kuroki, *Novel Process for Recycling Waste Plastics To Fuel Gas Using a Moving-Bed Reactor*. Energy Fuels, 2006. **20**(1): p. 155-158.DOI: 10.1021/ef0502655.
- 93. Bonalumi, D., Preliminary Study of Pyrolysis and Gasification of Biomass and Thermosetting Resins for Energy Production. Energy Procedia, 2016. **101**: p. 432-439.DOI: https://doi.org/10.1016/j.egypro.2016.11.055.
- 94. Bridgewater, A.V., *Biomass Pyrolysis*. 2007, International Energy Agency Bioenergy. Available from: http://www.ieabioenergy.com/iea-publications/task-libraries/.
- 95. Sharmina Begum, M.G. Rasul, and D. Akbar, *An Investigation on Thermo Chemical Conversions of SolidWaste for Energy Recovery*. World Academy of Science, Engineering and Technology, 2012. **62**: p. 624-630, http://www.waset.org/journals/waset/v62/v62-114.pdf.
- 96. Aguado, J., D.P. Serrano, and J.M. Escola, *Catalytic Upgrading of Plastic Wastes*, in *Feeds tock Recycling and Pyrolys is of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels* J. Scheirs and W. Kaminsky, Editors. 2006, John Wiley & Sons Ltd.,

http://f3.tiera.ru/3/Chemistry/Chemical%20engineering/Polymers/Scheirs%20J.,%20 Kaminsky%20W.%20(eds.)%20Feedstock%20Recycling%20and%20Pyrolysis%20of %20Waste%20Plastics%20(Wiley,%202006)(ISBN%200470021527)(792s).pdf. ISBN: 0-470-02152-7.

- 97. Al-Salem, S.M., P. Lettieri, and J. Baeyens, *Recycling and recovery routes of plastic solid waste (PSW): A review.* Waste Manage, 2009. **29**(10): p. 2625-2643.DOI: http://dx.doi.org/10.1016/j.wasman.2009.06.004.
- 98. Baeyens, J., A. Brems, and R. Dewil, *Recovery and recycling of post-consumer waste materials. Part 2. Target wastes (glass beverage bottles, plastics, scrap metal and steel cans, end-of-life tyres, batteries and household hazardous waste).* Int J Sustainable Eng, 2010. **3**(4): p. 232-245.DOI: 10.1080/19397038.2010.507885.
- 99. Brems, A., R. Dewil, J. Baeyens, and R. Zhang, *Gasification of plastic waste as waste-to-energy or waste-to-syngas recovery route*. Natural Science, 2013. **5**(6): p. 695-704, http://dx.doi.org/10.4236/ns.2013.56086.
- 100. Arena, U., L. Zaccariello, and M.L. Mastellone, *Fluidized bed gasification of wastederived fuels*. Waste Manage, 2010. **30**(7): p. 1212-1219.DOI: http://dx.doi.org/10.1016/j.wasman.2010.01.038.

- 101. Aznar, M.P., M.A. Caballero, J.A. Sancho, and E. Francés, *Plastic waste elimination by co-gasification with coal and biomass in fluidized bed with air in pilot plant*. Fuel Process Technol, 2006. **87**(5): p. 409-420.DOI: http://dx.doi.org/10.1016/j.fuproc.2005.09.006.
- 102. GTC. *Gasification Applications*. 2011, Available from: http://www.gasification.org/gasification-applications/chemicals-fertilizers-fuels/.
- 103. Gershman, Brickner, and Bratton, Gasification of Non-Recycled Plastics From Municipal Solid Waste in the United States 2013, GBB - Solid Waste Mananagement Consultants: Fairfax, VA. p. 1-66. T.A.C. Council Available from: http://plastics.americanchemistry.com/Sustainability-Recycling/Energy-Recovery/Gasification-of-Non-Recycled-Plastics-from-Municipal-Solid-Waste-inthe-United-States.pdf.
- 104. Tabak, S., M. Heinritz-Adrian, A. Brandl, U. GmbH, R. McGihon, M. Hindman, and X. Zhao. An Alternative Route for Coal To Liquid Fuel applying the ExxonMobil Methanol to Gasoline (MTG) Process. in Gasification Technologies Conference. 2008. USA, https://www.netl.doe.gov/sites/default/files/netl-file/26TABAK.pdf.
- 105. GSTC. *Gasification vs. Incineration*. Syngas Applications, Available from: https://www.globalsyngas.org/syngas-applications/gasification-vs-incineration/. Access Date: 08/08.
- 106. Pinto, F., C. Franco, R.N. André, C. Tavares, M. Dias, I. Gulyurtlu, and I. Cabrita, Effect of experimental conditions on co-gasification of coal, biomass and plastics wastes with air/steam mixtures in a fluidized bed system. Fuel, 2003. 82(15–17): p. 1967-1976.DOI: http://dx.doi.org/10.1016/S0016-2361(03)00160-1.
- 107. Arena, U., F. Di Gregorio, C. Amorese, and M.L. Mastellone, A techno-economic comparison of fluidized bed gasification of two mixed plastic wastes. Waste Manage, 2011. 31(7): p. 1494-1504.DOI: http://dx.doi.org/10.1016/j.wasman.2011.02.004.
- 108. Corella, J., A. Orío, and J.-M. Toledo, *Biomass Gasification with Air in a Fluidized Bed: Exhaustive Tar Elimination with Commercial Steam Reforming Catalysts.* Energy Fuels, 1999. **13**(3): p. 702-709.DOI: 10.1021/ef980221e.
- 109. Brage, C., K. Sjöström, Q. Yu, G. Chen, T. Liliedahl, and C. Rosén, *Biomass Gasification and Pyrolysis*. 1997. 227.
- 110. Abatzoglou, N., R. Evans, T.A. Milne, and n. Biomass Gasifier, *Tars*": *Their Nature, Formation and Conversion*. 1998.
- 111. Hirn, G., Generating syngas from plastic wastes. 2016, Federal Minisry for Economic Affairs and Energy (BMWi): Germany. Report Number: BINE-Projektinfo 05/2016. F. Karlsruhe Available from: http://www.bine.info/fileadmin/content/Publikationen/Projekt-Infos/2016/Projekt_05-2016/ProjektInfo_0516_engl_internetx.pdf.
- Bai, B., Y. Liu, Q. Wang, J. Zou, H. Zhang, H. Jin, and X. Li, *Experimental investigation on gasification characteristics of plastic wastes in supercritical water*. Renewable Energy, 2019. 135: p. 32-40.DOI: https://doi.org/10.1016/j.renene.2018.11.092.
- 113. Onwudili, J.A. and P.T. Williams, *Catalytic supercritical water gasification of plastics with supported RuO2: A potential solution to hydrocarbons–water pollution problem.* Process Saf Environ Prot, 2016. **102**: p. 140-149.DOI: https://doi.org/10.1016/j.psep.2016.02.009.
- 114. Onwudili, J.A. and P.T. Williams, Catalytic conversion of bio-oil in supercritical water: Influence of RuO2/γ-Al2O3 catalysts on gasification efficiencies and biomethane production. Appl Catal, B, 2016. 180: p. 559-568.DOI: https://doi.org/10.1016/j.apcatb.2015.06.058.

- 115. Straka, P. and O. Bičáková, *Hydrogen-rich gas as a product of two-stage co-gasification of lignite/waste plastics mixtures*. IJHE, 2014. **39**(21): p. 10987-10995.DOI: http://dx.doi.org/10.1016/j.ijhydene.2014.05.054.
- 116. Baloch, H.A., T. Yang, R. Li, S. Nizamuddin, X. Kai, and A.W. Bhutto, *Parametric study of co-gasification of ternary blends of rice straw, polyethylene and polyvinylchloride*. Clean Technol Environ Policy, 2016. **18**(4): p. 1031-1042.DOI: 10.1007/s10098-016-1092-4.
- 117. Brems, A., R. Dewil, J. Baeyens, and R. Zhang, *Gasification of plastic waste as waste-to-energy or waste-to-syngas recovery route*. Natural Science, 2013. **5**(6).DOI: 10.4236/ns.2013.56086.
- 118. Scheirs, J., Overview of Commercial Pyrolysis Processes for Waste Plastics, in Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels, 15, J. Scheirs and W. Kaminsky, Editors. 2006, John Wiley & Sons Ltd.: Chichester, West Sussex, England. p. 383-433. ISBN: 0-470-02152-7.
- 119. Diebold, J.P., A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils, S. Czernik, Editor. 2000, National Renewable Energy Laboratory (NREL). Report Number: NREL/SR-570-27613. U.S.D.o. Energy Available from: http://gisceu.net/PDF/U918.pdf.
- 120. Oasmaa, A. and D.C. Elliott. *Stability of fast pyrolysis bio-oils and upgraded products*. in *The International Conference on thermochemical conversion Science* (*tcbiomass2013*). 2013. Chicago, USA: VTT Technical Research Centre of Finland, http://www.gastechnology.org/tcbiomass2013/tcb2013/04-Oasmaa-tcbiomass2013presentation-Thur.pdf.
- 121. Oasmaa, A. and E. Kuoppala, *Fast Pyrolysis of Forestry Residue*. 3. Storage Stability of Liquid Fuel. Energy Fuels, 2003. **17**(4): p. 1075-1084.DOI: 10.1021/ef0300110.
- 122. FakhrHoseini, S.M. and M. Dastanian, *Predicting Pyrolysis Products of PE, PP, and PET Using NRTL Activity Coefficient Model.* J Chem, 2013. **2013**: p. 5.DOI: 10.1155/2013/487676.
- 123. Miandad, R., M. Rehan, A.-S. Nizami, M.A. El-Fetouh Barakat, and I.M. Ismail, *The Energy and Value-Added Products from Pyrolysis of Waste Plastics*, in *Recycling of Solid Waste for Biofuels and Bio-chemicals* O.P. Karthikeyan, K. Heimann, and S.S. Muthu, Editors. 2016, Springer Singapore: Singapore. p. 333-355.DOI: 10.1007/978-981-10-0150-5_12. ISBN: 978-981-10-0150-5.
- 124. Tulashie, S.K., E.K. Boadu, and S. Dapaah, *Plastic waste to fuel via pyrolysis: A key way to solving the severe plastic waste problem in Ghana*. Thermal Science and Engineering Progress, 2019. **11**: p. 417-424.DOI: https://doi.org/10.1016/j.tsep.2019.05.002.
- Al-Salem, S.M., A. Antelava, A. Constantinou, G. Manos, and A. Dutta, A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). J Environ Manage, 2017.
 197: p. 177-198.DOI: https://doi.org/10.1016/j.jenvman.2017.03.084.
- 126. Anuar Sharuddin, S.D., F. Abnisa, W.M.A. Wan Daud, and M.K. Aroua, *A review on pyrolysis of plastic wastes*. Energy Convers Manage, 2016. **115**: p. 308-326.DOI: https://doi.org/10.1016/j.enconman.2016.02.037.
- 127. Horvat, N. and F.T. Ng, *Tertiary polymer recycling: study of polyethylene thermolysis* as a first step to synthetic diesel fuel. Fuel, 1999. **78**(4): p. 459-470.DOI: https://doi.org/10.1016/S0016-2361(98)00158-6.
- 128. Ahmad, I., M.I. Khan, H. Khan, M. Ishaq, R. Tariq, K. Gul, and W. Ahmad, *Pyrolysis Study of Polypropylene and Polyethylene Into Premium Oil Products*. Int J Green Energy, 2015. **12**(7): p. 663-671.DOI: 10.1080/15435075.2014.880146.

- 129. Scott, D.S., S.R. Czernik, J. Piskorz, and D.S.A.G. Radlein, *Fast pyrolysis of plastic wastes*. Energy Fuels, 1990. **4**(4): p. 407-411.DOI: 10.1021/ef00022a013.
- Isoda, T., T. Nakahara, K. Kusakabe, and S. Morooka, *Catalytic cracking of polyethylene-liquefied oil over amorphous aluminosilicate catalysts*. Energy Fuels, 1998. 12(6): p. 1161-1167.DOI: 10.1021/ef980018j.
- 131. Bagri, R. and P.T. Williams, *Catalytic pyrolysis of polyethylene*. J Anal Appl Pyrolysis, 2002. **63**(1): p. 29-41.DOI: https://doi.org/10.1016/S0165-2370(01)00139-5.
- 132. López, A., I. de Marco, B.M. Caballero, M.F. Laresgoiti, and A. Adrados, *Dechlorination of fuels in pyrolysis of PVC containing plastic wastes*. Fuel Process Technol, 2011. **92**(2): p. 253-260.DOI: https://doi.org/10.1016/j.fuproc.2010.05.008.
- 133. Ma, S., J.U.N. Lu, and J. Gao, *Study on the Pyrolysis Dechlorination of PVC Waste*. EnS, 2004. **26**(4): p. 387-396.DOI: 10.1080/00908310390197352.
- 134. Zhou, J., B. Gui, Y. Qiao, J. Zhang, W. Wang, H. Yao, Y. Yu, and M. Xu, *Understanding the pyrolysis mechanism of polyvinylchloride (PVC) by characterizing the chars produced in a wire-mesh reactor*. Fuel, 2016. **166**: p. 526-532.DOI: https://doi.org/10.1016/j.fuel.2015.11.034.
- 135. Zhang, G.-H., J.-F. Zhu, and A. Okuwaki, Prospect and current status of recycling waste plastics and technology for converting them into oil in China. Resour Conserv Recycl, 2007. 50(3): p. 231-239.DOI: http://dx.doi.org/10.1016/j.resconrec.2006.11.007.
- 136. Akpanudoh, N.S., K. Gobin, and G. Manos, *Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts: Effect of polymer to catalyst ratio/acidity content.* J Mol Catal A: Chem, 2005. **235**(1–2): p. 67-73.DOI: http://dx.doi.org/10.1016/j.molcata.2005.03.009.
- 137. Makarichi, L., W. Jutidamrongphan, and K.-a. Techato, *The evolution of waste-to-energy incineration: A review*. Renewable Sustainable Energy Rev, 2018. **91**: p. 812-821.DOI: https://doi.org/10.1016/j.rser.2018.04.088.
- 138. Lu, J.-W., S. Zhang, J. Hai, and M. Lei, *Status and perspectives of municipal solid waste incineration in China: A comparison with developed regions.* Waste Manage, 2017. **69**: p. 170-186.DOI: https://doi.org/10.1016/j.wasman.2017.04.014.
- 139. Hopewell, J., R. Dvorak, and E. Kosior, *Plastics recycling: challenges and opportunities*. Philosophical transactions of the Royal Society of London Series B, Biological sciences, 2009. **364**(1526): p. 2115-2126.DOI: 10.1098/rstb.2008.0311.
- 140. Siddiqui, M.N. and H.H. Redhwi, *Catalytic coprocessing of waste plastics and petroleum residue into liquid fuel oils.* J Anal Appl Pyrolysis, 2009. **86**(1): p. 141-147.DOI: http://dx.doi.org/10.1016/j.jaap.2009.05.002.
- 141. Sundberg, J. and M. Olofsson, *Waste-to-Energy Incineration*. 2004, Profu consultancy firm: Gothenburg, Sweden. p. 1-36. S.A.o.W.M. (RVF) Available from: http://www.avfallsverige.se/fileadmin/uploads/Rapporter/Utveckling/U2004-15.pdf.
- 142. Gradus, R.H.J.M., P.H.L. Nillesen, E. Dijkgraaf, and R.J. van Koppen, *A Cost-effectiveness Analysis for Incineration or Recycling of Dutch Household Plastic Waste*. Ecol Econ, 2017. **135**: p. 22-28.DOI: https://doi.org/10.1016/j.ecolecon.2016.12.021.
- 143. Lea, W.R., *Plastic incineration versus recycling: a comparison of energy and landfill cost savings.* J Hazard Mater, 1996. **47**(1–3): p. 295-302.DOI: http://dx.doi.org/10.1016/0304-3894(95)00117-4.
- 144. World, W.M. Landfilled Plastics Could Power 5.2 Million U.S. Households. Waste to Energy 2011, Available from: http://www.waste-managementworld.com/articles/2011/10/landfilled-plastics-could-power-5-2-million-u-shouseholds.html. Access Date: 05/08.

- 145. Stelmachowski, M. and K. Słowiński, *Thermal and Thermo-Catalytic Conversion of Waste Polyolefins to Fuel-Like Mixture of Hydrocarbons*. Chemical and Process Engineering, 2012. **33**(1): p. 185-198.DOI: 10.2478/v10176-012-0016-z.
- 146. Sarker, M. and M.M. Rashid, *Alternative Liquid Hydrocarbon Fuel Production: Comparative Study for Polypropylene Waste Plastic and Standard Plastic.* http://acascipub.com/Books/Energy%20and%20Power/Alternative%20Liquid%20Hy drocarbon%20Fuel%20Production%20Comparative%20Study.pdf2013: Energy and Power. ISBN: 978-0-9886890-3-9.
- Maria, F.D. and G. Pavesi, *RDF to energy plant for a central Italian region SUW management system: Energetic and economical analysis.* Appl Therm Eng, 2006.
 26(11–12): p. 1291-1300.DOI: http://dx.doi.org/10.1016/j.applthermaleng.2005.10.024.
- 148. Halden, R.U., *Plastics and Health Risks*. Annu Rev Public Health, 2010. **31**(1): p. 179-194.DOI: 10.1146/annurev.publhealth.012809.103714.
- 149. Lang, I.A., T.S. Galloway, A. Scarlett, and et al., *Association of urinary bisphenol a concentration with medical disorders and laboratory abnormalities in adults.* JAMA, 2008. **300**(11): p. 1303-1310.DOI: 10.1001/jama.300.11.1303.
- 150. Avolio, R., F. Spina, G. Gentile, M. Cocca, M. Avella, C. Carfagna, G. Tealdo, and E.M. Errico, *Recycling Polyethylene-Rich Plastic Waste from Landfill Reclamation: Toward an Enhanced Landfill-Mining Approach*. Polymers, 2019. **11**(2).DOI: 10.3390/polym11020208.
- Krook, J., N. Svensson, and M. Eklund, Landfill mining: A critical review of two decades of research. Waste Manage, 2012. 32(3): p. 513-520.DOI: https://doi.org/10.1016/j.wasman.2011.10.015.
- 152. Zhou, C., W. Fang, W. Xu, A. Cao, and R. Wang, *Characteristics and the recovery potential of plastic wastes obtained from landfill mining*. J Cleaner Prod, 2014. **80**: p. 80-86.DOI: https://doi.org/10.1016/j.jclepro.2014.05.083.
- 153. Quaghebeur, M., B. Laenen, D. Geysen, P. Nielsen, Y. Pontikes, T. Van Gerven, and J. Spooren, *Characterization of landfilled materials: screening of the enhanced landfill mining potential.* J Cleaner Prod, 2013. 55: p. 72-83.DOI: https://doi.org/10.1016/j.jclepro.2012.06.012.
- 154. Zhang, X., H. Lei, L. Zhu, X. Zhu, M. Qian, G. Yadavalli, J. Wu, and S. Chen, *Thermal behavior and kinetic study for catalytic co-pyrolysis of biomass with plastics*. Bioresour Technol, 2016. **220**: p. 233-238.DOI: https://doi.org/10.1016/j.biortech.2016.08.068.
- Sebestyén, Z., E. Barta-Rajnai, J. Bozi, M. Blazsó, E. Jakab, N. Miskolczi, J. Sója, and Z. Czégény, *Thermo-catalytic pyrolysis of biomass and plastic mixtures using HZSM-*5. ApEn, 2017. 207: p. 114-122.DOI: https://doi.org/10.1016/j.apenergy.2017.06.032.
- 156. Ragaert, K., L. Delva, and K. Geem, *Mechanical and chemical recycling of solid plastic waste*. Waste Manage, 2017. **69**.DOI: 10.1016/j.wasman.2017.07.044.
- 157. George, N. and T. Kurian, *Recent Developments in the Chemical Recycling of Postconsumer Poly(ethylene terephthalate) Waste.* Ind Eng Chem Res, 2014. 53(37): p. 14185-14198.DOI: 10.1021/ie501995m.
- 158. Rochman, C.M., M.A. Browne, B.S. Halpern, B.T. Hentschel, E. Hoh, H.K. Karapanagioti, L.M. Rios-Mendoza, H. Takada, S. Teh, and R.C. Thompson, *Classify plastic waste as hazardous*. Nature, 2013. **494**(7436): p. 169-171.DOI: 10.1038/494169a.
- 159. Zhao, Y.-B., X.-D. Lv, and H.-G. Ni, *Solvent-based separation and recycling of waste plastics: A review.* Chemosphere, 2018. **209**: p. 707-720.DOI: https://doi.org/10.1016/j.chemosphere.2018.06.095.

- 160. Aguado, J. and D. Serrano, *Feedstock Recycling of Plastic Wastes*. RSC Clean Technology Monographs, ed. J.H. Clark. 1999, UK: The Royal Society of Chemistry. ISBN: 0-85404-531-7.
- 161. Bennett, G.F., Feedstock Recycling and Pyrolysis of Waste Plastics, J. Scheirs, W. Kaminsky (Eds.). John Wiley & amp; Sons Ltd., Chichester, West Sussex, England (2006), ISBN: 0-470-02152-7. J Hazard Mater, 2007. 147(1–2): p. 682-683.DOI: http://dx.doi.org/10.1016/j.jhazmat.2007.04.035.
- 162. Wong., S.L., N. Ngadi., and T.A.T. Abdullah., *Study on Dissolution of Low Density Polyethylene (LDPE)*. Applied Mechanics and Materials, 2015. **695**: p. 170-173.DOI: 10.4028/www.scientific.net/AMM.695.170.
- 163. Hadi., A.J., G. Faisal., Najmuddin., and I. Ahmed., Quality Restoration of Waste Polyolefin Plastic Material Through the Dissolution-Reprecipitation Technique. Chemical Industry & Chemical Engineering Quarterly, 2014. 20(2): p. 163-170.DOI: 10.2298/CICEQ120526119H.
- 164. Poulakis, J.G. and C.D. Papaspyrides, *The dissolution/reprecipitation technique applied on high-density polyethylene: I. Model recycling experiments.* Adv Polym Tech, 1995. **14**(3): p. 237-242.DOI: 10.1002/adv.1995.060140307.
- 165. Nauman, E.B. and J.C. Lynch, *Polymer recycling by selective dissolution*, U.S. Patent, Editor. 1992, Rensellaer Plytechnic Institute: USA, http://www.freepatentsonline.com/5278282.pdf.
- 166. Pappa, G., C. Boukouvalas, C. Giannaris, N. Ntaras, V. Zografos, K. Magoulas, A. Lygeros, and D. Tassios, *The selective dissolution/precipitation technique for polymer recycling: a pilot unit application*. Resour Conserv Recycl, 2001. **34**(1): p. 33-44.DOI: https://doi.org/10.1016/S0921-3449(01)00092-1.
- 167. Pappa, G., C. Boukouvalas, C. Giannaris, N. Ntaras, V. Zografos, K. Magoulas, A. Lygeros, and D. Tassios, *The selective dissolution/precipitation technique for polymer recycling: a pilot unit application*. Resources, Conservation and Recycling, 2001. 34: p. 33-44, http://ttpl.chemeng.ntua.gr/pdf/0111.pdf.
- 168. Altland, B.L., D. Cox, R.M. Enick, and E.J. Beckman, Optimization of the highpressure, near-critical liquid-based microsortation of recyclable post-consumer plastics. Resour Conserv Recycl, 1995. 15(3–4): p. 203-217.DOI: http://dx.doi.org/10.1016/0921-3449(95)00031-3.
- Weeden, G.S., N.H. Soepriatna, and N.-H.L. Wang, *Method for Efficient Recovery of High-Purity Polycarbonates from Electronic Waste*. Environ Sci Technol, 2015. **49**(4): p. 2425-2433.DOI: 10.1021/es5055786.
- 170. Turley, D.B., F.J. Areal, and J.E. Copeland, *The Opportunities for Use of Esters of Rapeseed Oil as Bio-Renewable Solvents*, in *HGCA Research Review No 52*. 2004: York. p. 1-51. Report Number: Project No. 2839. T.H.G.C.A. (HGCA) Available from: http://archive.hgca.com/publications/documents/cropresearch/RR52_Final_Review.pd f.
- Gonzalez, Y.M., P. de Caro, S. Thiebaud-Roux, and C. Lacaze-Dufaure, *Fatty Acid Methyl Esters as Biosolvents of Epoxy Resins: A Physicochemical Study.* JSCh, 2007. 36(4): p. 437-446, http://dx.doi.org/10.1007/s10953-007-9126-5.
- 172. Salehpour, S. and M.A. Dub'e, *Biodiesel: a green polymerization solvent*. The Royal Society of Chemistry, 2008. **10**: p. 321-326.DOI: 10.1039/b715047d.
- 173. Karuppannan Gopalraj, S. and T. Kärki, A review on the recycling of waste carbon fibre/glass fibre-reinforced composites: fibre recovery, properties and life-cycle analysis. SN Appl Sci, 2020. **2**(3): p. 433.DOI: 10.1007/s42452-020-2195-4.

- 174. Al-Sabagh, A.M., F.Z. Yehia, G. Eshaq, A.M. Rabie, and A.E. ElMetwally, *Greener routes for recycling of polyethylene terephthalate*. Egypt J Pet, 2016. **25**(1): p. 53-64.DOI: https://doi.org/10.1016/j.ejpe.2015.03.001.
- 175. Datta, J. and P. Kopczyńska, From polymer waste to potential main industrial products: Actual state of recycling and recovering. Crit Rev Environ Sci Technol, 2016. 46(10): p. 905-946.DOI: 10.1080/10643389.2016.1180227.
- 176. Carné Sánchez, A. and S.R. Collinson, *The selective recycling of mixed plastic waste of polylactic acid and polyethylene terephthalate by control of process conditions*. Eur Polym J, 2011. 47(10): p. 1970-1976.DOI: https://doi.org/10.1016/j.eurpolymj.2011.07.013.
- 177. Arjanggi, R.D. and J. Kansedo, *Recent advancement and prospective of waste plastics as biodiesel additives: A review.* J Energy Inst, 2019, https://doi.org/10.1016/j.joei.2019.08.005(in press).
- Calder, J., M.M. Roy, and W. Wang, Performance and emissions of a diesel engine fueled by biodiesel-diesel blends with recycled expanded polystyrene and fuel stabilizing additive. Energy, 2018. 149: p. 204-212.DOI: https://doi.org/10.1016/j.energy.2018.02.065.
- Hazrat, M., M. Rasul, M. Khan, N. Ashwath, and T. Rufford, *Emission Characteristics* of Polymer Additive Mixed Diesel-Sunflower Biodiesel Fuel. Energy Procedia, 2019. 156: p. 59-64.
- Zhang, Y., S.K. Mallapragada, and B. Narasimhan, *Dissolution of Styrene–Butadiene* Block Copolymers in Biodiesel. Journal of Applied Polymer Science, 2010. 118: p. 1859-1866.DOI: 10.1002/app.32572.
- 181. Mohammadi, P., A.M. Nikbakht, M. Tabatabaei, and K. Farhadi, A Novel Diesel Fuel Additive to Improve Fuel Properties and to Reduce Emissions. International Journal of Automotive Engineering, 2012. 2(3): p. 156-162.
- 182. Miller-Chou, B.A. and J.L. Koenig, *A review of polymer dissolution*. Prog Polym Sci, 2003. **28**(8): p. 1223-1270.DOI: https://doi.org/10.1016/S0079-6700(03)00045-5.
- 183. Singapati, A.Y., Master of Science, Dissolution of semicrystalline polymers: Numerical modeling and parametric analysis, in Department of Chemical and Biological Engineering. 2015, State University of New York at Buffalo: USA, Database Provider: CQUniversity, Document Number: 1594778, Available from: https://search.proquest.com/docview/1710098149?accountid=10016.
- 184. Narasimhan, B. and N.A. Peppas, *The physics of polymer dissolution: Modeling approaches and experimental behavior*, in *Polymer Analysis Polymer Physics*. 1997, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 157-207.DOI: 10.1007/3-540-61218-1_8. ISBN: 978-3-540-68374-2.
- 185. Miller-Chou, B., PhD, FT-IR imaging of polymer dissolution, in Department of Macromolecular Science and Engineering. 2003, Case Western Reserve University: USA, Database Provider: ProQuest Dissertations Publishing, Available from: https://search.proquest.com/docview/305346561/?pq-origsite=primo.
- Ueberreiter, K. and F. Asmussen, *Velocity of dissolution of polymers. Part I.* J Polym Sci, 1962. 57(165): p. 187-198.DOI: 10.1002/pol.1962.1205716515.
- 187. Narasimhan, B., *Mathematical models describing polymer dissolution: consequences for drug delivery*. Adv Drug Del Rev, 2001. **48**(2): p. 195-210.DOI: https://doi.org/10.1016/S0169-409X(01)00117-X.
- 188. Lodesova, D., A. Lodes, and A. PIkler, *Study of the diffusion process in the dissolution of poly (vinylidene chloride) in streaming organic solvents.* Chem Pap Chem Zvesti, 1978. **32**(2): p. 166-175, https://www.chempap.org/?id=7&paper=5170.

- Mallapragada, S.K. and N.A. Peppas, Crystal unfolding and chain disentanglement during semicrystalline polymer dissolution. AICHE J, 1997. 43(4): p. 870-876.DOI: 10.1002/aic.690430403.
- 190. Mallapragada, S., PhD, *Molecular analysis and experimental investigation of the dissolution mechanism of semicrystalline polymers*. 1996, Purdue University: USA, Database Provider: ProQuest Dissertations Publishing, Available from: https://search.proquest.com/docview/304263466?pq-origsite=primo.
- 191. Zhang, Y., S.K. Mallapragada, and B. Narasimhan, *A Novel High Throughput Method* to Investigate Polymer Dissolution. Macromol Rapid Commun, 2010. **31**: p. 385-390.DOI: 10.1002/marc.200900578.
- 192. Senichev, V.Y. and V.V. Tereshatov, *Effect of System Variables on Solubility*, in *Handbook of Solvents*, 4.2, G. Wypych, Editor. 2001, ChemTec Publishing: New York. p. 124-132, https://chemtec.org/products/1-895198-24-0. ISBN: 1-895198-24-0.
- 193. Kapila, S., V.J. Flanigan, M.F. Maples, and M.W. Mills, *Fatty acid esters to dissolve polystyrene for production of commodity material useful for production of polymers*, U.S. Patent, Editor. 2002, Google Patents: USA. p. 1-5, http://www.google.co.in/patents/US6337413.
- 194. Reduction, M.f.E.a.E., *Fuel Quality Standards (Biodiesel) Determination 2019*. 2019, Australian Government: Australia, https://www.legislation.gov.au/Details/F2019L01268/Download.
- 195. ASTM-D6751-19, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels. 2019, ASTM-International: USA.DOI: 10.1520/D6751-19.
- 196. van Krevelen, D.W., Cohesive Properties and Solubility, in Properties of Polymers Their Correlation With Chemical Structure; Their Numerical Estimation and Prediction From Additive Group Contributions,07, K. Te Nijenhuis, Editor. 2009, Elsevier. p. 189-227.DOI: 10.1016/B978-0-08-054819-7.00007-8. ISBN: 978-0-08-054819-7.
- 197. Bicerano, J., Prediction of polymer properties. 3rd ed., 2002, NY: Marcel Dekker Inc.
- 198. Vasile, C. and A.K. Kulshreshtha, eds. *Handbook of Polymer Blends and Composites*. Vol. 3. 2002, ChemTec Publishing Inc. : India. ISBN: 1-85957-303-7.
- 199. Dee, G.T. and B.B. Sauer, *The cohesive energy density of polymers and its relationship to surface tension, bulk thermodynamic properties, and chain structure.* J Appl Polym Sci, 2017. **134**(5).DOI: 10.1002/app.44431.
- 200. Bozdogan, A.E., A method for determination of thermodynamics and solubility parameters of polymers in dilute solutions from critical volume fractions. Polymer, 2003. 44(20): p. 6427-6430.DOI: https://doi.org/10.1016/S0032-3861(03)00678-5.
- 201. Li, C. and A. Strachan, *Cohesive energy density and solubility parameter evolution during the curing of thermoset.* Polymer, 2018. **135**: p. 162-170.DOI: https://doi.org/10.1016/j.polymer.2017.12.002.
- 202. Marcus, Y., *The internal pressure and cohesive energy density of two inorganic liquids: Bromine and carbon disulfide.* JChTh, 2016. **98**: p. 317-318.DOI: https://doi.org/10.1016/j.jct.2016.03.033.
- 203. Scatchard, G., Equilibria in Non-electrolyte Solutions in Relation to the Vapor Pressures and Densities of the Components. Chem Rev, 1931. 8(2): p. 321-333.DOI: 10.1021/cr60030a010.
- 204. Hildebrand, J.H., *Solubility*. J Am Chem Soc, 1916. **38**(8): p. 1452-1473.DOI: 10.1021/ja02265a002.
- 205. Barton, A.F.M., CRC handbook of solubility parameters and other cohesion parameters. 2nd ed., 1991, USA: CRC Press LLC. ISBN: 0-8493-0176-9.

