An Experimental Study of 2nd Generation Biodiesel as an Alternative Fuel for Diesel Engine

By

Muhammad Mostafa Kamal Bhuiya

A thesis submitted in fulfilment of the requirements for the award of

the degree of

Doctor of Philosophy

School of Engineering and Technology, Tertiary Education Division

Central Queensland University

Australia

March 2017

ABSTRACT

This study investigated the prospects of using 2nd generation biodiesel as an alternative fuel particularly the biodiesel produced from the Australian Beauty Leaf (BL) (*Calophyllum inophyllum* L.). Firstly, the study developed an optimised oil extraction method from BL kernel based on the kernel size and treatment conditions (for example, seed preparation and cracking, drying, whole kernel, grated kernel and moisture content). Mechanical method of using a screw press expeller and chemical method of using n-hexane were used for oil extraction. The results indicated that the grated kernels that were dried to 14.4% moisture content produced the highest oil yield from both methods. The highest oil recovery of 54% was obtained in n-hexane method from the grated kernel followed by 45% in screw press method. A comparison of fossil energy ratio (FER) (the ratio of energy produced from the biodiesel to the energy required for processing of the feedstocks) was made between n-hexane and screw press methods and the results revealed that the FER in-hexane method was 4.1 compared to 3.7 in screw press method, indicating that the n-hexane method is more efficient than the screw press technique. It should also be noted that the oil content of BL kernel was about 60% on dry weight basis.

Secondly, biodiesel was produced from the crude and refined BL oil. Two more oils namely, refined poppy oil (non-edible) and crude jojoba oil were also used for biodiesel production and comparison with BL biodiesels. A single stage (transesterification) and two-stage (acid–catalysed esterification and base-catalysed transesterification) processes were employed and various parameters, such as methanol to oil ratio, catalyst concentration, reaction temperature and reaction time were varied to optimise the biodiesel production process. The resulting fatty acid methyl ester (FAME; biodiesel) was characterised by gas chromatography (GC). The results of BL biodiesel yield and its physico-chemical properties were compared with those of poppy, mixture of poppy and waste cooking (poppy 80% and waste cooking 20%), and jojoba biodiesels. The conversion efficiencies of 91.1% for crude two-stage BL oil, 92.3% for refined BL oil, 82.8% for refined single stage BL oil, 93.4% for refined two stage poppy oil and 83.3% for crude two stage jojoba oil were found. The highest conversion efficiency was found for refined poppy oil (93.4%) followed by refined BL oil (92.3%).

Thirdly, engine performance, combustion and emission characteristics were studied using petrodiesel and biodiesel-diesel blends of B5, B10 and B20 for four biodiesels, viz. BL

biodiesel, poppy biodiesel, binary mixture of poppy and waste cooking biodiesel, and jojoba biodiesel. The testing was performed at engine speeds from 1200 rpm to 2400 rpm with a 200 rpm increment and engine loads of 25%, 50%, 75% and 100%.

The measured engine performance parameters are brake power (BP), torque, brake specific fuel consumption (BSFC), brake thermal efficiency (BTE) and brake mean effective pressure (BMEP). The results showed that the BP and BSFC increased, whereas the torque, BTE and BMEP decreased with an increase in engine speed for all biodiesels at full load. In terms of load, BP, torque, BTE and BMEP increased, while BSFC decreased with an increase in load. Amongst all the feedstocks, the poppy biodiesel showed better engine performance followed by BL biodiesel. The poppy biodiesel results indicated that the average reductions in BP, torque, BTE and BMEP were 0.90%, 0.75%, 0.40%, and 0.75%, respectively, and the average increase in BSFC was 1.15%, at B5 compared to petrodiesel over the entire range of engine speed. For BL biodiesel, the results indicated that the average decreases in BP, torque, BTE and BMEP were 4.15%, 2.6%, 3.95% and 2.6%, respectively, and the average increase in BSFC was 6.10%, at B5 as compared to petrodiesel over the range of speeds.

Engine combustion characteristics that were investigated are cylinder pressure (CP) and heat release rate (HRR). It was found that CPs of biodiesels tested in this study were higher than those of petrodiesel. Overall, the B20 formulation showed the highest CP compared to diesel, B5 and B10. At full load, an increase in CP for PB20 was 3.65%, and that for BLB20 was 3.40% as compared to diesel at 1400 rpm. On the other hand, the petrodiesel showed the highest HRR compared to B5, B10 and B20. At full load, a decrease in HRR for PB5 was 2.40%, and that for BL B5 was 3.8% at 1400 rpm. Both the CP and HRR increased with an increase in load varied from 25% to 100% for all tested fuels.

The emission characteristics that were evaluated are exhaust gas temperature (EGT), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbon (HC) and particulate matter (PM). The results showed that the EGT, NO_x and CO_2 increased, whereas the CO, HC and PM decreased with an increase in engine speed at full load for all tested biodiesels. The results also revealed that all emission parameters increased with an increase in engine load. Overall, the B5 performed better than other formulations for EGT, NO_x and CO_2 (that is, the increase in emission for these parameters was less for all biodiesel blends compared to diesel) while the B20 indicated better results for CO, HC and PM for all tested biodiesels as compared

to diesel (that is, reductions of these emissions were higher in biodiesels compared to diesel). Reduction in emission was higher for poppy B20 followed by BLB20 compared to other biodiesels. The highest reduction in CO emission was 8.10% for poppy B20 and 4.90% for BLB20 as compared to diesel.

Based on the above findings, it can be concluded that both poppy and BL biodiesels showed better engine performance, combustion and emissions characteristics, and they exhibit an excellent potential for use as 2nd generation biodiesels. The current study provided an experimental evidence and sound understanding of the use of poppy and BL biodiesels as potential 2nd generation biodiesels which is useful information for biodiesel producers and end users.

Keywords: 2nd generation biodiesel, alternative transport fuel, Biodiesel production, Engine performance and combustion characteristics, Engine emissions

DECLARATION OF AUTHORSHIP AND ORIGINALITY

I, the undersigned author, 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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March 2017

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LIST OF SYMBOLS

D   Engine displacement volume (m^3)

f Fuel consumption rate (g/hour)

H_2O Water

H_2SO_4 Sulphuric Acid

H_3PO_4 Phosphoric Acid

KOH   Potassium Hydroxide

NaOH   Sodium Hydroxide

Na_2SO_4 Sodium Sulphate

P Instantaneous cylinder pressure (Pa)

V Instantaneous cylinder volume (m^3)

γ Specific heat ratio

$\dfrac{dQ}{d\theta}$ Rate of heat release (J/°CA).

θ Crank angle (°CA)

η Efficiency

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
B5	5% Biodiesel and 95% Diesel
B10	10% biodiesel and 90% diesel
B20	20% biodiesel and 80% diesel
BL	Beauty Leaf
BLO	Beauty Leaf Oil
BLB	Beauty Leaf Blending
BMEP	Brake Mean Effective Pressure
BP	Brake Power
BSFC	Brake Specific Fuel Consumption
BTE	Brake Thermal efficiency
CBLO	Crude Beauty Leaf Oil
CEBLO	Crude Esterified Beauty Leaf Oil
CEJO	Crude Esterified Jojoba Oil
CETBLME	Crude Esterified Transesterified Beauty Leaf Methyl Ester
CH_3OK	Potassium Methoxide
CI	Compression Ignition
CJO	Crude Jojoba Oil
CO	Carbon monoxide
CO_2	Carbon Dioxide
CP	Cylinder Pressure
CV	Calorific vale
DI	Deionised Water
EGT	Exhaust Gas Temperature

EN	European Standard
FAME	Fatty Acid Methyl Ester
FER	Fossil Energy Ratio
FFA	Free Fatty Acid
FT	Fischer-Tropsch
GHG	Greenhouse Gas
GK	Grated Kernel
HC	Hydrocarbon
HCHO	Formaldehyde
HRR	Heat Release Rate
HV	Heat value
IEA	International Energy Agency
JB	Jojoba Blending
JME	Jojoba Methyl Ester
NO_x	Nitrogen Oxide
nPAH	Nnitrated Polycyclic Aromatic Hydrocarbon
PAH	Polycyclic Aromatic Hydrocarbons
PB	Poppy Blending
PC	Premixed Combustion
PM	Particulate Matter
PME	Poppy Methyl Ester
PPM	Parts Per Million
PWC	Poppy Waste Cooking
PWCB	Poppy Waste Cooking Blending
RBLO	Refined Beauty Leaf Oil
REBLO	Refined Esterified Beauty Leaf Oil

REPO	Refined Esterified Poppy Oil
RETBLME	Refined Esterified Transesterified Beauty Leaf Methyl Ester
RPO	Refined Poppy Oil
RTBLME	Refined Transesterified Beauty Leaf Methyl Ester
RWEBLO	Refined Without Esterified Beauty Leaf Oil
SD	Standard deviation
SE	Standard error
TBPD	Thousand Barrel per Day
WK	Whole Kernel

ACKNOWLEDGEMENTS

LIST OF PUBLICATIONS

The following articles were produced for publication during the course of my candidature. The authors' contributions in producing these papers are described below. It is to be noted that some papers have been put together before describing authors' contribution because similar contribution was made by each author in those papers.

Refereed Journal Papers

1. **Bhuiya, M.M.K,** Rasul, M.G., Khan, M.M.K., Ashwath, N., Azad, A.K. and Hazrat, M.A. (2016), Prospects on 2nd Generation Biodiesel as a Sustainable Fuel - Part: 2 Properties, Performance and Emission Characteristics, *Renewable and Sustainable Energy Reviews*, vol. 55, 2016, pp. 1129-1146.

2. **Bhuiya, M.M.K,** Rasul, M.G., Khan, M.M.K., Ashwath, N. and Azad, A.K. (2016), Prospects of 2nd Generation Biodiesel as a Sustainable Fuel - Part: 1 Selection of Feedstocks, Oil Extraction Techniques and Conversion Technologies, *Renewable and Sustainable Energy Reviews*, vol. 55, 2016, pp. 1109-1128.

3. **Bhuiya, M.M.K,** Rasul, M.G., Khan, M.M.K., Ashwath, N., Azad, A.K. and Hazrat, M.A. (2014), Second Generation Biodiesel: Potential Alternative to Edible Oil-derived Biodiesel, *Energy Procedia,* vol. 61, 2014, pp. 1969-1972.

Statement of Authors Contribution for papers 1, 2 and 3:

The development of each of these papers was initially discussed in fortnightly progress meetings between M.M.K. Bhuiya (student) and supervisory team (M.G. Rasul, M.M.K. Khan and N. Ashwath). Then, Bhuiya drafted the full manuscript of each of these papers including their relevant analysis and literature review. A/Prof M.G. Rasul (principal supervisor) initially reviewed these manuscripts and provided feedback for improvement and logical presentations of the contents. Then, Prof Khan and A/Prof Ashwath provided feedback on the second draft of each of these manuscripts and made valuable comments and suggestions for further improvement. Finally, discussion was made between Bhuiya and supervisory team for fine-tuning and finalising these manuscripts. A.K. Azad assisted Bhuiya during preparation of the initial drafts through collecting data and its analysis, formatting, discussion on contents and their sequential placement in the manuscripts. M.A. Hazrat assisted Bhuiya (for articles 1 and 3) in

collecting data and its analysis, and checking and configuring the full manuscripts. These papers were written from the literature review which is presented in chapter 2.

4. **Bhuiya, M.M.K,** Rasul, M.G., Khan, M.M.K., Ashwath, N., Azad, A.K. and Mofijur, M. (2015), Optimisation of Oil Extraction Process from Australian Native Beauty Leaf Seed (*Calophyllum inophyllum*), ***Energy Procedia,*** vol. 75, 2015, pp. 56-61.

Statement of Authors' Contribution for paper 4:

Initially, M.M.K. Bhuiya and supervisory team (M.G. Rasul, M.M.K. Khan and N. Ashwath) discussed about the methodology, and experimental design and data measurement for preparing these papers. M.M.K. Bhuiya conducted the experiments, measured the data, and performed the data and results analysis, and drafted these manuscripts. A/Prof M.G. Rasul (principal supervisor) assisted Bhuiya in analysing the data and their respective results and discussion. A/Prof Rasul first reviewed these manuscripts, and provided important suggestions and feedback for modification and improvement. Then, Prof Khan and A/Prof Ashwath reviewed the manuscripts, and made thoughtful comments and suggestions for further improvement and fine-tuning the contents. The other co-author A.K. Azad assisted Bhuiya in the experimental set up, measuring data and analysis. Then, M. Mofijur helped Bhuiya in final checking and compiling the whole manuscript. This article was written based on the contents presented in chapter 3.