- 206. Stefanis, E. and C. Panayiotou, *Prediction of Hansen Solubility Parameters with a New Group-Contribution Method*. IJT, 2008. **29**(2): p. 568-585.DOI: 10.1007/s10765-008-0415-z.
- 207. Hansen, C.M., *Hansen Solubility Parameters: A User's Handbook, Second Edition.* 2nd ed.,

http://www.crcpress.com/product/isbn/9780849372483?source=crcpress.com&utm_s ource=productpage&utm_medium=website&utm_campaign=RelatedTitles2007: CRC Press. 544. ISBN: 9780849372483.

- 208. van Krevelen, D.W., Properties of Polymers: Their Correlation with Chemical Structure, Their Numerical Estimation and Prediction from Additive Group Contributions. 4th ed. 10.1016/B978-0-08-054819-7.00007-820092009, UK: Elsevier. ISBN: 978-0-08-054819-7.
- Bozdogan, A.E., A method for determination of thermodynamic and solubility parameters of polymers from temperature and molecular weight dependence of intrinsic viscosity. Polymer, 2004. 45(18): p. 6415-6424.DOI: https://doi.org/10.1016/j.polymer.2004.04.065.
- 210. Database, P. *Cohesive energy density and Hildebrand parameter*. 2015, Available from: https://polymerdatabase.com/polymer%20physics/SolubilityParameter.html.
- 211. Hansen, C.M. and A. Beerbower, *Solubility Parameters*, in *Encyclopaedia of Chemical Technology* Kirk-Othmer, Editor. 1971, Interscience: New York.
- 212. Cataldo, F., Solubility of Fullerenes in Fatty Acids Esters: A New Way to Deliver In Vivo Fullerenes. Theoretical Calculations and Experimental Results, in Medicinal Chemistry and Pharmacological Potential of Fullerenes and Carbon Nanotubes, 13, F. Cataldo and T. Da Ros, Editors. 2008, Springer Netherlands. p. 317-335.DOI: 10.1007/978-1-4020-6845-4_13. ISBN: 978-1-4020-6844-7.
- 213. Hildebrand, J.H. and R.L. Scott, *The solubility of nonelectrolytes*. 3rd ed., http://www.amazon.co.uk/The-Solubility-Nonelectrolytes-Scott-
- Hildebrand/dp/B0007DW68O1950, New York: Reinhold Publishing.
- Senichev, V.Y. and V.V. Tereshatov, 5 Solubility of Selected Systems and Influence of Solutes, in Handbook of Solvents G. Wypych, Editor. 2001, ChemTec Publishing: Canada. p. 243-303.DOI: https://doi.org/10.1016/B978-1-927885-38-3.50006-1. ISBN: 978-1-927885-38-3.
- 215. Ajrash, M.J., M.Sc., Evaluation and prediction of latent heat of vaporization at various temperatures for pure components and binary mixtures, in Chem Eng. 2009, Al-Nahrain University: Iraq, Document Number: 2205, Available from: http://nahrainuniv.edu.iq/en/node/6785.
- 216. Watson, K.M., *Prediction of Critical Temperatures and Heats of Vaporization*. Ind Eng Chem, 1931. **23**(4): p. 360-364.DOI: 10.1021/ie50256a006.
- 217. Fedors, R.F., *A method for estimating both the solubility parameters and molar volumes of liquids*. Polym Eng Sci, 1974. **14**(2): p. 147-154.DOI: 10.1002/pen.760140211.
- 218. Khossravi, D. and K.A. Connors, *Solvent Effects on Chemical Processes, I: Solubility of Aromatic and Heterocyclic Compounds in Binary Aqueous—Organic Solvents.* J Pharm Sci, 1992. **81**(4): p. 371-379.DOI: https://doi.org/10.1002/jps.2600810418.
- 219. van Krevelen, D.W., *Properties of polymers*. 3rd ed., http://dx.doi.org/10.1002/polb.1991.0902913131990, New York: Elsevier Science Publishers. 875. ISBN: 978-0444881601.
- 220. Hansen, C.M., *The Three Dimensional Solubility Parameter and Solvent Diffusion coefficient.* https://hansen-solubility.com/contents/HSP1967-OCR.pdf1967, Copenhagen: Danish Technical Press.

- Machui, F., S. Abbott, D. Waller, M. Koppe, and C.J. Brabec, *Determination of Solubility Parameters for Organic Semiconductor Formulations*. MmCP, 2011. 212(19): p. 2159-2165.DOI: 10.1002/macp.201100284.
- 222. Lindvig, T., M.L. Michelsen, and G.M. Kontogeorgis, *Thermodynamics of paint-related systems with engineering models*. AICHE J, 2001. **47**(11): p. 2573-2584.DOI: 10.1002/aic.690471120.
- Gharagheizi, F. and M. Torabi Angaji, A New Improved Method for Estimating Hansen Solubility Parameters of Polymers. Journal of Macromolecular Science, Part B, 2006.
 45(2): p. 285-290.DOI: 10.1080/00222340500522372.
- 224. Hansen, C.M. and A. Beerbower, *Solubility Parameters*, in *Kirk-Othmer Encycl Chem Technol* A. Standen, Editor. 1971, Interscience: New York. p. 889-910.
- 225. Batista, M.M., R. Guirardello, and M.A. Krähenbühl, *Determination of the Solubility Parameters of Biodiesel from Vegetable Oils*. Energy Fuels, 2013. **27**(12): p. 7497-7509.DOI: 10.1021/ef401690f.
- 226. Refaat, A.A., *Correlation between the chemical structure of biodiesel and its physical properties.* Int J Environ Sci Technol (Tehran), 2009. **6**(4): p. 677-694.DOI: 10.1007/BF03326109.
- 227. Hoftyzer, P.J. and D.W. Van Krevelen, Properties of Polymers, 7. 1976. p. 152-155.
- 228. Small, P.A., *Some factors affecting the solubility of polymers*. J Appl Chem, 1953. **3**(2): p. 71-80.DOI: 10.1002/jctb.5010030205.
- 229. van Krevelen, D.W., Properties of Polymers Their Correlation With Chemical Structure; Their Numerical Estimation and Prediction From Additive Group Contributions 4ed, ed. K. Te Nijenhuis. 10.1016/B978-0-08-054819-7.00007-82009: Elsevier. 1-1031. ISBN: 978-0-08-054819-7.
- 230. Hansen, C.M., *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient. Their Importance in Surface Coating Formulation.* http://hansen-solubility.com/Contents/HSP1967-OCR.pdf1967, Copenhagen: Danish Technical Press.
- 231. Medina Gonzalez, Y., P. de Caro, S. Thiebaud-Roux, and C. Lacaze-Dufaure, *Fatty Acid Methyl Esters as Biosolvents of Epoxy Resins: A Physicochemical Study.* JSCh, 2007. **36**(4): p. 437-446.DOI: 10.1007/s10953-007-9126-5.
- 232. Hoy, K.L., *Solubility Parameter as a Design Parameter for Water Borne Polymers and Coatings.* J Ind Text, 1989. **19**(1): p. 53-67.DOI: 10.1177/152808378901900106.
- 233. Hoy, K.L., *New Values of the Solubility Parameters from Vapor Pressure Data*. Journal of Paint Technology, 1970. **42**(541): p. 76-118.
- 234. Lydersen, A., *Estimation of critical properties of organic compounds*. Univ Wisconsin Coll Eng, Eng Exp Stn Rep 3, 1955.
- 235. Schroeder, D.V., *An Introduction to Thermal Physics*. 2000, USA: Addison Wesley Longman. ISBN: 0-201-38027-7.
- 236. Flory, P.J., *Thermodynamics of High Polymer Solutions*. The Journal of Chemical Physics, 1942. **10**(1): p. 51-61.DOI: 10.1063/1.1723621.
- 237. Flory, P.J., *Principles of polymer chemistry*. 1953, USA: Cornell University Press. ISBN: 0-8014-0134-8.
- 238. Huggins, M.L., *Solutions of Long Chain Compounds*. The Journal of Chemical Physics, 1941. **9**(5): p. 440-440.DOI: 10.1063/1.1750930.
- 239. Huggins, M.L., *The Solubility of Nonelectrolytes. By Joel H. Hildebrand and Robert S. Scott.* The Journal of Physical Chemistry, 1951. **55**(4): p. 619-620.DOI: 10.1021/j150487a027.

- 240. Bristow, G.M. and W.F. Watson, *Cohesive energy densities of polymers. Part 1. Cohesive energy densities of rubbers by swelling measurements.* Trans Faraday Society, 1958. **54**(0): p. 1731-1741.DOI: 10.1039/TF9585401731.
- 241. Lindvig, T., M.L. Michelsen, and G.M. Kontogeorgis, A Flory-Huggins model based on the Hansen solubility parameters. Fluid Phase Equilib, 2002. **203**(1): p. 247-260.DOI: 10.1016/S0378-3812(02)00184-X.
- 242. Sigma-Aldrich, *Fatty acid standards*. 2014, Sigma-Aldrich Co. LLC.: USA, http://www.sigmaaldrich.com/catalog/product/supelco/1894?lang=en®ion=AU.
- 243. Lacey, P. and S. Westbrook, *Diesel Fuel Lubricity*. SAE Technical Paper, 1995. 10.4271/950248(950248).DOI: 10.4271/950248.
- 244. Wildes, S., *Methyl soyate: A new green alternative solvent*. Chem Health Saf, 2002. **9**(3): p. 24-26.DOI: http://dx.doi.org/10.1016/S1074-9098(02)00292-7.
- 245. Cataldo, F. and T. Braun, *The Solubility of C60 Fullerene in Long Chain Fatty Acids Esters.* Fullerenes, Nanotubes and Carbon Nanostructures, 2007. **15**(5): p. 331-339.DOI: 10.1080/15363830701512450.
- 246. Hu, Du, Z. Tang, and Min, *Study on the Solvent Power of a New Green Solvent: Biodiesel.* Ind Eng Chem Res, 2004. **43**(24): p. 7928-7931.DOI: 10.1021/ie0493816.
- 247. Kerton, F.M., Alternative Solvents for Green Chemistry. RSC Green Chemistry Book Series, ed. J.H. Clark and G.A. Kraus. 2009, UK: Royal Society of Chemistry. 238. ISBN: 978-0-85404-163-3.
- 248. Pereira, C.S.M., V.M.T.M. Silva, and A.E. Rodrigues, *Ethyl lactate as a solvent: Properties, applications and production processes - a review.* Green Chem, 2011.
 13(10): p. 2658-2671.DOI: 10.1039/C1GC15523G.
- 249. Greenhalgh, D.J., A.C. Williams, P. Timmins, and P. York, *Solubility parameters as predictors of miscibility in solid dispersions*. J Pharm Sci, 1999. **88**(11): p. 1182-1190.DOI: 10.1021/js9900856.
- 250. Bagley, E., T. Nelson, and J. Scigliano, *Three-dimensional solubility parameters and their relationship to internal pressure measurements in polar and hydrogen bonding solvents*. Journal of paint technology, 1971. **43**(555): p. 35-42.
- 251. Seymour, R.B., *Plastics Versus Corrosives (SPE monographs)*. 1982, USA: John Wiley & Sons Inc. ISBN: 10: 0471081825.
- 252. Elidrissi, A., S. El barkany, H. Amhamdi, A. Maaroufi, and B. Hammouti, New Approach to Prdict the Solubility of Polymers Application: Cellulose Acetate at Various DS, Prepared from Alfa "Stipa-tenassicima" of Eastern Morocco. J Mater Environ Sci, 2012. 3(2): p. 270-285, http://www.jmaterenvironsci.com/Document/vol3/vol3_N2/26-JMES-123-2011-Elidrissi.pdf.
- Thangaraj, B., P.R. Solomon, B. Muniyandi, S. Ranganathan, and L. Lin, *Catalysis in biodiesel production—a review*. Clean Energy, 2019. 3(1): p. 2-23.DOI: 10.1093/ce/zky020.
- 254. Chouhan, A.P.S. and A.K. Sarma, *Modern heterogeneous catalysts for biodiesel production: A comprehensive review*. Renewable Sustainable Energy Rev, 2011. 15(9): p. 4378-4399.DOI: 10.1016/j.rser.2011.07.112.
- 255. Atabani, A.E., A.S. Silitonga, I.A. Badruddin, T.M.I. Mahlia, H.H. Masjuki, and S. Mekhilef, A comprehensive review on biodiesel as an alternative energy resource and its characteristics. Renewable Sustainable Energy Rev, 2012. 16(4): p. 2070-2093.DOI: http://dx.doi.org/10.1016/j.rser.2012.01.003.
- 256. Ong, H.C., H.H. Masjuki, T.M.I. Mahlia, A.S. Silitonga, W.T. Chong, and K.Y. Leong, *Optimization of biodiesel production and engine performance from high free fatty acid*

Calophyllum inophyllum oil in CI diesel engine. Energy Convers Manage, 2014. **81**(0): p. 30-40.DOI: http://dx.doi.org/10.1016/j.enconman.2014.01.065.

- Sahoo, P.K., L.M. Das, M.K.G. Babu, and S.N. Naik, *Biodiesel development from high acid value polanga seed oil and performance evaluation in a CI engine*. Fuel, 2007. 86(3): p. 448-454.DOI: http://dx.doi.org/10.1016/j.fuel.2006.07.025.
- 258. Demirbas, A., *Biodiesel from waste cooking oil via base-catalytic and supercritical methanol transesterification*. Energy Convers Manage, 2009. **50**(4): p. 923-927.DOI: http://dx.doi.org/10.1016/j.enconman.2008.12.023.
- 259. Bhale, P.V., N.V. Deshpande, and S.B. Thombre, *Improving the low temperature properties of biodiesel fuel.* Renewable Energy, 2009. **34**(3): p. 794-800.DOI: http://dx.doi.org/10.1016/j.renene.2008.04.037.
- 260. Sahoo, P.K. and L.M. Das, *Combustion analysis of Jatropha, Karanja and Polanga based biodiesel as fuel in a diesel engine*. Fuel, 2009. **88**(6): p. 994-999.DOI: http://dx.doi.org/10.1016/j.fuel.2008.11.012.
- Atabani, A.E., T.M.I. Mahlia, I. Anjum Badruddin, H.H. Masjuki, W.T. Chong, and K.T. Lee, *Investigation of physical and chemical properties of potential edible and nonedible feedstocks for biodiesel production, a comparative analysis.* Renewable Sustainable Energy Rev, 2013. 21(0): p. 749-755.DOI: http://dx.doi.org/10.1016/j.rser.2013.01.027.
- 262. Energy, F. *Energy in Soybean Crushing and Transesterification*. 2012, Available from: http://www.extension.org/pages/26610/energy-in-soybean-crushing-and-transesterification. Access Date: 11/03/2014.
- 263. Al-Hamamre, Z. and J. Yamin, Parametric study of the alkali catalyzed transesterification of waste frying oil for Biodiesel production. Energy Convers Manage, 2014. 79(0): p. 246-254.DOI: http://dx.doi.org/10.1016/j.enconman.2013.12.027.
- 264. Viele, E.L., F.O. Chukwuma, and L. Uyigue, *Esterification of High Free Fatty Acid Crude Palm Kernel Oil as Feedstock for Base-Catalyzed Transesterification Reaction*. International Journal of Application or Innovation in Engineering & Management (IJAIEM), 2013. 2(12): p. 361-365, http://www.ijaiem.org/volume2issue12/IJAIEM-2013-12-31-100.pdf.
- Bazina, N. and J. He, Analysis of fatty acid profiles of free fatty acids generated in deepfrying process. J Food Sci Technol, 2018. 55(8): p. 3085-3092.DOI: 10.1007/s13197-018-3232-9.
- 266. Eze, V.C., A.P. Harvey, and A.N. Phan, *Determination of the kinetics of biodiesel* saponification in alcoholic hydroxide solutions. Fuel, 2015. **140**: p. 724-730.DOI: https://doi.org/10.1016/j.fuel.2014.10.001.
- 267. Theodorou, V., K. Skobridis, A.G. Tzakos, and V. Ragoussis, *A simple method for the alkaline hydrolysis of esters*. Tetrahedron Lett, 2007. **48**(46): p. 8230-8233.DOI: https://doi.org/10.1016/j.tetlet.2007.09.074.
- 268. Alenezi, R., M. Baig, J. Wang, R. Santos, and G. Leeke, *Continuous Flow Hydrolysis* of Sunflower Oil for Biodiesel. Energy Sources Part A Recovery Utilization and Environmental Effects, 2010. **32**: p. 460-468.DOI: 10.1080/15567030802612341.
- 269. Das, S., A.J. Thakur, and D. Deka, *Two-Stage Conversion of High Free Fatty Acid Jatropha curcas Oil to Biodiesel Using Brønsted Acidic Ionic Liquid and KOH as Catalysts*. The Scientific World Journal, 2014. **2014**: p. 9.DOI: 10.1155/2014/180983.
- Huber, G.W., S. Iborra, and A. Corma, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. Chem Rev, 2006. 106(9): p. 4044-4098.DOI: 10.1021/cr068360d.

- 271. Canakci, M. and J. van Gerpen, *Biodiesel Production from Oils and Fats with High Free Fatty Acids*. Trans ASAE, 2001. **44**(6): p. 1429-1436, http://seniordesign.engr.uidaho.edu/2007_2008/frenchfryfuel/paper_2.pdf.
- 272. ASTM, D664-04: Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration. 2004, ASTM International: USA.
- 273. Pomeranz, Y., *Food Analysis: Theory and Practice*. https://books.google.com.au/books?id=uOjiBwAAQBAJ2013: Springer US. ISBN: 9781461569985.
- 274. Saydut, A., A.B. Kafadar, F. Aydin, S. Erdogan, C. Kaya, and C. Hamamci, *Effect of homogeneous alkaline catalyst type on biodiesel production from soybean [Glycine max (L.) Merrill] oil.* Indian J Biotechnol, 2016. **15**: p. 596-600, http://nopr.niscair.res.in/handle/123456789/41020.
- 275. Aranda, D.A.G., R.T.P. Santos, N.C.O. Tapanes, A.L.D. Ramos, and O.A.C. Antunes, *Acid-Catalyzed Homogeneous Esterification Reaction for Biodiesel Production from Palm Fatty Acids*. CatL, 2008. **122**(1-2): p. 20-25.DOI: 10.1007/s10562-007-9318-z.
- 276. Hayyan, A., M.Z. Alam, M.E.S. Mirghani, N.A. Kabbashi, N.I.N.M. Hakimi, Y.M. Siran, and S. Tahiruddin, *Sludge palm oil as a renewable raw material for biodiesel production by two-step processes*. Bioresour Technol, 2010. **101**(20): p. 7804-7811.DOI: 10.1016/j.biortech.2010.05.045.
- 277. Romero, R., S.L. Martínez, and R. Natividad, *Biodiesel Production by Using Heterogeneous Catalysts*, in *Alternative Fuel* M. Manzanera, Editor. 2011, IntechOpen.DOI: 10.5772/23908.
- 278. Aghel, B., M. Mohadesi, and S. Sahraei, *Effect of Different Cosolvents on Transesterification of Waste Cooking Oil in a Microreactor*. Chemical Engineering & Technology, 2018. **41**(3): p. 598-605.DOI: 10.1002/ceat.201700025.
- 279. Sharma, S., V. Saxena, A. Baranwal, P. Chandra, and L.M. Pandey, *Engineered nanoporous materials mediated heterogeneous catalysts and their implications in biodiesel production*. Mater Sci Energy Technol, 2018. 1: p. 11-21.DOI: 10.1016/j.mset.2018.05.002.
- Xie, W., X. Huang, and H. Li, Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst. Bioresour Technol, 2007. 98(4): p. 936-939.DOI: https://doi.org/10.1016/j.biortech.2006.04.003.
- 281. Marwaha, A., A. Dhir, S.K. Mahla, and S.K. Mohapatra, *An overview of solid base heterogeneous catalysts for biodiesel production*. CarRv, 2018. **60**(4): p. 594-628.DOI: 10.1080/01614940.2018.1494782.
- 282. Khurshid, S.N.A., MSc., Biodiesel production by using heterogeneous catalyst, in Department of Chemical Engineering and Technology. 2014, Royal Institute of Technology (KTH), Available from: https://www.divaportal.org/smash/get/diva2:721123/FULLTEXT01.pdf.
- 283. Nasreen, S., M. Nafees, L.A. Qureshi, M.S. Asad, A. Sadiq, and S.D. Ali, *Review of Catalytic Transesterification Methods for Biodiesel Production*. 2018, InTech.DOI: 10.5772/intechopen.75534.
- Lee, A.F., J.A. Bennett, J.C. Manayil, and K. Wilson, *Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification*. ChSRv, 2014. 43: p. 7887-7916.DOI: 10.1039/C4CS00189C.
- 285. Haigh, K.F., G.T. Vladisavljević, J.C. Reynolds, Z. Nagy, and B. Saha, *Kinetics of the pre-treatment of used cooking oil using Novozyme 435 for biodiesel production*. Chem Eng Res Des, 2014. 92(4): p. 713-719.DOI: https://doi.org/10.1016/j.cherd.2014.01.006.
- 286. Kusdiana, D. and S. Saka, *Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol.* Fuel, 2001. **80**(5): p. 693-698.DOI: https://doi.org/10.1016/S0016-2361(00)00140-X.
- 287. Babcock, R., P. I. E. C. Clausen, M. Popp, and I. W. Brent Schulte, Yield Characteristics of Biodiesel Produced from Chicken Fat-Tall Oil Blended Feedstocks. 2008, University of Arkansas: USA. Report Number: Project Number MBTC-2092. Available https://www.researchgate.net/publication/253638502_Yield_Characteristics_of_Biodi esel_Produced_from_Chicken_Fat-Tall_Oil_Blended_Feedstocks.
- 288. Permsuwan, A., N. Tippayawong, T. Kiatsiriroat, C. Thararux, and S. Wangkarn, *Reaction Kinetics of Transesterification Between Palm Oil and Methanol under Subcritical Conditions*. Energy Science and Technology, 2011. **2**(1): p. 35-42.DOI: http://dx.doi.org/10.3968/j.est.1923847920110201.672.
- 289. Alleman, T.L., R.L. McCormick, E.D. Christensen, G. Fioroni, K. Moriarty, and J. Yanowitz, *Biodiesel Handling and Use Guide (Fifth Edition)*. 2016, United States Department of Energy (USDOE): USA. Report Number: DOE/GO-102016-4875. USDOE Available from: https://afdc.energy.gov/files/u/publication/biodiesel handling use guide.pdf.
- 290. Jääskeläinen, H. *Biodiesel Standards & Properties*. 2009. https://www.dieselnet.com/tech/fuel_biodiesel_std.php.
- 291. Alleman, T.L., L. Fouts, and G. Chupka, *Quality Parameters and Chemical Analysis* for Biodiesel Produced in the United States in 2011. 2013, National Renewable Energy Laboratory (NREL). Report Number: NREL/TP-5400-57662. Available from: https://www.nrel.gov/docs/fy130sti/57662.pdf.
- 292. Rutz, D. and R. Janssen, *Overview and Recommendations on Biofuel Standards for Transport in the EU*, in *Project: BiofuelMarketplace*. 2006, WIP Renewable Energies: Germany. Report Number: EIE/05/022/SI2.420009. Available from: https://ec.europa.eu/energy/intelligent/projects/sites/ieeprojects/files/projects/documents/biofuel_marketplace_biofuel_standards_for_transpo rt_in_the_eu.pdf.
- 293. CEN, EN 14214:2012 Liquid petroleum products Fatty acid methyl esters (FAME) for use in diesel engines and heating applications - Requirements and test methods, in IS EN 14214:2012+A1:2014&AC:2014. 2012, European Committee For Standardization: Belgium. Available from: https://infostore.saiglobal.com/preview/98708742874.pdf?sku=861350_SAIG_NSAI_ NSAI_2049227.
- 294. SA.GOV.AU. *Biodiesel (B5, B20 and B100)*. Available from: https://www.lowemissionvehicles.sa.gov.au/knowledge_bank/transport_fuels/biodiese 1_b5,_b20_and_b100.
- 295. Schober, S., I. Seidl, and M. Mittelbach, *Ester content evaluation in biodiesel from animal fats and lauric oils*. Eur J Lipid Sci Technol, 2006. **108**(4): p. 309-314.DOI: 10.1002/ejlt.200500324.
- 296.Chin, H.-L.L., N. Lingga, and C. Lahey Determination of FAME Content in Palm Oil
Biodiesel by Gas Chromatography.2008.https://solutions.shimadzu.co.jp/an/n/en/gc/apc108006.pdf.2008.
- 297. ASTM, Designation: E2997–16: Standard Test Method for Analysis of Biodiesel Products by Gas ChromatographyMass Spectrometry. 2016, ASTM International: USA.DOI: 10.1520/E2997-16.
- 298. Kalayasiri, P., N. Jeyashoke, and K. Krisnangkura, *Survey of seed oils for use as diesel fuels*. Journal of the American Oil Chemists' Society, 1996. **73**(4): p. 471-474.

- 299. Mohibbe Azam, M., A. Waris, and N.M. Nahar, Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. Biomass Bioenergy, 2005. 29(4): p. 293-302.DOI: https://doi.org/10.1016/j.biombioe.2005.05.001.
- 300. Krisnangkura, K., A simple method for estimation of cetane index of vegetable oil methyl esters. J Am Oil Chem Soc, 1986. **63**(4): p. 552-553.
- 301. Giakoumis, E.G. and C.K. Sarakatsanis, *Estimation of biodiesel cetane number, density, kinematic viscosity and heating values from its fatty acid weight composition.* Fuel, 2018. 222: p. 574-585.DOI: https://doi.org/10.1016/j.fuel.2018.02.187.
- 302. Andreo-Martínez, P., N. García-Martínez, M.d.M. Durán-del-Amor, and J. Quesada-Medina, Advances on kinetics and thermodynamics of non-catalytic supercritical methanol transesterification of some vegetable oils to biodiesel. Energy Convers Manage, 2018. 173: p. 187-196.DOI: https://doi.org/10.1016/j.enconman.2018.07.069.
- 303. Zeng, Z., L. Cui, W. Xue, J. Chen, and Y. Che, *Recent Developments on the Mechanism and Kinetics of Esterification Reaction Promoted by Various Catalysts* in *Chemical Kinetics*, 12, V. Patel, Editor. 2012, InTech: Croatia, http://library.umac.mo/ebooks/b28113640.pdf. ISBN: 978-953-51-0132-1.
- 304. Bates, D.M. and D.G. Watts, Nonlinear Regression Analysis and Its Applications. Wiley Series in Probability and Statistics. 10.1002/97804703167571988: John Wiley & Sons, Inc. ISBN: 9780470316757
- 305. Freedman, B., E.H. Pryde, and T.L. Mounts, *Variables affecting the yields of fatty esters from transesterified vegetable oils*. J Am Oil Chem Soc, 1984. **61**(10): p. 1638-1643.DOI: 10.1007/BF02541649.
- 306. Anwar, M., M. Rasul, N. Ashwath, and M.M. Rahman, *Optimisation of Second-Generation Biodiesel Production from Australian Native Stone Fruit Oil Using Response Surface Method.* Vol. 11. 2018. 2566.
- 307. Kostić, M.D., A.V. Veličković, N.M. Joković, O.S. Stamenković, and V.B. Veljković, Optimization and kinetic modeling of esterification of the oil obtained from waste plum stones as a pretreatment step in biodiesel production. Waste Manage, 2016. 48: p. 619-629.DOI: https://doi.org/10.1016/j.wasman.2015.11.052.
- 308. Hasni, K., Z. Ilham, S. Dharma, and M. Varman, Optimization of biodiesel production from Brucea javanica seeds oil as novel non-edible feedstock using response surface methodology. Energy Convers Manage, 2017. 149: p. 392-400.DOI: https://doi.org/10.1016/j.enconman.2017.07.037.
- 309. Milano, J., H.C. Ong, H.H. Masjuki, A.S. Silitonga, W.-H. Chen, F. Kusumo, S. Dharma, and A.H. Sebayang, *Optimization of biodiesel production by microwave irradiation-assisted transesterification for waste cooking oil-Calophyllum inophyllum oil via response surface methodology*. Energy Convers Manage, 2018. **158**: p. 400-415.DOI: https://doi.org/10.1016/j.enconman.2017.12.027.
- 310. Sastri, V.S., J.-C. BÜNzli, V.R. Rao, G.V.S. Rayudu, and J.R. Perumareddi, *chapter 7 Kinetics And Mechanisms of Rare Earth Complexation*, in *Modern Aspects of Rare Earths and Their Complexes* V.S. Sastri, J.-C. BÜNzli, V.R. Rao, G.V.S. Rayudu, and J.R. Perumareddi, Editors. 2003, Elsevier: Amsterdam. p. 481-567.DOI: https://doi.org/10.1016/B978-044451010-5/50021-3. ISBN: 978-0-444-51010-5.
- 311. El Seoud, O.A., W.J. Baader, and E.L. Bastos, *Practical Chemical Kinetics in Solution*, in *Encyclopedia of Physical Organic Chemistry* Z. Wang, U. Wille, and E. Juaristi, Editors. 2016, John Wiley & Sons, Inc. p. 1-68.DOI: 10.1002/9781118468586.epoc1012.
- 312. Ptáček, P., T. Opravil, and F. Šoukal, A Brief Introduction to the History of Chemical Kinetics, in Introducing the Effective Mass of Activated Complex and the Discussion

on the Wave Function of this Instanton,1, P. Ptáček, Editor. 2018, Intechopen. p. 1-25.DOI: http://dx.doi.org/10.5772/intechopen.78704.

- Alexander, A. and R. Zare, *Anatomy of an Elementary Chemical Reaction*. Journal of Chemical Education - J CHEM EDUC, 1998. **75**(9): p. 1105-1118.DOI: 10.1021/ed075p1105.
- 314. Zhou, L., Master of Applied Science, Reaction Kinetics of Biodiesel Production by Using Low Quality Feedstock, in Environmental Systems Engineering. 2013, University of Regina: Regina, Saskatchewan, Available from: https://ourspace.uregina.ca/bitstream/handle/10294/5484/Zhou_Ling_200260947_MA SC_EVSE_Spring2014.pdf.
- 315. Berrios, M., J. Siles, M.A. Martín, and A. Martín, *A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil.* Fuel, 2007. **86**(15): p. 2383-2388.DOI: https://doi.org/10.1016/j.fuel.2007.02.002.
- 316. Ma, F., L.D. Clements, and M.A. Hanna, *The effect of mixing on transesterification of beef tallow*. Bioresour Technol, 1999. **69**(3): p. 289-293.DOI: https://doi.org/10.1016/S0960-8524(98)00184-9.
- 317. Fischer, E. and A. Speier, *Darstellung der Ester*. Ber Dtsch Chem Ges, 1895. **28**(3): p. 3252-3258.DOI: 10.1002/cber.189502803176.
- 318. Gjiri, E. *The Fischer esterification*. Available from: https://www.name-reaction.com/fischer-esterification. Access Date: 11/02.
- Sarve, A., M.N. Varma, and S.S. Sonawane, Optimization and Kinetic Studies on Biodiesel Production from Kusum (Schleichera triguga) Oil Using Response Surface Methodology. J Oleo Sci, 2015. 64(9): p. 987-997.DOI: https://doi.org/10.5650/jos.ess15069.
- 320. Berrios, M., J. Siles, M. Martin, and A. Martin, *A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil.* Fuel, 2007. **86**(15): p. 2383-2388.DOI: 10.1016/j.fuel.2007.02.002.
- 321. Prasanna Rani, K.N., T.S.V. Ramana Neeharika, T.P. Kumar, B. Satyavathi, and C. Sailu, *Kinetics of Non-Catalytic Esterification of Free Fatty Acids Present in Jatropha Oil.* J Oleo Sci, 2016. 65(5): p. 441-445.DOI: 10.5650/jos.ess15255.
- 322. Su, C.-H., *Kinetic study of free fatty acid esterification reaction catalyzed by recoverable and reusable hydrochloric acid.* Bioresour Technol, 2013. **130**: p. 522-528.DOI: https://doi.org/10.1016/j.biortech.2012.12.090.
- 323. Trinh, H., S. Yusup, and Y. Uemura, *Optimization and kinetic study of ultrasonic assisted esterification process from rubber seed oil*. Bioresour Technol, 2018. **247**: p. 51-57.DOI: 10.1016/j.biortech.2017.09.075.
- 324. Cheng, J., Y. Li, S. He, W. Shen, Y. Liu, and Y. Song, *Reaction Kinetics of Transesterification between Vegetable Oil and Methanol under Supercritical Conditions*. Energy Sources Part A, 2008. **30**(8): p. 681-688.DOI: 10.1080/15567030601082084.
- 325. Lieu, T., S. Yusup, and M. Moniruzzaman, *Kinetic study on microwave-assisted esterification of free fatty acids derived from Ceiba pentandra Seed Oil.* Bioresour Technol, 2016. **211**: p. 248-256.DOI: https://doi.org/10.1016/j.biortech.2016.03.105.
- Ataya, F., M. Dubé, and M. Ternan, Acid-Catalyzed Transesterification of Canola Oil to Biodiesel under Single- and Two-Phase Reaction Conditions. Energy Fuels, 2007. 21(4).DOI: 10.1021/ef0701440.
- 327. Sendzikiene, E., V. Makareviciene, P. Janulis, and S. Kitrys, *Kinetics of free fatty acids esterification with methanol in the production of biodiesel fuel*. Eur J Lipid Sci Technol, 2004. **106**(12): p. 831-836.DOI: 10.1002/ejlt.200401011.

- 328. Kocsisová, T., J. Cvengroš, and J. Lutišan, *High-temperature esterification of fatty acids with methanol at ambient pressure*. Eur J Lipid Sci Technol, 2005. **107**(2): p. 87-92.DOI: 10.1002/ejlt.200401077.
- 329. L. Cardoso, A., S. Braga, and M. da Silva, *Esterification of Oleic Acid for Biodiesel Production Catalyzed by SnCl2: A Kinetic Investigation*. Energies, 2008. 1(2).DOI: 10.3390/en1020079.
- 330. Diasakou, M., A. Louloudi, and N. Papayannakos, *Kinetics of the non-catalytic transesterification of soybean oil.* Fuel, 1998. **77**(12): p. 1297-1302.DOI: https://doi.org/10.1016/S0016-2361(98)00025-8.
- 331. Sivakumar, P., S. Sindhanaiselvan, N.N. Gandhi, S.S. Devi, and S. Renganathan, *Optimization and kinetic studies on biodiesel production from underutilized Ceiba Pentandra oil.* Fuel, 2013. 103: p. 693-698.DOI: https://doi.org/10.1016/j.fuel.2012.06.029.
- 332. Araújo, B.Q., R.C.d.R. Nunes, C.V.R. de Moura, E.M. de Moura, A.M.d.G.L. Citó, and J.R. dos Santos Júnior, *Synthesis and Characterization of Beef Tallow Biodiesel*. Energy Fuels, 2010. 24(8): p. 4476-4480.DOI: 10.1021/ef1004013.
- 333. Rincón, L.E., J.J. Jaramillo, and C.A. Cardona, Comparison of feedstocks and technologies for biodiesel production: An environmental and techno-economic evaluation. Renewable Energy, 2014. 69(Comparison of feedstocks and technologies for biodiesel production: An environmental and techno-economic evaluation): p. 479-487.DOI: https://doi.org/10.1016/j.renene.2014.03.058.
- Bencinar, J.M., N. Sánchez, G. Martínez, and L. García, *Study of biodiesel production from animal fats with high free fatty acid content*. Bioresour Technol, 2011. 102(23): p. 10907-10914.DOI: https://doi.org/10.1016/j.biortech.2011.09.068.
- 335. Doğan, T.H. and H. Temur, *Effect of fractional winterization of beef tallow biodiesel* on the cold flow properties and viscosity. Fuel, 2013. **108**: p. 793-796.DOI: https://doi.org/10.1016/j.fuel.2013.02.028.
- 336. Chuah, L.F., A. Bokhari, S. Yusup, J.J. Klemeš, B. Abdullah, and M.M. Akbar, *Optimisation and Kinetic Studies of Acid Esterification of High Free Fatty Acid Rubber Seed Oil.* Arabian Journal for Science and Engineering, 2016. **41**(7): p. 2515-2526.DOI: 10.1007/s13369-015-2014-1.
- Chai, M., Q. Tu, M. Lu, and Y.J. Yang, *Esterification pretreatment of free fatty acid in biodiesel production, from laboratory to industry*. Fuel Process Technol, 2014. 125: p. 106–113.DOI: 10.1016/j.fuproc.2014.03.025.
- 338. Öner, C. and Ş. Altun, Biodiesel production from inedible animal tallow and an experimental investigation of its use as alternative fuel in a direct injection diesel engine. ApEn, 2009. 86(10): p. 2114-2120.DOI: https://doi.org/10.1016/j.apenergy.2009.01.005.
- 339. Peng-Lim, B., S. Ganesan, G.P. Maniam, and M. Khairuddean, *Sequential conversion of high free fatty acid oils into biodiesel using a new catalyst system*. Energy, 2012. 46(1): p. 132-139.DOI: https://doi.org/10.1016/j.energy.2012.09.013.
- 340. Ma, F., L. D. Clements, and M. A. Hanna, *The Effects of Catalyst, Free Fatty Acids, and Water on Transesterification of Beef Tallow*. Trans ASAE, 1998. **41**(5): p. 1261-1264.DOI: https://doi.org/10.13031/2013.17292.
- 341. Ferdous, K., A. Deb, J. Rumky, M. Uddin, M. Khan, and M.A. Islam, Preparation of Biodiesel from Higher FFA Containing Castor Oil. Int J Sci Eng Res, 2013. 4: p. 401-406.
- 342. Nasreen, S., M. Nafees, L.A. Qureshi, M.S. Asad, A. Sadiq, and S.D. Ali, *Review of Catalytic Transesterification Methods for Biodiesel Production*, in *Biofuels: State of*

Development,6, K. Biernat, Editor. 2018, IntechOpen. p. 93-119.DOI: 10.5772/intechopen.75534. ISBN: 978-1-78923-347-6.

- Banga, S. and P. Varshney, *Effect of impurities on performance of biodiesel: A review*.
 J Sci Ind Res, 2010. 69: p. 575-579, https://www.researchgate.net/publication/228859806_Effect_of_impurities_on_perfor mance_of_biodiesel_A_review.
- 344. Trejo-Zárraga, F., F.d.J. Hernández-Loyo, J.C. Chavarría-Hernández, and R. Sotelo-Boyás, *Kinetics of Transesterification Processes for Biodiesel Production*, in *Biofuels* State of Development K. Biernat, Editor. 2018, IntechOpen.DOI: 10.5772/intechopen.75927.
- 345. Xinyu, Z., X. Guizhuan, Y. Yongchang, Y. Xiaobin, and Z. Bailiang, Optimization of transesterification of beef tallow for biodiesel production catalyzed by solid catalysts. Transactions of the Chinese Society of Agricultural Engineering, 2013. 29(17): p. 196-203.DOI: 10.3969/j.issn.1002-6819.2013.17.026
- 346. LLC., M. *Interpret all statistics and graphs for Simple Regression*. Minitab Express Support 2019, Available from: https://support.minitab.com/en-us/minitab-express/1/help-and-how-to/modeling-statistics/regression/how-to/simple-regression/interpret-the-results/all-statistics-and-graphs/#vif. Access Date: 08/03.
- 347. Zhang, Y., S.K. Mallapragada, and B. Narasimhan, *Dissolution of waste plastics in biodiesel*. Polym Eng Sci, 2010. **50**(5): p. 863-870.DOI: 10.1002/pen.21598.
- 348. Búcsi, A., J. Oremusová, and D. Uhríková *Kinetics of Dissolution of Solid Substances*. Class Tutorial Exercise. https://www.fpharm.uniba.sk/fileadmin/faf/Pracoviskasubory/KFCHL/ENG/lectures/Physical_Chemistry/Exercise_4___Kinetics_of_dissolu tion_of_solid_substances.pdf.
- 349. COMSOL, *Diffusion Equation*, in *Multiphysics Cyclopedia*. 2015, COMSOL Inc., https://www.comsol.com/multiphysics/diffusion-equation.
- 350. Shi, Y., A. Wan, Y. Shi, Y. Zhang, and Y. Chen, *Experimental and Mathematical Studies on the Drug Release Properties of Aspirin Loaded Chitosan Nanoparticles*. Biomed Res Int, 2014. **2014**: p. 8.DOI: 10.1155/2014/613619.
- 351. McMahon, N., PhD, *The Mechanics of Drug Dissolution*, in *School of Computing*. 2008, Dublin City University: Ireland, Available from: http://doras.dcu.ie/590/1/nmcmahon_2008.pdf.
- 352. Noyes, A.A. and W.R. Whitney, *The rate of solution of solid substances in their own solutions*. J Am Chem Soc, 1897. **19**(12): p. 930-934.DOI: 10.1021/ja02086a003.
- 353. Smith, B.T., *Solubility and dissolution*, in *Physical Pharmacy*, 3, R. Education, Editor. 2016, Pharmaceutical Press: USA. p. 31-50, https://www.pharmpress.com/files/docs/remington-education-physical-pharmacysample-chapter-3.pdf.
- 354. Dokoumetzidis, A. and P. Macheras, *A century of dissolution research: From Noyes and Whitney to the Biopharmaceutics Classification System.* Int J Pharm, 2006. **321**(1): p. 1-11.DOI: https://doi.org/10.1016/j.ijpharm.2006.07.011.
- 355. Lu, J.X. and J. Murray, *Biochemistry, Dissolution and Solubility*, in *NCBI Bookshelf*. Updated 2019, StatPearls Publishing LLC: USA, https://www.ncbi.nlm.nih.gov/books/NBK431100/.
- 356. Jarusuwannapoom, T., W. Hongrojjanawiwat, S. Jitjaicham, L. Wannatong, M. Nithitanakul, C. Pattamaprom, P. Koombhongse, R. Rangkupan, and P. Supaphol, *Effect of solvents on electro-spinnabilityof polystyrene solutions and morphological appearance of resulting electrospun polystyrene fibers*. Eur Polym J, 2005. **41**: p. 409-421.DOI: 10.1016/j.eurpolymj.2004.10.010.

- 357. TFX. TFX Engine Pressure Analysis Systems In Cylinder Pressures (ICP) & In Port Pressures (IPP). Available from: https://www.tfxengine.com/.
- 358. Kubota Operator's Manual Kubota Diesel Engine. 2013. https://www.kubota.com.au/wp-content/uploads/2015/10/V3300.V3800.V3300-T.V3800-T.pdf.
- 359. Yamada, H., K. Misawa, D. Suzuki, K. Tanaka, J. Matsumoto, M. Fujii, and K. Tanaka, *Detailed analysis of diesel vehicle exhaust emissions: Nitrogen oxides, hydrocarbons and particulate size distributions.* Proc Combust Inst, 2011. **33**(2): p. 2895-2902.DOI: https://doi.org/10.1016/j.proci.2010.07.001.
- 360. Lapuerta, M., O. Armas, and J. Rodríguez-Fernández, *Effect of biodiesel fuels on diesel engine emissions*. PrECS, 2008. **34**(2): p. 198-223.DOI: http://dx.doi.org/10.1016/j.pecs.2007.07.001.
- Srinivasan, G.R., V. Shankar, and R. Jambulingam, *Experimental study on influence of dominant fatty acid esters in engine characteristics of waste beef tallow biodiesel.* Energy Explor Exploit, 2019. **37**(3): p. 1098-1124.DOI: 10.1177/0144598718821791.
- Jambulingam, R., V. Shankar, S. Palani, and G.R. Srinivasan, *Effect of Dominant Fatty Acid Esters on Emission Characteristics of Waste Animal Fat Biodiesel in CI Engine*. Front Energy Res, 2019. 7: p. 63, https://www.frontiersin.org/article/10.3389/fenrg.2019.00063.
- 363. Ashok, B. and K. Nanthagopal, 15 Eco friendly biofuels for CI engine applications, in Advances in Eco-Fuels for a Sustainable Environment K. Azad, Editor. 2019, Woodhead Publishing. p. 407-440.DOI: https://doi.org/10.1016/B978-0-08-102728-8.00015-2. ISBN: 978-0-08-102728-8.
- 364. Palash, S.M., M.A. Kalam, H.H. Masjuki, M.I. Arbab, B.M. Masum, and A. Sanjid, Impacts of NOx reducing antioxidant additive on performance and emissions of a multicylinder diesel engine fueled with Jatropha biodiesel blends. Energy Convers Manage, 2014. 77(0): p. 577-585.DOI: http://dx.doi.org/10.1016/j.enconman.2013.10.016.
- 365. Tan, P.-q., Z.-y. Hu, D.-m. Lou, and Z.-j. Li, *Exhaust emissions from a light-duty diesel* engine with Jatropha biodiesel fuel. Energy, 2012. **39**(1): p. 356-362.DOI: http://dx.doi.org/10.1016/j.energy.2012.01.002.
- 366. Abed, K.A., A.K. El Morsi, M.M. Sayed, A.A.E. Shaib, and M.S. Gad, *Effect of waste cooking-oil biodiesel on performance and exhaust emissions of a diesel engine*. Egypt J Pet, 2018. **27**(4): p. 985-989.DOI: https://doi.org/10.1016/j.ejpe.2018.02.008.
- 367. Vijay Kumar, M., A. Veeresh Babu, and P. Ravi Kumar, *The impacts on combustion, performance and emissions of biodiesel by using additives in direct injection diesel engine*. Alexandria Engineering Journal, 2018. 57(1): p. 509-516.DOI: https://doi.org/10.1016/j.aej.2016.12.016.
- 368. Ong, H.C., H.H. Masjuki, T.M.I. Mahlia, A.S. Silitonga, W.T. Chong, and T. Yusaf, Engine performance and emissions using Jatropha curcas, Ceiba pentandra and Calophyllum inophyllum biodiesel in a CI diesel engine. Energy, 2014. 69: p. 427-445.DOI: https://doi.org/10.1016/j.energy.2014.03.035.
- 369. Aboelazayem, O., N.S. El-Gendy, A.A. Abdel-Rehim, F. Ashour, and M.A. Sadek, Biodiesel production from castor oil in Egypt: Process optimisation, kinetic study, diesel engine performance and exhaust emissions analysis. Energy, 2018. 157: p. 843-852.DOI: https://doi.org/10.1016/j.energy.2018.05.202.
- 370. Abdul Malik, S.M., I.A. Shaiful, S.M. Mohd. Ismail, N.M. Mohd Jaafar, and A. Mohamad Sahar, *Combustion and Emission Characteristics of Coconut-Based Biodiesel in a Liquid Fuel Burner*. Energies, 2017. **10**(4).DOI: 10.3390/en10040458.

- 371. Kalam, M.A., H.H. Masjuki, M.H. Jayed, and A.M. Liaquat, *Emission and performance characteristics of an indirect ignition diesel engine fuelled with waste cooking oil.* Energy, 2011. **36**(1): p. 397-402.DOI: https://doi.org/10.1016/j.energy.2010.10.026.
- 372. Chuah, L.F., A. Aziz, Y. Suzana, A. Bokhari, J. Klemeš, and C.Z. Abdullah, *Performance and emission of diesel engine fuelled by waste cooking oil methyl ester derived from palm olein using hydrodynamic cavitation*. Clean Technol Environ Policy, 2015. 10.1007/s10098-015-0957-2.DOI: 10.1007/s10098-015-0957-2.
- 373. Venu, H. and M. Dinesh Babu, *Improvement of ternary fuel combustion with various injection pressure strategies in a toroidal re-entrant combustion chamber*. Environ Sci Pollut Res, 2018. **25**(32): p. 32024-32043.DOI: 10.1007/s11356-018-3174-9.
- 374. Coronado, C.R., J.A. de Carvalho, and J.L. Silveira, *Biodiesel CO2 emissions: A comparison with the main fuels in the Brazilian market*. Fuel Process Technol, 2009.
 90(2): p. 204-211.DOI: https://doi.org/10.1016/j.fuproc.2008.09.006.
- 375. Sheehan, J., V. Camobreco, J. Duffield, M. Graboski, and H. Shapouri, An Overview of Biodiesel and Petroleum Diesel Life Cycles. 1998, National Renewable Energy Laboratory: USA. Report Number: NREL/TP-580-24772. Available from: https://www.nrel.gov/docs/legosti/fy98/24772.pdf.
- 376. Rizwanul Fattah, I.M., H.H. Masjuki, M.A. Kalam, M. Mofijur, and M.J. Abedin, *Effect* of antioxidant on the performance and emission characteristics of a diesel engine fueled with palm biodiesel blends. Energy Convers Manage, 2014. **79**: p. 265-272.DOI: https://doi.org/10.1016/j.enconman.2013.12.024.
- 377. Semakula, M. and F. Inambao, *The Formation, Effects and Control of Oxides of Nitrogen in Diesel Engines*. International Journal of Applied Engineering Research, 2018. 13(6): p. 3200-3209, https://www.ripublication.com/Volume/ijaerv13n6.htm.
- 378. Jeevahan, J., G. Mageshwaran, G.B. Joseph, R.B.D. Raj, and R.T. Kannan, Various strategies for reducing Nox emissions of biodiesel fuel used in conventional diesel engines: A review. ChEnC, 2017. 204(10): p. 1202-1223.DOI: 10.1080/00986445.2017.1353500.
- 379. Mirhashemi, F.S. and H. Sadrnia, *NOX emissions of compression ignition engines fueled with various biodiesel blends: A review.* J Energy Inst, 2020. **93**(1): p. 129-151.DOI: https://doi.org/10.1016/j.joei.2019.04.003.
- 380. Hazrat, M., M. Rasul, M. Khan, N. Ashwath, and T. Rufford, *Emission characteristics* of waste tallow and waste cooking oil based ternary biodiesel fuels. Energy Procedia, 2019. **160**: p. 842-847.
- 381. Elshaib, A.A., M.M. Kamal, and A.A. Elahwany, *Performance of a diesel engine fueled* by waste cooking oil biodiesel. J Energy Inst, 2014. **87**(1): p. 11-17.DOI: https://doi.org/10.1016/j.joei.2014.02.001.
- 382. Heywood, J.B., *Internal Combustion Engine Fundamental*. 1988, USA: McGraw-Hill Inc. ISBN: 0-07-028637-X.
- 383. Pulkrabek, W.W., Engineering fundamentals of the internal combustion engine. 2 ed., http://www.amazon.com/Engineering-Fundamentals-Internal-Combustion-Edition/dp/01314057052003, Upper Saddle River, New Jersey: Prentice Hall. 1-425. ISBN: 978-0131405707.
- 384. Sakurai, H., K. Park, P.H. McMurry, D.D. Zarling, D.B. Kittelson, and P.J. Ziemann, Size-Dependent Mixing Characteristics of Volatile and Nonvolatile Components in Diesel Exhaust Aerosols. Environ Sci Technol, 2003. 37(24): p. 5487-5495.DOI: 10.1021/es034362t.
- Kittelson, D.B., W.F. Watts, and J.P. Johnson, On-road and laboratory evaluation of combustion aerosols—Part1: Summary of diesel engine results. JAerS, 2006. 37(8): p. 913-930.DOI: http://dx.doi.org/10.1016/j.jaerosci.2005.08.005.

- 386. Schneider, J., N. Hock, S. Weimer, S. Borrmann, U. Kirchner, R. Vogt, and V. Scheer, Nucleation Particles in Diesel Exhaust: Composition Inferred from In Situ Mass Spectrometric Analysis. Environ Sci Technol, 2005. 39(16): p. 6153-6161.DOI: 10.1021/es049427m.
- 387. Maricq, M.M., R.E. Chase, N. Xu, and P.M. Laing, The Effects of the Catalytic Converter and Fuel Sulfur Level on Motor Vehicle Particulate Matter Emissions: Light Duty Diesel Vehicles. Environ Sci Technol, 2001. 36(2): p. 283-289.DOI: 10.1021/es0109621.
- 388. Mohankumar, S. and P. Senthilkumar, *Particulate matter formation and its control methodologies for diesel engine: A comprehensive review*. Renewable Sustainable Energy Rev, 2017. **80**: p. 1227-1238.DOI: https://doi.org/10.1016/j.rser.2017.05.133.
- 389. Karavalakis, G., S. Stournas, and E. Bakeas, *Light vehicle regulated and unregulated emissions from different biodiesels*. Sci Total Environ, 2009. **407**(10): p. 3338-3346.DOI: http://dx.doi.org/10.1016/j.scitotenv.2008.12.063.
- 390. Lapuerta, M., O. Armas, R. Ballesteros, and J. Fernández, Diesel emissions from biofuels derived from Spanish potential vegetable oils. Fuel, 2005. 84(6): p. 773-780.DOI: http://dx.doi.org/10.1016/j.fuel.2004.11.010.
- 391. Park, S., H. Kim, and B. Choi, *Emission characteristics of exhaust gases and nanoparticles from a diesel engine with biodiesel-diesel blended fuel (BD20)*. J Mech Sci Technol, 2009. **23**(9): p. 2555-2564.DOI: 10.1007/s12206-009-0704-x.
- 392. Lapuerta, M., J. Rodríguez-Fernández, and J.R. Agudelo, *Diesel particulate emissions from used cooking oil biodiesel*. Bioresour Technol, 2008. **99**(4): p. 731-740.DOI: http://dx.doi.org/10.1016/j.biortech.2007.01.033.
- 393. Kim, D.S. and C.S. Lee, *Improved emission characteristics of HCCI engine by various premixed fuels and cooled EGR*. Fuel, 2006. **85**(5–6): p. 695-704.DOI: http://dx.doi.org/10.1016/j.fuel.2005.08.041.
- 394. Elkelawy, M., H. Alm-Eldin Bastawissi, K.K. Esmaeil, A.M. Radwan, H. Panchal, K.K. Sadasivuni, D. Ponnamma, and R. Walvekar, *Experimental studies on the biodiesel production parameters optimization of sunflower and soybean oil mixture and DI engine combustion, performance, and emission analysis fueled with diesel/biodiesel blends.* Fuel, 2019. 255: p. 115791.DOI: https://doi.org/10.1016/j.fuel.2019.115791.
- 395. Arunkumar, M., M. Kannan, and G. Murali, *Experimental studies on engine performance and emission characteristics using castor biodiesel as fuel in CI engine*. Renewable Energy, 2019. 131: p. 737-744.DOI: https://doi.org/10.1016/j.renene.2018.07.096.
- 396. Boubel, R.W. and L.A. Ripperton, *Oxides of Nitrogen and Unburned Hydrocarbons Produced During Controlled Combustion.* J Air Pollut Control Assoc, 1965. **15**(6): p. 270-273.DOI: 10.1080/00022470.1965.10468377.
- 397. Abed, K.A., M.S. Gad, A.K. El Morsi, M.M. Sayed, and S.A. Elyazeed, *Effect of biodiesel fuels on diesel engine emissions*. Egypt J Pet, 2019. 28(2): p. 183-188.DOI: https://doi.org/10.1016/j.ejpe.2019.03.001.
- 398. Musthafa, M.M., T.A. Kumar, T. Mohanraj, and R. Chandramouli, *A comparative study on performance, combustion and emission characteristics of diesel engine fuelled by biodiesel blends with and without an additive.* Fuel, 2018. **225**: p. 343-348.DOI: https://doi.org/10.1016/j.fuel.2018.03.147.
- 399. Ma, F., C. Zhao, F. Zhang, Z. Zhao, Z. Zhang, Z. Xie, and H. Wang, An Experimental Investigation on the Combustion and Heat Release Characteristics of an Opposed-Piston Folded-Cranktrain Diesel Engine. Energies, 2015. 8(7).DOI: 10.3390/en8076365.

- 400. Imtenan, S., M. Varman, H.H. Masjuki, M.A. Kalam, H. Sajjad, M.I. Arbab, and I.M. Rizwanul Fattah, *Impact of low temperature combustion attaining strategies on diesel engine emissions for diesel and biodiesels: A review*. Energy Convers Manage, 2014.
 80: p. 329-356.DOI: https://doi.org/10.1016/j.enconman.2014.01.020.
- 401. E, J., M. Pham, D. Zhao, Y. Deng, D. Le, W. Zuo, H. Zhu, T. Liu, Q. Peng, and Z. Zhang, *Effect of different technologies on combustion and emissions of the diesel engine fueled with biodiesel: A review*. Renewable Sustainable Energy Rev, 2017. 80: p. 620-647.DOI: https://doi.org/10.1016/j.rser.2017.05.250.
- 402. Dharmaraja, J., D.D. Nguyen, S. Shobana, G.D. Saratale, S. Arvindnarayan, A.E. Atabani, S.W. Chang, and G. Kumar, *Engine performance, emission and bio characteristics of rice bran oil derived biodiesel blends*. Fuel, 2019. **239**: p. 153-161.DOI: https://doi.org/10.1016/j.fuel.2018.10.123.
- 403. Usta, N., An experimental study on performance and exhaust emissions of a diesel engine fuelled with tobacco seed oil methyl ester. Energy Convers Manage, 2005.
 46(15): p. 2373-2386.DOI: https://doi.org/10.1016/j.enconman.2004.12.002.
- 404. Ashraful, A.M., H.H. Masjuki, M.A. Kalam, H.K. Rashedul, M. Habibullah, M.M. Rashed, M.H. Mosarof, and A. Arslan, *Impact of edible and non-edible biodiesel fuel properties and engine operation condition on the performance and emission characteristics of unmodified DI diesel engine*. Biofuels, 2016. **7**(3): p. 219-232.DOI: 10.1080/17597269.2015.1132365.
- 405. Kalam, M.A., M. Husnawan, and H.H. Masjuki, *Exhaust emission and combustion evaluation of coconut oil-powered indirect injection diesel engine*. Renewable Energy, 2003. **28**(15): p. 2405-2415.DOI: https://doi.org/10.1016/S0960-1481(03)00136-8.
- 406. Liaquat, A., H. Masjuki, M. Kalam, M. Varman, M. Hazrat, M. Shahabuddin, and M. Mofijur, *Application of blend fuels in a diesel engine*. Energy Procedia, 2012. **14**: p. 1124-1133.
- 407. Dynatronix^{TM,} D., *Diesel Dynamometer/Mechatronics Educational Trainer*, T.T. Ltd, Editor. 2016, Turbine Technologies Ltd, http://www.turbinetechnologies.com/Portals/0/pdfs/Diesel%20DynaTronics%20Curri culum%20Sample.pdf.
- 408. Tech, C. *What Is Engine Torque? It's Characteristics & Formula*. Technical Anatomy 2019, Available from: https://carbiketech.com/engine-torque/.
- 409. Alwi, A., N.W. Zulkifli, N.L. Sukiman, A. Yusoff, Z. Zakaria, M. Jamshaid, M.H. Hasnul, and M.S. Amzar, *Evaluation of engine performance and exhaust emission characteristics in a diesel engine using isobutanol—Calophyllum inophyllumbiodiesel—diesel ternary blends*. Environ Sci Pollut Res, 2019. **26**(12): p. 11815-11826.DOI: 10.1007/s11356-019-04603-6.
- 410. Lahane, S. and K.A. Subramanian, Effect of different percentages of biodiesel-diesel blends on injection, spray, combustion, performance, and emission characteristics of a diesel engine. Fuel, 2015. 139: p. 537-545.DOI: https://doi.org/10.1016/j.fuel.2014.09.036.
- 411. Ashok, B., K. Nanthagopal, and D. Sakthi Vignesh, *Calophyllum inophyllum methyl ester biodiesel blend as an alternate fuel for diesel engine applications*. Alexandria Engineering Journal, 2018. 57(3): p. 1239-1247.DOI: https://doi.org/10.1016/j.aej.2017.03.042.
- Boehman, A.L., D. Morris, J. Szybist, and E. Esen, *The Impact of the Bulk Modulus of Diesel Fuels on Fuel Injection Timing*. Energy Fuels, 2004. 18(6): p. 1877-1882.DOI: 10.1021/ef049880j.
- 413. Ozsezen, A.N. and M. Canakci, *Determination of performance and combustion characteristics of a diesel engine fueled with canola and waste palm oil methyl esters.*

Energy Convers Manage, 2011. **52**(1): p. 108-116.DOI: https://doi.org/10.1016/j.enconman.2010.06.049.