Refereed Conference Papers

5. **Bhuiya, M.M.K,** Rasul, M.G., Khan, M.M.K., Ashwath, N. (2015), Comparison of Oil Refining and Biodiesel Production Process between Screw press and n-hexane Techniques from Beauty Leaf Feedstock, 11th International Conference on Mechanical Engineering 2015 (ICME 2015), Paper ID-582, 18-20 December, Dhaka, Bangladesh.

6. **Bhuiya, M.M.K,** Rasul, M.G., Khan, M.M.K., Ashwath, N. (2015), Beauty Leaf Oil Refining and Conversion into Biodiesel from Australian Native 2nd Generation Feedstock, 3rd International Conference on Mechanical Engineering and Renewable Energy 2015, (ICMERE 2015), Paper ID-270, 26-29 November, Chittagong, Bangladesh.

Statement of Authors Contribution for papers 5 and 6:

M.M.K. Bhuiya developed the methodology, designed the experimental measurement procedures, conducted the experiments and measured the data, and analysed the data. Bhuiya also developed the contents of the papers and drafted the manuscript. A/Prof M.G. Rasul (principal supervisor) assisted in analysing data. Initially, A/Prof M.G. Rasul reviewed these manuscripts and provided guidance and valuable feedback for modification of the manuscripts. Then, Prof Khan and A/Prof Ashwath reviewed the second draft of these manuscripts, and made comments and suggestions for further development. These papers were finalised though further discussion between Bhuiya and supervisory team. These papers were written based on the contents of chapters 4 and 5, respectively.

7. **Bhuiya, M.M.K,** Rasul, M.G., Ashwath, N., Khan, M.M.K. (2014), Recent development in producing biodiesel from non-edible oil feedstocks, 2nd International Conference on Mechanical Engineering and Renewable Energy 2013, (ICMERE 2013), Paper Id-268, 1-3 May, Chittagong, Bangladesh.

Statement of Author Contribution for paper 7:

M.M.K. Bhuiya developed the contents of the manuscript and prepared the manuscript with literature review and relevant analysis. Initial feedback on the draft was made by A/Prof M.G. Rasul (principal supervisor) for improvement and logical presentation of the contents. Then, A/Prof Ashwath and Prof Khan made valuable comments and suggestions for further improvement. Finally, in a group discussion between Bhuiya and supervisory team was done for further revision and finalising the manuscript. This paper was written from the literature review presented in chapter 2.

CHAPTER 1

INTRODUCTION

1.1 Motivation and Background

The world energy demand is increasing continuously. Nowadays, it is a key challenge to meet the growing energy demand in a benign, eco-friendly and cost effective way as energy, economy and environment are the multidisciplinary concern. Energy is broadly categorised into two groups which are non-renewable and renewable energy. The non-renewable energy sources (crude oil, coal, and natural gas and so on) are playing a vital role in the growth of industrial development, agricultural sector, power generation sector, urban and rural sites, transportation and in fulfilling other primary human needs. The world primary energy consumption has reached 535 EJ (or 12,730 million tonnes of oil equivalent (Mtoe) which is a 28% increase yearly over the energy consumption in 2013 (Xia et al. 2016). In 2013, the total primary energy consumption was 87%, which came mainly from the fossil fuels as these were the dominant energy source (BP 2016b). The world energy consumption from 1990 to 2015 and its prediction till 2035 can be seen in Figure 1.1 (Portal 2016). In 2015, the majority of the world energy consumption which is 85.76% came from natural gas (24.36%), coal (28.93%) and liquids (32.45%).

It is projected that the use of renewable energy would reduce the world fossil energy consumption to 81.27% (Natural gas 26.11%, coal 26.14% and liquids 29.01%) although the world energy consumption is increasing day by day and is expected to continue till 2035 (Portal, 2016). According to the International Energy Outlook (IEO), it was predicted that the world consumption of petroleum and other liquid fuels will increase to 100 million barrels per day (b/d) in 2020 and 121 million b/d in 2040 (IEO 2016) while it was 90 million b/d in 2012. It has been reported that about one-third of total energy consumption converted from fossil fuels (coal, oil, gas and so on) is linked with transport fuel through liquid fuels (petrol and diesel) (IEA 2015). In addition, it can also be noted that the transport sector globally occupies the 3rd place when total energy consumption and greenhouse gas (GHG) emissions are considered (after the industry and the building sectors). Currently, world liquids demand (petroleum oil, biofuels and other liquids) is about 20 Mb/d, which will increase to 112 Mb/d by 2035 of which transport will accounts for over 60% of the growth (BP 2016a).
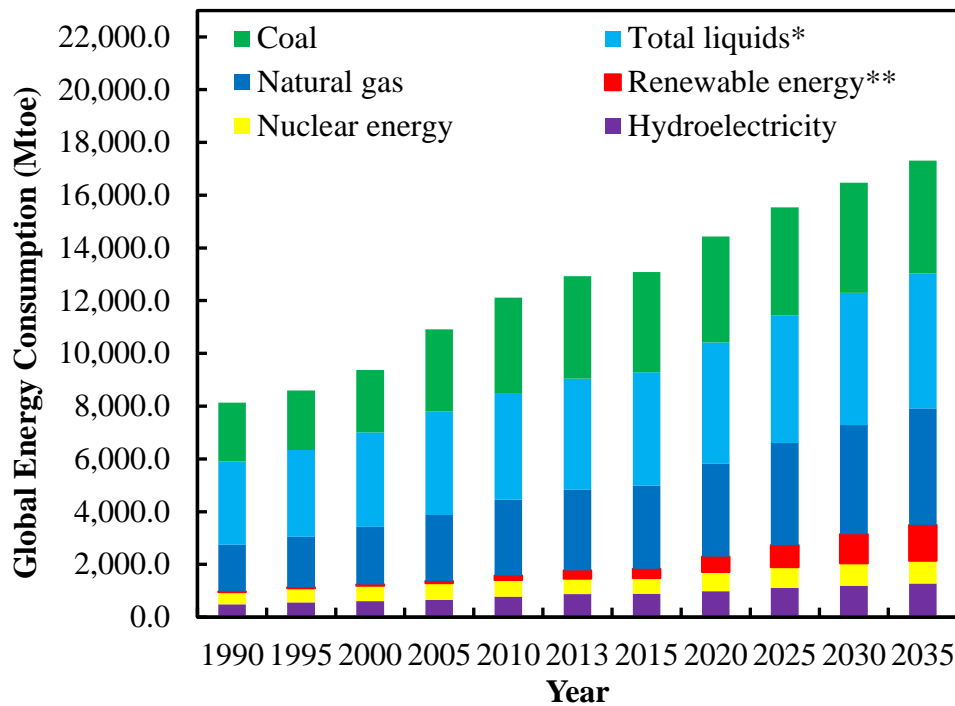
Figure 1.1: World energy consumption from 1990-2035 in Mtoe. * Includes petroleum oil, biofuels, gas-to-liquids and coal-to-liquids. ** Includes wind power, solar electricity and other renewables (Portal 2016).

This increase in world energy consumption is primarily due to population growth, industrialisation and exposure to better living standards. In particular, Australia's demand for oil has increased steadily over recent decades which is mainly due to the increasing demand for transport (Department of Industry and Science 2014). As predicted, the transport sector consumed 26% of energy which was the 2nd largest energy consumer in 2012-2013 (BoRaEE 2014). It has been reported that the world petroleum oil reserves declined by 2.4 billion barrels in 2015 to 1697.6 billion barrels which indicates an increase by 24% over the 2005 supply (Oil reserves 2016).

The amount of non-renewable energies, that is, fossil fuel reserves, are depleting gradually due to the continuous and increasing energy demand and consumption. In addition, due to climate change, environmental pollution and CO_2 emission from petroleum fuels, the world is shifting towards alternative sources of energy which are renewable, locally available, cost effective and environmentally friendly. The search for alternative sources of energy has escalated since the introduction of Mandatory Renewable Energy Target in 2001 (MRET 2001). Thus, the pressure is building up amongst the fuel industries to explore alternative sources of feedstock, to meet

at least the 2% target. Amongst many alternatives, biofuel is considered as one of the emerging renewable sources of energy for meeting increasing global energy demand, especially transport energy demand and its capability of reducing green house gas (GHG) emissions significantly. Moreover, the use of biofuel could increase and can play a significant role into fulfilling this increasing demand at a large scale which is predicted to increase from 5.26% in 2015 to 13.02% in 2035 as shown in Figure 1.2 (BP 2016a, Sajjadi et al. 2016, p. 3).
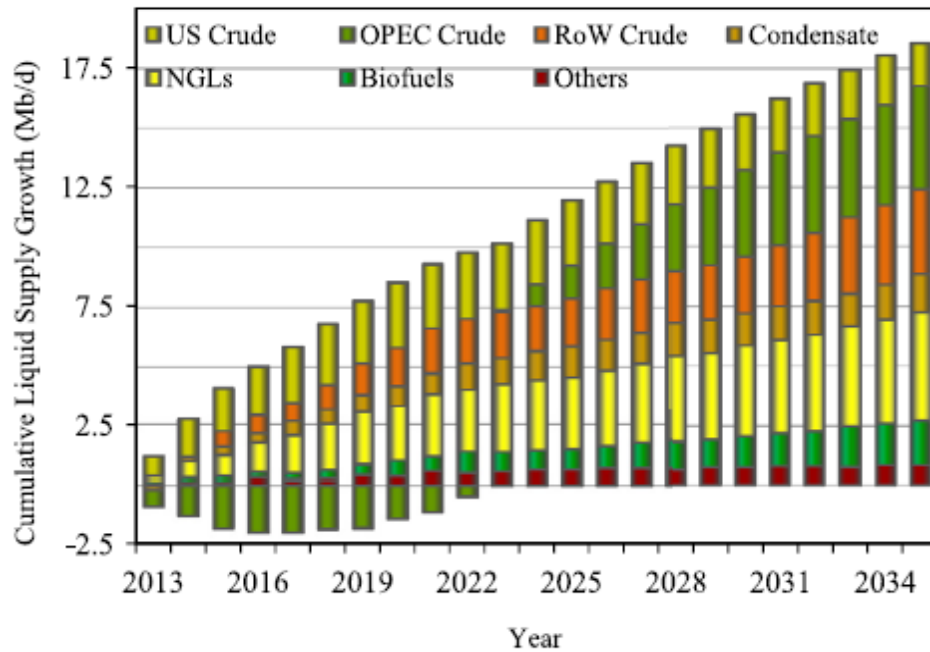
Figure 1.2: World liquid energy supply growth till 2035. * Includes gas-to-liquid, coal-to-liquid and refinery volume gain (BP 2016a, Sajjadi et al. 2016, p. 3).

The International Energy Agency (IEA) predicts that it is possible to meet more than a quarter of world energy demand for transportation using biofuels (Alternative Energy 2016). In addition, with increasing global warming temperature continuously, the use of biofuels is increasing, which assists the locally produced fuels to reduce the dependency on imported oil and the import cost to a large extent (Nigam & Singh 2011, Stephenson et al. 2008). It can be noted that the world's total biodiesel production has been growing steadily over the last decade from 123.9 Thousand Barrels per Day (TBPD) in 2006 to 561 TBPD in 2016 as shown in Figure 1.3 (EIA 2017, IEA 2017). In particular, Australia's total biodiesel production has also been increased significantly from 0.4 TBPD in 2006 to 2 TBPD in 2016 as presented in Figure 1.4 (EIA 2017, IEA 2017).
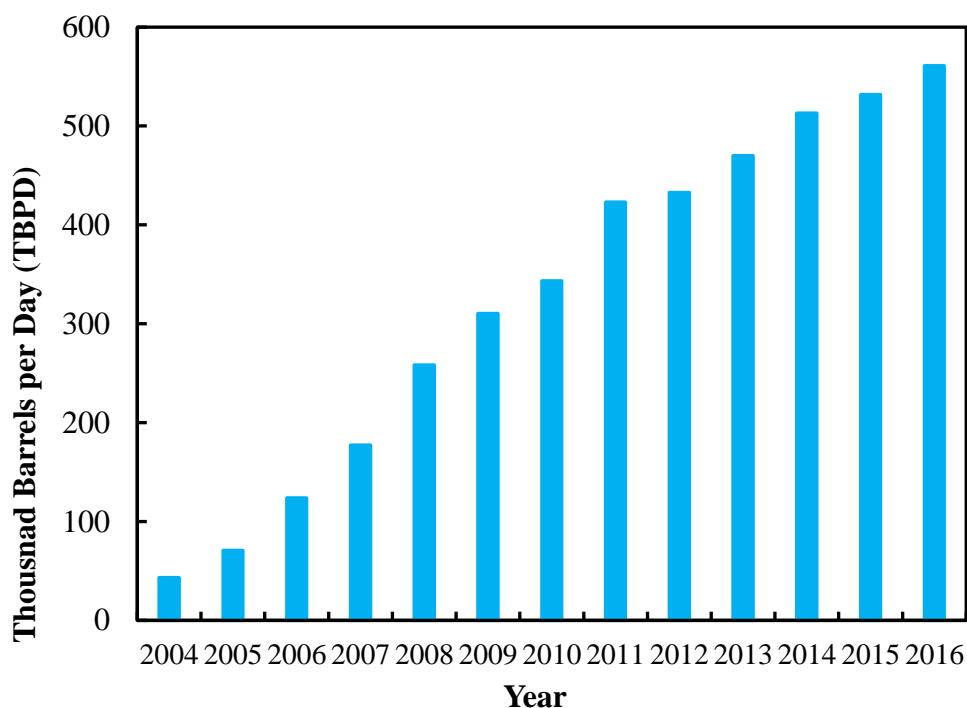
Figure 1.3: Total biodiesel production in worldwide (EIA 2017, IEA 2017)
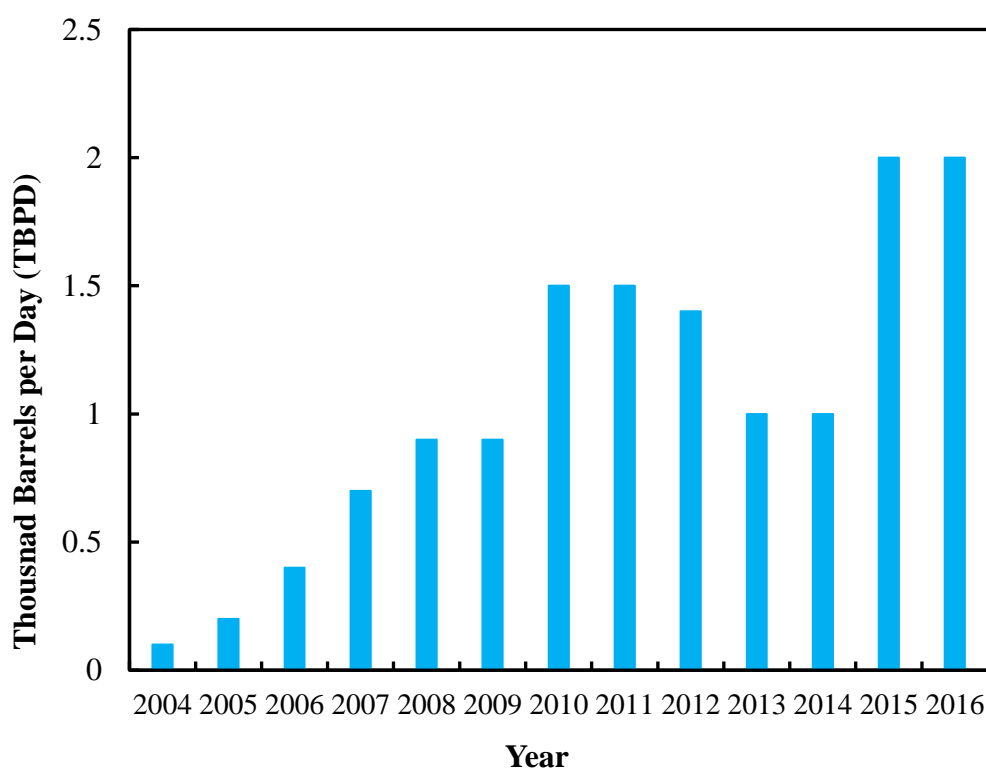
Figure 1.4: Total biodiesel production in Australia (EIA 2017, IEA 2017)

The renewable biofuel resources could help reduce the world's dependency on oil to a great extent. Biofuels which are alternative to fossil fuels can be considered as a promising source

of future generation fuel. It's have the ability to increase the security of supply, reduce engine emissions and provides a steady income for farmers. For example, the reductions in CO and HC emissions for *Callophyllum inophyllum* biodiesel at a biodiesel-diesel blend of B10 are 7.9% and 7.79% which are lower than the petroleum diesel (Mosarof et al. 2016). Hence, the possibility of use of biofuels as an alternative transport fuel, more specifically 2nd generation biodiesels, is being explored in this study.

1.2 Biofuel

Biofuels, which are predominantly produced from biomass sources, are classified to as liquid, gas or solid fuels. These are produced from biomass resources which include biodiesel, bioethanol, methanol, and Fischer-Tropsch (FT) diesel, and gaseous fuels (hydrogen, syngas and methane and so on) (Demirbas 2008b). Liquid biofuels are primarily used in engine or are used in fuel cells for power generation. These are the good choice of fuel owing to their renewability, biodegradability and lower emissions of exhaust gases (Bhatti et al. 2008). These are mainly categorised as primary and secondary biofuels as shown in Figure 1.5 (Nigam & Singh 2011).
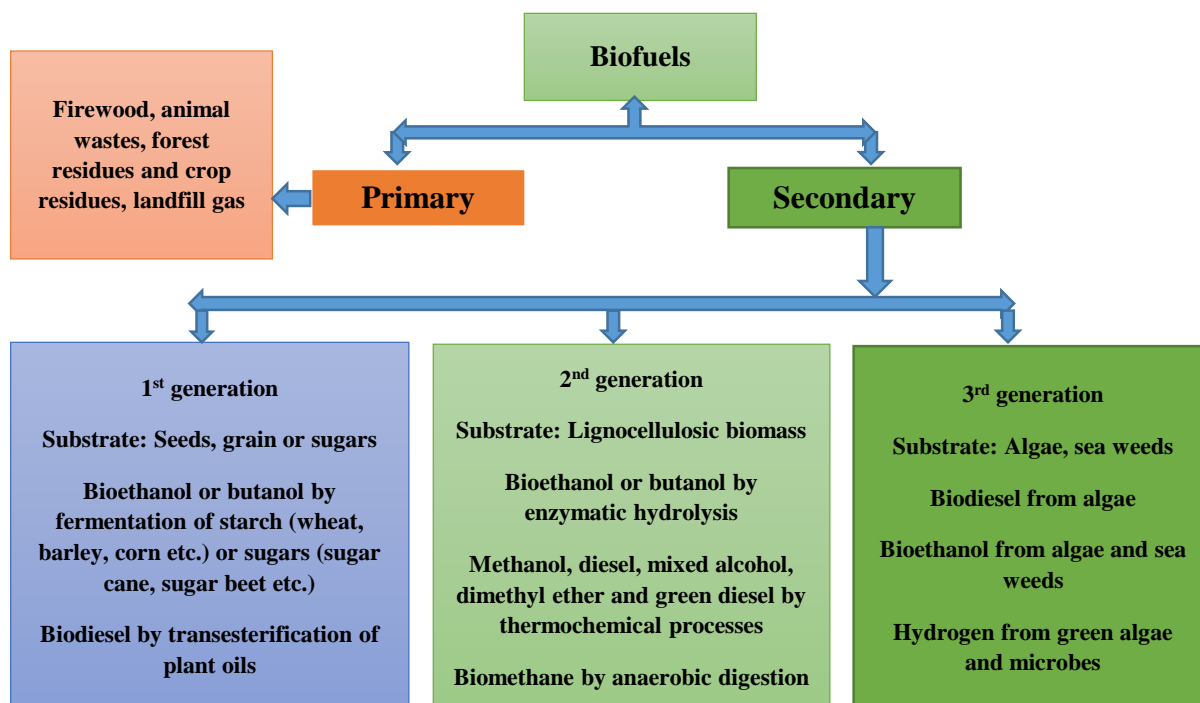
Figure 1.5: Classification of biofuels (Nigam & Singh 2011)

The secondary or liquid biofuels are subdivided into 1st generation biofuels, 2nd generation biofuels and 3rd generation biofuels. The distinction among those biofuels is the feedstock used.

The detailed advantages, and disadvantages of 1st and 2nd generation biofuels are shown in Figure1.6 (Naik et al. 2010). Research has recently begun on 3rd generation biofuels. Among different liquid biofuels, biodiesel is regarded as one of the promising alternative resources to meet the future transport energy demand nationally and internationally.

1st generation fuel:

Technology: Economical

Feedstocks: Vegetable oils and corn sugar etc.
Products:
FAME or biodiesel, corn ethanol, sugar alcohol
Problems: 1. Limited feedstock (food vs fuel)
2. Blended partly with conventional fuel
Benefits: Environmentally friendly, economic and social security

Petroleum Refinary:
Feedstocks:
Crude Petroleum

Products:
CNG, LPG, Diesel, Petrol, Kerosene and Jet fuel

Problems:
1. Deplation of petroleum reserve
2. Environment pollution
3. Economics and ecological problems

2nd generation biofuel:

Feedstocks: Non food, cheap and abundant plant waste biomass, grass and water hyacinth etc.

Products: Hydrotreating oil, bio-oil, FT oil, ethanol, butanol, mixed alcohols

Advantages:
1. Not competing with food
2. Advance technology still under development to reduce the cost of conversion.
3. Environmentally friendly

Figure 1.6: Comparison of 1st and 2nd generation biofuel and petroleum fuel (Naik et al. 2010).

1.3 Biodiesel

Biodiesel (fatty acid methyl esters) is derived from vegetable oils as well as animal fat through esterification and transesterification reactions of free fatty acids (FFAs) and triglycerides, respectively (Demirbas 2009c, Janaun & Ellis 2010, McNeff et al. 2008). In other words, biodiesel is a mixture of alkyl esters of long chain fatty acids, which are synthesised through esterification and transesterification of free fatty acids (FFAs) and triglycerides (TG), respectively (Borugadda & Goud 2012, Leung et al. 2010, McNeff et al. 2008, Murugesan et al. 2009).

The biodiesels that are produced from edible oil feedstocks, such as soybean, palm oil, sunflower, safflower, rapeseed, coconut, peanut and so on are defined as 1st generation biodiesel feedstocks (Atabani et al. 2012, Rashid & Anwar 2008). The biodiesels which are generally produced from non-edible feedstocks, such as waste vegetable oils and fats, non-food crops, forestry residues, biomass sources, algae and so on (Posten & Schaub 2009) are termed as 2nd generation biodiesels. In this study, 2nd generation biodiesel feedstocks are considered as prospective feedstocks.

1.4 Selection of Biodiesel Feedstock for this Study

The selection of biodiesel feedstock is a vital issue nowadays to ensure low cost, availability, and energy supply and balance of feedstock for biodiesel production. The 1st genertaion feedstock which is produced from edible oil sources influences the global imbalance to the market demand and food supply due to their high prices. In addition, the abundant use of edible oil sources for biodiesel production causes a reduction in food sources all over the globe. Thus, the focus has been shifted to 2nd generation feedstocks nowadays as these are easily available in nature, efficient, environmentally favourable and are likely to be more economical compared to the 1st generation feedstocks (Atabani et al. 2012, Demirbas 2009b). In addition, these feedstocks are not used as a food commodity for human owing to the presence of toxic components. Moreover, these are significant because these could reduce the demand for edible oils for biodiesel production to a great extent (Ong et al. 2013). The 2nd generation feedstocks especially produced from non-edible oil plants could be considered as a potential source for production of biodiesel (Jena et al. 2010, Kafuku & Mbarawa 2010b, Kumar & Sharma 2011, Wan Ghazali et al. 2015, Wang et al. 2011).