- Sajjad, H., H.H. Masjuki, M. Varman, M.A. Kalam, M.I. Arbab, S. Imtenan, and A.M. 414. Ashraful, Influence of gas-to-liquid (GTL) fuel in the blends of Calophyllum inophyllum An biodiesel and diesel: analysis of combustion-performance-emission 2015. **97**: 42-52.DOI: characteristics. Energy Convers Manage, p. https://doi.org/10.1016/j.enconman.2015.02.037.
- Hojati, A. and A. Shirneshan, *Effect of compression ratio variation and waste cooking oil methyl ester on the combustion and emission characteristics of an engine*. Energy Environ, 2019. 10.1177/0958305X19893045: p. 0958305X19893045.DOI: 10.1177/0958305X19893045.
- 416. S.S, N., *Analysis of noise emitted from diesel engines*. J Phys Conf Ser, 2015. **662**: p. 012018.DOI: 10.1088/1742-6596/662/1/012018.
- 417. El-Kasaby, M. and M.A. Nemit-allah, *Experimental investigations of ignition delay period and performance of a diesel engine operated with Jatropha oil biodiesel.* Alexandria Engineering Journal, 2013. 52(2): p. 141-149.DOI: https://doi.org/10.1016/j.aej.2012.12.006.
- 418. Ferguson, C.R. and A.T. Kirkpatrick, *Internal Combustion Engines: Applied Thermosciences*. 3rd ed., https://www.wiley.com/en-au/Internal+Combustion+Engines%3A+Applied+Thermosciences%2C+3rd+Edition-p-97811189265292016, UK: John Wiley & Sons Ltd. ISBN: 978-1-118-92652-9.
- 419. Krieger, R.B. and G.L. Borman, *The computation of apparent heat release for internal combustion engines*. ASME, 1966, (ASME 66-WA/DGP-4).
- 420. G.Abbaszadehmosayebi, PhD, *Diesel engine heat release analysis by using newly defined dimensionless parameters*, in *School of Engineering and Design*. 2014, Brunel University: UK, Available from: https://bura.brunel.ac.uk/bitstream/2438/9201/1/FulltextThesis.pdf.
- 421. Hosamani, B.R. and V.V. Katti, *Experimental analysis of combustion characteristics* of CI DI VCR engine using mixture of two biodiesel blend with diesel. Engineering Science and Technology, an International Journal, 2018. **21**(4): p. 769-777.DOI: https://doi.org/10.1016/j.jestch.2018.05.015.
- 422. Li, Y., H. Xu, R. Cracknell, R. Head, and S. Shuai, *An experimental investigation into combustion characteristics of HVO compared with TME and ULSD at varied blend ratios.* Fuel, 2019. **255**: p. 115757.DOI: https://doi.org/10.1016/j.fuel.2019.115757.
- 423. Bednarski, M., P. Orliński, M.K. Wojs, and M. Sikora, *Evaluation of methods for determining the combustion ignition delay in a diesel engine powered by liquid biofuel.* J Energy Inst, 2019. 92(4): p. 1107-1114.DOI: https://doi.org/10.1016/j.joei.2018.06.007.
- 424. Keating, E.L., ed. *Applied Combustion*. 2nd ed. Mech Eng, ed. L.L. Faulkner. 2007, Taylor & Francis Group LLC: USA. ISBN: 1-5744-640-1.
- 425. Assanis, D., Z. Filipi, S. Fiveland, and M. Syrimis, A Methodology for Cycle-By-Cycle Transient Heat Release Analysis in a Turbocharged Direct Injection Diesel Engine. SAE Special Publication Series, 2000. SP-1530(SAE Paper No. 2000-01-1185).DOI: 10.4271/2000-01-1185.
- 426. Nieto Garzón, N.A., A.A.M. Oliveira, and E. Bazzo, *An ignition delay correlation for compression ignition engines fueled with straight soybean oil and diesel oil blends*. Fuel, 2019. **257**: p. 116050.DOI: https://doi.org/10.1016/j.fuel.2019.116050.
- 427. Rothamer, D.A. and L. Murphy, *Systematic study of ignition delay for jet fuels and diesel fuel in a heavy-duty diesel engine*. Proc Combust Inst, 2013. **34**(2): p. 3021-3029.DOI: https://doi.org/10.1016/j.proci.2012.06.085.

- 428. Bodisco, T.A., PhD, *In-Cylinder Pressure and Inter-Cycle Variability Analysis for a Compression Ignition Engine: Bayesian Approaches*, in *School of Chemistry, Physics and Mechanical Engineering*. 2013, Queensland University of Technology (QUT): Australia, Available from: https://eprints.qut.edu.au/62064/11/Timothy_Bodisco_Thesis.pdf.
- 429. Bodisco, T., S. Low Choy, and R.J. Brown, *A Bayesian approach to the determination* of ignition delay. Appl Therm Eng, 2013. **60**(1): p. 79-87.DOI: https://doi.org/10.1016/j.applthermaleng.2013.06.048.
- 430. Alptekin, E., *Emission, injection and combustion characteristics of biodiesel and oxygenated fuel blends in a common rail diesel engine.* Energy, 2017. **119**: p. 44-52.DOI: https://doi.org/10.1016/j.energy.2016.12.069.
- 431. Assanis, D.N., Z.S. Filipi, S.B. Fiveland, and M. Syrimis, *A Predictive Ignition Delay Correlation Under Steady-State and Transient Operation of a Direct Injection Diesel Engine*. J Eng Gas Turbines Power, 2003. **125**(2): p. 450-457.DOI: 10.1115/1.1563238.
- 432. Reddy, P.R., D.M. Krishna, K.G. Mallan, and V. Ganesan, *Evaluation of combustion parameters in direct injection diesel engines-an easy and reliable method.* SAE Technical Paper, 1993. https://doi.org/10.4271/930605(Technical Paper 930605).DOI: https://doi.org/10.4271/930605.
- 433. Katrašnik, T., S. Rodman Opresnik, F. Trenc, and N. Škifić, *A new criterion to determine the start of combustion in diesel engine*. Proceedings of the 2004 Fall Technical Conference of the ASME Internal Combustion Engine Division, 2004: p. 235-241.
- 434. Checkel, M. and J. Dale, *Computerized Knock Detection from Engine Pressure Records*, in *SAE International Congress and Exposition*. 1986, SAE International: USA.DOI: https://doi.org/10.4271/860028.
- 435. Wong, C.L. and D.E. Steere. *The Effects of Diesel Fuel Properties and Engine Operating Conditions on Ignition Delay.* in *1982 SAE International Fall Fuels and Lubricants Meeting and Exhibition.* 1982. United States: SAE International.DOI: https://doi.org/10.4271/821231.
- 436. Karst, D. and Y. Yang, *Using the solubility parameter to explain disperse dye sorption on polylactide*. J Appl Polym Sci, 2005. **96**(2): p. 416-422.DOI: 10.1002/app.21456.
- 437. ChemicalBook. *Carboxylic acids esters and derivatives*. 2016, Available from: https://www.chemicalbook.com/ProductCatalog_EN/131916-2.htm.
- 438. Lee, B., D. Jung, and Y.-W. Kim. *Physics-Based Control Oriented Mean Value Model* for Diesel Combustion Process With EGR Sensitivity. in ASME 2011 Dynamic Systems and Control Conference and Bath/ASME Symposium on Fluid Power and Motion Control. 2011.DOI: 10.1115/dscc2011-6089.
- 439. Nagele, P., *Misuse of standard error of the mean (SEM) when reporting variability of a sample. A critical evaluation of four anaesthesia journals.* Br J Anaesth, 2003. 90(4): p. 514-6.DOI: 10.1093/bja/aeg087.
- 440. Altman, D.G. and J.M. Bland, *Standard deviations and standard errors*. BMJ (Clinical research ed), 2005. **331**(7521): p. 903-903.DOI: 10.1136/bmj.331.7521.903.
- 441. McHugh, M.L., *Standard error: meaning and interpretation*. Biochem Med (Zagreb), 2008. **18**(1): p. 7-13.DOI: https://doi.org/10.11613/BM.2008.002.
- 442. Le, C.T. and L.E. Eberly, *Introductory Biostatistics*. Second ed., 2016, USA and Canada: John Wiley & Sons, Inc. ISBN: 9781118595985.
- 443. Moffat, R.J., *Describing the uncertainties in experimental results*. Exp Therm Fluid Sci, 1988. **1**(1): p. 3-17.DOI: https://doi.org/10.1016/0894-1777(88)90043-X.

444. Moffat, R.J., *Contributions to the Theory of Single-Sample Uncertainty Analysis*. Transactions of the ASME, 1982. **104**: p. 250-258, http://fluidos-lfa.usuarios.rdc.puc-rio.br/metexp-pos/Paper_Moffat.pdf.

APPENDIX A1

Groups	$\phi_{di}(MPa)^{1/2}.cm^3.mol^{-1}$	$\phi_{pi} (MPa)^{1/2}.cm^3.mol^{-1}$	E _{hi}	E_{coh}
			J.mol ⁻¹	J.mol ⁻¹
-CH ₃	420	0	0	9640
CH ₂	270	0	0	4190
>CH-	80	0	0	420
>C<	-70	0	0	-5580
CH ₂ =	400	0	0	
-CH=	200	0	0	
>C=	70	0	0	
-0-	100	400	3000	6290
-СОН	470	800	4500	
HCOO-	530	-	-	
-СООН	530	420	10000	-
-COO-	390	490	7000	3410
>C=0	290	770	2000	-
$-NO_2$	500	1070	1500	
$=PO_4$	740	1890	13000	
–OH	210	500	20000	-
$-NH_2$	280	-	8400	
-NH-	160	210	3100	
>N-	20	800	5000	
–C≡N	430	1100	2500	25000
-S-	440	-	-	8800
-F	(220)	-	-	4470
Cl	450	550	400	12990
-Br	(550)	-	-	15500
Ring	190	-	-	
$-C_6H_{11}$ $- \bigcirc$ cyclohexyl	1620	0	0	-
$-C_6H_5 \longrightarrow benzyl$	1430	110	0	31000
$\textbf{-}C_6H_4\textbf{-}CH_{3(o,m,p)}$	1270	110	0	

Table A1-1 Molar attraction constants for group contribution method by Hoftyzer-vanKerevelen [196, 219, 227, 229]

Groups	E _{coh} (J/mol)	V (cm ³ /mol)	Groups	E _{coh} (J/mol)	V (cm ³ /mol)
-CH ₃	4710	33.5	-0-	3350	3.8
CH ₂	4940	16.1	-CHO (aldehyde)	21350	22.3
>CH-	3430	-1.0	-CO-	17370	10.8
>C<	1470	-19.2	–COOH	27630	28.5
CH ₂ =	4310	28.5	-COO-	18000	18.0
-CH=	4310	13.5	-CO ₃ - (carbonate)	17580	22.0
>C=	4310	-5.5	-C ₂ O ₃ - (anhydride)	30560	30.0
-C≡	7070	6.5	-HCOO- (formate)	18000	32.5
Phenyl	31,940	71.4	-CO2CO2- (oxalate)	26790	37.3
Phenylene (o, m, p)	31,940	52.4	-HCO3	12560	18.0
Ring closure 5 or more atoms	1050	16.0	-COF	13400	29.0
Ring closure 3 or 4 atoms	3140	18.0	-COCl	17580	38.1
Conjugation in ring for each double bond	1670	-2.2	–COBr	24,150	41.6
Halogen attached to carbon atom with	-20% of Ecoh of halogen	4.0	-COI	29,300	48.7
double bond					
–F	4190	18.0	-NH ₂	12560	19.2
-F (distributed)	3560	20.0	-NH-	8370	4.5
-F (trisubstituted)	2300	22.0	>N-	4190	-9.0
-CF2- (for perfluoro compounds)	4270	23.0	-N=	11720	5.0
-CF3 (for perfluoro compounds)	4270	57.5	-N=C	18,840	23.1
Cl	11550	24.0	-NF2	7660	33.1
-Cl (distributed)	9630	26.0	-NF-	5070	24.5
-Cl (trisubstituted)	7530	27.3	-CONH2	41,860	17.5

Table A1-2 Group contributions to the cohesive energy and molar volume by Fedors [196, 217]

-Br	15490	30	-CONH-	33,490	9.5
-Br (distributed)	12350	31	-CON<	29510	-7.7
-Br (trisubstituted)	10670	32.4	HCON<	27,630	11.3
-I	19050	31.5	HCONH-	43950	27.0
-I (distributed)	16740	33.5	-NHCOO-	26370	18.5
-I (trisubstituted)	16330	37.0	-NHCONH-	50,230	-
–C≡N	25530	24.0	-NHCON<	41,860	-
–OH	29800	10.0	>NCON<	20,930	-14.5
-OH (disubstituted or on adjacent C atoms)	21850	13.0	NH2COO-	37,000	_
–SH	14,440	28.0	-NCO	28,460	35.0
-S-	14,150	12	-ONH2	19,050	20.0
-S2-	23,860	23.0	>C=NOH	25,120	11.3
	13,400	47.2	-CH=NOH	25,120	24.0
>SO	39,140	_	-NO2 (aliphatic)	29,300	24.0
–SO3	18,840	27.6	-NO2 (aromatic)	15,360	32.0
-SO4	28,460	31.6	-NO2 (nitrite)	11,720	33.5
–SO2Cl	37,070	43.5	-NO3	20,930	33.5
–SCN	20,090	37.0	–NH NO2	39,770	28.7
-NCS	25,120	40.0	-NNO-	27,210	10
Р	9420	-1.0	Si	3390	0
-PO3	14,230	22.7	SiO4	21,770	20.0
–PO4	20,930	28.0	В	13,810	-2.0
–PO3(OH)	31,810	32.2	BO3	0	20.4
Al	13,810	-2.0	Ga	13,810	-2.0
In	13,810	-2.0	TI	13,810	-2.0
Ge	8080	-1.5	Sn	11300	1.5
Pb	17160	2.5	As	12980	7.0
Sb	16330	8.9	Bi	21350	9.5
Se	17160	16.0	Те	20090	17.4
Zn	14480	2.5	Cd	17790	6.5
Hg	22810	7.5	-N=N-	4190	_

Groups	E _{coh} (J/mol)	V _m (cm ³ /mol)	Groups	E _{coh} (J/mol)	V _m (cm ³ /mol)
-CH ₃	9640	33.5	NO _{2 (aromatic)}	15355	32.0
-CH ₂ -	4190	16.1	-0-	3347	3.8
>CH-	3431	-1.0	–OH	29790	10.0
>C<	1464	-19.2	S	14142	12.0
H ₂ C= (olefin)	4310	28.5	-SO-	39140	0.0
-CH= (olefin)	4310	13.5	$-SO_4-$	28451	31.6
>C= (olefin)	4310	-5.5	$-\mathbf{F}$	4184	18.0
HC≡	3849	27.4	Cl	11548	24.0
-C≡	7071	6.5	–Br	15481	30.0
Phenyl	31924	71.4	I	19037	31.5
Phenylene (o, m, p)	31924	52.4	-NH-	8368	4.5
Phenyl (trisubstituted)	31924	33.4	Ν	4184	-9.0
Phenyl (tetrasubstituted)	31924	14.4	-N=	11715	5.0
Phenyl (pentasubstituted)	31924	-4.6	-N=N-	4188	0.0
Phenyl (hexasubstituted)	31924	-23.6	–C≡N	25522	24.0
Ring closure 5 or more atoms	1046	16.0	-СООН	27614	28.5
Ring closure 3 or 4 atoms	3138	18.0	-CO ₂ -	17991	18.0
Conjugation in ring for each double bond	1674	-2.2	-CO-	17364	10.8
$-NH_2$	12552	19.2	-CONH-	33472	9.5

Table A1-3 Group contributions to E_{coh} and V used to estimate the solubility parameter at 298 K as listed by Karst **[217, 436**]1-

Table A1-4 Hansen Solubility Parameters (HSP) Components of Fatty Acid Me	thyl Esters
(FAME) by van Krevelen-Hoftyzer methodology	

FAME	FAME From the calculation of Cataldo [212] (MPa) ^{1/2}		n of	From Go (MPa) ^{1/2}	onzalez <i>e</i>	et al. [23]	1]	From Batista <i>et al.</i> [225] (MPa) ^{1/2}			225]	
	δ_d	δ_p	δ_{h}	δ_t	δ_d	δ_p	δ_{h}	δ_t	δ_{d}	δ_{p}	δ_{h}	δ_t
C8:0	-	-	-	-	16.58	2.4	5.85	17.74	14.9	2.6	6.0	16.3
C10:0	-	-	-	-	-	-	-	-	15.9	2.3	5.7	17.0
C12:0	-	-	-	-	16.54	2.06	5.43	17.53	16.0	2.0	5.3	17.0
C14:0	16.1	5.6	9.0	19.2	16.51	1.81	5.08	17.37	16.0	1.8	5.0	16.9

C16:0	15.5	4.8	8.3	18.3	16.48	1.61	4.8	17.24	15.9	1.5	4.5	16.6
C16:1	-	-	-	-	-	-	-	-	-	-	-	-
C18:0	15.6	4.3	7.9	18.0	16.46	1.45	4.56	17.14	15.8	1.4	4.5	16.5
C18:1	16.3	4.7	8.2	18.8	16.45	1.49	4.61	17.15	16.0	1.5	4.6	16.7
C18:2	16.1	4.8	8.2	18.7	16.45	1.53	4.67	17.17	15.9	1.5	4.6	16.6
C18:3	16.0	4.8	8.3	18.7	-	-	-	-	15.7	1.5	4.6	16.4
C18:1(OH)	-	-	-	-	-	-	-	-	16.1	2.1	8.9	18.5
C20:0	-	-	-	-	-	-	-	-	-	-	-	-
Glyceryl trioleate	16.1	1.5	4.7	16.9	-	-	-	-	-	-	-	-
Glyceryl tristearate	16.1	1.5	4.7	16.9	-	-	-	-	-	-	-	-

Table A1-5 Molar	Volume and Molar	Attraction Constants	of various	groups (He	oy method)
	(Data	collected from [196])			

Groups	Molar Volume from Density Measurement, V _m (cm ³ /mol)	Molar Attraction/cohesion Constant, ϕ_t [(MPa) ^{1/2} mol ⁻¹]	$\begin{array}{l} Polar \ Cohesion \\ Constant, \ \phi_p \\ [(MPa)^{1/2}mol^{-1}] \end{array}$	Lydersen const. Δ_T	Lydersen polar const. Δ_T^p
-CH ₃	21.548	303.5	0	0.023	0.022
CH2	15.553	269.0	0	0.020	0.020
>CH-	9.577	176.0	0	0.012	0.013
>C<	3.562	65.5	0	0	0.040
CH ₂ = (olefin)	19.173	259	67	0.018	0.019
-CH= (olefin)	13.178	249	59.5	0.018	0.0185
>C= (olefin)	7.183	173	63	0	0.013
–CH= (aromatic)	13.417	241	62.5	0.011	0.018
–C= (aromatic)	7.422	201	65	0.011	0.015
-НС=О	23.3	600	532	0.048	0.045
>C=0	17.3	538	525	0.040	0.040
–COOH (acid)	26.102	565	415	0.039	0.039
–COO– (ester)	23.728	640	528	0.047	0.050
-CO-O-CO-	41.0	1160	1160	0.086	0.086
–C≡N	23.1	725	725	0.060	0.054
-N=C=O	25.9	736	8.2	0.054	0.054
HCON<	35.8	1020	725	0.062	0.055
-CONH ₂	34.3	1200	900	0.071	0.084

-CONH-	28.3	1131	895	0.054	0.073
-OCONH-	34.8	1265	890	0.078	0.094
$-OH \rightarrow (H bonded)$	10.65	485	485	0.082	0.034
–OH (Primary)	12.45	675	675	0.082	0.049
–OH (Secondary)	12.45	591	591	0.082	0.049
–OH (Tertiary)	12.45	500	500	0.082	0.049
–OH (aromatic/ phenolic)	12.45	350	350	0.031	0.006
–O– (ether)	6.462	235	216	0.021	0.018
–O– (acetal)	6.462	236	102	0.018	0.018
–O– (epoxide)	6.462	361	156	0.027	0.027
$-NH_2$	17.0	464	464	0.031	0.035
-NH-	11.0	368	368	0.031	0.0275
>N-	12.6	125	125	0.014	0.009
-S-	18.0	428	428	0.015	0.032
–F	11.2	845	73.5	0.018	0.006
-Cl (primary)	19.5	419.5	307	0.017	0.031
–Cl (secondary)	19.5	426	315	0.017	0.032
–Cl (aromatic)	19.5	330	81.5	0.017	0.025
Cl ₂	39.0	705	572	0.034	0.052
-Br	25.3	528	123	0.010	0.039
–Br (aromatic)	25.3	422	100	0.010	0.031
Conjugation Isomerism	-	475	-19.8	0	0.0035
Cis	-	-14.6	-14.6	0	-0.001
Trans	-	-27.6	-27.6	0	-0.002
Aromatic Subst	itution				
Ortho	-	-13.3	-13.3	0	0.0015
Meta	-	-24.3	-24.3	0	0.0010
Para	-	-34.0	-34.0	0	0.006
Ring size (non-a	aromatic)				
4-membered	-	159	203	0	0.012
5-membered	-	43	85	0	0.003
6-membered	-	-48	61	0	-0.0035
7-membered	-	92	0	0	0.007

Acid Chain	Chain formula	Saturation	Linear Structure	Molecular weight (g/mol)
Caprylic	C8:0	Saturated	CH ₃ (CH ₂) ₆ COOH	144.21
Capric	C10:0	Saturated	CH ₃ (CH ₂) ₈ COOH	172.26
Lauric	C12:0	Saturated	CH ₃ (CH ₂) ₁₀ COOH	200.32
Myristic	C14:0	Saturated	CH ₃ (CH ₂) ₁₂ COOH	228.37
Pentadecanoic	C15:0	Saturated	CH ₃ (CH ₂) ₁₃ COOH	242.4
Palmitic	C16:0	Saturated	CH ₃ (CH ₂) ₁₄ COOH	256.42
Palmitoleic	C16:1	Unsaturated	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOH	254.41
Heptadecanoic	C17:0	Saturated	CH ₃ (CH ₂) ₁₅ COOH	270.45
Stearic	C18:0	Saturated	CH ₃ (CH ₂) ₁₆ COOH	284.48
Oleic	C18:1	Unsaturated	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	282.46
Linoleic	C18:2	Unsaturated	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOH	280.45
Linolenic	C18:3	Unsaturated	CH ₃ CH ₂ CH=CHCH ₂ CH=CHCH ₂ CH=CH (CH ₂) ₇ COOH	278.43
Ricinoleic	C18:1(OH)	Unsaturated	$CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COOH$	298.46
Arachidic	C20:0	Saturated	CH ₃ (CH ₂) ₁₈ COOH	312.53
Eicosenoic	C20:1	Unsaturated	CH ₃ (CH2) ₇ CH=CH(CH ₂) ₉ COOH	310.51
Behenic	C22:0	Saturated	CH ₃ (CH ₂) ₂₀ COOH	340.58
Erucic	C22:1	Unsaturated	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₁₁ COOH	338.57
Lignoceric acid	C24:0	Saturated	CH ₃ (CH ₂) ₂₂ COOH	368.64

Table A1-6 Structural Formula and molecular weight for Fatty Acids [242]

Chain formula	Saturation	Linear Structure of FAMEs	Molecu lar weight [242]	Density @25 ^o C (g/cm ³) [242, 437]
C8:0	Saturated	CH ₃ (CH ₂) ₆ COOCH ₃ (Methyl caprylate/ Caprylic acid methyl ester)	158.24	0.877
C10:0	Saturated	$CH_3(CH_2)_8COOCH_3$ (Methyl caprate/ Capric acid methyl ester)	186.29	0.871
C12:0	Saturated	CH ₃ (CH ₂) ₁₀ COOCH ₃ (Methyl laurate/ Lauric acid methyl ester)	214.34	0.87
C14:0	Saturated	CH ₃ (CH ₂) ₁₂ COOCH ₃ (Methyl myristate/ Myristic acid methyl ester)	242.40	0.86
C15:0	Saturated	CH ₃ (CH ₂) ₁₃ COOCH ₃ (Methyl pentadecanoate/ Pentadecanoic acid Methyl ester)	256.42	0.86
C16:0	Saturated	CH ₃ (CH ₂) ₁₄ COOCH ₃ (Methyl palmitate/ Palmitic acid methyl ester)	270.45	0.85
C16:1	Unsaturated	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl palmitoleate/ Palmitoleic acid methyl ester)	268.43	0.875
C17:0	Saturated	CH ₃ (CH ₂) ₁₅ COOCH ₃ (/ Methyl margarate/ Methyl heptadecanoate/ Heptadecylic acid methyl ester)	284.48	0.78
C18:0	Saturated	CH ₃ (CH ₂) ₁₆ COOCH ₃ (Methyl stearate/ Stearic acid methyl ester)	298.50	0.85
C18:1	Unsaturated	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl oleate/ Oleic acid methyl ester)	296.49	0.87
C18:2	Unsaturated	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl linoleate/ Linoleic acid methyl ester)	294.47	0.889
C18:3	Unsaturated	CH ₃ CH ₂ CH=CHCH ₂ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOC H ₃	292.46	0.895
C18:1 (OH)	Unsaturated	(Methyl inforenate/ Linorenic acid methyl ester) CH ₃ (CH ₂) ₅ CH(OH)CH ₂ CH=CH(CH ₂) ₇ COO-CH ₃ (Methyl ricinoleate / Methyl 12-hydroxyoleate/ Ricinoleic acid methyl ester)	314.49	0.9
C20:0	Saturated	CH ₃ (CH ₂) ₁₈ COOCH ₃ (Methyl arachidate / Methyl eicosanoate/ Arachidic acid methyl ester)	326.56	0.883
C20:1	Unsaturated	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₉ COOCH ₃ (Methyl cis-11- eicosenoate/ Methyl eicosenoate/ Eicosenoic acid methyl ester)	324.54	0.871
C22:0	Saturated	CH ₃ (CH ₂) ₂₀ COOCH ₃ (Methyl behenate / Methyl docosanoate / Docosanoic acid methyl ester/ Behenic acid methyl ester)	354.61	0.878
C22:1	Unsaturated	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₁₁ COOCH ₃ (Methyl erucate/ Erucic aid methyl ester)	352.59	0.870

Table A1-7 Chemical formula, molecular weight and density of fatty acid methyl esters (FAME) [242]

Group increment	Mi (g∕mol)	V _{wi} (cm³∕mol)	Group increment	Mi (g∕mol)	V _{wi} (cm³∕mol)
-CH2-	14.03	10.23	-0-	16.00	(5.5)
					(5.0)
CH(CH3)	28.05	20.45	-NH-	15.02	(4)
-CH(iso-C3H7)-	56.11	40.9	-S-	32.06	10.8
-CH(ter-C ₄ H ₉)-	70.13	51.1	- S- S-	64.12	22.7
-CH(C ₆ H ₅)-	90.12	52.6	•		
CH(C ₆ H ₄ CH ₃)	104.14	63.8		64.06	20.3
-CH(OH)-	30.03	14.8		01.00	20.0
-CH(OCH ₃)-	44.05	25.5	0		
-CH(OCOCH ₃)-	72.06	37.0	-COO-	44.01	15.2
-CH(COOCH ₃)-	72.06	37.0	-0000-	60.01	18.9
-CH(CN)-	39.04	21.5	-CONH-	43.03	(13)
CHF	32.02	12.5	-OCONH-	59.03	(18)
			-NHCONH-	58.04	(18)
-CHCl-	48.48	19.0	-Si(CH ₃) ₂ -	58.15	42.2
	42.08	30.7		00.14	
-C(CH ₂)(C ₄ H ₂)-	104.1	62.8		82.14	53.3
-C(CH ₂)	86.05	46.7			
(COOCH ₂)-	00.00	10.0	\uparrow	76.09	43.3
-CF ₂ -	50.01	14.8			
-CFCI-	66.47	21.0		76.09	43.3
-CCl ₂ -	82.92	27.8			
CU_CU	26.04	16.0			
	20.04	10.9		104.14	6E 6
$-CH=C(CH_3)-CH=C(CH_$	40.00	27.2		104.14	05.0
	00.49	25.7			
-L=L- 	24.02	10.1			
0, ral.	28.01	(95	C ₆ H₅		
_С"— 1 _{аг.}	20.01	117		220.20	120
		(11.7		220.20	130
				126.18	69.9
				214.13	94.5
			o o		

Figure A1-1 Molar mass and van der Waals volume of bivalent groups [208]

Group increment	Mi (g∕mol)	V _{wi} (cm³∕mol)	Group increment	Mi (g∕mol)	V _{wi} (cm³∕mol)			
Group increments of	mass and	Van der Waa	als volume (Non-biva	lent group:	s)			
Monovalent			Aromatic ("3/2"-valent)					
-H	1.008	3.44						
-CH ₃	15.03	13.67	CH _{ar}	13.02	8.05			
$-CH(CH_3)_2$	43.09	34.1	C _{ar} (exo)	12.01	5.55			
$-C(CH_3)_3$	57.11	44.35	C [*] _{ar} (endo)	12.01	4.75			
–C≡CH	25.02	19.5	N _{ar} (pyrid)	14.00	5.2			
-C≡N	26.02	14.7	Trivalent					
-0H	22.07	0.0 14 9						
-5n _F	19.07	14.0 57	<u>\Сн_</u>	13.02	68			
(al	35.45	(116		15.02	0.0			
$-Cl \left\{ ar \right\}$	35.45	{12.0	-CH=C<	25.03	13.5			
-CF ₃	69.01	21.3		20.00	10.0			
-CHCl	83.93	31.3						
-CH ₂ Cl	49.48	21.85	-N<	14.01	4.3			
-CCl ₃	118.38	38.2		-				
$-NO_2$	46.01	16.8	Tetravalent					
\rightarrow	77.10	45.85	>C<	12.01	3.3			
			=C=	12.01	6.95			
<>(-C ₆ H ₁₁)	83.15	56.8	<u> </u>	12.02	(0)			
(-C₅H₀)	69.12	46.5	- C ≡	13.02	(8)			
- N	78.07	43.0	$\sum_{i=1}^{n}$	74.08	38.3			
	127.2	71.45		74.08	38.3			
-N	166.4	88.7	 i	28.09	16.6			
-SO4	96.06	35.1						

Figure A1-2 Molar mass and van der Waals volume of non-bivalent groups [208]



Figure A1-3 Cetane Number (CN) variation of various diesel-biodiesel and diesel-biodiesel-PS fuel blends



Figure A1-4 Density variation of various diesel-biodiesel and diesel-biodiesel-PS fuel blends



Figure A1-5 Characteristics of kinematic viscosity variation of various diesel-biodiesel and diesel-biodiesel-PS fuel blends



Figure A1-6 Variation of lower heating values of various diesel-biodiesel and diesel-biodiesel-PS fuel blends

APPENDIX A2

Table A2-1 Solubility parameter range, molar volume and cohesive energy of various thermoplastics published by different group contribution methods **[196]**

Polymer	δ_t range (J/cm ³) ^{1/2}	V	E _{coh} (J/mol)							
	or (MPa) ^{1/2}	(cm ³ /mol)	Fedors	Small	Van	Hoy	Hoftyzer	Avg.		
					Krevelen		-van	E_{coh}		
							Krevelen			
Polyethylene	15.8~17.1	32.9	9880	9000	9500	8800	8380	9112		
Polypropylene	16.8~18.8	49.1	13080	12000	14400	11400	14250	13026		
Polystyrene	17.4~19.0	98.0	40310	34300	38300	34700	35610	36644		
Polyvinyl	19.2~22.1	45.2	19920	17200	17600	16500	17600	17764		
chloride										
Polyethylene	19.9~21.9	143.2	77820	69600	61200	76800	163420	89768		
terephthalate										

Plastic	Repeating unit	Molar volume of the repeating units, V_m	Cohesive energy of the repeating units, E_{coh}	Solubility Parameter,
polymers		(cm ³ /mol)	(J/mol)	$\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5} (\text{MPa})^{1/2}$
LDPE	-(CH ₂ -CH ₂)-	2x16.1=32.2	2x4940=9880	17.52
HDPE	-(CH ₂ -CH ₂)-	2x16.1=32.2	2x4940=9880	17.52
PP	-[CH ₂ -CH(CH ₃)]-	(1x16.1)+(1x(-1.0)) +(1x33.5) =48.6	(1x4710)+(1x4940)+(1x3430)=13080	16.41
PVC	-{ CH ₂ - CH-} I Cl	(1x16.1)+(1x(-1.0)) +(1x24.0) =39.1	(1x4940)+(1x3430)+(1x11550) =19920	22.57
PS	- [CH ₂ - CH] -	(1x16.1)+(1x(-1.0)) +(1x71.4) =86.5	(1x4940)+(1x3430)+(1x31940) =40310	21.59
EPS	- [CH ₂ - CH] -	(1x16.1)+(1x(-1.0)) +(1x71.4) =86.5	(1x4940)+(1x3430)+(1x31940) =40310	21.59
PET	- [0 - (CH ₂) ₂ - 0 - C - O - O	(2x18.0)+(2x16.1)+(1x71.4) =139.6	(2x4940)+(2x18000)+(1x31940) =77820	23.61

Table A2-2 Hildebrand solubility parameters of thermoplastics group contibution method (Fedors' method, [217])