Several researchers (Atabani et al. 2013b, Demirbas 2009c, Sajjadi et al. 2016, Yadav et al. 2016) are trying to identify the non-edible oil seed plants which have the potential to be used as a 2nd generation biodiesel feedstocks. Amongst different 2nd generation biodiesel feedstocks, beauty leaf (BL), poppy, jojoba oil, and binary mixture of poppy and waste cooking oil have been used as prospective biodiesel feedstocks in this study. The reason for using these feed stocks are outlined below.

The BL plants can be easily grown in marginal as well as barren or unused lands. It is a low cost feedstock. It consumes less water and requires less maintenance, and less fertile soil. These trees can be grown in diverse climatic conditions, are easy to cultivate and maintain (Ashwath

2010). It can be easily cultivated in lands that are unsuitable for human food crops at a lower cost compared to other edible feedstocks (Gui et al. 2008). BL tree has the potential to produce large quantities of fruits and seeds twice a year. Due to its high oil content in the kernel and higher heating value of the oil, it is considered as one of the most significant feedstocks for biodiesel production (Atabani & César 2014, Fadhlullah et al. 2015, Friday & Okano 2006a, Hathurusingha & Ashwath 2007). In addition, its oil can be considered as an important raw material for biodiesel production due to its low feedstock cost (Azad & Uddin 2013, Gui et al. 2008, Leung et al. 2010, Silitonga et al. 2014).

The seeds of opium poppy have high oil content (about 50%) (Aksoy 2011b, Mahdavi-Damghani et al. 2010, Rashid et al. 2016). The poppy oil which was with residual alkaloids (non-edible oil) was used in this study. Generally, poppy plants grow under a wide range of soil and climatic conditions. These cannot withstand extreme cold weather. It is a highly sensitive plant to environmental conditions (Shukla et al. 2015). The yield potential of the poppy seed is impressive and it yields about 0.8 tonnes of oil per hectare (Larkin 2007, Prochazka & Smutka 2012). Jojoba is considered as one of the renewable alternative energy sources which are not yet widely known (Al Awad et al. 2014). The jojoba oil is highly stable (Bisht et al. 1993) with very high resistance to oxidation over a relatively wide range of temperature (40-200 °C) (Allawzi et al. 1998) and that is why it can keep its chemical structure and kinematic viscosity upon heating. The cultivation of these plants could be an alternative way of reversing deforestation. In addition, planting of these trees would reduce CO_2 concentrations in the atmosphere (Banković-Ilić et al. 2012, Karmakar et al. 2010).

In addition, waste cooking oil (WCO) available from restaurants and households are attracting attention as an alternative feedstock due to the high cost of crude and refined vegetable oils for biodiesel production (Borugadda & Goud 2012). Moreover, the production of biodiesel from WCO to partially substitute petroleum fuel is one of the ways of solving the problems of environmental pollution which is caused by illegal dumping of large amounts of WCO into rivers and landfills (Balat & Balat 2010, Chen et al. 2009). Furthermore, the biodiesel produced from those feedstocks can be easily integrated with current fossil fuel based transport sector by different blending compostions.

1.5 Research Problems and Gaps

Based on the available literature, it can be noted that the 2nd generation biodiesel especially biodiesel produced from BL feedstock is a prospective feedstock to use as a transport fuel. However, there are several factors involved in BL feedstock which includes seed/kernel sizes, treatments, oil extraction techniques and optimisation, biodiesel production and optimisation, performance, combustion and emission outputs of engine. Moreover, the potential of Australian beauty leaf (BL) feedstock is still unexploited. Therefore, it is necessary to examine its viability as an alternative fuel to diesel engine. Although several studies have been conducted on oil extraction and optimisation, and biodiesel production from BL oil to evaluate engine performance, combustion and emission characteristics, there are still several issues unresolved on oil extraction and optimisation, for instance, effective oil extraction technique, how the oil extraction process can be optimised, what processing and kernel sizes are more suitable for maximization of oil extraction and so on. In addition, there are issues on biodiesel production and optimisation, for example, produce quality biodiesel with high yield which could minimise the technical problems (high density and viscosity) of engines with minimal power loss.

Although there are several 2nd generation biodiesel feedstocks are used nowadays for biodiesel production and its optimization to assess the engine performance, combustion and emission characteristics, however; it is necessary to look for efficient feedstocks which are available in nature, have high oil content, and lower prices for a sustainable biodiesel production. Beauty leaf (BL), poppy and jojoba oil can be considered as emerging feedstocks due to above mentioned characteristics. However, more research is still needed to clarify the above mentioned issues and to explore the real benefits using those feedstocks in terms of engine performance, combustion and emission characteristics.

Based on all of the above issues the following research gaps are identified in this study:

- A very few studies have been conducted on oil extraction and optimisation on the basis of kernel sizes and treating conditions from BL feedstock.
- A few studies have been done on biodiesel production using both crude and refined oil by both single and two stage processes.

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- A very few researches have been done to assess the full potential of BL biodiesel as an alternative source of petroleum diesel, starting from the extraction through to testing in full scale four cylinder engine dynamometer test bed.
- A few studies have been conducted on biodiesel production and optimisation regarding poppy and jojoba oil.
- Little attention has been paid to poppy and jojoba biodiesel-diesel blend to assess the engine performance, combustion and emission characteristics.
- To the best of the author's knowledge from the available literature, no study has been conducted yet to evaluate the engine performance, combustion and emission characteristics using PWC biodiesel-diesel blend.

1.6 Aims and Objectives

The overall aim of this study is to investigate the potential of 2nd generation biodiesel produced from BL feedstock as an alternative fuel in diesel engine, starting from BL oil extraction and biodiesel production through to engine testing. The results of BL biodiesel on its production process (transesterification), physico-chemical properties and engine performance, emission and combustion characteristics are compared with that of poppy and jojoba biodiesel to identify the best performer feedstock. The specific objectives of the study are to:

- Extract oil from different sizes of BL kernel using screw press and n-hexane techniques at different moisture contents and optimise the extraction processes. This would provide a better understanding of the oil extraction process at a large scale.
- Refine crude BL oil for biodiesel production with an aim to achieve a highest yield of biodiesel.
- Produce biodiesel from crude and refined BL oil by single stage (transesterification) and 2 stage processes (esterification and transesterification), and produce biodiesel from poppy and jojoba oil by 2 stage processes.
- Optimise the biodiesel production by changing different affecting parameters, such as methanol to oil ratio molar ratio, catalyst concentration, reaction temperature and time to achieve a maximum yield of biodiesel (methyl ester).
- Compare the yield of BL biodiesel with those of poppy and jojoba biodiesel at optimum operating conditions.

- Characterise the physico-chemical properties of BL, poppy, jojoba and one more biodiesel defined by PWC (mixture of 80% poppy and 20% waste cooking biodiesel).
- Compare the fatty acid methyl esters (FAMEs) and properties of BL biodiesel with those of poppy, jojoba and PWC biodiesel.
- Perform experiment using CI engine (that is, diesel engine) fuelled with BL, poppy, jojoba and PWC biodiesel-diesel blends (B5, B10 and B20) to evaluate the engine performance, combustion and emission characteristics. The results of BL biodiesel are compared with those of poppy, jojoba and PWC biodiesel.
- Identify and recommend the best performer feedstock based on engine performance, combustion and emission features which would provide useful information for biodiesel producer and end users.

1.7 Scope and Limitation of the Study

This research focused on the potentiality study of 2nd generation biodiesel as an alternative fuel source for petroleum diesel. The use of native species such as BL tree provides an excellent opportunity, as this could be planted in large areas of degraded and cleared lands that are readily available. This quality makes BL a preferred species by the environmentalists, as the production of BL species will not compete with food crops either for the land or for the use of plant products. The cultivation of these plants could be an alternative way of reforestation rather than forest clearing. In addition, planting of these trees would reduce CO_2 concentrations (Banković-Ilić et al. 2012, Karmakar et al. 2010). On a large scale, BL cultivation and biodiesel production could create a new economy directly via introducing biodiesel, and indirectly through reducing import of fossil fuel.

The poppy plant previously called "Diesel Tree" is grown in Northern Queensland and Tasmania, Australia at a large scale to produce biodiesel from poppy seed (Poppy Oil 2016). The poppy seeds contain high-quality oil, however, crude poppy oil is not suitable for human consumption due to the presence of alkaloids (Macquarie Oil Company 2016).

The proposed research will contribute to clear understanding of biodiesel production from BL. The methodology which was developed for BL biodiesel production could be transferred to other species suitable for 2nd generation biodiesel production and to the regions outside of

tropical/sub-tropical zones. The proposed research is technologically and scientifically innovative.

This research will provide a new insight in to biodiesel-diesel blend for BL, poppy, poppy and waste cooking (PWC), and jojoba biodiesel in terms of engine performance, combustion and emission characteristics. With a sustainable biodiesel production at a cheaper cost, these feedstocks can meet the future transport energy demand to a great extent.

There were some limitations in this study which are described below:

The screw press that was used for oil extraction from BL feedstock was not especially designed for that feedstock. That is why some adjustments were done during the oil extraction. In n-hexane oil extraction technique, there was no available facility to recover n-hexane which was used as a solvent. In biodiesel production for all feedstocks, methanol (used as a reagent) recovery was not possible due to lack of recycling facility. In engine testing, up to 20% of biodiesel-diesel blends were used for beauty leaf (BL), poppy, binary mixture of poppy and waste cooking (PWC) and jojoba which is the acceptable international standard to use in compression ignition (CI) engine. Economic analysis was not considered within the scopes of the project.

1.8 Thesis Outline

This thesis contains nine chapters. The arrangement of these chapters are briefly summarised below:

In Chapter 1, an overview of the energy consumption and growth, energy consumption in transportation sector, and the motivation of this study are presented. The research problems and gaps, aims and objectives, and scope and limitation of the study are also stated.

In Chapter 2, the literature reviews relevant to the present study are reported. The literature review covers biodiesel, the necessity of 2nd generation biodiesel, potential resources of 2nd generation biodiesel feedstock, selection of feedstock, oil extraction and refining, biodiesel conversion technologies, engine performance, combustion and emission characteristics.

In Chapter 3, the steps for oil extraction from BL kernel using mechanical and chemical methods, and optimisation of oil extraction processes including optimising parameters are discussed.

In Chapter 4, refining of BL crude oil, such as degumming, alkali neutralisation and dewaxing processes are illustrated. The mass and energy balances are also explained in this chapter.

In Chapter 5, biodiesel production and optimisation in terms of the parameters influencing biodiesel yield are presented. Fatty acid methyl ester (FAME) composition using gas chromatography (GC) and physico-chemical properties of biodiesel are also explained

In Chapter 6, engine performance characteristics, such as brake power (BP), torque, brake thermal efficiency (BTE), brake specific fuel consumption (BSFC), brake mean effective pressure (BMEP) for all biodiesel-diesel blends (B5, B10 and B20) of poppy, PWC, BL and jojoba in terms of engine operating conditions (speed and load) are analysed and presented. In addition, a comparison is made of the results between diesel and biodiesel-diesel blends.

In Chapter 7, engine combustion characteristics, such as cylinder pressure (CP) and heat release rate (HRR) for all biodiesel blends are analysed and discussed. Also, a comparison of the results between diesel and biodiesel-diesel blends is presented.

In Chapter 8, engine emission characteristics, such as exhaust gas tempertaure (EGT), nitrogen oxides (NO_x), Carbon dioxide (CO_2), carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) as a function of engine speed and load for all biodiesel blends and diesel are presented, discussed and compared.

In Chapter 9, the findings and concluding remarks of the proposed research are summarised. The recommendations for further study and future line of research are also outlined in this chapter.

CHAPTER 2

LITERATURE REVIEW

The literature review was done on the basis of importance of 2nd generation biodiesel, biodiesel feedstock, oil extraction and optimisation, biodiesel production and optimisation and to identify the efficient production technology for production of biodiesel which would substitute the current dependency on fossil fuel worldwide to a great extent. In addition, in this review emphasis was given to evaluate engine performance, combustion and exhaust emission characteristics. The effect of biodiesel and biodiesel-diesel blend on engine performances, such as brake power (BP), torque, brake thermal efficiency (BTE), brake specific fuel consumption (BSFC) and brake mean effective pressure (BMEP), combustion characteristics which include cylinder pressure (CP) and heat release rate (HRR), and exhaust emission characteristics, such as exhaust gas temperature (EGT), nitrogen oxides (NO_x), carbon dioxide (CO_2), carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) are presented in this review. This review would contribute to the greater understanding of the recent development and prospects of BL biodiesel as a future transport fuel. Moreover, this study provides a comparative baseline to make an easy comparison of the feedstocks used in terms of fuel properties, engine performance, combustion and emission features.