Table A2-3 Solubility parameter of thermoplastics using group contribution method (Hoy's method, [67, 232])

Plastic polymers	Molecular mass of repeating unit, M	Molecular density of the repeating unit, ρ	Sum of Molar Attraction Constant of the components, $\sum \phi$ (cal ^{1/2} cm ^{-3/2}).mol ⁻¹	Solubility Parameter, $\delta_t = \frac{\rho \sum \varphi}{M}$ (cal ^{1/2} cm ^{-3/2})	$\delta_t (\mathrm{MPa})^{1/2}$
LDPE	28	0.92	2x131.5=263.0	8.64	17.68
HDPE	28	0.95	2x131.5=263.0	8.92	18.25
PP	42.08	0.9	(1x131.5)+(1x86.0)+(1x148.0)=365.5	7.82	16.0
PVC	62.50	1.4	(1x131.5)+(1x86.0)+(1x208.0)=425.5	9.53	19.50

PS	104.1	1.06	(1x131.5)+(1x86.0)+(6x117.0)+(1x(-23.5))=896.5	9.12	18.66
EPS	104.1	0.93	(1x131.5)+(1x86.0)+(6x117.0)+(1x(-23.5))=896.5	8.0	16.36
PET	192.2	1.36	(2x326.5)+(2x131.5)+(6x117.0)+(1x(-23.5))=1594.7	11.28	23.09

Table A2-4 Calculation of Hansen solubility parameter components of various plastics using group contribution method (van Krevelen-Hoftyzermethod [196])

Plastic polymers	$\sum \! \phi_{di} \left(MPa \right)^{1/2} .cm^3.mol^{\cdot 1}$	$\sum (\phi_{pi})^2$ (MPa) ^{1/2} .cm ³ .mol ⁻¹	$\sum E_{hi}$ J.mol ⁻¹	$\sum V_{\rm m}$ (cm ³ /mol)	$\begin{array}{l} \delta_d = \\ \sum \phi_{di} / \sum V_m \\ (MPa)^{1/2} \end{array}$	$\delta_p = \frac{\left(\Sigma \varphi_p^2\right)^{0.5}}{\Sigma v_m}$ (MPa) ^{1/2}	$\delta_h = \left[\frac{\sum E_h}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	δ_t (MPa) ^{1/2}
LDPE	2x270=540.0	0	0	2x16.1=32.2	16.77	0	0	16.77
HDPE	2x270=540.0	0	0	2x16.1=32.2	16.77	0	0	16.77
PP	(1x270)+(1x80)+(1x420) =770.0	0	0	(1x16.1)+(1x(-1.0)) +(1x33.5) =48.6	15.84	0	0	15.84
PVC	(1x270)+(1x80)+(1x450) =800.0	$(1x0) + (1x0) + (1x(550)^2)$ =302500.00	(1x0)+(1x0)+(1x400) =400	(1x16.1)+(1x(-1.0)) +(1x24.0) =39.1	20.46	14.07	3.19	25.04
PS	(1x270)+(1x80)+(1x1430) =1780	$(1x0)+(1x0)+(1x(110)^2)$ =12100.00	(1x0)+(1x0)+(1x0) =0	(1x16.1)+(1x(-1.0)) +(1x71.4) =86.5	20.57	1.27	0	20.61
EPS	(1x270)+(1x80)+(1x1430) =1780	$(1x0)+(1x0)+(1x(110)^2)$ =12100.00	(1x0)+(1x0)+(1x0) =0	(1x16.1)+(1x(-1.0)) +(1x71.4) =86.5	20.57	1.27	0	20.61
PET	(2x390)+(2x270)+(1x1430) =2750.0	$(2x(490)^2)+(2x0)+(1x(110)^2)$ =492300.00	(2x7000)+(2x0)+(1x0) =14000.0	(2x18.0)+(2x16.1)+(1x71.4) =139.6	19.70	5.02	10.01	22.66

		Fedor's group contrib parameter	oution, Hildebrand solubi	lity	Hoftyzer-van Krevelen group contribution for molar additive constants of Hansen's solubility parameters			
FAME Group	Linear Structure	V _m (cm ³ /mol)	E _{coh} (J/mol)	$\begin{array}{l} \delta = \\ [E_{coh}/V_{m}]^{0.5} \end{array}$	$\begin{array}{l} \sum \phi_{di} \\ (MPa)^{1/2}.cm^3. \\ mol^{-1} \end{array}$	$\sum (\phi_{pi})^2$ (MPa) ^{1/2} .cm ³ .mol ⁻¹	$\sum E_{hi}$ J.mol ⁻¹	
C8:0	CH ₃ (CH ₂) ₆ COOCH ₃ (Methyl caprylate)	(2x33.5)+(6x16.1)+ (1x18)=181.6	(2x4710)+(6x4940)+ (1x18000) = 57060	17.73	(2x420)+(6x27) 0)+(1x390.0) =2850.0	$(2x0)+(6x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(6x0)+(1x7000) =7000.0	
C10:0	CH ₃ (CH ₂) ₈ COOCH ₃ (Methyl caprate)	(2x33.5)+(8x16.1)+ (1x18)=213.8	(2x4710)+(8x4940)+ (1x18000) = 66940	17.69	(2x420)+(8x27 0)+(1x390.0) =3390.0	$(2x0)+(8x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(8x0)+(1x7000) =7000.0	
C12:0	CH ₃ (CH ₂) ₁₀ COOCH ₃ (Methyl laurate)	(2x33.5)+(10x16.1) +(1x18.0) =246	(2x4710)+(10x4940) +(1x18000) = 76820	17.67	(2x420)+(10x2 70)+(1x390.0) =3930.0	$(2x0)+(10x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(10x0)+(1x7000) =7000.0	
C14:0	CH ₃ (CH ₂) ₁₂ COOCH ₃ (Methyl myristate)	(2x33.5)+(12x16.1) +(1×18.0) =278.2	(2x4710)+(12x4940) +(1x18000) = 86700	17.65	(2x420)+(12x2 70)+(1x390.0) =4470	$(2x0)+(12x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(12x0)+(1x7000) =7000.0	
C15:0	CH ₃ (CH ₂) ₁₃ COOCH ₃ (Methyl pentadecanoate)	(2x33.5)+(13x16.1) +(1x18.0) =294.3	(2x4710)+(13x4940) +(1x18000) = 91640	17.65	(2x420)+(13x2 70)+(1x390) = 4740	$(2x0)+(13x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(13x0)+(1x7000) =7000.0	
C16:0	CH ₃ (CH ₂) ₁₄ COOCH ₃ (Methyl palmitate)	(2x33.5)+(14x16.1) +(1x18.0) =310.4	(2x4710)+(14x4940) +(1x18000) = 96580	17.64	(2x420)+(14x2) 70)+(1x390.0) =5010.0	$(2x0)+(14x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(14x0)+(1x7000) =7000.0	
C16:1	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl palmitoleate)	(2x33.5)+(12x16.1) +(1x18.1)+(2x13.5) =305.2	(2x4710)+(12x4940) +(2x4310)+ (1x18000) =95320	17.67	(2x420)+(12x2 70)+(1x390) +(2x(200)) =4870.0	$(2x0)+(12x0)+(1x(490.0)^2)+(2x0) = 240100.0$	(2x0)+(12x0)+(1x7000) +(2x0) =7000.0	

Table A2-5 Calculation of Hildebrand solubility parameters (Fedor's method) and Hansen solubility parameters of fatty acid methyl esters by component group contributions (Hoftyzer-van Krevelen methods) [196, 212, 213, 217, 245]

C17:0	CH ₃ (CH ₂) ₁₅ COOCH ₃ (Methyl pentadecanoate)	(2x33.5)+(15x16.1) +(1x18.0) =326.5	(2x4710)+(15x4940) +(1x18000) = 101520	17.63	(2x420)+(15x2) 70)+(1x390.0) =5280	$(2x0)+(15x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(15x0)+(1x7000) =7000.0
C18: 0	CH ₃ (CH ₂) ₁₆ COOCH ₃ (Methyl stearate)	(2x33.5)+(16x16.1) +(1x18.0) =342.6	(2x4710)+(16x4940) +(1x18000) = 106460	17.63	(2x420)+(16x2 70)+(1x390.0) =5550.0	$(2x0)+(16x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(16x0)+(1x7000) =7000.0
C18: 1	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl oleate)	(2x33.5)+(14x16.1) +(1x18)+(2x13.5) =337.4	(2x4710)+(14x4940) +(2x4310)+(1x18000)=105200	17.66	(2x420)+(14x2) 70)+(1x390) +(2x(200)) =5410.0	$(2x0)+(14x0)+(1x(490.0)^2)+$ (2x0) = 240100.0	(2x0)+(14x0)+(1x7000) +(2x0) =7000.0
C18: 2	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl linoleate)	(2x33.5)+(12x16.1) +(1x18)+(4x13.5) =332.2	(2x4710)+(12x4940) +(4x4310)+(1x18000)=103940	17.69	(2x420)+(12x2) 70)+(1x390) +(4x(200)) =5270	$(2x0)+(12x0)+(1x(490.0)^2)+$ (4x0) = 240100.0	(2x0)+(12x0)+(1x7000) +(4x0) =7000.0
C18: 3	CH ₃ CH ₂ CH=CHCH ₂ C H=CHCH ₂ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl linolenate)	(2x33.5)+(10x16.1) +(1x18)+(6x13.5) =327	(2x4710)+(10x4940) +(6x4310)+(1x18000)=102680	17.72	(2x420)+(10x2) 70)+(1x390) +(6x(200)) =5130.0	$(2x0)+(10x0)+(1x(490.0)^2)+(6x0) = 240100.0$	(2x0)+(10x0)+(1x7000) +(6x0) =7000.0
C18:1 (OH)	CH ₃ (CH ₂) ₅ CH(OH)CH ₂ CH=CH(CH ₂) ₇ COOCH ₃ (Methyl ricinoleate)	(2x33.5)+(13x16.1) +(1x18)+(2x(13.5)) +(1x-1.0))+ (1x10.0) =330.3	(2x4710)+(13x4940) +(1x3430)+(1x29800)+(1x18000)+(2x431 0)=133490	20.10	(2x420)+(13x2) 70)+(1x390) +(2x(200))+(1) x80)+(1x210) =5430.0	$(2x0)+(13x0)+(1x(490.0)^2)+(2x0)+(1x0)+(1x(500)^2)=$ 490100.0	(2x0)+(13x0)+(1x7000) +(2x0)+(1x0)+(1x20000))=27000.0
C20: 0	CH ₃ (CH ₂) ₁₈ COOCH ₃ (Methyl arachidate)	(2x33.5)+(18x16.1) +(1x18.0) =374.8	(2x4710)+(18x4940) +(1x18000) = 116340	17.62	(2x420)+(18x2 70)+(1x390.0) =6090.0	$(2x0)+(18x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(18x0)+(1x7000) =7000.0
C20: 1	CH ₃ (CH2) ₇ CH=CH(CH ₂) ₉ COOCH ₃ (Methyl cis-11- eicosenoate)	(2x33.5)+(16x16.1) +(1x18)+(2x13.5) =369.6	(2x4710)+(16x4940) +(2x4310)+(1x18000)=115080	17.65	(2x420)+(16x2 70)+(1x390) +(2x(200)) =5950.0	$(2x0)+(16x0)+(1x(490.0)^2)+$ (2x0) = 240100.0	(2x0)+(16x0)+(1x7000) +(2x0) =7000.0
C22: 0	CH ₃ (CH ₂) ₂₀ COO CH ₃ (Methyl behenate)	(2x33.5)+(20x16.1) +(1x18.0) =407	(2x4710)+(20x4940) +(1x18000) = 126220	17.61	(2x420)+(20x2 70)+(1x390.0) =6630.0	$(2x0)+(20x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(20x0)+(1x7000) =7000.0

C22: 1	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₁₁ COOCH ₃ (Methyl erucate)	(2x33.5)+(18x16.1) + $(1x18.1)+(2x13.5)$ = 401.8	(2x4710)+(18x4940) +(2x4310)+(1x18000)=124960	17.64	(2x420)+(20x2 70)+(1x390) +(2x(200)) =7030.0	$(2x0)+(20x0)+(1x(490.0)^2)+$ (2x0) = 240100.0	(2x0)+(20x0)+(1x7000) +(2x0) =7000.0
C24:0	CH ₃ (CH ₂) ₂₂ COOCH ₃ (Methyl tetracosanoate)	(2x33.5)+(22x16.1) +(1x18.0) =439.2	(2x4710)+(22x4940) +(1x18000) = 136100	17.60	(2x420)+(22x2 70)+(1x390.0) =7170.0	$(2x0)+(22x0)+(1x(490.0)^2)$ =240100.0	(2x0)+(22x0)+(1x7000) =7000.0

Table A2-6 Calculation of solubility parameters and HSP components of FAMEs (Fedors and Hoftyzer–Van Krevelen methods)

	Fedors' group contribution for Hildebrand solubility parameters		Hoftyzer-va	Hoftyzer-van Krevelen group contribution method for Hansen solubility parameters								
FAME Group	$\frac{\sum V_m}{(cm^{3/} mol)}$	E _{coh} (J/mol)	$\begin{array}{l} \delta_1 = \\ [Ecoh/\\Vm]^{0.5} \end{array}$	$\begin{array}{l} \sum \phi di \\ (MPa)^{1/2} . \\ cm^3 . \ mol^{-1} \end{array}$	$\begin{array}{l} \sum (\phi_{pi})^2 \\ (MPa)^{1/2}. \\ cm^3. \ mol^{-1} \end{array}$	∑Ehi J.mol⁻¹	$\begin{array}{l} \delta_d = (\sum \phi_{di} / \\ \sum V_m) \\ (MPa)^{1/2} \end{array}$	$\delta_p = \frac{\left(\Sigma \varphi_p^2\right)^{0.5}}{\Sigma v_m}$ MPa) ^{1/2}	$\delta_h = \left[\frac{\sum E_h}{V_m}\right]^{0.5} $ (MPa) ^{1/2}	$\begin{array}{l} \delta_{2} = \\ (\delta_{d}{}^{2} + \delta_{p}{}^{2} + \\ \delta_{h}{}^{2})^{0.5} \\ (MPa)^{1/2} \end{array}$	parameter, $\delta_t = 0.5 x (\delta_1 + \delta_2)$ (MPa) ^{1/2}	
C8:0	181.6	57060	17.73	2850	240100	7000	15.69	2.70	1.20	15.97	16.85	
C10:0	213.8	66940	17.69	3390	240100	7000	15.86	2.29	1.19	16.06	16.88	
C12:0	246	76820	17.67	3930	240100	7000	15.98	1.99	1.18	16.14	16.91	
C14:0	278.2	86700	17.65	4470	240100	7000	16.07	1.76	1.17	16.21	16.93	
C15:0	294.3	91640	17.65	4740	240100	7000	16.11	1.66	1.17	16.23	16.94	
C16:0	310.4	96580	17.64	5010	240100	7000	16.14	1.58	1.17	16.26	16.95	
C16:1	305.2	95320	17.67	4870	240100	7000	15.96	1.61	1.17	16.08	16.88	
C17:0	326.5	101520	17.63	5280	240100	7000	16.17	1.50	1.17	16.28	16.96	
C18: 0	342.6	106460	17.63	5550	240100	7000	16.20	1.43	1.16	16.30	16.97	
C18: 1	337.4	105200	17.66	5410	240100	7000	16.03	1.45	1.16	16.14	16.90	
C18: 2	332.2	103940	17.69	5270	240100	7000	15.86	1.48	1.16	15.97	16.83	
C18: 3	327	102680	17.72	5130	240100	7000	15.69	1.50	1.17	15.80	16.76	

C18:1(OH)	330.3	133490	20.10	5430	490100	27000	16.44	2.12	1.25	16.62	18.36	
C20: 0	374.8	116340	17.62	6090	240100	7000	16.25	1.31	1.16	16.34	16.98	
C20: 1	369.6	115080	17.65	5950	240100	7000	16.10	1.33	1.16	16.19	16.92	
C22: 0	407	126220	17.61	6630	240100	7000	16.29	1.20	1.15	16.37	16.99	
C22: 1	401.8	124960	17.64	7030	240100	7000	17.50	1.22	1.15	17.58	17.61	
C24:0	439.2	136100	17.60	7170	240100	7000	16.33	1.12	1.15	16.40	17.00	

Table A2-7 Hoy's method to determine the solubility parameter for FAMEs

FAME Groups	Molar Volume from Density Measurement, V _m (cm ³ /mol)	φ _t [(MPa) ^{1/2} mol ⁻¹]	$\delta_t = \frac{\varphi_t + B}{v_m},$ B=227	FAME Groups	Molar Volume from Density Measurement, V _m (cm ³ /mol)	$\begin{array}{l} \phi_t \\ [(MPa)^{1/2}mol^{-1}] \end{array}$	$\delta_t = \frac{\varphi_t + B}{V_m},$ B=227
C8:0	160.14	2861	19.28	C18: 1	310.92	5511	18.45
C10:0	191.25	3399	18.96	C18: 2	306.17	5471	18.61
C12:0	222.35	3937	18.73	C18: 3	301.42	5431	18.77
C14:0	253.46	4475	18.55	C18:1(OH)	317.40	6093	19.91
C15:0	269.01	4744	18.48	C20: 0	346.78	6089	18.21
C16:0	284.57	5013	18.41	C20: 1	342.03	6049	18.35
C16:1	279.82	4973	18.58	C22: 0	377.88	6627	18.14
C17:0	300.12	5282	18.36	C22: 1	373.13	6587	18.26
C18: 0	315.67	5551	18.30	C24:0	408.99	7165	18.07

FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters of FAMEs by Hoy, $\delta_t = \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$	WTB FAME fraction, x _i = (% Quantity/ 100)	Solubility Parameters of FAMEs by Fedors $\delta = \operatorname{xi} \left[\frac{E_{\text{coh}}}{V_m} \right]^{0.5} (\text{MPa})^{1/2}$	Solubility parameters of FAMEs by Hoy, $\delta_t = xi \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$
C14:0	17.65	18.55	0.0403	0.71	0.75
C15:0	17.65	18.48	0.0103	0.18	0.19
C16:0	17.64	18.41	0.235	4.15	4.33
C16:1	17.67	18.58	0.0382	0.68	0.71
C17:0	17.63	18.36	0.0308	0.54	0.57
C18: 0	17.63	18.30	0.2819	4.97	5.16
C18: 1	17.66	18.45	0.3321	5.86	6.13
C18: 2	17.69	18.61	0.0148	0.26	0.28
C18: 3	17.72	18.77	0.0167	0.30	0.31
			δt=sum	17.65	18.42

Table A2-8 Hildebrand solubility parameters of the FAME compositions of WTB biodiesel fuel by Fedors, and Hoy methods

Table A2-9 Hildebrand solubility parameters of the FAME compositions of WCB biodiesel fuel by Fedors, and Hoy methods

FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5} (MPa)^{1/2}$	Solubility parameters of FAMEs by Hoy, $\delta_t = \frac{\varphi_t + B}{V_m} (\text{MPa})^{1/2}$	WCB FAME fraction, x _i = (% Quantity/100)	Solubility Parameters of FAMEs by Fedors $\delta =$ xi $\left[\frac{E_{coh}}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters of FAMEs by Hoy, $\delta_t = xi \frac{\varphi_t + B}{V_m} (\text{MPa})^{1/2}$
C14:0	17.65	18.55	0.048	0.85	0.89
C16:0	17.64	18.41	0.165	2.91	3.04

C16:1	17.67	18.58	0.019	0.34	0.35
C18: 0	17.63	18.30	0.041	0.72	0.75
C18: 1	17.66	18.45	0.441	7.79	8.14
C18: 2	17.69	18.61	0.235	4.16	4.37
C18: 3	17.72	18.77	0.0399	0.71	0.75
C20: 0	17.62	18.21	0.0041	0.07	0.07
C22: 0	17.61	18.14	0.0069	0.12	0.13
			δt=sum(δti)	17.66	18.49

Table A2-10 Hildebrand solubility parameters of the FAME compositions of CaB biodiesel fuel by Fedors, and Hoy methods

FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5} (MPa)^{1/2}$	Solubility parameters of FAMEs by Hoy, $\delta_t = \frac{\varphi_t + B}{V_m} (\text{MPa})^{1/2}$	CaB FAME fraction, x _i = (% Quantity/100)	Solubility Parameters by Fedors $\delta = xi \left[\frac{E_{coh}}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters by Hoy $\delta_t = xi \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$
C16:0	17.64	18.41	0.0074	0.13	0.14
C18: 0	17.63	18.30	0.0055	0.10	0.10
C18: 1	17.66	18.45	0.0385	0.68	0.71
C18: 2	17.69	18.61	0.0558	0.99	1.04
C18: 3	17.72	18.77	0.0046	0.08	0.09
C18:1(OH)	20.10	19.91	0.8853	17.80	17.63
C20: 0	17.62	18.21	0.0031	0.05	0.06
			δt=sum(δti)	19.83	19.76

FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{v_m}\right]^{0.5} (MPa)^{1/2}$	Solubility parameters of FAMEs by Hoy, $\delta_t = \frac{\varphi_t + B}{V_m} (\text{MPa})^{1/2}$	PB FAME fraction, x _i = (% Quantity/100)	Solubility Parameters by Fedors $\delta = xi \left[\frac{E_{coh}}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters of FAMEs by Hoy, $\delta_t = xi \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$
C16:0	17.64	18.41	0.092	1.62	1.69
C16:1	17.67	18.58	0.0022	0.04	0.04
C18: 0	17.63	18.30	0.027	0.48	0.49
C18: 1	17.66	18.45	0.153	2.70	2.82
C18: 2	17.69	18.61	0.719	12.72	13.38
C18: 3	17.72	18.77	0.0069	0.12	0.13
			δt=sum(δti)	17.68	18.56

Table A2-11 Hildebrand solubility parameters of the FAME compositions of PB biodiesel fuel by Fedors, and Hoy methods

Table A2-12 Hildebrand solubility parameters of the FAME compositions of SB biodiesel fuel by Fedors, and Hoy methods

FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5} (MPa)^{1/2}$	Solubility parameters of FAMEs by Hoy, $\delta_t = \frac{\varphi_t + B}{V_m} (\text{MPa})^{1/2}$	SB FAME fraction, xi = (% Quantity/100)	Solubility Parameters by Fedors $\delta = xi \left[\frac{E_{coh}}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters of FAMEs by Hoy, $\delta_t = xi \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$
C16:0	17.64	18.41	0.1215	2.14	2.24
C18: 0	17.63	18.30	0.0383	0.68	0.70
C18: 1	17.66	18.45	0.2677	4.73	4.94
C18: 2	17.69	18.61	0.5415	9.58	10.08
C20: 0	17.62	18.21	0.0309	0.54	0.56
			δt=sum(δti)	17.67	18.52
FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5} (MPa)^{1/2}$	Solubility parameters of FAMEs by Hoy, $\delta_t = \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$	CB FAME fraction, xi = (% Quantity/100)	Solubility Parameters by Fedors $\delta = xi \left[\frac{E_{coh}}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters of FAMEs by Hoy, $\delta_t = xi \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$
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C8:0	17.73	19.28	0.0019	0.03	0.04
C10:0	17.69	18.96	0.001	0.02	0.02
C12:0	17.67	18.73	0.001	0.02	0.02
C14:0	17.65	18.55	0.001	0.02	0.02
C16:0	17.64	18.41	0.0635	1.12	1.17
C18: 0	17.63	18.30	0.0565	1.00	1.03
C18: 1	17.66	18.45	0.4247	7.50	7.84
C18: 2	17.69	18.61	0.1665	2.95	3.10
C18: 3	17.72	18.77	0.2785	4.94	5.23
C20: 0	17.62	18.21	0.002	0.04	0.04
C22: 0	17.61	18.14	0.002	0.04	0.04
C22: 1	17.64	18.26	0.0014	0.02	0.03
			δt=sum(δti)	17.68	18.56

Table A2-13 Hildebrand solubility parameters of the FAME compositions of CB biodiesel fuel by Fedors, and Hoy methods

FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5} (MPa)^{1/2}$	Solubility parameters of WTC FAME fraction, xi FAMEs by Hoy, = (% Quantity/100) $\delta_t = \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$		Solubility Parameters by Fedors $\delta = xi \left[\frac{E_{coh}}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters of FAMEs by Hoy, $\delta_t = xi \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$
C14:0	17.65	18.55	0.0428	0.76	0.79
C15:0	17.65	18.48	0.0072	0.13	0.13
C16:0	17.64	18.41	0.2126	3.75	3.91
C16:1	17.67	18.58	0.0321	0.57	0.60
C17:0	17.63	18.36	0.0209	0.37	0.38
C18: 0	17.63	18.30	0.2048	3.61	3.75
C18: 1	17.66	18.45	0.3669	6.48	6.77
C18: 2	17.69	18.61	0.0853	1.51	1.59
C18: 3	17.72	18.77	0.0241	0.43	0.45
C20: 0	17.62	18.21	0.0013	0.02	0.02
C22: 0	17.61	18.14	0.0022	0.04	0.04
			$\delta t=sum(\delta ti)$	17.65	18.45

Table A2-14 Hildebrand solubility parameters of the FAME compositions of WTC biodiesel fuel by Fedors, and Hoy methods

Table A2-15 Hildebrand solubility parameters of the FAME compositions of WTP biodiesel fuel by Fedors, and Hoy methods

FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{v_m}\right]^{0.5} (MPa)^{1/2}$	Solubility parameters of FAMEs by Hoy, $\delta_t = \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$	WTP FAME fraction, xi = (% Quantity/100)	Solubility Parameters by Fedors $\delta = xi \left[\frac{E_{coh}}{V_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters of FAMEs by Hoy, $\delta_t = xi \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$
C14:0	17.65	18.55	0.0274	0.48	0.51
C15:0	17.65	18.48	0.0071	0.13	0.13

C16:0	17.64	18.41	0.1893	3.34	3.49
C16:1	17.67	18.58	0.0265	0.47	0.49
C17:0	17.63	18.36	0.0211	0.37	0.39
C18: 0	17.63	18.30	0.2003	3.53	3.67
C18: 1	17.66	18.45	0.2751	4.86	5.08
C18: 2	17.69	18.61	0.2401	4.25	4.47
C18: 3	17.72	18.77	0.0136	0.24	0.26
			$\Delta t=sum(\delta ti)$	17.67	18.47

Table A2-16 Hildebrand solubility parameters of the FAME compositions of PWC biodiesel fuel by Fedors, and Hoy methods

FAME Group	Solubility Parameters of FAMEs by Fedors $\delta = \left[\frac{E_{coh}}{V_m}\right]^{0.5} (MPa)^{1/2}$	Solubility parameters of FAMEs by Hoy, $\delta_t = \frac{\varphi_t + B}{V_m} (\text{MPa})^{1/2}$	PWC FAME fraction, xi = (% Quantity/100)	Solubility Parameters by Fedors $\delta = xi \left[\frac{E_{coh}}{v_m}\right]^{0.5}$ (MPa) ^{1/2}	Solubility parameters of FAMEs by Hoy, $\delta_t = xi \frac{\varphi_t + B}{V_m} (MPa)^{1/2}$
C14:0	17.65	18.55	0.0149	0.26	0.28
C16:0	17.64	18.41	0.1146	2.02	2.11
C16:1	17.67	18.58	0.0074	0.13	0.14
C18: 0	17.63	18.30	0.0313	0.55	0.57
C18: 1	17.66	18.45	0.2421	4.27	4.47
C18: 2	17.69	18.61	0.5691	10.07	10.59
C18: 3	17.72	18.77	0.0172	0.30	0.32
C20: 0	17.62	18.21	0.0013	0.02	0.02
C22: 0	17.61	18.14	0.0021	0.04	0.04
			δt=sum(δti)	17.67	18.54

FAME Group	$\begin{array}{l} \sum \phi_{di} \\ (MPa)^{1/2}.c \\ m^3.mol^{-1} \end{array}$	$\frac{\sum(\phi_{pi})2}{(MPa)^{1/2}.c} \\ m^3.mol^{-1}$	∑E _{hi} J.mol ⁻¹	V _m (cm ³ /m ol)	WTB FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = \frac{\left(\sum_i (x_i \varphi_{di}) \right)}{V_m}$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{V_m}$ $(MPa)^{1/2}$	$\delta_h = \left[\sum_i \frac{x_i E_{hi}}{V_m}\right]^{0.5}$ $(MPa)^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$ $(\text{MPa})^{1/2}$
C14:0	4470	240100	7000	278.2	0.0403	180.141	9676.03	282.1	0.65	0.35	1.01	1.25
C15:0	4740	240100	7000	294.3	0.0103	48.822	2473.03	72.1	0.17	0.17	0.49	0.55
C16:0	5010	240100	7000	310.4	0.235	1177.35	56423.5	1645	3.79	0.77	2.30	4.50
C16:1	4870	240100	7000	305.2	0.0382	186.034	9171.82	267.4	0.61	0.31	0.94	1.16
C17:0	5280	240100	7000	326.5	0.0308	162.624	7395.08	215.6	0.50	0.26	0.81	0.99
C18: 0	5550	240100	7000	342.6	0.2819	1564.55	67684.2	1973.3	4.57	0.76	2.40	5.21
C18: 1	5410	240100	7000	337.4	0.3321	1796.66	79737.2	2324.7	5.33	0.84	2.62	6.00
C18: 2	5270	240100	7000	332.2	0.0148	77.996	3553.48	103.6	0.23	0.18	0.56	0.63
C18: 3	5130	240100	7000	327	0.0167	85.671	4009.67	116.9	0.26	0.19	0.60	0.68
					sum				16.10	3.83	11.73	20.97
	Hansen's so	lubility param	eters of W	TB by Hof	tyzer- van Kre	evelen metho	od		δd	бр	δh	δt (MPa) ^{1/2}

Table A2-17 Hansen solubility parameters of the FAME compositions of WTB biodiesel fuel by Hoftyzer-van Krevelen methods

Table A2-18 Hansen solubility parameters of the FAME compositions of WCB biodiesel fuel by Hoftyzer-van Krevelen methods

FAME Group	$\sum \phi_{di} (MPa)^{1/2} .cm^3.m$ ol ⁻¹	$\begin{array}{c} \sum(\phi_{pi})2\\ (MPa)^{1/2}.\\ cm^{3}.mol^{-1} \end{array}$	$\sum E_{hi}$ J.mol ⁻¹	V _m (cm ³ / mol)	WCB FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = \frac{\sum_i (x_i \varphi_{di})}{V_m}$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{V_m}$ (MPa) ^{1/2}	$\delta_h = \left[\sum_i \frac{x_i E_{hi}}{v_m}\right]^{0.5}$ $(MPa)^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5} (\text{MPa})^{1/2}$
C14:0	4470	240100	7000	278.2	0.048	214.56	11524.8	336	0.77	0.39	1.10	1.40
C16:0	5010	240100	7000	310.4	0.165	826.65	39616.5	1155	2.66	0.64	1.93	3.35

C16·1	4870	240100	7000	305.2	0.019	92 53	4561.9	133	0.30	0.22	0.66	0.76
010.1	1070	210100		505.2	0.019	2.55	150115	155	0.50	0.22	0.00	0.76
C18:0	5550	240100	7000	342.6	0.041	227.55	9844.1	287	0.66	0.29	0.92	1.17
C18:1	5410	240100	7000	337.4	0.441	2385.81	105884.1	3087	7.07	0.96	3.02	7.75
C18:2	5270	240100	7000	332.2	0.235	1238.45	56423.5	1645	3.73	0.72	2.23	4.40
C18:3	5130	240100	7000	327	0.0399	204.687	9579.99	279.3	0.63	0.30	0.92	1.16
C20:0	6090	240100	7000	374.8	0.0041	24.969	984.41	28.7	0.07	0.08	0.28	0.30
C22:0	6630	240100	7000	407	0.0069	45.747	1656.69	48.3	0.11	0.10	0.34	0.38
					sum				16.01	3.70	11.40	20.65
Hansen's solubility parameters of WCB by Hoftyzer- van Krevelen method								δd	δр	δh	δt (MPa) ^{1/2}	

Table A2-19 Hansen solubility parameters of the FAME compositions of CaB biodiesel fuel by Hoftyzer-van Krevelen methods

FAME Group	$\begin{array}{c} \sum \phi_{di} \\ (MPa)^{1/} \\ {}^2.cm^3.m \\ ol^{-1} \end{array}$	$\begin{array}{l} \sum (\phi_{pi}) 2 \\ (MPa)^{1/2}. \\ cm^3.mol^{-1} \end{array}$	$\sum E_{hi}$ J.mol ⁻¹	V _m (cm ³ /m ol)	CaB FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = (\sum_i (x_i \varphi_{di}) / V_m)$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{V_m}$ $(MPa)^{1/2}$	$\delta_h = \left[\sum_i \frac{x_i E_{hi}}{v_m}\right]^{0.5}$ $(MPa)^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$ $(\text{MPa})^{1/2}$
C18:0	5550	240100	7000	342.6	0.0055	30.525	1320.55	38.5	0.09	0.11	0.34	0.36
C18:1	5410	240100	7000	337.4	0.0385	208.285	9243.85	269.5	0.62	0.28	0.89	1.12
C18:2	5270	240100	7000	332.2	0.0558	294.066	13397.58	390.6	0.89	0.35	1.08	1.44
C18:3	5130	240100	7000	327	0.0046	23.598	1104.46	32.2	0.07	0.10	0.31	0.34
C18:1 (OH)	5430	490100	27000	330.3	0.8853	4807.18	433885.53	23903.1	14.55	1.99	8.51	16.98
C20:0	6090	240100	7000	374.8	0.0031	18.879	744.31	21.7	0.05	0.07	0.24	0.26
					sum				16.39	3.04	11.78	20.94
	Hansen	's solubility	parameters	s of CaB b	y Hoftyzer- van	Krevelen me	ethod		δd	бр	δh	δt (MPa) ^{1/2}

FAME Group	$\begin{array}{l} \sum \phi_{di} \\ (MPa)^{1/2}.c \\ m^3.mol^{-1} \end{array}$	$\begin{array}{l} \sum (\phi_{pi}) 2 \\ (MPa)^{1/2}. \\ cm^3.mol^{-1} \end{array}$	$\sum_{hi} E_{hi}$ J.mol ⁻¹	V _m (cm ³ /m ol)	PB FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = \frac{\sum_i (x_i \varphi_{di})}{V_m}$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{v_m}$ (MPa) ^{1/2}	$\delta_h = \left[\sum_i \frac{x_i E_{hi}}{v_m}\right]^{0.5}$ $(\text{MPa})^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$ $(\text{MPa})^{1/2}$
C16:0	5010	240100	7000	310.4	0.092	460.92	22089.2	644	1.48	0.48	1.44	2.12
C16:1	4870	240100	7000	305.2	0.0022	10.714	528.22	15.4	0.04	0.08	0.22	0.24
C18:0	5550	240100	7000	342.6	0.027	149.85	6482.7	189	0.44	0.24	0.74	0.89
C18:1	5410	240100	7000	337.4	0.153	827.73	36735.3	1071	2.45	0.57	1.78	3.08
C18:2	5270	240100	7000	332.2	0.719	3789.13	172631.9	5033	11.41	1.25	3.89	12.12
C18:3	5130	240100	7000	327	0.0069	35.397	1656.69	48.3	0.11	0.12	0.38	0.42
					sum				15.93	2.73	8.47	18.88
	Hansen's s	olubility para	ameters of	PB by Hof	tyzer- van Kre	evelen metho	od		δ_d	δ_p	δ_h	$\delta_t (MPa)^{1/2}$

Table A2-20 Hansen solubility parameters of the FAME compositions of PB biodiesel fuel by Hoftyzer-van Krevelen methods

Table A2-21 Hansen solubility parameters of the FAME compositions of SB biodiesel fuel by Hoftyzer-van Krevelen methods

FAME Group	$\begin{array}{l} \sum \phi_{di} \\ (MPa)^{1/2}.c \\ m^3.mol^{-1} \end{array}$	$\begin{array}{l} \sum (\phi_{pi}) 2 \\ (MPa)^{1/2}.c \\ m^3.mol^{-1} \end{array}$	∑E _{hi} J.mol ⁻¹	V _m (cm ³ / mol)	SB FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = \frac{\sum_i (x_i \varphi_{di})}{V_m}$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{V_m}$ $(MPa)^{1/2}$	$\delta_h = \left[\sum_i \frac{x - E_{hi}}{v_m}\right]^{0.5}$ $(MPa)^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$ $(\text{MPa})^{1/2}$
C14:0	4470	240100	7000	278.2	0.0403	180.141	9676.03	282.1	0.65	0.35	1.01	1.25
C15:0	4740	240100	7000	294.3	0.0103	48.822	2473.03	72.1	0.17	0.17	0.49	0.55
C16:0	5010	240100	7000	310.4	0.235	1177.35	56423.5	1645	3.79	0.77	2.30	4.50
C16:1	4870	240100	7000	305.2	0.0382	186.034	9171.82	267.4	0.61	0.31	0.94	1.16
C17:0	5280	240100	7000	326.5	0.0308	162.624	7395.08	215.6	0.50	0.26	0.81	0.99
C18:0	5550	240100	7000	342.6	0.2819	1564.55	67684.2	1973.3	4.57	0.76	2.40	5.21

C18:1	5410	240100	7000	337.4	0.3321	1796.66	79737.2	2324.7	5.33	0.84	2.62	6.00
C18:2	5270	240100	7000	332.2	0.0148	77.996	3553.48	103.6	0.23	0.18	0.56	0.63
C18:3	5130	240100	7000	327	0.0167	85.671	4009.67	116.9	0.26	0.19	0.60	0.68
					sum				16.10	3.83	11.73	20.97
	Hansen	's solubility par	ameters of	SB by Ho	oftyzer- van	Krevelen meth	iod		δ_d	δ_p	δ_{h}	$\delta_t(MPa)^{1/2}$

Table A2-22 Hansen solubility parameters of the FAME compositions of CB biodiesel fuel by Hoftyzer-van Krevelen methods

FAME Group	$\begin{array}{c} \sum \phi_{di} \\ (MPa)^{1/2}.c \\ m^3.mol^{-1} \end{array}$	$\frac{\sum(\phi_{pi})2}{(MPa)^{1/2}}.\\ cm^{3}.mol^{-1}$	$\sum_{hi} E_{hi}$ J.mol ⁻¹	V _m (cm ³ /m ol)	CB FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = \frac{\sum_i (x_i \varphi_{di})}{V_m}$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{V_m}$ (MPa) ^{1/2}	$\delta_h = \left[\sum_i \frac{x_i E_{hi}}{v_m}\right]^{0.5}$ $(MPa)^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$ $(MPa)^{1/2}$
C8:0	2850	240100	7000	181.6	0.0019	5.415	456.19	13.3	0.03	0.12	0.27	0.30
C10:0	3390	240100	7000	213.8	0.001	3.39	240.1	7	0.02	0.07	0.18	0.20
C12:0	3930	240100	7000	246	0.001	3.93	240.1	7	0.02	0.06	0.17	0.18
C14:0	4470	240100	7000	278.2	0.001	4.47	240.1	7	0.02	0.06	0.16	0.17
C16:0	5010	240100	7000	310.4	0.0635	318.14	15246.4	444.5	1.02	0.40	1.20	1.63
C18:0	5550	240100	7000	342.6	0.0565	313.58	13565.7	395.5	0.92	0.34	1.07	1.45
C18:1	5410	240100	7000	337.4	0.4247	2297.63	101970.5	2972.9	6.81	0.95	2.97	7.49
C18:2	5270	240100	7000	332.2	0.1665	877.46	39976.7	1165.5	2.64	0.60	1.87	3.29
C18:3	5130	240100	7000	327	0.2785	1428.71	66867.9	1949.5	4.37	0.79	2.44	5.07
C20:0	6090	240100	7000	374.8	0.002	12.18	480.2	14	0.03	0.06	0.19	0.20
C22:0	6630	240100	7000	407	0.002	13.26	480.2	14	0.03	0.05	0.19	0.20
C22:1	7030	240100	7000	401.8	0.0014	9.842	336.14	9.8	0.02	0.05	0.16	0.16
					sum				15.93	3.54	10.87	20.33
	Hansen's s	olubility par	ameters of	CB by Ho	ftyzer- van Kro	evelen metho	bd		δ_d	δ_p	δ_h	$\delta_t (MPa)^{1/2}$

FAME Group	$\begin{array}{l} \sum \phi_{di} \\ (MPa)^{1/2}. \\ cm^3.mol^{-1} \end{array}$	$\frac{\sum (\phi_{pi})2}{(MPa)^{1/2}}.\\ cm^{3}.mol^{-1}$	$\sum E_{hi}$ J.mol ⁻¹	V _m (cm ³ /m ol)	WTC FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = \frac{\delta_d}{(\sum_i (x_i \varphi_{di}) / V_m)}$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{V_m}$ (MPa) ^{1/2}	$\delta_h = \left[\sum_i \frac{x_i E_{hi}}{v_m}\right]^{0.5}$ $(MPa)^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$ $(\text{MPa})^{1/2}$
C14:0	4470	240100	7000	278.2	0.0428	191.316	10276.28	299.6	0.69	0.36	1.04	1.30
C15:0	4740	240100	7000	294.3	0.0072	34.128	1728.72	50.4	0.12	0.14	0.41	0.45
C16:0	5010	240100	7000	310.4	0.2126	1065.126	51045.26	1488.2	3.43	0.73	2.19	4.14
C16:1	4870	240100	7000	305.2	0.0321	156.327	7707.21	224.7	0.51	0.29	0.86	1.04
C17:0	5280	240100	7000	326.5	0.0209	110.352	5018.09	146.3	0.34	0.22	0.67	0.78
C18:0	5550	240100	7000	342.6	0.2048	1136.64	49172.48	1433.6	3.32	0.65	2.05	3.95
C18:1	5410	240100	7000	337.4	0.3669	1984.929	88092.69	2568.3	5.88	0.88	2.76	6.56
C18:2	5270	240100	7000	332.2	0.0853	449.531	20480.53	597.1	1.35	0.43	1.34	1.95
C18:3	5130	240100	7000	327	0.0241	123.633	5786.41	168.7	0.38	0.23	0.72	0.84
C20:0	6090	240100	7000	374.8	0.0013	7.917	312.13	9.1	0.02	0.05	0.16	0.16
C22:0	6630	240100	7000	407	0.0022	14.586	528.22	15.4	0.04	0.06	0.19	0.21
					sum				16.07	4.03	12.38	21.38
Hansen's solubility parameters of WTC by Hoftyzer- van Krevelen method δ_d						δ_d	δ _p	δ_h	$\delta_t (MPa)^{1/2}$			

Table A2-23 Hansen solubility parameters of the FAME compositions of WTC biodiesel fuel by Hoftyzer-van Krevelen methods

FAME Group	$\begin{array}{l} \sum \phi_{di} \\ (MPa)^{1/2}. \\ cm^3.mol^{-1} \end{array}$	$\begin{array}{c} \sum(\phi_{pi})2 \\ (MPa)^{1/2}. \\ cm^{3}.mol^{-1} \end{array}$	$\sum E_{hi}$ J.mol ⁻¹	V _m (cm ³ /m ol)	WTP FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = \frac{\sum_i (x_i \varphi_{di})}{V_m}$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{V_m}$ $(MPa)^{1/2}$	$\delta_h = \left[\sum_i \frac{x_i E_{hi}}{v_m}\right]^{0.5}$ $(MPa)^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$ $(\text{MPa})^{1/2}$
C14:0	4470	240100	7000	278.2	0.0274	122.478	6578.74	191.8	0.44	0.29	0.83	0.98
C15:0	4740	240100	7000	294.3	0.0071	33.654	1704.71	49.7	0.11	0.14	0.41	0.45
C16:0	5010	240100	7000	310.4	0.1893	948.393	45450.93	1325.1	3.06	0.69	2.07	3.75
C16:1	4870	240100	7000	305.2	0.0265	129.055	6362.65	185.5	0.42	0.26	0.78	0.92
C17:0	5280	240100	7000	326.5	0.0211	111.408	5066.11	147.7	0.34	0.22	0.67	0.79
C18:0	5550	240100	7000	342.6	0.2003	1111.665	48092.03	1402.1	3.24	0.64	2.02	3.88
C18:1	5410	240100	7000	337.4	0.2751	1488.291	66051.51	1925.7	4.41	0.76	2.39	5.07
C18:2	5270	240100	7000	332.2	0.2401	1265.327	57648.01	1680.7	3.81	0.72	2.25	4.48
C18:3	5130	240100	7000	327	0.0136	69.768	3265.36	95.2	0.21	0.17	0.54	0.61
					sum				16.05	3.90	11.96	20.93
	Hansen's	solubility pa	arameters o	of WTP by	Hoftyzer- van	Krevelen met	hod		δ_d	δ _p	δ_h	$\delta_t (MPa)^{1/2}$

Table A2-24 Hansen solubility parameters of the FAME compositions of WTP biodiesel fuel by Hoftyzer-van Krevelen methods

FAME Group	$\begin{array}{l} \sum \phi_{di} \\ (MPa)^{1/2}.c \\ m^3.mol^{-1} \end{array}$	$\begin{array}{l} \sum (\phi_{pi}) 2 \\ (MPa)^{1/2}. \\ cm^3.mol^{-1} \end{array}$	$\sum E_{hi}$ J.mol ⁻¹	V _m (cm ³ /m ol)	PWC FAME fractions	$\sum_i x_i \varphi_{di}$	$\sum_i x_i \varphi_{pi}^2$	$\sum_i x_i \varphi_{pi}^2$	$\delta_d = \frac{\sum_i (x_i \varphi_{di})}{V_m}$ (MPa) ^{1/2}	$\delta_p = \frac{\left(\sum_i x_i \varphi_{pi}^2\right)^{0.5}}{v_m}$ $(MPa)^{1/2}$	$\delta_h = \left[\sum \frac{x_i E_{hi}}{V_m}\right]^{0.5}$ $(MPa)^{1/2}$	$\delta_t = \left(\delta_d^2 + \delta_p^2 + \delta_h^2\right)^{0.5}$ $(MPa)^{1/2}$
C14:0	4470	240100	7000	278.2	0.0149	66.603	3577.49	104.3	0.24	0.21	0.61	0.69
C16:0	5010	240100	7000	310.4	0.1146	574.146	27515.46	802.2	1.85	0.53	1.61	2.51
C16:1	4870	240100	7000	305.2	0.0074	36.038	1776.74	51.8	0.12	0.14	0.41	0.45
C18:0	5550	240100	7000	342.6	0.0313	173.715	7515.13	219.1	0.51	0.25	0.80	0.98
C18:1	5410	240100	7000	337.4	0.2421	1309.76	58128.21	1694.7	3.88	0.71	2.24	4.54
C18:2	5270	240100	7000	332.2	0.5691	2999.16	136640.9	3983.7	9.03	1.11	3.46	9.73
C18:3	5130	240100	7000	327	0.0172	88.236	4129.72	120.4	0.27	0.20	0.61	0.69
C20:0	6090	240100	7000	374.8	0.0013	7.917	312.13	9.1	0.02	0.05	0.16	0.16
C22:0	6630	240100	7000	407	0.0021	13.923	504.21	14.7	0.03	0.06	0.19	0.20
					sum				15.95	3.27	10.09	19.96
	Hansen's s	olubility par	ameters of	PWC by H	loftyzer- van H	Krevelen met	thod		δ_d	δ _p	δ_h	$\delta_t (MPa)^{1/2}$

Table A2-25 Hansen solubility parameters of the FAME compositions of PWC biodiesel fuel by Hoftyzer-van Krevelen methods

FAME Group	FAME fraction= (% Ouantity/100)	Solubility Parameters by	Solubility parameters by	Hoftyzer-van Krev		Average $(MPa)^{1/2}$		
		Fedors $\delta = [Ecoh/Vm]^{0.5}$ $(MPa)^{1/2}$	Hoy (MPa) ^{1/2} $\delta_t = \frac{\varphi_t + B}{V_m}$	$\delta_d \!\!=\! \sum \! \phi_{di} \! / \! \sum \! V_m$	$\delta_p = \frac{\left(\Sigma \varphi_p^2\right)^{0.5}}{\Sigma v_m}$	$\delta_h = [(\sum E_h)/V_m]^{0.5}$	$\begin{array}{l} \delta = \\ (\delta_d{}^2 + \delta_p{}^2 + \\ \delta_h{}^2)^{0.5} \end{array}$	ot, (111 a)
C14:0	0.0403	0.71	0.75	0.65	0.07	0.05	0.65	0.70
C15:0	0.0103	0.18	0.19	0.17	0.02	0.01	0.17	0.18
C16:0	0.235	4.15	4.33	3.79	0.37	0.27	3.82	4.10
C16:1	0.0382	0.68	0.71	0.61	0.06	0.04	0.61	0.67
C17:0	0.0308	0.54	0.57	0.50	0.05	0.04	0.50	0.54
C18: 0	0.2819	4.97	5.16	4.57	0.40	0.33	4.60	4.91
C18: 1	0.3321	5.86	6.13	5.33	0.48	0.39	5.36	5.78
C18: 2	0.0148	0.26	0.28	0.23	0.02	0.02	0.24	0.26
C18: 3	0.0167	0.30	0.31	0.26	0.03	0.02	0.26	0.29
	Sum	17.65	18.42	16.10	1.50	1.17	16.21	17.43

Table A2-26 Solubility parameters of the FAME compositions of WTB biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

FAME Group	Group FAME fraction= (% Solubility Parameters Quantity/100) by Fedors δ =[Ecoh/Vm] ^{0.5}		Solubility parameters by	Hoftyzer-van Kreve		Average δt		
		$\delta = [E \cosh / V m]^{0.3}$ (MPa) ^{1/2}	$\delta_t = \frac{\varphi_t + B}{v_m}$	$\delta_{d} \!\!=\! \sum \! \phi_{di} \! / \! \sum \! V_{m}$	$\delta_p = \frac{\left(\sum \varphi_p^2\right)^{0.5}}{\sum v_m}$ δp	$\begin{split} \delta_h &= \left[(\Sigma E_h) / V_m \right]^{0.5} \\ \delta \mathbf{h} \end{split}$	$\begin{array}{l} \delta = \\ (\delta_d{}^2 + \delta_p{}^2 + \\ \delta_h{}^2)^{0.5} \end{array}$	
C14:0	0.048	0.85	0.89	0.77	0.08	0.06	0.78	0.84
C16:0	0.165	2.91	3.04	2.66	0.26	0.19	2.68	2.88
C16:1	0.019	0.34	0.35	0.30	0.03	0.02	0.31	0.33
C18: 0	0.041	0.72	0.75	0.66	0.06	0.05	0.67	0.71
C18: 1	0.441	7.79	8.14	7.07	0.64	0.51	7.12	7.68
C18: 2	0.235	4.16	4.37	3.73	0.35	0.27	3.75	4.09
C18: 3	0.0399	0.71	0.75	0.63	0.06	0.05	0.63	0.70
C20: 0	0.0041	0.07	0.07	0.07	0.01	0.00	0.07	0.07
C22: 0	0.0069	0.12	0.13	0.11	0.01	0.01	0.11	0.12
	δt=sum(δti)	17.66	18.49	16.01	1.49	1.17	16.12	17.42

Table A2-27 Solubility parameters of the FAME compositions of WCB biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

FAME Group	FAME fraction = (% Quantity/100)	Solubility Parameters by Fedors δ=[Ecoh/Vm] ^{0.5}	Solubility parameters by Hoy (MPa) ^{1/2}	Hoftyzer-van Kre	Average δt, (MPa) ^{1/2}			
		(MPa) ^{1/2}	$\delta_t = \frac{\varphi_t + B}{V_m}$	$\delta_{d}{=}\sum\!\phi_{di}{/}{\sum}V_{m}$	$\delta_{p} = \frac{\left(\Sigma \varphi_{p}^{2}\right)^{0.5}}{\Sigma v_{m}}$ δp	$\delta_{\hbar} = \left[(\sum E_{\hbar}) / V_m \right]^{0.5} \delta \mathbf{h}$	$\begin{split} \delta &= \\ (\delta_d{}^2 + \delta_p{}^2 + \\ \delta_h{}^2)^{0.5} \end{split}$	
C16:0	0.0074	0.13	0.14	0.12	0.01	0.01	0.12	0.13
C18: 0	0.0055	0.10	0.10	0.09	0.01	0.01	0.09	0.10
C18: 1	0.0385	0.68	0.71	0.62	0.06	0.04	0.62	0.67
C18: 2	0.0558	0.99	1.04	0.89	0.08	0.06	0.89	0.97
C18: 3	0.0046	0.08	0.09	0.07	0.01	0.01	0.07	0.08
C18:1(OH)	0.8853	17.80	17.63	14.55	1.88	1.10	14.72	16.71
C20: 0	0.0031	0.05	0.06	0.05	0.00	0.00	0.05	0.05
	δt=sum(δti)	19.83	19.76	16.39	2.05	1.24	16.56	18.72

Table A2-28 Solubility parameters of the FAME compositions of CaB biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

Table A2-29 Solubility parameters of the FAME compositions of PB biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

FAME Group	FAME fraction = (% Quantity/100)	Solubility Parameters by Fedors $\delta = [Ecoh/Vm]^{0.5}$ (MPa) ^{1/2}	Solubility parameters by Hoy (MPa) ^{1/2} $\delta_t = \frac{\varphi_t + B}{V_m}$	Hoftyzer-van Kre	Average $(MD_{r})^{1/2}$			
				$\delta_d \!\!=\! \sum \! \phi_{di} \! / \! \sum \! V_m$	$\delta_p = \frac{\left(\sum \varphi_p^2\right)^{0.5}}{V_m}$	$\delta_h = \left[\frac{\sum E_h}{V_m}\right]^{0.5}$	$\begin{split} \delta &= \\ (\delta_d{}^2 + \delta_p{}^2 + \\ \delta_h{}^2)^{0.5} \end{split}$	• ot, (MPa)**
C16:0	0.092	1.62	1.69	1.48	0.15	0.11	1.50	1.60

C16:1	0.0022	0.04	0.04	0.04	0.00	0.00	0.04	0.04
C18: 0	0.027	0.48	0.49	0.44	0.04	0.03	0.44	0.47
C18: 1	0.153	2.70	2.82	2.45	0.22	0.18	2.47	2.66
C18: 2	0.719	12.72	13.38	11.41	1.06	0.84	11.49	12.53
C18: 3	0.0069	0.12	0.13	0.11	0.01	0.01	0.11	0.12
	δt=sum(δti)	17.68	18.56	15.93	1.48	1.16	16.04	17.43

Table A2-30 Solubility parameters of the FAME compositions of SB biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

FAME Group	FAME fraction = (100)	Solubility	Solubility	Hoftyzer-van Kre	Average			
	(% Quantity/100)	Fedors $\delta = [Ecoh/Vm]^{0.5}$ $(MPa)^{1/2}$	hoy (MPa) ^{1/2} $\delta_t = \frac{\varphi_t + B}{V_m}$	$\delta_{d} \!\!=\! \sum \! \phi_{di} \! / \! \sum \! V_{m}$	$\delta_p = \frac{\left(\Sigma \varphi_p^2\right)^{0.5}}{\Sigma v_m}$	$\delta_h = \left[(\sum E_h) / V_m \right]^{0.5}$	$\begin{array}{l} \delta = \\ (\delta_d{}^2 \!\!+ \delta_p{}^2 \!\!+ \\ \delta_h{}^2)^{0.5} \end{array}$	δt, (MPa) ^{1/2}
C16:0	0.1215	2.14	2.24	1.96	0.19	0.14	1.98	2.12
C18: 0	0.0383	0.68	0.70	0.62	0.05	0.04	0.62	0.67
C18: 1	0.2677	4.73	4.94	4.29	0.39	0.31	4.32	4.66
C18: 2	0.5415	9.58	10.08	8.59	0.80	0.63	8.65	9.44
C20: 0	0.0309	0.54	0.56	0.50	0.04	0.04	0.50	0.54
	δt=sum(δti)	17.67	18.52	15.97	1.47	1.16	16.08	17.42

FAME Group	FAME fraction = (% Quantity/100)	Solubility Parameters by	Solubility parameters by	Hoftyzer-van Kre	velen method, δ (M	Pa) ^{1/2}		Average $(MD_{-})^{1/2}$
	(/o Quantity/100)	Fedors	Hoy $(MPa)^{1/2}$		0.5		δ=	- ot, (MPa) ²
		$\delta = [Ecoh/Vm]^{0.3}$ $(MPa)^{1/2}$	$\delta_t = \frac{\varphi_t + B}{V_m}$	$\delta_{d} \!\!= \sum \! \phi_{di} \! / \! \sum \! V_{m}$	$\delta_p = \frac{(\Sigma \varphi_p^2)^{0.5}}{\Sigma v_m}$	$\delta_h = \left[(\sum E_h) / V_m \right]^{0.5}$	$\begin{array}{c} (\delta_d{}^2\!\!+\delta_p{}^2\!\!+\\ \delta_h{}^2)^{0.5} \end{array}$	
C8:0	0.0019	0.03	0.04	0.03	0.01	0.00	0.03	0.03
C10:0	0.001	0.02	0.02	0.02	0.00	0.00	0.02	0.02
C12:0	0.001	0.02	0.02	0.02	0.00	0.00	0.02	0.02
C14:0	0.001	0.02	0.02	0.02	0.00	0.00	0.02	0.02
C16:0	0.0635	1.12	1.17	1.02	0.10	0.07	1.03	1.11
C18: 0	0.0565	1.00	1.03	0.92	0.08	0.07	0.92	0.98
C18: 1	0.4247	7.50	7.84	6.81	0.62	0.49	6.86	7.40
C18: 2	0.1665	2.95	3.10	2.64	0.25	0.19	2.66	2.90
C18: 3	0.2785	4.94	5.23	4.37	0.42	0.32	4.40	4.85
C20: 0	0.002	0.04	0.04	0.03	0.00	0.00	0.03	0.03
C22: 0	0.002	0.04	0.04	0.03	0.00	0.00	0.03	0.03
C22: 1	0.0014	0.02	0.03	0.02	0.00	0.00	0.02	0.02
	δt=sum(δti)	17.68	18.56	15.93	1.48	1.16	16.04	17.42

Table A2-31 Solubility parameters of the FAME compositions of CB biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

Table A2-32 Solubility parameters of the FAME compositions of WTC biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

	FAME Group	FAME fraction = (% Quantity/100)	Solubility Parameters by	Hoftyzer-van Krevelen method, δ (MPa) ^{1/2}	Average
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		Fedors $\delta = [Ecoh/Vm]^{0.5}$ $(MPa)^{1/2}$	Solubility parameters by Hoy (MPa) ^{1/2} $\delta_t = \frac{\varphi_t + B}{V_m}$	$\delta_d \!\!=\! \sum \! \phi_{di} \! / \! \sum \! V_m$	$\delta_p = \frac{\left(\Sigma \varphi_p^2\right)^{0.5}}{\Sigma V_m}$	$\delta_h = [(\sum E_h)/V_m]^{0.5}$	$\begin{array}{l} \delta = \\ (\delta_d{}^2 \!$	δt, (MPa) ^{1/2}
C14:0	0.0428	0.76	0.79	0.69	0.08	0.05	0.69	0.75
C15:0	0.0072	0.13	0.13	0.12	0.01	0.01	0.12	0.13
C16:0	0.2126	3.75	3.91	3.43	0.34	0.25	3.46	3.71
C16:1	0.0321	0.57	0.60	0.51	0.05	0.04	0.52	0.56
C17:0	0.0209	0.37	0.38	0.34	0.03	0.02	0.34	0.36
C18: 0	0.2048	3.61	3.75	3.32	0.29	0.24	3.34	3.57
C18: 1	0.3669	6.48	6.77	5.88	0.53	0.43	5.92	6.39
C18: 2	0.0853	1.51	1.59	1.35	0.13	0.10	1.36	1.49
C18: 3	0.0241	0.43	0.45	0.38	0.04	0.03	0.38	0.42
C20: 0	0.0013	0.02	0.02	0.02	0.00	0.00	0.02	0.02
C22: 0	0.0022	0.04	0.04	0.04	0.00	0.00	0.04	0.04
	δt=sum(δti)	17.65	18.45	16.07	1.50	1.17	16.19	17.43

Table A2-33 Solubility parameters of the FAME compositions of WTP biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

FAME Group	Hoftyzer-van Krevelen method, δ (MPa) ^{1/2}	Average

	FAME fraction = (% Quantity/100)	Solubility Parameters by Fedors δ =[Ecoh/Vm] ^{0.5} (MPa) ^{1/2}	Solubility parameters by Hoy (MPa) ^{1/2} $\delta_t = \frac{\varphi_t + B}{V_m}$	$\delta_d \!\!=\! \sum \! \phi_{di} \! / \! \sum \! V_m$	$\delta_p = \frac{\left(\Sigma \varphi_p^2\right)^{0.5}}{\Sigma v_m}$	$\delta_h = [(\Sigma E_h)/V_m]^{0.5}$	$\begin{array}{l} \delta = \\ (\delta_d{}^2 \!\!+ \delta_p{}^2 \!\!+ \\ \delta_h{}^2)^{0.5} \end{array}$	δt, (MPa) ^{1/2}
C14:0	0.0274	0.48	0.51	0.44	0.05	0.03	0.44	0.48
C15:0	0.0071	0.13	0.13	0.11	0.01	0.01	0.12	0.12
C16:0	0.1893	3.34	3.49	3.06	0.30	0.22	3.08	3.30
C16:1	0.0265	0.47	0.49	0.42	0.04	0.03	0.43	0.46
C17:0	0.0211	0.37	0.39	0.34	0.03	0.02	0.34	0.37
C18: 0	0.2003	3.53	3.67	3.24	0.29	0.23	3.27	3.49
C18: 1	0.2751	4.86	5.08	4.41	0.40	0.32	4.44	4.79
C18: 2	0.2401	4.25	4.47	3.81	0.35	0.28	3.84	4.18
C18: 3	0.0136	0.24	0.26	0.21	0.02	0.02	0.21	0.24
	δt=sum(δti)	17.67	18.47	16.05	1.49	1.17	16.16	17.43

Table A2-34 Solubility parameters of the FAME compositions of PWC biodiesel fuels by Fedors, Hoy and Hoftyzer-van Krevelen methods

FAME Group	FAME fraction = (% Quantity/100)	Solubility Parameters by	Hoftyzer-van Krevelen method, $\delta (MPa)^{1/2}$	Average