2.1 Introduction

The increasing demand for energy, and the problem of diminishing petroleum reserves as well as the increasing awareness of environmental pollution from petroleum fuel emissions have led to the urge to find renewable alternative fuels as a substitute for petroleum-based fuel (Azad et al. 2014a, Bhuiya et al. 2016a, Bhuiya et al. 2016b, Sajjadi et al. 2016). In addition, the emissions produced due to the combustion of petroleum fuel have an adverse effect on human health. Global warming is increasing rapidly due to the emission of greenhouse gases (GHGs) including methane, NO_x and CO_2. It has been reported that if the average global temperature is increased by more than 2 °C, hundreds of millions of people will lose their lives (Liaquat et al. 2010, Mofijur et al. 2013a). CO, HC, formaldehyde (HCHO), NO_x, PM and organic gases other than methane (non-methane organic gases, that is, NMOG) that are emitted from internal combustion engines have been ascertained as harmful to human health and environmental

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degradation (Mofijur et al. 2013a). The impact of engine exhaust emissions on humans are summarised in Table 2.1 (Mofijur et al. 2013a, Okona-Mensah et al. 2005, Zhang & Zhu 2010).

Table 2.1: Impact of engine exhaust emissions on human being (Mofijur et al. 2013a, Okona-Mensah et al. 2005, Zhang & Zhu 2010)

Exhaust emissions	Impact on human being	References
PM	Can cause lung cancer and cardiopulmonary deaths.	(Zhang & Zhu 2010)
NO_x	Irritates lungs and causes oedema, bronchitis and pneumonia and results in increased sensitivity to dust and pollen in asthmatics.	(Faiz et al. 1990)
CO	Affects foetal growth in pregnant women and tissue development of young children. It has a synergistic action with other pollutants to promote morbidity in people with respiratory or circulatory problems.	(Faiz et al. 1990)
HC	Causes eye irritation, coughing and sneezing, drowsiness and symptoms akin to drunkenness. Some hydrocarbons have a close affinity for diesel particulates and may contribute to lung disease.	(Faiz et al. 1990)
PAHs	Can lead to eye and nose irritation, coughing, nausea and shortness of breath.	(Okona-Mensah et al. 2005)
Formaldehyde	Can cause eye and nose irritation, coughing, nausea and shortness of breath.	(Onursal & Gautam 1997)

All these issues have made renewable energy an attractive alternative renewable fuel for the future. Furthermore, for a sustainable future of the planet, it is essential to look for renewable fuel sources which implicitly include reliable fuel sources. Biodiesel can be considered as one of the promising alternative resources for diesel engines especially from non-edible oil (2nd generation) feedstock. Biodiesel, an alternative fuel to petro-diesel, is a renewable, technically feasible, economically competitive, environmental friendly, non-toxic, portable, eco-friendly

fuel and easily available (Abbaszaadeh et al. 2012, Agarwal 2007, Atabani et al. 2013b, Balat 2011, Demirbas 2009c, Lapuerta et al. 2008b, Ong et al. 2013, Sajjadi et al. 2016, Singh & Singh 2010, Yusuf et al. 2011). Nowadays, it is gaining worldwide acceptance in the market as an environmentally benign alternative diesel fuel. In addition, it can be used as a blending component or a direct replacement for diesel in vehicle engines (Demirbas 2009c). Furthermore, biodiesel has a great potential to be a part of a sustainable energy mix in the future (Abbaszaadeh et al. 2012, Canakci & Sanli 2008, Ong et al. 2013).

One of the important attractions of biodiesel is its biodegradability, essentially no sulphur and aromatic contents, offers promise to reduce PM, HC, CO, sulphates, polycyclic aromatic hydrocarbons (PAH), nPAH (nitrated polycyclic aromatic hydrocarbon), toxic emissions and being more environmentally favourable than the fossil fuels (Balat & Balat 2010, Janaun & Ellis 2010). Moreover, biodiesel is taken into account to be carbon neutral since the carbon dioxide released into the atmosphere during its utilization as a fuel has been recycled and reused for the growth of crop plants (Barnwal & Sharma 2005, Koh & Mohd. Ghazi 2011). Biodiesel has the potential to reduce GHG emission significantly which is about 80% (Mofijur et al. 2015b). As a transport fuel, numerous studies have been conducted on safety, health and environmental outcomes of biodiesel emissions (Gaffney & Marley 2009, Liu et al. 2009a). In addition, it can offer several advantages which include higher flash point, higher cetane number and reduced exhaust emissions significantly as compared to the conventional petroleum diesel (Fazal et al. 2013, Sajjadi et al. 2016, Tan et al. 2015). Moreover, biodiesel methyl esters improve the lubrication properties of the diesel fuel blend. It is a good lubricant which is about 66% better than petro-diesel (Demirbas 2008c, Demirbas 2009c, Moecke et al. 2016). However, the higher cost of biodiesel production than petroleum diesel is the main drawback for the commercialisation of biodiesel (Abbaszaadeh et al. 2012). Therefore, it is necessary to find new biodiesel feedstocks that would be able to grow in marginal lands with minimum agricultural inputs. The detailed advantages and disadvantages of biodiesel are listed in Table 2.2.

Table 2.2: Advantages and disadvantages of biodiesel (Atadashi et al. 2010, Balat 2011, Balat & Balat 2010, Demirbas 2009c, Jena et al. 2010, Kafuku & Mbarawa 2010b, No 2011, Saloua et al. 2010, Shahid & Jamal 2011, Silitonga et al. 2011)

Advantages	Disadvantages
Biodiesel is produced from renewable sources, such as vegetable oils as well as animal fats.	It creates food crisis in some countries as biofuels are made from vegetable and animal fats, and more demand for those products may raise prices.
Biodiesel is renewable, non-toxic, non-flammable, portable, readily available, biodegradable, sustainable, eco-friendly and free from sulphur and aromatic content.	Biodiesel has 12% lower energy content than diesel and this leads to an increase in fuel consumption of about 2-10%.
It reduces greenhouse gas emissions significantly. The use of biodiesel instead of petroleum diesel can reduce GHGs up to 78%.	It has lower volatilities which causes the formation of deposits in engine due to incomplete combustion characteristics.
Biodiesel content 10-11% of oxygen which makes it a fuel with high combustion characteristics.	It is not suitable to use in low temperatures as biodiesel gels in cold weather.
It can be used in existing diesel engines with a little modification. It also can be used in different blends with petroleum diesel, for example, B10, B20 and B30 etc.	Biodiesel causes excessive carbon deposition and gum formation in engines and the oil gets contaminated and creates flow problem.
It improves engine lubrication and increases engine life as it is virtually sulphur free.	Biodiesel has relatively higher viscosity and lower volatility than diesel.
It can reduce the dependency on foreign suppliers of oil with locally/domestic energy crops.	Oxidation stability of biodiesel is lower than diesel. That is why it can be oxidised into fatty acids with the presence of air and causes corrosion of fuel tank, pipe and injector.
It produces less soot (particulate matter), carbon monoxide, unburned hydrocarbons and sulphur dioxide compared to petroleum diesel.	Due to the higher oxygen content in biodiesel, it produces relatively higher NO_x emissions than the petroleum products.

Biodiesel helps rural development to restore degraded lands over a period.	It has the variation in quality since it is produced from variety of biofuel sources.
It has a positive economic impact. As biofuels are produced locally, thousands of people are employed in biofuel production plant.	It clogs in engine. Biodiesel cleans dirt from the engine and later this dirt gets collected in fuel filter and clogs it.
Biodiesel has higher cetane number than petroleum diesel which reduces the ignition delay.	Some regions are not suitable for oil producing crops and they need to be transported to the factories which increase the cost and amount of emission associated with the production and transportation.
Production can be raised easily and is less time consuming.	Biodiesel can cause corrosion in vehicle material (copper and brass) such as fuel system blockage, seal failures, filter clogging, and deposits at injection pumps.
Biodiesel is safe for transportation, handling, distribution, utilization and storage due to its higher flash point (above 70-170 °C) than petroleum diesel (60-80 °C).	Lower engine speed and power, high price, high engine wear and engine compatibility
Biodiesel reduces the environmental effect of a waste product.	Use of biodiesel in IC engine may lead to engine durability problems high includes injector cocking, filter plugging, and piston ring sticking etc.

Biodiesel has some disadvantages against other renewable sources which include regional suitability (use of water use and invasiveness), use of fertiliser, food security, and deforestation and so on. The use of biodiesel can be tricky as this operate differently in cars than the regular petroleum-based fuel. Lin et al. (2011a) pointed out the three key driving forces and challenges to develop biodiesel industry such as (i) biodiesel fuel will play a more important role in strengthening the nation's energy security with the global energy crisis approaching; (ii) as a renewable energy biodiesel can contribute to the reduction of greenhouse-gas (GHG) emissions significantly when replacing fossil oil; (iii) the increased demand for oil crops for biodiesel production clearly has a positive impact on net farm income and reduces the government outlays to farmers by raising the market price of oil crops. However, with the global increase

in the scale of biodiesel production, biodiesel has become a methodical risk with respect to its economic, ecological, and socio-political impacts. It is reported that opportunities, challenges and even threats have been raised. Especially, those linked to the 1st generation biodiesel have also received considerable criticisms recently, most notably the biodiesel potential to increase food prices and damage biodiversity; their continuing need for significant government support and subsidies; and greenhouse gas emissions (Florin & Bunting 2009, IEA 2008, Lin et al. 2011a). While the biodiesel industry is being established in many parts of the world, it has also been hit by the current global economic crisis. In order to overcome the adversities of the economic background, it is critical for the biodiesel industry to continuously improve on aspects that will strengthen the prospects of better market penetration (Janaun & Ellis 2010). The important aspects of biodiesel which revealed its prospect as the next generation green fuel, include: (i) cost and environmental impact of conversion process; (ii) key drivers and challenges of biodiesel industry development; (iii) efforts towards environmentally benign and cleaner emissions; (iv) diversification of products derived from biodiesel glycerol; and (v) policy and government incentives (Janaun & Ellis 2010, Lin et al. 2011a).

2.2 Why 2nd Generation Biodiesel?

The biodiesels usually produced from edible oil resources, such as soybeans, palm oil, sunflower, safflower, rapeseed, coconut and peanut are considered as the 1st generation biodiesel feedstocks. In many countries of the world, edible oils are not produced in sufficient amounts to meet the local requirements of human food and therefore, have to be imported from other places. On the other hand, the biodiesels which are generally produced from non-edible feedstocks, such as waste vegetable oils and fats, non-food crops, forestry residues, biomass sources, algae and so on are termed as the 2nd generation biodiesels. The use of non-edible vegetable oils is of significance because this would reduce the demand for edible oils. Therefore, the 2nd generation biodiesel which is mainly produced from non-edible oils, and besides, produced from waste or recycled oils and animal fats has become more attractive and promising for the sustainable production of biodiesel (Atabani et al. 2013b, Azad et al. 2014c, Azad et al. 2015, Bhuiya et al. 2014b, Demirbas 2009c, Ong et al. 2013).

There are many reasons for not using the 1st generation (edible oil) as feedstocks for biodiesel production. The use of 1st generation feedstock for biodiesel production influences the global imbalance to the market demand and the food supply by their high prices and the reduction in

food sources (Banković-Ilić et al. 2012). Thus, focus has to be shifted to 2nd generation feedstocks that are not used as food items and could be grown in the barren lands. In addition, the oils produced from these resources are unsuitable for human consumption due to presence of toxic components in the oils. Apart from low cost and impossibility of their use for human consumption, the other reasons for biodiesel production from these resources include: (i) oil plants produce large amounts of non-edible oils in nature all over the world; (ii) non-edible oil plants can be easily cultivated in lands unsuitable for human crops at a lower cost than those of the edible oil crops (Gui et al. 2008); and (iii) establishment of these plants reduces CO_2 concentrations in the atmosphere (Banković-Ilić et al. 2012, Karmakar et al. 2010).

Although the non-edible oils are not providing sufficient assurance to nullify the competition with food or feed as well as forest clearing, these possess the potential of minimising these factors. For instance, non-edible oil resources have not been used as food sources due to toxicity in most of the countries around the world. There are many factors involved in the growing of non-edible/edible oil plants, such as production yield, fertile land and water, but non-edible oil plants can be easily cultivated in marginal as well as barren or unused lands which require less maintenance, low cost, less soil fertility and less water as opposed to arable lands which is generally suitable for growing edible vegetable oils. Moreover, plantation of non-edible oils by using those lands could be an alternative way of reforestation rather than forest clearing. However, it is noted that non-edible feedstocks can also be grown in arable lands, but that is not a general practice and is not recommended.

On the other hand, edible oil based plants are not generally produced in marginal as well as barren or unused lands due to the concern of soil fertility and product yield. Although these might be grown on abandoned/polluted land in some cases, this is not the general practice to fulfill the current needs or demands of oil. Moreover, in the case of edible oils, they have received considerable criticisms - most notably the biodiesel potential to damage biodiversity; their relatively low GHG abatement capacity yet high marginal carbon abatement costs and related greenhouse gas emissions (Florin & Bunting 2009, IEA 2008, Lin et al. 2011a). Furthermore, when forested land is cleared or food crops are displaced to make way for bioenergy feedstock crops, it is likely that bioenergy production will indirectly increase GHG emissions (Florin & Bunting 2009).

The main parameter that determines the cost of biodiesel production derived from vegetable oil is the cost of feedstock. This is why non-edible vegetable oils can be taken into account as a prospective sustainable fuel over the edible vegetable oils due to its low feedstocks cost (Azad & Uddin 2013, Gui et al. 2008, Leung et al. 2010). It has been found that the price of biodiesel mainly depends on the cost of feedstocks which makes up 70%-95% of the total production cost (Balat 2011, Demirbas 2007, Gui et al. 2008, Leung et al. 2010). Janaun & Ellis (2010) reported that using low-cost feedstocks is one of the key issues including improving efficiency of the production process, developing a cost-effective catalyst and managing agricultural land. Therefore, the use of cost-effective non-edible oils can be a way to improve the economy of biodiesel production and its commercial production at an industrial scale. Zhang et al. (2003a) reported that the price of biodiesel is about US$ 0.5 per litre compared to US$ 0.35 per litre for petroleum diesel. However, it is believed that the use of non-edible oils can bring down the price and meet the world energy demand and reduce dependency on edible oils (Ong et al. 2013).

In evaluating the quality of biodiesel, it is important to take into account several other factors, such as raw material, driving cycle, nature of purification, its storage, and vehicle technology (Abbaszaadeh et al. 2012). However, due to the concern associated with food versus fuel, environmental and economic issues related to edible oils, the non-edible oil feedstocks are gaining popularity for biodiesel production. The used cooking or frying oils are of increasing interest day by day, as it is an inexpensive feedstock for biodiesel production in most of the countries of the world except European Union (EU). Moreover, waste cooking oil (WCO) is a promising alternative option to vegetable oil and one of the good feedstocks for biodiesel production, as it is not suitable for human consumption. The price of WCO is relatively cheaper in comparison with fresh vegetable oils (Demirbas 2009c). Its price is 2-3 times cheaper than the virgin vegetable oils in most of the countries of the world except EU (Phan & Phan 2008). However, it is to be noted that the feedstocks cost for the 2nd generation biofuels especially WCO is higher than that of the fresh vegetable oil due to the Renewable Energy Directive (RED) policy in EU (European Biofuels 2015). Zhang et al. (2003b) reported that the total manufacturing cost of biodiesel can be significantly reduced by using waste cooking oil. It has also been reported that the use of used cooking oil is one of the options to make the biodiesel production cost effective (Demirbas 2009c, Math et al. 2010). Therefore, WCO could be a good choice to use as raw material than the virgin oils.

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The wide range of available feedstocks in terms of 2nd generation feedstocks represents one of the most significant factors for biodiesel production (Atabani et al. 2012, Ong et al. 2011, Silitonga et al. 2013c). Furthermore, it could be noted in a broader sense that biodiesel production especially from 2nd generation feedstock is one of the effective and alternative ways to overcome the problems linked with the energy crisis as the demand for energy is increasing day by day and the associated global warming which is caused by the emissions of fossil fuel and ultimately impacts on the environment (Abbaszaadeh et al. 2012, Canakci & Sanli 2008).

2.3 Biodiesel Feedstocks

A considerable amount of research has been conducted on alternative feedstocks for biodiesel production all over the world (Kumar & Sharma 2011). However, selecting the cheapest feedstock is a vital issue to ensure low production cost of biodiesel (Atabani et al. 2012). As much as possible, the biodiesel feedstock should fulfill two requirements for production of biodiesel; these are low production costs and large production scale (Silitonga et al. 2013c). The availability of feedstock for biodiesel production depends on the regional climate, geographical locations, local soil conditions and agricultural practices of any country (Atabani et al. 2012, Kumar & Sharma 2011, Singh & Singh 2010).

In general, biodiesel feedstock can be categorised into four groups: (i) edible vegetable oil, (ii) non-edible vegetable oil, (iii) waste or recycled oil and (iv) animal fats (Ahmad et al. 2011, Atabani et al. 2012, Azad et al. 2012b, Balat & Balat 2010, Berchmans & Hirata 2008, Chisti 2007, Demirbas 2008a, Demirbas 2009c, Friday & Okano 2006b, Haas et al. 2001, Juan et al. 2011, Kafuku & Mbarawa 2010b, Karmee & Chadha 2005, Knothe & Steidley 2009, Kumar et al. 2013, Lim & Teong 2010, Pinto et al. 2005, Ramadhas et al. 2005, Rashid et al. 2008, Silitonga et al. 2011, Singh & Singh 2010). Among those, non-edible vegetable oils (Atabani et al. 2013b, Demirbas 2009c, Ong et al. 2013), waste or recycled oil as well as animal fats (Atabani et al. 2012, Berchmans & Hirata 2008, Chisti 2007, Demirbas 2009c, Haas et al. 2001, Knothe & Steidley 2009, Kumar et al. 2013, Lim & Teong 2010, Ramadhas et al. 2005) are regarded as the 2nd generation biodiesel feedstocks. The various 2nd generation biodiesel feedstocks are shown in Table 2.3 (Balat 2011, Chisti 2007, Moser 2009, No 2011, Singh & Singh 2010, Wan Ghazali et al. 2015). The feedstocks are subdivided into conventional and alternative feedstocks.

Table 2.3: Feedstock categories for 2nd generation biodiesel production (Balat 2011, Chisti 2007, Moser 2009, No 2011, Singh & Singh 2010, Wan Ghazali et al. 2015)

Category		Feedstocks	References
1. Non-edible oil seeds	A:	Jatropha, Karanja, Mahua, Linseed, Cottonseed, Neem, Camelina, Putranjiva, Tobacco, Polanga, Cardoon, Deccan Hemp, Castor, Jojoba, Moringa, Poon, Koroch seed, Desert date, *Eruca sativa gars*, Sea mango, Pilu, Crambe, Syringa, Milkweed, Field pennycress, Stillingia, Radish Ethiopian mustard, Tomato seed, Kusum, Cuphea, Camellia, Paradise, Terminalia, *Michelia champaca*, *Garcinia indica*, *Zanthoxylum bungeanum*, Beauty leaf, Jojoba and Poppy.	(Atabani & César 2014, Azam et al. 2005, Balat & Balat 2010, Carlsson 2009, Chapagain et al. 2009, Demirbas 2009c, Deshmukh & Bhuyar 2009, Devan & Mahalakshmi 2009a, Devan & Mahalakshmi 2009b, Devan & Mahalakshmi 2009c, Devan & Mahalakshmi 2009d, Encinar et al. 1999, Giannelos et al. 2005, Hebbal et al. 2006, Holser & Harry-O'Kuru 2006, Hosamani et al. 2009, Jain & Sharma 2010b, Kansedo et al. 2009b, Knothe et al. 2009, Li et al. 2009, Liu et al. 2009b, Machacon et al. 2001, Macquarie Oil Company 2016, Moser et al. 2009, No 2011, Raghu et al. 2009, Rashid et al. 2008, Sahoo et al. 2007, Sarin et al. 2010, Sarma et al. 2005, Shao & Chu 2008, Sharma & Singh 2010, Singh & Singh 2010, Yang et al. 2008)
2. Animal fats	C:	Beef tallow, pork lard, yellow grease	(Goodrum et al. 2003, Lim & Teong 2010, Ma & Hanna 1999, No 2011, Singh & Singh 2010, Tashtoush et al. 2004)
	A:	Waste salmon, melon bug, sorghum bug, chicken fat and by-products from fish oil	(Fukuda et al. 2001, Goodrum et al. 2003, Kamini et al. 2000, Lim & Teong 2010, Moser 2009, No 2011, Singh & Singh 2010)
3.Waste materials	C:	Cooking oil, frying oil	(Enweremadu & Mbarawa 2009, Goodrum et al. 2003, Kulkarni & Dalai 2006, No 2011, Singh & Singh 2010)
	A:	Vegetable oil soapstocks, acid oils, tall oil, dried distiller's grains (DDG), pomace oil	(Çaynak et al. 2009, Haas 2005, Moser 2009, No 2011)

A: alternative; C: conventional

It is very important to consider some parameters when comparing different feedstocks. Each feedstock should be evaluated based on a full life-cycle analysis. These include: (1) availability of land, (2) cultivation practices, (3) energy supply and balance, (4) emission of greenhouse gases, (5) injection of pesticides, (6) soil erosion and fertility, (7) contribution to biodiversity value losses, (8) logistics costs (transport and storage), (9) direct economic value of the feedstocks considering the co-products, (10) creation or maintenance of employment, (11) water requirements and water availability, and (12) the effects of feedstock on air quality (Ahmad et al. 2011, Atabani et al. 2012, Balat 2011, Chisti 2007).

2.3.1 Non-Edible Oil Resources

Non-edible oil resources are gaining popularity worldwide as they are easily available in many parts of the world and can be grown in degraded lands that are not suitable for raising food crops, are more efficient, more environmentally favourable, produce useful by-products and are likely to be more economical compared to edible oils (Atabani et al. 2012). It has been observed throughout the world that large amounts of non-edible oil plants are available in nature (Demirbas 2009b).

There are a large number of oil plants that produce non-edible oils. Azam et al. (2005) reported that 75 plant species contain more than 30% oil in their seeds and 26 species of them were found most suitable for the use of biodiesel that can be employed for the synthesis of fatty acid methyl ester (FAME). Currently, edible oils are the main resources for world biodiesel production (more than 95%) (Gui et al. 2008). Various oils extracted from different kernels of seeds of non-edible crops are the potential feedstocks for biodiesel production. The main sources for biodiesel production from non-edible oils are: jatropha (*Jatropha curcas*), karanja or honge or koroch seed (*Pongamia pinnata*), beauty leaf (*Calophyllum inophyllum*), neem (*Azadirachta indica*), mahua (*Madhuca indica* and *Madhuca longifolia*), tobacco seed (*Nicotiana tabacum*), jojoba (*Simmondsia chinensis*) and poppy (*Papaver somniferum*) (Atabani et al. 2013b, Balat & Balat 2010, Demirbas 2009c, No 2011, Sajjadi et al. 2016).

2.3.1.1 Beauty Leaf Oil (BLO)

Beauty leaf (*Calophyllum inophyllum)* seed is recognised as one of the most significant feedstocks for biodiesel production because of its high oil content (Fadhlullah et al. 2015). Its oil has higher heating value (Atabani & César 2014). In addition, its low feedstock cost makes

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it an important raw material for biodiesel production (Silitonga et al. 2014). It is regarded as a prospective species to produce 2nd generation biodiesel due to its potential to produce large quantities of fruits and high oil content in the seeds (kernels). It can be grown on degraded lands in a variety of climatic conditions, and is easy to cultivate and maintain (Ashwath 2010). Furthermore, the BL grows in free draining, less fertile soils in different regions of southern and central Asia, such as Sri Lanka and India and in Australia (CSIRO 2010). The BL tree with fruits is shown in Figure 2.1 (Ong et al. 2014a, p. 3).