		Fedors $\delta = [Ecoh/Vm]^{0.5}$ $(MPa)^{1/2}$	Solubility parameters by Hoy (MPa) ^{1/2} $\delta_t = \frac{\varphi_t + B}{V_m}$	$\delta_d \!\!= \sum \!\! \phi_{di} \! / \! \sum \! V_m$	$\delta_p = \frac{\left(\Sigma \varphi_p^2\right)^{0.5}}{\Sigma v_m}$	$\delta_h = [(\sum E_h)/V_m]^{0.5}$	$\begin{array}{l} \delta = \\ (\delta_d{}^2 + \delta_p{}^2 + \\ \delta_h{}^2)^{0.5} \end{array}$	δt, (MPa) ^{1/2}
C14:0	0.0149	0.26	0.28	0.24	0.03	0.02	0.24	0.26
C16:0	0.1146	2.02	2.11	1.85	0.18	0.13	1.86	2.00
C16:1	0.0074	0.13	0.14	0.12	0.01	0.01	0.12	0.13
C18: 0	0.0313	0.55	0.57	0.51	0.04	0.04	0.51	0.54
C18: 1	0.2421	4.27	4.47	3.88	0.35	0.28	3.91	4.22
C18: 2	0.5691	10.07	10.59	9.03	0.84	0.66	9.09	9.92
C18: 3	0.0172	0.30	0.32	0.27	0.03	0.02	0.27	0.30
C20: 0	0.0013	0.02	0.02	0.02	0.00	0.00	0.02	0.02
C22: 0	0.0021	0.04	0.04	0.03	0.00	0.00	0.03	0.04
	δt=sum(δti)	17.67	18.54	15.95	1.48	1.16	16.06	17.42

APPENDIX A3



(a) CO emission by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) CO emission by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load







(d) CO emission by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-1 Carbon monoxide (CO) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition







(b) CO emission by diesel, diesel-CaB, and diesel-CaB-PS blends at idle crank load

(c) CO emission by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load

WTC5PS5

WTC15

Diesel

WTC10PS10

WTC5

WTC10PS15

Engine Speed (RPM)

WTC5PS10

WTC15PS5

WTC5PS15

WTC15PS10

375

2400

■WTC10PS5

SWTC10

WTC15PS15



(d) CO emission by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-2 Carbon monoxide (CO) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) CO₂ emission by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) CO₂ emission by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load



(c) CO₂ emission by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) CO₂ emission by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-3 Brake specific carbon dioxide (CO₂) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) CO₂ emission by diesel, diesel-WTB and diesel-WTB-PS blends at idle crank load





(c) CO₂ emission by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load



(d) CO₂ emission by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-4 Brake specific carbon dioxide (CO₂) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) NO_x emission by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) NO_x emission by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load



(c) NO_x emission by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) NO_x emission by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-5 Nitrogen Oxides (NO_x) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) NO_x emission by diesel, diesel-WTB and diesel-WTB-PS blends at idle crank load





(b) NO_x emission by diesel, diesel-CaB, and diesel-CaB-PS blends at idle crank load

(c) NO_x emission by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load



(d) NO_x emission by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-6 Nitrogen Oxides (NO_x) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) PM emission by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) PM emission by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load



(c) PM emission by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) PM emission by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-7Particulate matters (PM) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) PM emission by diesel, diesel-WTB and diesel-WTB-PS blends at idle crank load





(b) PM emission by diesel, diesel-CaB, and diesel-CaB-PS blends at idle crank load

(c) PM emission by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load



(d) PM emission by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load
 Figure A3-8 Particulate matters (PM) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS

blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) HC emission by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) HC emission by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load



(c) HC emission by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) HC emission by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-9 Unburnt hydrocarbons (HC) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition


(a) HC emission by diesel, diesel-WTB and diesel-WTB-PS blends at idle crank load



(b) HC emission by diesel, diesel-CaB, and diesel-CaB-PS blends at idle crank load





(d) HC emission by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-10 Unburnt hydrocarbons (HC) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition







(c) O₂ emission by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) O₂ emission by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-11Excess oxygen (O₂) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition







(c) O₂ emission by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load



(d) O₂ emission by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-12 Excess oxygen (O₂) emission by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) EGT characteristics by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) EGT characteristics by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load



(c) EGT characteristics by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) EGT characteristics by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-13Exhaust gas temperature (EGT) characteristics by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) EGT characteristics by diesel, diesel-WTB and diesel-WTB-PS blends at idle crank load



(b) EGT characteristics by diesel, diesel-CaB, and diesel-CaB-PS blends at idle crank load



(c) EGT characteristics by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load



(d) EGT characteristics by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-14 Exhaust gas temperature (EGT) characteristics by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) BP vs engine speed by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) BP vs engine speed by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load



(c) BP vs engine speed by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) BP vs engine speed by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-15 Relationship between brake power (BP) and engine speed by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) BP vs engine speed by diesel, diesel-WTB and diesel-WTB-PS blends at idle crank load



(b) BP vs engine speed by diesel, diesel-CaB, and diesel-CaB-PS blends at idle crank load



(c) BP vs engine speed by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load



(d) BP vs engine speed by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-16 Relationship between brake power (BP) and engine speed by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) T vs engine speed by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) T vs engine speed by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load



(c) T vs engine speed by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) T vs engine speed by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-17 Relationship between Torque (T) and engine speed by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) T vs engine speed by diesel, diesel-WTB and diesel-WTB-PS blends at idle crank load



(b) T vs engine speed by diesel, diesel-CaB, and diesel-CaB-PS blends at idle crank load



(c) T vs engine speed by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load



(d) T vs engine speed by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-18 Relationship between Torque (T) and engine speed by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) BSFC vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at part (50%) load



(b) BSFC vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at part (50%) load



(c) BSFC vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at part (50%) load



(d) BSFC vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at part (50%) load

Figure A3-19 Brake specific fuel consumption (BSFC) characteristics at various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) BSFC vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at idle load





(b) BSFC vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at idle load

(c) BSFC vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at idle load



(d) BSFC vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at idle load

Figure A3-20 Brake specific fuel consumption (BSFC) characteristics at various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) BTE vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at part load



(b) BTE vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at part load



(c) BTE vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at part load



(d) BTE vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at part load

Figure A3-21 Brake thermal efficiency (BTE) characteristics at various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) BTE vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at idle crank load



load



(c) BTE vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at idle crank load



(d) BTE vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at idle crank load

Figure A3-22 Brake thermal efficiency (BTE) characteristics at various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) BMEP vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at part load



(b) BMEP vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at part load



(c) BMEP vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at part load



(d) BMEP vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at part load

Figure A3-23 Characteristics of Brake Mean Effective Pressure (BMEP) for various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) BMEP vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at idle load



(b) BMEP vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at idle load



(c) BMEP vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at idle load



(d) BMEP vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at idle load

Figure A3-24 Characteristics of Brake Mean Effective Pressure (BMEP) for various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



(a) BSEC vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at part load



(b) BSEC vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at part load



(c) BSEC vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at part load



(d) BSEC vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at part load

Figure A3-25 Characteristics of Brake Specific Fuel Consumption (BSEC) for various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at part (50%) load condition



(a) BSEC vs engine speeds by diesel, diesel-WTB and diesel-WTB-PS blends at idle load



(b) BSEC vs engine speeds by diesel, diesel-CaB, and diesel-CaB-PS blends at idle load



(c) BSEC vs engine speeds by diesel, diesel-WTC, and diesel-WTC-PS blends at idle load



(d) BSEC vs engine speeds by diesel, diesel-PWC and diesel-PWC-PS blends at idle load

Figure A3- 26 Characteristics of Brake Specific Fuel Consumption (BSEC) for various engine speeds by diesel, (a) diesel-WTB and diesel-WTB-PS blends, (b) diesel-CaB and diesel-CaB-PS blends, (c) diesel-WTC and diesel-WTC-PS blends, and (d) diesel-PWC and diesel-PWC-PS blends at idle crank load condition



Figure A3-27 In-Cylinder pressure (CP) variation with Crank Angle (CA) variation for diesel, diesel-WTC and diesel-WTC-PS fuel blends for Part (50%) load conditon at, (a) 1200 rpm, (b) 1500 rpm, (c) 2100 rpm (d) 2400 rpm



Figure A3-28 In-Cylinder pressure (CP) variation with Crank Angle (CA) variation for diesel, diesel-WTC and diesel-WTC-PS fuel blends for Idle Crank load conditon at (a) 1200 rpm, (b) 1500 rpm, (c) 2100 rpm (d) 2400 rpm


Figure A3-29 Apparent heat release rate (HRR) variation with Crank Angle (CA) variation for diesel, diesel-WTC and diesel-WTC-PS fuel blends for Part (50%) load conditon at (a) 1200 rpm, (b) 1500 rpm, (c) 2100 rpm (d) 2400 rpm



Figure A3-30 Apparent heat release rate (HRR) variation with Crank Angle (CA) variation for diesel, diesel-WTC and diesel-WTC-PS fuel blends for Idle crank load conditon at (a) 1200 rpm, (b) 1500 rpm, (c) 2100 rpm (d) 2400 rpm



Figure A3-31 Ignition delay (ms) variation with engine speed for diesel, diesel-WTB and diesel-WTB-PS fuel blends at Full Load, Part (50%) Load and Idle Crank Load condition



Figure A3-32 Ignition delay (ms) variation with engine speed for diesel, diesel-PWC and diesel-PWC-PS fuel blends at Full Load, Part (50%) Load and Idle Crank Load condition



Figure A3-33 Ignition delay (ms) variation with engine speed for diesel, diesel-CaB and diesel-CaB-PS fuel blends at Full Load, Part (50%) Load and Idle Crank Load condition

APPENDIX A4



Figure A4-1 Stages of particulate matters formation (Adapted from [388])



Figure A4-2 Typical diesel fuel combustion stages and HRR variation (adapted from [438])



Figure A4-3 Start of Injection (SOI) and Start of Combustion (SOC) detection from Pressure grandients from in cylinder pressure data (adapated from [426])

	Speed (rpm)	WTC5	WTC5PS5	WTC5PS10	WTC5PS15	WTC10	WTC10PS5	WTC10PS10	WTC10PS15	WTC15	WTC15PS5	WTC15PS10	WTC15PS15
	1200	65.77	68.72	68.11	66.64	67.59	69.55	70.80	67.42	68.83	70.28	68.16	67.90
load	1500	64.98	65.33	64.98	64.81	64.63	66.51	67.71	64.90	66.26	67.65	64.66	65.36
Full	1800	66.72	67.07	66.37	66.46	67.33	69.28	70.53	66.90	68.30	69.74	67.77	67.37
	2100	68.72	68.03	69.33	69.16	68.90	70.90	72.17	69.07	70.52	72.00	68.13	69.56
	2400	66.98	66.29	66.72	66.11	66.37	68.30	69.53	66.37	67.77	69.19	65.47	66.85
	Speed (rpm)	WTC5	WTC5PS5	WTC5PS10	WTC5PS15	WTC10	WTC10PS5	WTC10PS10	WTC10PS15	WTC15	WTC15PS5	WTC15PS10	WTC15PS15
	1200	69.75	69.16	70.38	68.11	69.42	71.43	72.72	68.72	70.17	71.64	69.34	69.21
load	1500	64.63	65.59	67.33	65.94	65.42	67.31	68.53	66.72	68.12	69.55	67.32	67.20
Part	1800	64.46	63.85	65.85	64.90	63.94	65.79	66.98	64.98	66.35	67.74	65.58	65.44
	2100	66.72	66.46	65.85	67.59	67.51	69.46	70.71	68.46	69.90	71.37	69.11	68.95
	2400	65.77	65.07	65.59	64.29	64.90	66.78	67.98	64.81	66.17	67.56	65.36	66.73
	Speed (rpm)	WTC5	WTC5PS5	WTC5PS10	WTC5PS15	WTC10	WTC10PS5	WTC10PS10	WTC10PS15	WTC15	WTC15PS5	WTC15PS10	WTC15PS15
	1200	66.32	65.70	66.39	66.29	65.24	65.93	67.12	65.68	67.06	68.47	66.27	66.15
load	1500	69.06	68.71	69.43	64.37	64.29	64.93	66.10	65.42	66.79	68.19	66.01	65.88
Idle	1800	64.77	64.39	65.07	64.20	64.55	66.42	67.62	64.72	66.08	67.47	65.32	65.18
	2100	67.20	66.80	67.51	66.98	67.33	69.28	70.53	67.77	69.19	70.64	68.41	68.25
	2400	64.34	63.96	64.63	64.11	64.37	66.24	67.43	64.63	65.99	67.38	65.18	66.55

Table A4-1 Peak in-cylinder pressure (bar) for combustion of diesel, diesel-WTC and diesel-WTC-PS fuel blends at various speeds and loads

Table A4-2 Peak in-cylinder pressure (bar) for combustion of diesel, diesel-WTB and diesel-WTB-PS fuel blends at various speeds and loads

	Speed (rpm)	WTB5	WTB5PS5	WTB5PS10	WTB5PS15	WTB10	WTB10PS5	WTB10PS10	WTB10PS15	WTB15	WTB15PS5	WTB15PS10	WTB15PS15
ad	1200	68.16	69.56	69.41	66.64	66.82	68.76	70.00	68.76	70.20	71.68	69.71	69.25
ul lo	1500	65.17	66.96	66.81	64.81	63.90	65.75	66.93	66.19	67.58	68.99	67.10	66.66
Fu	1800	67.89	69.02	68.87	66.46	66.56	68.49	69.73	68.23	69.66	71.12	69.17	68.71
	2100	69.47	71.27	71.11	69.16	68.11	70.09	71.35	70.44	71.92	73.43	71.42	70.95

	2400	66.93	68.48	68.33	66.11	65.62	67.52	68.74	67.69	69.12	70.57	68.63	68.18
	Speed (rpm)	WTB5	WTB5PS5	WTB5PS10	WTB5PS15	WTB10	WTB10PS5	WTB10PS10	WTB10PS15	WTB15	WTB15PS5	WTB15PS10	WTB15PS15
_	1200	70.00	70.91	70.75	68.11	68.63	70.62	71.89	70.09	71.56	73.06	71.06	70.59
loac	1500	65.96	68.84	68.69	65.94	64.67	66.55	67.75	68.05	69.48	70.94	68.99	68.53
Part	1800	64.47	67.05	66.90	64.90	63.21	65.04	66.21	66.27	67.67	69.09	67.19	66.75
	2100	68.07	70.64	70.48	67.59	66.74	68.67	69.91	69.82	71.29	72.79	70.79	70.32
	2400	65.44	66.87	66.72	64.29	64.16	66.02	67.20	66.10	67.49	68.90	67.01	66.57
	Speed (rpm)	WTB5	WTB5PS5	WTB5PS10	WTB5PS15	WTB10	WTB10PS5	WTB10PS10	WTB10PS15	WTB15	WTB15PS5	WTB15PS10	WTB15PS15
	1200	65.79	67.76	67.62	66.29	64.50	65.18	66.35	66.98	68.39	69.83	67.91	67.46
load	1500	64.82	67.50	67.35	64.37	63.55	64.19	65.34	66.72	68.12	69.55	67.64	67.19
dle	1800	65.09	66.78	66.63	64.20	63.81	65.66	66.84	66.01	67.39	68.81	66.92	66.48
_	2100	67.89	69.92	69.77	66.98	66.56	68.49	69.73	69.11	70.57	72.05	70.07	69.61
	2400	64.91	66.69	66.54	64.11	63.64	65.49	66.66	65.92	67.30	68.72	66.83	66.39

Table A4-3 Peak in-cylinder pressure (bar) for combustion of diesel, diesel-CaB and diesel-CaB-PS fuel blends at various speeds and loads

	Speed (rpm)	CaB5	CaB5PS5	CaB5PS10	CaB5PS15	CaB10	CaB10PS5	CaB10PS10	CaB10PS15	CaB15	CaB15PS5	CaB15PS10	CaB15PS15
	1200	65.84	64.48	65.16	66.64	66.29	65.41	64.55	66.96	68.36	69.80	68.08	67.43
oad	1500	64.61	63.27	63.94	64.81	63.68	62.84	62.01	64.32	65.67	67.05	65.40	64.78
l llu ⁵	1800	65.93	64.56	65.24	66.46	65.42	64.55	63.70	66.08	67.47	68.88	67.19	66.55
ц	2100	68.92	67.49	68.20	69.16	68.38	67.47	66.58	69.07	70.52	72.00	70.23	69.56
	2400	66.90	65.51	66.20	66.11	65.85	64.98	64.12	66.52	67.91	69.34	67.63	66.99
	Speed (rpm)	CaB5	CaB5PS5	CaB5PS10	CaB5PS15	CaB10	CaB10PS5	CaB10PS10	CaB10PS15	CaB15	CaB15PS5	CaB15PS10	CaB15PS15
	1200	69.36	67.92	6co8.64	68.11	67.42	66.53	65.65	68.10	69.53	70.99	69.24	68.58
load	1500	67.16	65.77	66.46	65.94	66.20	65.33	64.46	66.87	68.27	69.71	67.99	67.35
Part]	1800	64.17	62.84	63.50	64.90	64.20	63.35	62.51	64.85	66.21	67.60	65.94	65.31
Η	2100	67.87	66.46	67.16	67.59	67.16	66.27	65.39	67.84	69.26	70.72	68.98	68.32

	Speed (rpm)	CaB5	CaB5PS5	CaB5PS10	CaB5PS15	CaB10	CaB10PS5	CaB10PS10	CaB10PS15	CaB15	CaB15PS5	CaB15PS10	CaB15PS15
	1200	64.26	62.93	63.59	66.29	70.12	69.19	68.28	70.82	72.31	73.83	72.01	71.33
load	1500	65.58	64.22	64.90	64.37	63.59	62.75	61.92	64.23	65.58	66.96	65.31	64.69
Idle	1800	64.70	63.36	64.03	64.20	63.76	62.92	62.09	64.41	65.76	67.14	65.49	64.87
	2100	67.43	66.03	66.72	66.98	66.55	65.67	64.80	67.22	68.63	70.07	68.35	67.70
	2400	64.61	63.27	63.94	64.11	64.46	63.61	62.77	65.11	66.48	67.88	66.21	65.58

Table A4-4 Peak in-cylinder pressure (bar) for combustion of diesel, diesel-PWC and diesel-PWC-PS fuel blends at various speeds and loads

	Speed (rpm)	PWC5	PWC5PS5	PWC5PS10	PWC5PS15	PWC10	PWC10PS5	PWC10PS10	PWC10PS15	PWC15	PWC15PS5	PWC15PS10	PWC15PS15
	1200	66.02	64.65	65.33	66.64	65.77	64.90	64.04	65.07	66.44	67.83	66.16	65.53
oad	1500	64.44	63.10	63.76	64.81	65.59	64.73	63.87	64.72	66.08	67.47	65.81	65.18
I Ilu ⁵	1800	66.11	64.74	65.42	66.46	65.50	64.64	63.79	65.50	66.88	68.28	66.60	65.97
щ	2100	69.71	68.27	68.98	69.16	68.38	67.47	66.58	68.55	69.99	71.46	69.70	69.04
	2400	66.81	65.43	66.11	66.11	66.20	65.33	64.46	65.77	67.15	68.56	66.87	66.23
	Speed (rpm)	PWC5	PWC5PS5	PWC5PS10	PWC5PS15	PWC10	PWC10PS5	PWC10PS10	PWC10PS15	PWC15	PWC15PS5	PWC15PS10	PWC15PS15
	1200	69.18	67.75	68.46	68.11	68.03	67.13	66.24	68.81	70.26	71.73	69.97	69.30
load	1500	66.20	64.82	65.50	65.94	65.77	64.90	64.04	65.50	66.88	68.28	66.60	65.97
Part]	1800	65.32	63.96	64.63	64.90	67.24	66.36	65.48	67.59	69.01	70.46	68.73	68.07
Т	2100	68.66	67.23	67.94	67.59	66.80	65.91	65.04	66.66	68.06	69.49	67.78	67.13
	2400	65.58	64.22	64.90	64.29	64.20	63.35	62.51	65.24	66.61	68.01	66.34	65.71
	Speed (rpm)	PWC5	PWC5PS5	PWC5PS10	PWC5PS15	PWC10	PWC10PS5	PWC10PS10	PWC10PS15	PWC15	PWC15PS5	PWC15PS10	PWC15PS15
	1200	64.97	63.62	64.29	66.29	65.14	64.28	63.43	67.57	68.99	70.43	68.70	68.05
load	1500	62.59	61.29	61.94	64.37	62.76	61.93	61.11	65.62	66.99	68.40	66.72	66.08
[dle]	1800	64.17	62.84	63.50	64.20	64.35	63.50	62.66	65.44	66.81	68.22	66.54	65.90
	2100	67.51	66.11	66.81	66.98	67.69	66.80	65.92	68.28	69.71	71.17	69.42	68.76
	2400	65.14	63.79	64.46	64.11	65.31	64.45	63.60	65.35	66.72	68.12	66.45	65.81

	Speed (rpm)	WTC5	WTC5PS5	WTC5PS10	WTC5PS15	WTC10	WTC10PS5	WTC10PS10	WTC10PS15	WTC15	WTC15PS5	WTC15PS10	WTC15PS15
_	1200	208.77	185.31	208.38	199.53	206.90	212.90	216.73	215.05	219.57	224.18	217.85	216.58
loac	1500	228.88	178.69	181.59	194.50	216.86	223.15	227.17	212.43	216.89	221.45	215.19	213.94
Full	1800	211.25	213.64	202.35	204.23	195.38	201.04	204.66	199.18	203.37	207.64	231.06	200.60
	2100	234.35	239.57	236.42	214.08	239.31	246.25	250.68	221.44	226.09	230.84	236.29	223.02
	2400	229.33	233.40	228.02	247.37	214.26	220.47	224.44	225.14	229.87	234.70	228.07	226.74
	Speed (rpm)	WTC5	WTC5PS5	WTC5PS10	WTC5PS15	WTC10	WTC10PS5	WTC10PS10	WTC10PS15	WTC15	WTC15PS5	WTC15PS10	WTC15PS15
_	1200	197.06	195.40	205.21	196.05	202.58	208.45	212.20	186.08	189.99	193.98	187.76	187.40
loac	1500	202.30	191.99	186.41	206.99	197.25	202.97	206.63	206.12	210.45	214.87	207.98	207.59
Part	1800	198.35	191.02	205.02	226.07	202.79	208.67	212.43	217.64	222.21	226.88	219.64	219.19
	2100	249.51	247.47	205.02	235.17	229.41	236.06	240.31	241.93	247.01	252.20	244.23	243.65
	2400	297.62	300.51	250.61	297.77	248.31	255.51	260.11	302.64	309.00	315.49	305.22	311.63
	Speed (rpm)	WTC5	WTC5PS5	WTC5PS10	WTC5PS15	WTC10	WTC10PS5	WTC10PS10	WTC10PS15	WTC15	WTC15PS5	WTC15PS10	WTC15PS15
_	1200	123.31	122.27	123.55	123.36	131.36	132.74	325.74	119.75	122.26	124.83	120.83	120.60
loac	1500	166.35	165.50	167.24	124.24	154.86	156.40	159.22	162.05	165.45	168.93	163.51	163.20
Idle	1800	177.61	176.57	178.42	166.72	166.67	171.50	174.59	168.61	172.15	175.77	170.16	169.81
	2100	202.08	200.90	203.01	197.31	194.19	199.82	203.42	174.47	178.14	181.88	176.13	175.71
	2400	198.94	197.77	199.85	194.01	190.47	195.99	199.52	176.47	180.17	183.96	177.97	181.70

Table A4-5 Peak in-cylinder HRR (J/^OCA) for combustion of diesel, diesel-WTC and diesel-WTC-PS fuel blends at various speeds and loads

Table A4-6 Peak in-cylinder HRR (J/^OCA) for combustion of diesel, diesel-WTB and diesel-WTB-PS fuel blends at various speeds and loads

	Speed (rpm)	WTB5	WTB5PS5	WTB5PS10	WTB5PS15	WTB10	WTB10PS5	WTB10PS10	WTB10PS15	WTB15	WTB15PS5	WTB15PS10	WTB15PS15
5	1200	208.62	221.88	221.39	199.53	204.54	210.47	214.26	219.32	223.93	228.63	222.35	220.88
l loa	1500	218.67	219.18	218.70	194.50	214.39	220.60	224.58	216.66	221.21	225.85	219.64	218.20
Full	1800	197.00	205.51	205.06	204.23	193.15	198.75	202.33	203.14	207.41	211.76	205.94	204.59
	2100	241.30	228.48	227.98	214.08	236.58	243.44	247.82	225.85	230.59	235.43	228.96	227.45
	2400	216.04	232.29	231.78	247.37	211.82	217.96	221.88	229.62	234.44	239.36	232.78	231.25

	Speed (rpm)	WTB5	WTB5PS5	WTB5PS10	WTB5PS15	WTB10	WTB10PS5	WTB10PS10	WTB10PS15	WTB15	WTB15PS5	WTB15PS10	WTB15PS15
	1200	204.26	191.99	191.57	196.05	200.27	206.07	209.78	189.78	193.77	197.83	192.40	191.13
load	1500	198.89	212.67	212.20	206.99	195.00	200.66	204.27	210.22	214.63	219.14	213.12	211.71
Part	1800	204.48	224.55	224.06	226.07	200.48	206.29	210.01	221.97	226.63	231.39	225.03	223.54
	2100	231.32	249.62	249.07	235.17	226.80	233.37	237.57	246.74	251.92	257.22	250.15	248.50
	2400	250.38	312.26	311.57	297.77	245.48	252.60	257.14	308.66	315.14	321.76	312.92	310.86
	Speed (rpm)	WTB5	WTB5PS5	WTB5PS10	WTB5PS15	WTB10	WTB10PS5	WTB10PS10	WTB10PS15	WTB15	WTB15PS5	WTB15PS10	WTB15PS15
	1200	132.46	123.55	123.28	123.36	129.87	131.23	322.02	122.13	124.69	127.31	123.81	123.00
load	1500	156.15	167.20	166.83	124.24	153.09	154.62	157.40	165.27	168.74	172.29	167.55	166.45
Idle	1800	168.05	173.97	173.58	166.72	164.77	169.54	172.60	171.96	175.57	179.26	174.33	173.19
	2100	195.81	180.01	179.62	197.31	191.98	197.55	201.10	177.94	181.68	185.49	180.40	179.21
	2400	192.06	182.07	181.67	194.01	188.30	193.76	197.25	179.97	183.75	187.61	182.46	181.25

Table A4-7 Peak in-cylinder HRR (J/^OCA) for combustion of diesel, diesel-CaB and diesel-CaB-PS fuel blends at various speeds and loads

	Speed (rpm)	CaB5	CaB5PS5	CaB5PS10	CaB5PS15	CaB10	CaB10PS5	CaB10PS10	CaB10PS15	CaB15	CaB15PS5	CaB15PS10	CaB15PS15
	1200	215.38	210.91	213.13	199.53	196.93	194.33	191.76	198.92	203.09	207.36	202.26	200.33
load	1500	198.42	194.30	196.35	194.50	205.71	202.99	200.31	207.79	212.15	216.61	211.28	209.27
IluF	1800	209.55	205.20	207.36	204.23	215.79	212.94	210.13	217.97	222.55	227.22	221.63	219.52
-	2100	211.53	207.15	209.33	214.08	229.26	226.23	223.25	231.58	236.44	241.41	235.47	233.23
	2400	232.34	227.52	229.92	247.37	218.37	215.48	212.64	220.57	225.21	229.94	224.28	222.14
	Speed (rpm)	CaB5	CaB5PS5	CaB5PS10	CaB5PS15	CaB10	CaB10PS5	CaB10PS10	CaB10PS15	CaB15	CaB15PS5	CaB15PS10	CaB15PS15
	1200	219.24	214.69	216.95	196.05	199.86	197.22	194.61	201.88	206.12	210.45	205.27	203.31
load	1500	197.71	193.61	195.65	206.99	205.76	203.05	200.36	207.84	212.21	216.66	211.33	209.32
Part	1800	238.12	233.18	235.63	226.07	232.98	229.91	226.87	235.34	240.28	245.32	239.29	237.01
н	2100	237.56	232.63	235.08	235.17	238.04	234.89	231.79	240.44	245.49	250.64	244.48	242.15
	2400	261.54	256.12	258.81	297.77	288.08	284.27	280.52	290.99	297.10	303.34	295.87	293.06

	Speed (rpm)	CaB5	CaB5PS5	CaB5PS10	CaB5PS15	CaB10	CaB10PS5	CaB10PS10	CaB10PS15	CaB15	CaB15PS5	CaB15PS10	CaB15PS15
	1200	140.41	137.50	138.95	123.36	204.92	202.21	199.54	206.99	211.34	215.77	210.46	208.46
load	1500	164.15	160.75	162.44	124.24	158.42	156.33	154.27	160.02	163.38	166.82	162.71	161.16
Idle	1800	175.50	171.86	173.67	166.72	184.15	181.72	179.32	186.01	189.92	193.91	189.14	187.34
	2100	209.25	204.91	207.07	197.31	227.94	224.93	221.96	230.24	235.08	240.01	234.11	231.88
	2400	209.22	204.88	207.04	194.01	189.36	186.86	184.39	191.28	195.29	199.40	194.49	192.64

Table A4-8 Peak in-cylinder HRR (J/^OCA) for combustion of diesel, diesel-PWC and diesel-PWC-PS fuel blends at various speeds and loads

	Speed (rpm)	PWC5	PWC5PS5	PWC5PS10	PWC5PS15	PWC10	PWC10PS5	PWC10PS10	PWC10PS15	PWC15	PWC15PS5	PWC15PS10	PWC15PS15
	1200	201.73	197.54	199.62	199.53	189.19	186.69	184.22	192.92	196.97	201.10	196.15	194.29
load	1500	199.03	194.90	196.95	194.50	202.85	200.17	197.53	188.73	192.69	196.74	191.90	190.07
Full]	1800	210.28	205.92	208.09	204.23	207.78	205.04	202.33	200.68	204.89	209.19	204.05	202.10
Π	2100	236.97	232.06	234.50	214.08	226.34	223.35	220.40	231.39	236.25	241.21	235.27	233.03
	2400	298.67	292.48	295.56	247.37	237.96	234.82	231.72	230.25	235.09	240.02	234.12	231.89
	Speed (rpm)	PWC5	PWC5PS5	PWC5PS10	PWC5PS15	PWC10	PWC10PS5	PWC10PS10	PWC10PS15	PWC15	PWC15PS5	PWC15PS10	PWC15PS15
	1200	218.30	213.77	216.02	196.05	203.31	200.63	197.98	202.08	206.33	210.66	205.48	203.52
load	1500	206.70	202.41	204.54	206.99	187.06	184.58	182.15	200.70	204.92	209.22	204.07	202.13
Part	1800	211.66	207.27	209.45	226.07	222.96	220.02	217.11	212.18	216.64	221.19	215.74	213.69
Π	2100	251.91	246.69	249.28	235.17	245.08	241.84	238.65	244.58	249.72	254.97	248.69	246.32
	2400	312.33	305.85	309.06	297.77	197.25	194.65	192.07	242.68	247.78	252.98	246.76	244.41
	Speed (rpm)	PWC5	PWC5PS5	PWC5PS10	PWC5PS15	PWC10	PWC10PS5	PWC10PS10	PWC10PS15	PWC15	PWC15PS5	PWC15PS10	PWC15PS15
	1200	112.37	110.04	111.19	123.36	112.67	111.18	109.71	125.74	128.38	131.08	127.85	126.64
load	1500	126.71	124.08	125.39	124.24	127.05	125.37	123.71	126.63	129.29	132.01	128.76	127.53
dle	1800	158.33	155.04	156.67	166.72	158.75	156.65	154.58	169.93	173.50	177.14	172.79	171.14
-	2100	180.58	176.83	178.69	197.31	181.06	178.67	176.31	201.11	205.34	209.65	204.49	202.54
	2400	185.41	181.57	183.48	194.01	185.91	183.45	181.03	197.75	201.90	206.14	201.07	199.16

APPENDIX A5

While determining the uncertainty of the experimentally derived data sets, the following theoretical background was reviewed briefly.

The experimental values presented in this study are the mean values of the sample measurements for each of the cases. Therefore, the uncertainty analysis has been expressed in terms of the standard error of the mean (SEM) rather than the standard deviation values. SEM can simply describe how the population mean can be confidently determined from the sample means [439-441]. When there are complex sets of data, the central limit theorem [442] explains the uncertainty around the mean value of a population size (N) if the standard deviation (SD) of the set of sample means is known. SEM is indeed the standard deviation of the distribution of sample means, it reduces the statistical variability of a distribution with the increase in population size. Thus, the SEM can be expressed per the Eq. A5-1.

$$SEM = \frac{SD}{\sqrt{N}}$$
 (Eq. A5-1)

Where SD is the standard deviation of the set of sample means and N is the population size. Here SD is determined from the Eq. A5-2.

Where $\overline{x_l}$ is the sample mean of a sample size, $\mu_{\overline{x}}$ is the mean of the set of sample means, and n is the number of sample means in the set.

Once the SEM is determined, the 95% confidence interval (CI₉₅) of the whole population size can be determined from the Eq. A5-3.

$$CI_{95} = \bar{x} \pm (1.96 \times SEM)$$
 (Eq. A5-3)

So, the 95% CI of any population size can be found within the range of $\pm (1.96 \times SEM)$ of the sample means, \bar{x} .

In most cases, the CI₉₅ of a sample distribution is described as the double of the SD of the distribution around the mean value [443], i.e. $CI_{95} = \bar{x} \pm (2 \times SD)$.

In case of a studied result (R), if the result is dependent on single or multiple variables (i.e. $x_1, x_2, x_3 \dots x_n$) then the uncertainty in the R can be determined by the following formula (Eq. A5-4a, or Eq. A5-4b) [443, 444].

$$\delta R = \sqrt{\left(\frac{\partial R}{\partial x_1} \delta x_1\right)^2 + \left(\frac{\partial R}{\partial x_2} \delta x_2\right)^2 + \dots + \left(\frac{\partial R}{\partial x_n} \delta x_n\right)^2} \dots (\text{Eq. A5-4a})$$

Or, $\delta R = \sqrt{\sum_{i=1}^n \left(\frac{\partial R}{\partial x_i} \delta x_i\right)^2} \dots (\text{Eq. A5-4b})$

Here, Eq. A5-4b is known as the root-sum-square (RSS) method for uncertainty analysis for a studied result depending on any number of independent variables [443, 444]. This equation can be well simply stated as, "the uncertainty of a result is the sum of square root of the uncertainties of each of the independent variables measured individually". In case of the expressing the uncertainties as a fraction of the derived result, the result is purely considered as a product of each of the dependent variable to determine the relative uncertainty of the resultant [443, 444].

Therefore, if the resulting function is expressed as in Eq. A5-5a, the relative uncertainty can be determined by following Eq. A5-5b as follows.

$$R = x_1^a x_2^b \dots \dots x_n^m \dots (\text{Eq. A5-5a})$$
$$\frac{\delta R}{R} = \sqrt{\left(a\frac{\partial x_1}{x_1}\right)^2 + \left(b\frac{\partial x_2}{x_2}\right)^2 + \dots \dots + \left(m\frac{\partial x_m}{x_m}\right)^2} \dots (\text{Eq. A5-5b})$$

Eq. A5-5b can be used to determine the uncertainties of the measured components as percentile form of the result in the same unit.

The following tables present the uncertainty analysis of the experimentally derived data sets in this study.

Properties	Mean of the sample means, \bar{x}	Standard deviation of means (SD)	Standard error of means (SEM)	Instrument error (±E)	Higher uncertainty (SEM+E)	Lower uncertainty (SEM-E)
Kinematic Viscosity (mm2/s, at 40 °C)	5.648	3.098	0.566	0.350	0.916	0.216
Density (g/cm3, at 15 °C)	0.881	0.018	0.003	0.005	0.008	-0.002
Higher Heating Value (MJ/kg, HHV)	41.252	1.517	0.277	0.001	0.318	0.236
Lower Heating Value (MJ/kg, LHV)	39.798	0.846	0.155	0.001	0.194	0.115
Oxidation Stability (hours, at 110 °C)	12.316	10.544	1.925	0.010	1.935	1.915
Flash Point (°C)	163.252	32.669	5.964	0.100	6.064	5.864
Pour Point (°C)	-4.776	8.298	1.515	0.100	1.615	1.415
Cloud Point (°C)	1.409	7.762	1.417	0.100	1.517	1.317
Cold filter plugging point (°C, CFPP)	-1.528	7.352	1.342	0.100	1.442	1.242
Cetane Number (CN)	57.346	4.302	0.786	0.130	0.916	0.656
Iodine Value (IV, g I2/100g oil)	96.962	27.216	5.238	3.500	8.738	1.738
Saponification Value (SV, mg KOH/ g oil)	202.760	2.572	0.495	2.900	3.395	-2.405
Acid Value (AV, mg KOH/g oil)	0.431	0.455	0.083	0.001	0.084	0.082

Table A5- 1 Uncertainty analysis of physico-chemical properties of the biodiesel fuels as presented in the Table 5-20

	Mean Dissolution Time (minutes) of 3 repeats at												
			V	arious Temp	peratures								
Biodiesel Solvents	Polymer Content	60 °C	70 °C	85 °C	100 °C	120 °C	Average of the Means, , \bar{x}	Standard Deviatio n of the Means, SD	Standard Error of the Means, SEM=SD/sqrt(N), (N is total sample size = 3*5 = 15)				
	Ca100PS5	198	153	109	92	57	122	49.05	21.94				
Ca	Ca100PS10	287	194	151	125	95	170	66.75	29.85				
	Ca100PS15	335	289	203	175	132	227	74.58	33.35				
	WCO100PS5	180	130	103	63	49	105	47.23	21.12				
WCO	WCO100PS10	278	231	161	139	102	182	63.73	28.50				
	WCO100PS15	351	277	221	192	155	239	68.67	30.71				
	PWC100PS5	194	165	149	120	105	147	31.71	14.18				
PWC	PWC100PS10	276	205	177	163	133	191	48.51	21.69				
	PWC100PS15	294	271	226	208	199	240	36.82	16.46				
	C100PS5	217	192	178	114	65	153	55.69	24.91				
С	C100PS10	271	205	193	126	87	176	64.15	28.69				
	C100PS15	293	270	203	140	96	200	74.80	33.45				
	PB100PS5	255	205	99	55	52	133	82.30	36.81				
PB	PB100PS10	261	246	131	61	55	151	88.14	39.42				
	PB100PS15	316	258	135	85	61	171	99.38	44.45				
	WTP100PS5	272	170	75	59	44	124	86.08	38.49				
WTP	WTP100PS10	303	239	99	77	58	155	97.56	43.63				
	WTP100PS15	339	284	120	94	70	181	108.80	48.66				
	WTB100PS5	283	177	61	52	37	122	94.65	42.33				
WTB	WTB100PS10	320	257	79	65	54	155	111.09	49.68				
	WTB100PS15	351	299	91	78	66	177	122.21	54.65				
	WTC100PS5	275	155	56	49	32	113	91.56	40.95				
WTC	WTC100PS10	321	251	76	62	49	152	112.11	50.14				
	WTC100PS15	338	285	83	75	58	168	118.80	53.13				
	SF100PS5	109	75	47	43	36	62	26.98	12.07				
SF	SF100PS10	245	188	68	47	37	117	83.82	37.48				
	SF100PS15	316	258	135	72	61	168	101.74	45.50				

Table A5-2 Experimental uncertainty in terms of standard error of the means (SEM) of dossolution profile of PS into various biodiesel solvents

Mean Dissolution Time (minutes) of 3 repeats at Various Temperatures										
Biodiesel Solvents	Polymer content	85 °C	100 °C	120 °C	135 °C	150 °C	Average of the Means, \bar{x}	St D M	candard eviation of the leans, SD	Standard Error of the Means, SEM=SD/sqrt(N); (N is total sample size = 3*5 = 15)
	Ca100PE5	361	298	233	181	123	239	83	3.93	21.67
Ca	Ca100PE10	578	482	352	305	211	386	12	29.94	33.55
	Ca100PE15	645	618	586	452	348	530	11	12.53	29.05
Biodiesel Solvents	Polymer content	85 °C	100 °C	120 °C	C 135 °	C 150 °	Aver C of th Mea	rage e ns, <i>x</i> ̄	Standard Deviation of the Means, SD	Standard Error of the Means, SEM=SD/sqrt(N); (N is total sample size = 3*5 = 15)
	WCO100PE5	288	210	180	132	117	185		61.14	15.79
WCO	WCO100PE10	489	395	321	257	219	336		97.00	25.05
	WCO100PE15	621	565	432	349	282	450		127.45	32.91
	PWC100PE5	338	290	211	163	120	224		80.07	20.67
PWC	PWC100PE10	505	370	290	226	168	312		117.67	30.38
	PWC100PE15	597	534	443	337	235	429		130.80	33.77
	C100PE5	384	288	219	181	107	236		94.41	24.38
С	C100PE10	495	342	290	235	170	306		110.28	28.47
	C100PE15	551	457	350	274	205	367		124.21	32.07
	PB100PE5	361	268	182	134	106	210		93.32	24.09
PB	PB100PE10	449	325	263	201	119	271		111.95	28.91
	PB100PE15	490	340	297	217	161	301		113.06	29.19
	WTP100PE5	445	406	314	194	114	295		125.01	32.28
WTP	WTP100PE10	517	493	407	238	142	359		146.26	37.76
	WTP100PE15	547	518	431	275	189	392		138.79	35.84
	WTB100PE5	449	407	325	197	129	301		121.75	31.44
WTB	WTB100PE10	539	510	406	248	161	373		146.96	37.94
	WTB100PE15	570	535	433	293	205	407		139.59	36.04
	WTC100PE5	435	395	313	190	125	292		118.14	30.50
WTC	WTC100PE10	530	490	392	240	156	362		143.41	37.03
	WTC100PE15	552	521	420	285	195	395		136.56	35.26
Biodiesel Solvents	Polymer content	85 °C	100 °C	2 110 °C	C 120 °	C 135 °	Aver C of th Mea	age e ns, <i>x</i>	Standard Deviation of the Means, SD	Standard Error of the Means, SEM=SD/sqrt(N); (N is total sample size = 3*5 = 15)
	SF100PE5	391	293	197	125	69	215		115.59	29.84
SF	SF100PE10	464	349	269	165	88	267		132.65	34.25
	SF100PE15	515	380	295	189	108	297		142.69	36.84

Table A5- 3 Experimental uncertainty in terms of standard error of the means (SEM) of dossolution profile of PE into various biodiesel solvents

		Mean Di Various 7	ssolution T Femperatur	ime (minut res	es) of 3 rep	eats at			
Biodiesel Solvents	Polymer content	100 °C	120 °C	135 °C	145 °C	155 °C	Average of the Means, \bar{x}	Standard Deviation of the Means, SD	Standard Error of the Means, SEM=SD/sqrt(N); (N is total sample size = 3*5 = 15)
	Ca100PP5	441	346	268	179	145	276	108.41	27.99
Ca	Ca100PP10	548	521	426	316	257	414	112.96	29.17
	Ca100PP15	810	621	542	371	318	532	177.21	45.76
	WCO100PP5	541	364	250	199	160	303	137.43	35.48
WCO	WCO100PP10	606	486	380	334	267	415	119.34	30.81
	WCO100PP15	861	683	512	462	345	573	180.59	46.63
	PWC100PP5	398	320	240	183	141	256	92.81	23.96
PWC	PWC100PP10	695	491	406	272	216	416	169.88	43.86
	PWC100PP15	820	651	579	458	306	563	173.85	44.89
	C100PP5	410	316	247	198	140	262	93.83	24.23
С	C100PP10	560	441	377	281	209	374	122.45	31.62
	C100PP15	713	590	472	360	241	475	166.05	42.87
	PB100PP5	535	400	312	206	160	323	135.09	34.88
PB	PB100PP10	693	590	380	265	189	423	190.97	49.31
	PB100PP15	872	636	520	340	240	522	222.78	57.52
	WTP100PP5	641	517	446	304	197	421	156.27	40.35
WTP	WTP100PP10	839	647	518	321	233	512	218.87	56.51
	WTP100PP15	1001	840	553	358	255	601	282.20	72.86
	WTB100PP5	571	459	386	321	213	390	121.35	31.33
WTB	WTB100PP10	865	628	472	333	254	510	218.29	56.36
	WTB100PP15	1068	870	510	377	279	621	300.21	77.51
	WTC100PP5	564	440	371	312	209	379	119.50	30.85
WTC	WTC100PP10	842	605	455	325	247	495	211.90	54.71
	WTC100PP15	1050	840	498	392	269	610	290.81	75.09
Biodiesel Solvents	Polymer content	100 °C	110 °C	125 °C	135 °C	150 °C	Average of the Means, <i>x</i> ̄	Standard Deviation of the Means, SD	Standard Error of the Means, SEM=SD/sqrt(N); (N is total sample size = 3*5 = 15)
	SF100PP5	476	407	348	207	146	317	123.03	31.77
SF	SF100PP10	570	467	399	244	175	371	144.32	37.26
	SF100PP15	945	723	532	310	218	546	266.08	68.70

Table A5- 4 Experimental uncertainty in terms of standard error of the means (SEM) of dossolution profile of PP into various biodiesel solvents

Kinematic Viscosity (mm²/s, at 40 °C)	WTB	WCB	CaB	РВ	SB	СВ	WTC	WTP	PWC
Mean of the sample means (\bar{x})	172.90	170.46	515.91	145.01	154.08	158.95	171.16	153.03	158.61
Standard deviation of means (SD)	192.23	189.52	573.59	161.23	171.30	176.73	190.29	170.14	176.34
Standard error of means (SEM)	55.49	54.71	165.58	46.54	49.45	51.02	54.93	49.12	50.90
Instrumental error (±E)	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Higher uncertainty (SEM+E)	55.84	55.06	165.93	46.89	49.80	51.37	55.28	49.47	51.25
Lower uncertainty (SEM-E)	55.14	54.36	165.23	46.19	49.10	50.67	54.58	48.77	50.55

Table A5-5 Uncertainty of the experimentally derived mean viscosity of various PS-biodiesel solutions as presented in the Table 6-2

Table A5-6 Uncertainty of the experimentally derived mean HHV of various PS-biodiesel solutions

Higher Heating Value (MJ/kg, HHV)	WTB	WCB	CaB	PB	SB	СВ	WTC	WTP	PWC
Pure biodiesel	41.400	40.160	40.650	40.590	40.520	40.990	41.100	41.120	40.320
Biodiesel with 5% (w/v) PS	41.397	40.221	40.686	40.629	40.563	41.008	41.113	41.131	40.373
Biodiesel with 10% (w/v) PS	41.493	40.376	40.817	40.763	40.700	41.123	41.223	41.241	40.520
Biodiesel with 15% (w/v) PS	41.498	40.443	40.860	40.809	40.749	41.149	41.243	41.260	40.579
Mean of the sample means (\bar{x})	41.45	40.30	40.75	40.70	40.63	41.07	41.17	41.19	40.450
Standard deviation of means (SD)	0.049	0.114	0.087	0.091	0.094	0.069	0.064	0.063	0.105
Standard error of means (SEM)	0.014	0.033	0.025	0.026	0.027	0.020	0.018	0.018	0.030
Instrumental error (±E)	0.041	0.040	0.041	0.041	0.041	0.041	0.041	0.041	0.040
Higher uncertainty (SEM+E)	0.055	0.073	0.066	0.067	0.068	0.061	0.060	0.059	0.071
Lower uncertainty (SEM-E)	-0.027	-0.007	-0.016	-0.015	-0.013	-0.021	-0.023	-0.023	-0.010

Speed	$BS\ CO_2$	СО	HC	NOx	PM	O2	AFR	EGT	Fuel flow	Fuel power	Brake Power	Torque	BSFC	BTE	BSEC	BMEP	BMEP	HRR
(rpm)	gm/kWh	(% vol.)	(ppm)	(ppm)	(mg/m³)	(% vol.)	Air/Fuel	(C)	kg/h	kW	kW	Nm	gm/kWh	%	J/Wh	kPa	MPa	(J/°CA)
800	854.88	0.2	16.95	99	25.91	15.02	49.65	401	4.98	58.52	18.35	219.04	271.39	31.36	11.48	829.57	0.83	71.33
1200	751.87	0.92	18.01	327	99.72	1.39	15.05	488	6.91	81.19	28.95	230.38	238.69	35.66	10.10	872.51	0.87	66.64
1500	704.09	0.59	13.59	372	28.02	2.56	16.41	496	8.04	94.47	35.97	228.99	223.52	38.08	9.45	867.27	0.87	64.81
1800	774.88	0.43	11.94	440	11.89	3.68	17.48	511	9.67	113.62	39.31	208.55	245.99	34.60	10.41	789.83	0.79	66.46
2100	807.48	0.29	11.14	489	6.59	3.72	17.51	521	11.72	137.71	45.72	207.90	256.34	33.20	10.84	787.39	0.79	69.16
2400	844.53	0.15	10.89	417	4.5	3.4	17.21	571	12.81	150.52	47.78	190.11	268.10	31.74	11.34	720.01	0.72	66.11
Mean of sample means, M	789.62	0.430	13.75	357.33	29.44	4.96	22.22	498.00	9.02	106.00	36.01	214.16	250.67	34.11	10.60	811.10	0.81	67.42
Standard deviation of the means (SD)	52.52	0.264	2.79	126.23	32.67	4.57	12.30	50.89	2.70	31.75	10.05	13.88	16.67	2.32	0.71	52.57	0.05	2.18
Standard error of means (SEM)	12.38	0.062	0.66	29.75	7.70	1.08	2.90	12.00	0.64	7.48	2.37	3.27	3.93	0.55	0.17	12.39	0.01	0.51
Measurement uncertainty, E (±%)	0.30	0.020	1.00	1.00	0.10	0.20	2.00	1.00	0.40	0.41	0.41	0.02	2.01	1.90	0.20	1.90	1.18	2.00
Higher limit of uncertainty (M+ (SEM+E))	804.37	0.49	14.55	390.66	37.17	6.05	25.56	514.98	9.69	113.92	38.53	217.47	259.64	35.30	10.79	838.90	0.83	69.28
Lower limit of uncertainty (M-(SEM- E))	779.61	0.37	13.23	331.15	21.77	3.89	19.76	490.98	8.42	98.96	33.79	210.93	251.78	34.21	10.46	814.12	0.81	68.25

Table A5-7 Uncertainty analysis of combustion, emission and performance parameters of diesel fuel at full load condition

Speed	$BS \ CO_2$	СО	HC	NOx	PM	O2	AFR	EGT	Fuel flow	Fuel power	Brake Power	Torque	BSFC	BTE	BSEC	BMEP	BMEP	HRR
(rpm)	gm/kWh	(% vol.)	(ppm)	(ppm)	(mg/m³)	(% vol.)		(C)	kg/h	kW	kW	Nm	gm/kWh	%	J/Wh	kPa	MPa	(J/°CA)
800	866.65	0.13	12.12	106.45	22.74	16.04	50.68	398.45	5.29	62.14	18.27	218.12	289.56	29.41	12.24	826.11	0.83	214.74
1200	755.32	0.63	15.52	410.27	35.04	2.91	17.24	478.45	7.22	84.77	28.60	227.62	252.36	33.74	10.67	862.07	0.86	208.62
1500	720.11	0.36	12.85	449.26	9.30	4.64	18.82	492.85	8.55	100.42	35.54	226.25	240.60	35.39	10.17	856.89	0.86	218.67
1800	788.66	0.30	11.36	532.84	3.04	5.99	19.89	501.86	10.23	120.19	38.84	206.05	263.50	32.32	11.14	780.38	0.78	197.00
2100	823.61	0.21	9.73	557.38	2.50	5.16	19.70	518.67	12.38	145.39	44.99	204.59	275.18	30.95	11.63	774.84	0.77	241.30
2400	856.88	0.10	8.16	511.88	2.11	4.67	18.98	596.25	13.38	157.12	46.73	185.95	286.30	29.74	12.10	704.25	0.70	216.04
Mean of sample means, M	801.87	0.288	11.62	428.01	12.45	6.57	24.22	497.76	9.51	111.67	35.50	211.43	267.92	31.92	11.33	800.76	0.80	216.06
Standard deviation of the means (SD)	52.79	0.178	2.33	152.17	12.39	4.34	11.87	58.33	2.82	33.11	9.76	14.44	17.64	2.14	0.75	54.70	0.05	13.32
Standard error of means (SEM)	12.44	0.042	0.55	35.87	2.92	1.02	2.80	13.75	0.66	7.81	2.30	3.40	4.16	0.50	0.18	12.89	0.01	3.14
Measurement uncertainty, E (±%)	0.30	0.020	1.00	1.00	0.10	0.20	2.00	1.00	0.40	0.41	0.41	0.02	2.01	1.90	0.20	1.90	1.18	2.00
Higher limit of uncertainty (M+ (SEM+E))	816.72	0.33	12.29	468.16	15.39	7.60	27.50	516.48	10.21	119.93	37.94	214.88	277.46	33.04	11.52	828.87	0.82	223.52
Lower limit of uncertainty (M-(SEM- E))	791.84	0.25	11.19	396.43	9.55	5.56	21.91	488.98	8.88	104.32	33.34	208.07	269.14	32.03	11.17	803.08	0.80	217.24

Table A5-8 Uncertainty analysis of combustion, emission and performance parameters of WTB5 fuel at full load condition

Speed	BS CO ₂	CO	HC	NOx	PM	O2	AFR	EGT	Fuel flow	Fuel power	Brake Power	Torque	BSFC	BTE	BSEC	BMEP	BMEP	HRR
(rpm)	gm/kWh	(% vol.)	(ppm)	(ppm)	(mg/m³)	(% vol.)		(C)	kg/h	kW	kW	Nm	gm/kWh	%	J/Wh	kPa	MPa	(J/°CA)
800	872.80	0.10	5.90	77.71	33.88	13.96	54.74	378.53	4.82	56.45	17.27	206.18	278.76	30.60	11.77	780.41	0.78	210.54
1200	800.19	0.50	7.56	283.09	36.79	2.53	17.15	454.53	7.18	84.21	28.10	223.64	255.57	33.37	10.79	846.48	0.85	204.54
1500	762.90	0.29	6.26	305.49	9.02	5.52	18.72	480.53	8.51	99.75	34.92	222.29	243.66	35.01	10.28	841.39	0.84	214.39
1800	835.52	0.23	5.53	346.35	3.67	6.76	20.49	486.80	10.18	119.39	38.16	202.44	266.85	31.96	11.26	766.26	0.77	193.15
2100	872.55	0.14	4.74	352.82	2.73	5.67	20.29	503.11	12.32	144.43	44.20	201.01	278.68	30.61	11.76	760.83	0.76	236.58
2400	883.08	0.08	3.97	348.08	2.22	4.06	20.12	578.36	13.31	156.08	47.20	187.81	282.04	30.24	11.90	710.86	0.71	211.82
Mean of sample means, M	837.84	0.226	5.66	285.59	14.72	6.42	25.25	480.31	9.39	110.05	34.98	207.23	267.60	31.97	11.29	784.37	0.78	211.83
Standard deviation of the means (SD)	43.80	0.143	1.14	96.38	14.77	3.63	13.24	59.44	2.92	34.24	10.04	12.49	13.99	1.73	0.59	47.28	0.05	13.06
Standard error of means (SEM)	10.32	0.034	0.27	22.72	3.48	0.86	3.12	14.01	0.69	8.07	2.37	2.94	3.30	0.41	0.14	11.14	0.01	3.08
Measurement uncertainty, E (±%)	0.30	0.020	1.00	1.00	0.10	0.20	2.00	1.00	0.40	0.41	0.41	0.02	2.01	1.90	0.20	1.90	1.18	2.00
Higher limit of uncertainty (M+ (SEM+E))	850.68	0.26	5.98	311.16	18.21	7.29	28.88	499.12	10.11	118.57	37.49	210.21	276.27	32.98	11.46	810.42	0.80	219.15
Lower limit of uncertainty (M-(SEM- E))	830.03	0.19	5.45	265.73	11.25	5.58	22.64	471.10	8.74	102.43	32.75	204.33	269.68	32.17	11.18	788.13	0.78	212.99

Table A5-9 Uncertainty analysis of combustion, emission and performance parameters of WTB5PS5 fuel at full load condition

Speed	$BS \ CO_2$	CO	HC	NOx	PM	O2	AFR	EGT	Fuel flow	Fuel power	Brake Power	Torque	BSFC	BTE	BSEC	BMEP	BMEP	HRR
(rpm)	gm/kWh	(% vol.)	(ppm)	(ppm)	(mg/m³)	(% vol.)		(C)	kg/h	kW	kW	Nm	gm/kWh	%	J/Wh	kPa	MPa	(J/°CA)
800	906.12	0.10	6.49	75.77	35.57	12.79	55.83	386.66	5.27	61.85	17.36	207.21	303.56	28.07	12.83	784.31	0.78	216.64
1200	761.29	0.46	8.32	276.01	38.63	2.32	17.50	464.29	7.19	84.37	28.19	224.31	255.04	33.41	10.78	849.02	0.85	210.47
1500	725.81	0.26	6.88	297.86	9.47	5.06	19.10	490.84	8.52	99.95	35.02	222.96	243.15	35.04	10.27	843.91	0.84	220.60
1800	794.90	0.21	6.08	337.69	3.86	6.20	20.90	497.25	10.19	119.62	38.27	203.05	266.30	32.00	11.25	768.56	0.77	198.75
2100	830.12	0.13	5.21	344.00	2.86	5.20	20.69	513.91	12.33	144.71	44.34	201.61	278.10	30.64	11.75	763.11	0.76	243.44
2400	840.14	0.07	4.37	339.37	2.33	3.72	20.52	590.78	13.32	156.39	47.34	188.37	281.45	30.27	11.89	712.99	0.71	217.96
Mean of sample means, M	809.73	0.21	6.23	278.45	15.45	5.88	25.76	490.62	9.47	111.15	35.09	207.92	271.27	31.57	11.46	786.98	0.79	217.98
Standard deviation of the means (SD)	58.08	0.13	1.25	93.97	15.51	3.32	13.50	60.72	2.81	32.96	10.06	12.52	19.46	2.25	0.82	47.40	0.05	13.44
Standard error of means (SEM)	13.69	0.03	0.29	22.15	3.66	0.78	3.18	14.31	0.66	7.77	2.37	2.95	4.59	0.53	0.19	11.17	0.01	3.17
Measurement uncertainty, E (±%)	0.30	0.02	1.00	1.00	0.10	0.20	2.00	1.00	0.40	0.41	0.41	0.02	2.01	1.90	0.20	1.90	1.18	2.00
Higher limit of uncertainty (M+ (SEM+E))	825.85	0.24	6.58	303.38	19.12	6.67	29.45	509.84	10.17	119.37	37.60	210.91	281.30	32.70	11.68	813.11	0.81	225.50
Lower limit of uncertainty (M-(SEM- E))	798.47	0.18	5.99	259.09	11.81	5.11	23.09	481.22	8.85	103.83	32.86	205.01	272.13	31.64	11.29	790.77	0.79	219.17

Table A5-10 Uncertainty analysis of combustion, emission and performance parameters of WTB5PS10 fuel at full load condition

Speed	$BS \ CO_2$	CO	HC	NOx	PM	O2	AFR	EGT	Fuel flow	Fuel power	Brake Power	Torque	BSFC	BTE	BSEC	BMEP	BMEP	HRR
(rpm)	gm/kWh	(% vol.)	(ppm)	(ppm)	(mg/m³)	(% vol.)		(C)	kg/h	kW	kW	Nm	gm/kWh	%	J/Wh	kPa	MPa	(J/°CA)
800	909.63	0.09	6.34	74.78	35.93	12.15	55.60	389.75	5.31	62.35	17.39	207.61	305.14	27.89	12.91	785.80	0.79	220.54
1200	764.01	0.42	8.12	272.42	39.02	2.20	17.42	468.01	7.24	85.06	28.25	224.80	256.29	33.21	10.84	850.88	0.85	214.26
1500	728.40	0.24	6.72	293.99	9.56	4.81	19.02	494.77	8.58	100.77	35.10	223.45	244.35	34.83	10.34	845.77	0.85	224.58
1800	796.94	0.20	5.94	333.30	3.90	5.89	20.81	501.23	10.27	120.60	38.40	203.70	267.34	31.84	11.31	771.02	0.77	202.33
2100	833.09	0.12	5.09	339.53	2.89	4.94	20.61	518.02	12.42	145.90	44.43	202.05	279.47	30.46	11.82	764.79	0.76	247.82
2400	843.14	0.07	4.27	334.96	2.35	3.53	20.44	595.51	13.42	157.67	47.45	188.78	282.84	30.09	11.96	714.56	0.71	221.88
Mean of sample means, M	812.53	0.19	6.08	274.83	15.61	5.58	25.65	494.55	9.54	112.06	35.17	208.40	272.57	31.39	11.53	788.81	0.79	221.90
Standard deviation of the means (SD)	58.40	0.12	1.22	92.75	15.66	3.16	13.44	61.20	2.83	33.23	10.09	12.54	19.59	2.24	0.83	47.46	0.05	13.68
Standard error of means (SEM)	13.77	0.03	0.29	21.86	3.69	0.74	3.17	14.43	0.67	7.83	2.38	2.96	4.62	0.53	0.20	11.19	0.01	3.22
Measurement uncertainty, E (±%)	0.30	0.02	1.00	1.00	0.10	0.20	2.00	1.00	0.40	0.41	0.41	0.02	2.01	1.90	0.20	1.90	1.18	2.00
Higher limit of uncertainty (M+ (SEM+E))	828.74	0.22	6.43	299.44	19.32	6.34	29.33	513.92	10.24	120.35	37.69	211.40	282.67	32.51	11.75	814.98	0.81	229.56
Lower limit of uncertainty (M-(SEM- E))	801.21	0.16	5.86	255.72	11.93	4.85	22.99	485.07	8.91	104.69	32.94	205.49	273.43	31.45	11.36	792.61	0.79	223.12

Table A5-11 Uncertainty analysis of combustion, emission and performance parameters of WTB5PS15 fuel at full load condition

Overall Relative Uncertainty of the Engine Test Bed System:

In case of the overall relative uncertainty of the fuel combustion, performance, and emission characterisation by various equipment, which consist of the engine test bed system, the overall relative uncertainty can be derived by Eq. A5-4a.

The values of the individual uncertainties of the derived parameters from the engine test bed system are already mentioned in the Table A5-12 as the relative measurement uncertainty (E).

Measurements	Relative Measurement Uncertainty (±%)
Fuel flow	0.4
Engine speed	0.02
Cylinder Pressure (CP)	0.03
Crank Angle	0.01
AFR	
EGT	1
BP	0.41
Torque	0.02
BSFC	2.01
O ₂	0.2
NOx	1
СО	0.02
CO ₂	0.3
HC	1
PM	0.1
Overall measurement uncertainty (Root-sum-square):	2.74

Table A5-12 Individual relative uncertainties of the engine test bed system

Based on the RSS method referred in the Eq. A5-4a the overall uncertainty of the system is as follows:

$$Overall \ measurement \ uncertainty = \left[\left(E_{fuel \ flow} \right)^2 + \left(E_{AFR} \right)^2 + \left(E_{engine \ speed} \right)^2 + \left(E_{crank \ angle} \right)^2 + \left(E_{cylinder \ pressure} \right)^2 + \left(E_{CO2} \right)^2 + \left(E_{CO} \right)^2 + \left(E_{HC} \right)^2 + \left(E_{NOx} \right)^2 + \left(E_{PM} \right)^2 + \left(E_{O2} \right)^2 + \left(E_{EGT} \right)^2 + \left(E_{Torque} \right)^2 + \left(E_{BP} \right)^2 + \left(E_{BSFC} \right)^2 \right]^{\frac{1}{2}} = \pm 2.74\%$$