The BL is native to Australia and is non-intrusive; it does not compete with other native species (Hathurusingha 2012). It also exhibits geo-climatic adaptability/elasticity, requires less maintenance and is tolerant to most of the ordinary pests (Friday & Okano 2006a). The BL attains reproductive maturity in 5 years-7 years and can yield fruits for more than 200 years (Friday & Okano 2006a). Based on the fatty acid composition of BL oil, it has been established that the biodiesel produced from this species abides by the American Society for Testing and Materials (ASTM) and European Union (EN) biofuel standards (Azam et al. 2005). Based on the above features, its oil could be considered as a potential source for biodiesel production.

Tree

Fresh fruits

Dried fruits

Seeds after peeling

Seeds before peeling

Figure 2.1: Beauty leaf tree, fruit, seeds and kernels (Ong et al. 2014a, p. 3).

2.3.1.2 Jojoba Oil

Jojoba (*Simmondisa chincnsis*), a semi-arid evergreen perennial shrub that grows naturally in deserts, is gaining popularity as an industrial crop in some countries around the world (Bouaid et al. 2007). It is grown in the desert of south-western United States, Central and South America, South Africa and north-western Mexico (Al-Widyan & Al-Muhtaseb 2010). Moreover, it is planted in some countries of the Middle East and Latin American countries now. Jojoba seed contains about 40%-50% of oil in which straight chain monoesters are the main components in the range of C20-C44 (Al-Widyan & Al-Muhtaseb 2010).

Jojoba tree is 0.7 m-1.0 m high and can be easily recognised by its characteristics, such as thickness, leatheries, bluish green leaves and dark brown nutlike fruit. Its growing rate is slow and was unknown for a long time to use it as a commercial agricultural product (Al-Muhtaseb 2005, Al-Zoubi 1996). Under good conditions, it's have a life span of up to 100 years (Al-Muhtaseb 2005, Al-Zoubi 1996). Actually, it is considered as a liquid wax not oil and is pronounced as "hoho-ba". In addition, its seed contains oil with distinctive characteristics compared to other vegetable oil plants. Generally, the jojoba seed is nut shaped and is around 1 cm to 2 cm long. Therefore, it is considered as an exceptional commercially promising crop. In addition, it has the potential to become an important cash crop around the world in huge-tracts of semi-arid land. It is a beneficial plant as it is grown in robust, drought tolerant and soils of marginal fertility. It requires less water, low maintenance cost and low fertilizer. It can withstand salinity and desert heat without demanding much water or shade. However, water is needed to meet the lack of rainfall in deserts, especially during the dry season. This plant persists as small stunted bushes and survives temperatures of up to 45 °C in the desert area while the amount of rainfall is less than 100 mm per year.

Jojoba oil can be used as a perfect constituent within soap, cream, lotion, balm and massage oil formulations for all skin at it highly penetrates the skin (Aussie Soap Supplies 2016). Jojoba oil is used mainly in the field of cosmetic applications which include soap, cream, body butter, lotion, balm, massage oil, foot and hair care products, pharmaceuticals industry and lubricants (Al-Widyan & Al-Muhtaseb 2010, Bouaid et al. 2007). It assists to restore the regular pH level of the skin due to its high penetration and close looks like the natural sebum characteristics. It is used for skin care and scalp treatment, and it helps to smooth and soften. It can be used in formulations for arthritis and rheumatism due to the presence of natural anti-inflammatory

myristic acid (Aussie Soap Supplies 2016). Moreover, it is considered as very good natural anti-oxidants. In automobile applications, jojoba oil is used as a good lubricant in high-speed machines, tool work and metal cutting.

The volumetric composition of the oil is 97% of waxed ester and 3% FFAs (Abu-Arabi et al. 2000, Al-Hamamre & Al-Salaymeh 2014, Canoira et al. 2006, Radwan et al. 2007). Therefore, it is more preferably considered as a wax; however, jojoba oil-wax is the term in common use. As jojoba oil-wax contains less amounts of FFAs and alcohols, phytosterols, tecopherols, phospholipids and traces of triacylglycerol; and therefore, these have to be analysed carefully (Busson-Breysse et al. 1994, Canoira et al. 2006). The physico-chemical properties of jojoba oil-wax product are very important as the jojoba oil–wax has a low chemical activity and a very high normal boiling point (398 °C). The oil is highly stable (Bisht et al. 1993) with very high resistance to oxidation over a relatively wide range of temperature (40 °C-200 °C) (Allawzi et al. 1998) and that is why it can keep its chemical structure and viscosity upon heating.

Jojoba is considered as one of the renewable alternative energy sources which are not yet widely known (Al Awad et al. 2014). It is consisted of esters of fatty acids and fatty alcohols but not composed of triglycerides. Jojoba biodiesel can be safely used as an alternative fuel to diesel in diesel engines by decreasing its high viscosity within the accepted limit of biodiesel standards. It has a lot of advantages as a renewable energy source, such as widely available, contains less sulphur and nitrogen, and is more environmentally friendly compared to fossil fuels (Al-Widyan & Al-Muhtaseb 2010, Al-Widyan et al. 2002b).

2.3.1.3 Poppy Oil

The poppy (*Papaver somniferum* L.) is a plant of the dicot family Papaveraceae which is cultivated for seed, oil and opium (Mahdavi-Damghani et al. 2010). The plant is an erect, annual herb, 30 cm-170 cm tall; flower buds are ovate, dropping before anthesis; the fruit looks like a capsule which contains a huge number of very small seeds (Keskin et al. 2015). The opium poppy species belongs to the family of *Papaver somniferum* L. and includes 44 genera and 760 species (Rashid et al. 2016).

The opium poppy is planted in Turkey, India, Australia, France, Spain and Hungary as a legal producer under the regulation of the United Nations Organisation (Keskin et al. 2015). The

United Nations Organisation has already designated Turkey and India as traditional opium poppy producers. A significant amount of poppy (about 47%) is produced in Turkey compared to the other parts of the world (Report 2014). The poppy plants are also grown in the wild, some parts of Pakistan, Afghanistan and Myanmar (Rashid et al. 2016, Tian et al. 2011). Asia origin opium poppy is grown in many places around the world having the same physical features. It has been observed that most species are found in the northern hemisphere (Bozan & Temelli 2003). Generally, these plants grow under a wide range of soil and climatic conditions. These cannot withstand extreme cold weather. It is a highly sensitive plant to environmental conditions (Shukla et al. 2015). Medium textured soils treated with manure or well fertilised are suitable for growing of poppy plants. The opium poppy family is outstanding due to its ornamental and pharmaceutical importance (Rashid et al. 2016).

The opium poppy is regarded as one of the important alkaloids species in which five major alkaloids named as morphine, codeine, thebaine, narcotine and papaverine are existent, which are important because of their immense medicinal values (Chaterjee et al. 2010, Facchini & Park 2003, Kumar & Patra 2012, Shukla & Singh 2004). Opiate alkaloids and their synthetic derivatives (oxycodone, hydrocodone and pholcodine) are broadly used in medicine as these components are produced in hundreds of tons in the medicine industry (Francis et al. 2008, Holzer 2009). The opium poppy is used as a sedative, anaesthetic and anti-diarrheal matter for humans for about thousands of years (Aksoy 2011b). In addition, it could be a representative of medicinal plants as this is one of the geographically-widespread species having several medicinal properties (Verma et al. 2011).

The seeds of opium poppy have a high ratio of oil content (Aksoy 2011b). The poppy seed contains about 50% oil, mainly in the form of oleic and linoleic acids (Aksoy 2011b, Mahdavi-Damghani et al. 2010, Rashid et al. 2016). Opium poppy is a significant industrial plant not only due to its high oil content which is used for nutrition but also it contains alkaloid which is used in medicine and science (Keskin et al. 2015). Due to presence of high amounts of polyunsaturated fatty acids in the poppy oil, sometimes it is used as a food for human consumption (Musa Özcan & Atalay 2006). In Europe, poppy seeds which are free of alkaloids are used in confectionary and bakery as a culinary ingredient, and are widely used in perfume, cosmetic and medicinal industries. The oil extracted from poppy seeds which is also free of alkaloids, is generally used as an ingredient in production of bakery products. It contains 22% protein, 18% carbohydrate and 5% moisture. The yield potential of the poppy seed is

impressive and it yields about 0.8 tonnes of oil per hectare (Larkin 2007, Prochazka & Smutka 2012). The performance of yield is the most important parameter in biodiesel production through transesterification.

Poppy oil is considered as non-edible oil due to the presence of residual alkaloids. This oil is not suitable for human or stock consumption as it contains residual alkaloids. It could be noted that poppy seed is a by-product of the alkaloid extraction process which is processed at Macquarie Oil Company (Macquarie Oil Company 2016).

There are some abridgements of non-edible vegetable oils as a diesel fuel such as higher viscosity, lower volatility, the reactivity of unsaturated hydrocarbon chains as well as a higher percentage of carbon residue (Balat 2011, Demirbas 2009b, No 2011, Srivastava & Verma 2008). Furthermore, it has been found that some of the non-edible oils contain a high amount of free fatty acids (FFAs) which ultimately increases the cost of biodiesel production (Banković-Ilić et al. 2012, Leung et al. 2010).

2.3.2 Waste Cooking Oil (WCO)

A great economic advantage could be achieved by using more economical feedstock, such as waste cooking or frying oil for the production of biodiesel (Abbaszaadeh et al. 2012, Azad et al. 2014b, Haas et al. 2006, Ma & Hanna 1999). It has been observed that the WCO available from restaurants and households is attracting attention as an alternative feedstock due to the high cost of crude and refined vegetable oils for biodiesel production (Borugadda & Goud 2012). Its usage significantly reduces the cost of biodiesel production. Nowadays, it has been noticed that there is a large amount of waste lipids generated from restaurants, food processing industries, fast food shops and households. The production of biodiesel from WCO to partially substitute petroleum fuel is one of the ways of solving the problems of environmental pollution which is caused by illegal dumping of large amounts of WCO into rivers and landfills (Balat & Balat 2010, Chen et al. 2009). Therefore, biodiesel produced from WCO could obtain a commercial patent as an alternative fuel to petroleum-based diesel for diesel engines in the European and US markets (Balat & Balat 2010).

The amounts of WCO produced in homes and restaurants are increasing rapidly due to the exceptional growth in human population (Chen et al. 2009, Yaakob et al. 2013). In addition, the increment in food consumption has a great impact on the production of WCO. The chemical

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and physical properties of the waste cooking oil are slightly different from those obtained from fresh oils due to changes in the properties during frying (Cvengroš & Cvengrošová 2004). WCO is obtained after using edible vegetable oils (Campanelli et al. 2010) such as palm, sunflower and corn oils by frying several times.

It has been observed that conversion of WCO into methyl esters (biodiesels) through the transesterification process approximately reduces the molecular weight to one-third, viscosity one-seventh, flash point slightly, pour point considerably, and increases the volatility marginally (Balat & Balat 2010, Demirbas 2009a, Demirbas 2009c). However, some drawbacks of using WCO as feedstock for biodiesel production are that it contains several solid impurities, such as FFAs and water (Meng et al. 2008, Tan et al. 2011, Yaakob et al. 2013). In addition, the presence of water in the oil often leads to hydrolysis, and a high FFA content leads to saponification.

2.4 Properties and Characteristics of Non-edible Oil

All alternative biodiesel fuels should meet the international standard specification of biodiesel such as American Society of Testing and Materials (ASTM) 6751, European Standard (EN) 14214, and so on. These standards specify certain physical and chemical characteristics of biodiesels, which include cetane number, density (kg/m^3), viscosity (mm^2/s), calorific value (MJ/kg), cloud and pour points (°C), flash point (°C), acid value (mg KOH/g-oil), ash content (%), copper corrosion, carbon residue, water content and sediment, distillation range, sulphur content, glycerine (%m/m), phosphorus content (mg/kg) and oxidation stability (Atabani et al. 2013b, Atadashi et al. 2010, Sanford et al. 2009). The biodiesel obtained from non-edible feedstocks have been reviewed from several viewpoints (Atabani et al. 2013b, Kumar & Sharma 2011, Sharma et al. 2011). The properties of non-edible biodiesel depend on the type of feedstock, their chemical compositions as well as fatty acid compositions which influence engine performance and emission (Atabani et al. 2012, Atabani et al. 2013b, No 2011). The physico-chemical properties of various non-edible biodiesels are summarised in Table 2.4 (Atabani et al. 2013b).

Table 2.4: Physico-chemical properties of biodiesel produced from various non-edible feedstocks

Feedstocks of non-edible methyl ester	Pour point (°C)	Cloud point, (°C)	Flash point, (°C)	CFPP (°C)	Kinematic viscosity at 40 °C (mm²/s)	Specific gravity	Cetane number	Calorific value (MJ/kg)	Cold soak filtration (s) (mL Remaining)	Density
Asclepias syriaca (milkweed)	-6	-0.95	-	-	4.6-5.2	-	50	-	-	-
Brassica carinata (Ethiopian mustard)	-	-	> 120	-	4.5	-	52	-	-	879 kg/m³
Balanites aegyptiaca (desert date)	-	3 -7	122-131	1-3	3.7-4.2	-	53.56	-	-	870-890 kg/m³
Calophyllum inophyllum (polanga)	4.3	13.2	151	-	4	-	57.3	-	-	888.6 kg/m³
Camellia japonica	-	-	193	-	4.7	-	54	-	-	877 kg/m³
Camelina sativa	-8	1.5	> 160	-1	4.365	-	-	-	223	-
Cuphea viscosissima	-	-	-	-	-	-	-	-	-	-
Eruca sativa gars	-10	-	127	-	5	0.879	49	38.67	-	-
Eruca sativa L. (taramira)	-	-	52	-	5.9	-	48	-	-	0.881 at 15 °C g/cm³
Euphorbia lathyris L.	-	-	181	-11	4.63	-	59.6	-	-	876 at 20 °C kg/m³

Guizotia abyssinica L. (niger)		-	4	157	-	4.30	-	57	-	-	-
Hevea brasiliensis (rubber seed)	8	-	4	130	-	5.81	0.842	-	36.5	-	860 kg/m^3
Hibiscus sabdariffa L. (rosella)	1	-	-	> 130	-	4.58	-	-	-	-	880.1 kg/m^3
Idesia polycarpa var. *vestita*		*-*	*-4*	*> 174*	*-2*	*4.12*	*-*	*47*	*-*	*-*	886.2 kg/m^3
Jatropha curcas L. (jatropha)		-	4	163		4.4	-	57.1	41.17	-	880 kg/m^3
Lesquerella fendleri		-	-11.6	> 160	-6	10.02	-	-	-	> 720 (190 mL)	-
Madhuca indica (mahua)	6	5		129	-	3.98	0.916	51	39.4	-	916 kg/m3
Michelia champaca		-	-	-	-	-	-	50.28	-	-	-
Nicotiana tabacum (tobacco)		-	-	165.4	-5	4.23	-	51.6	39.81	-	888.5 kg/m3
Pongamia pinnata (karanja)		-	-	180	-7	4.85	0.878	58	35.56	-	0.89 g/cc
Putranjiva roxburghii (putranjiva)	3	-	-	48	-		0.918	54.99	39.58	-	-
Pongamia glabra (koroch seed)	6		-	55	-	3.28	-	45.39	43.42	-	0.8661 g/cc
Rice bran		-	0.3	> 160	-3	4.95	-	73.6	36.05	111	877 kg/m^3

Ricinus communis (castor)	-	-13.4	> 160	7	15.25	-	-	38.7	> 720 (216 mL)	0.913 g/ml
Simarouba glauca (paradise tree)	2	-	141.2	-	5.4	-	64	-	-	0.8752 g/cc
Jojoba (*Simmondsia chinensis*)	-	-	61	-	19.2	-	63.5	47.38	-	0.866 g/ml
Sapium sebiferum L. Roxb. (stillingia)	-	-13	137	-10	4.81	-	50	-	-	0.900 g/cm^3
Sterculia foetida L. (poon)	0.14	-	162	-	6	-	54	-	-	0.875 g/cm^3
Terminalia catappa	6	-	90	-	4.3	-	57.1	36.97	-	873 at 20 °C g/cm^3
Terminalia belerica Roxb.	6	-	90	-	5.17	-	53	39.22	-	882.8 kg/m^3
Thlaspi arvense L. (field pennycress)	18	-10	-	-17	5.24	-	59.8	-	-	-
Vernicia fordii	-	-	185	-	2.5	-	53	-	-	864 kg/m^3

Iodine number (g I$_2$/100 g)	Sulphated ash content (%mass)	Ash content (%mass)	Carbon residue (%mass)	Water and sediment (vol.%)	Visual inspection	Free glycerin (%mass)	Monoglycerides (%mass)	Diglycerides (%mass)	Triglycerides (%mass)	Total glycerin (%mass)	Copper corrosion
-	-	-	-	-	-	-	-	-	-	-	-

128	< 0.01	-	0.09	-	-	38	0.53	0.13	0.07	-	-
97-100	-	-	0.1-0.2	410-450 (mg/kg)	-	-	-	-	-	-	1
85	0.026	-	0.434	0	-	-	-	-	-	0.232	1b
-	-	-	0.02	-	-	0.01	-	-	-	0.04	-
-	< 0.005	-	0.075	< 0.005	1	0.002	0.222	0.125	0.022	0.080	1a
-	-	-	-	-	-	0.002	0.780	0.089	0.000	0.218	-
-	-	-	-	-	-	-	-	-	-	-	-
-	-	-	-	0.05	-	-	-	-	-	-	1
-	-	-	-	400 (mg/kg)	-	0.01	-	-	-	0.09	1a
-	0.0016	-	0.018	-	-	0.002	-	-	-	0.017	1
144	-	0.01	-	-	-	-	-	-	-	-	-
62	< 0.005	-	0.84	< 0.005	-	0	0.5733	0.0163	0	0.11	1a
-	-	-	0.3	-	-	-	-	-	-	-	1a
-	max. 0.02	-	-	0.05	-	0.01	-	-	-	0.02	1
-	0.01	-	0.109	0.075	2	0.055	0.559	0.710	0.023	0.307	1a

74.2	-	0 .01	0.20	0.04	-	-	-	-	-	-	-
104.0	-	-	-	-	-	-	-	-	-	-	-
136	0.0004	-	0.029	-	-	0.002	0.54	0.13	0.17	0.23	1a
89	0.005	-	0.002	-	-	0.022	0.65	0.16	0.12	-	1a
82.9	-	-	< 0.1	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-	-	-
-	< 0.005	-	0.047	< 0.005	1	0.001	0.281	0.059	0.000	0.083	1a
-	0.034	-	0.110	< 0.005	1	0.367	0.258	0.479	0.023	0.507	1a
46	-	-	0.18	0.05	-	-	-	-	-	-	1
-	0.01	0.037	0.26	300 (mg/kg)	-	0.01	0.359	-	0.000	0.09	1a
-	-	-	-	-	-	0.000	0.359	0.423	0.000	0.156	-
98	-	-	-	-	-	-	-	-	-	-	-
83.2	-	-	-	-	-	-	-	-	-	-	-
77.8	-	0.0005	0.0085	-	-	-	-	-	-	-	-
-	-	-	-	-	-	0.005	-	-	-	0.041	-
-	-	-	0.02	-	-	0.01	-	-	-	0.04	-

Phosphorus (ppm)	Calcium (ppm)	Magnesium (ppm)	Acid number (mg KOH/g)	Methanol content (mg/kg)	Ester content (wt.%)	Moisture (wt%)	Sulphur (ppm)	Oxidation stability (hour)	Distillation temperature (%)	Lubricity (HFRR; mm)	References
-	0.3	-	-	-	-	-	-	-	-	-	(Pinzi et al. 2009)
-	-	-	0.08	50	13	-	< 10 mg/kg	-	-	-	(Cardone et al. 2003)
1.1-2.2	-	1.0-1.5	-	-	-	-	2-5 mg/kg	-	-	124-126	(Chapagain et al. 2009)
0.223	-	-	-	-	-	-	-	-	-	-	(Pinzi et al. 2009)
-	-	-	0.16	-	97.7	-	-	-	-	-	(Chung 2010)
< 0.1	0.8	1.1	0.338	-	-	0.04	0.6% mass	1.7	-	122	(Moser & Vaughn 2010)
< 0.1	< 0.1	0.2	2.141	-	-	0.050	-	13.3	-	-	(Sanford et al. 2009)
-	-	-	-	-	-	-	-	-	-	-	(Li et al. 2009)
-	-	-	0.40	-	97	-	0.02 % mass	8	-	-	(Chakrabarti et al. 2011)
-	-	-	0.19	97.61	97.6	-	-	10.4	-	-	(Wang et al. 2011)

< 0.001 % mass	Max. < 1 mg/kg	Max. < 1 mg/kg	0.15	0.003	-	-	0.003 % mass	3.23	1.02	-	(Sarin et al. 2009)
-	-	-	0.9	-	-	-	-	-	-	-	(Ikwuagwu et al. 2000)
-	-	-	0.43	0.01	-	-	0.00021 % mass	2.58	-	-	(Nakpong & Wootthikanokkhan 2010)
-	-	-	0.27	-	-	-	-	-	354.5	-	(Yang et al. 2009)
< 0.001 % mass	-	-	0.48	-	-	-	Max. 0.005 % mass	mi. 6 h	-	-	(Kumar Tiwari et al. 2007)
< 0.1	< 0.1	0.7	0.630	-	-	0.073	180	10.5	-	-	(Sanford et al. 2009)
-	-	-	-	-	-	-	-	-	-	-	(Saravanan et al. 2010a)
-	-	-	-	-	-	-	-	-	-	-	(Azam et al. 2005)
4 mg/kg	< 2 mg/kg	< 2 mg/kg	0.3	< 0.01	98.6	-	8 mg/kg	0.8	-	-	(Usta et al. 2011)
-	-	-	0.42	0.005	-	-	0.003 % mass	6	348	-	(Pinzi et al. 2009)
-	-	-	-	-	-	-	-	-	-	-	(Azam et al. 2005)

-	-	-	-	-	-	-	274	-	-	-	(Gogoi & Baruah 2011)
< 0.1	0.6	0.9	0.586	0.29	-	0.015	6 % mass	0.4	-	-	(Sanford et al. 2009)
< 0.1	< 0.1	< 0.1	0.996	-	-	0.053	1.3 % mass	1.1	-	-	(Panwar et al. 2010, Sanford et al. 2009)
-	-	-	-	-	-	-	0.13 % mass	-	-	-	(Devan & Mahalakshmi 2009d)
< 0.1	4	2.4	-	-	-	0.026	0.3 % mass	56.9	-	-	(Sanford et al. 2009)
< 0.1	0.5	0.4	0.708	-	-	0.052	15 % mass	0.6	-	125	(Liu et al. 2009b)
-	-	-	0.14	-	-	-	-	-	-	-	(Devan & Mahalakshmi 2009a)
-	0.5	0.4	0.001	-	-	0.067	13.3 % mass	0.4	-	-	(Pinzi et al. 2009)
-	-	-	0.23	-	-	-	96	-	-	-	(Chakraborty et al. 2009)
0.0	-	-	0.04	-	-	-	7	4.4	-	-	(Moser et al. 2009)
-	-	-	0.19	-	96.1	-	-	-	-	-	(Chung 2010)

2.5 Biodiesel Production

A lot of efforts have been made to develop and improve vegetable oil derivatives in order to achieve the properties and performance of hydrocarbon-based diesel fuel. It has been remarked that high viscosity, low volatility and polyunsaturated characters are the main barriers that prevent the use of direct vegetable oils in conventional diesel engines (Demirbas 2009c, Singh & Singh 2010). However, direct use of vegetable oils has been deemed unsatisfactory due to the presence of high viscosity, FFA content and the presence of carbon deposits (Ma & Hanna 1999, Nigam & Singh 2011). In addition, refinement is necessary to turn those vegetable oils into quality fuel. In order to overcome those problems, many technologies and methods have been employed nowadays to produce biodiesel from various non-edible feedstocks (Atabani et al. 2012, Atabani et al. 2013b) as well as waste materials (Balat 2011, Gürü et al. 2009, Gürü et al. 2010, Phan & Phan 2008, Yaakob et al. 2013). These include: pyrolysis, dilution, micro-emulsification and transesterification (Agarwal 2007, Atabani et al. 2012, Atabani et al. 2013b, Balat & Balat 2010, Canakci & Sanli 2008, Chauhan et al. 2010, Demirbas 2008a, Demirbas 2009c, Demirbas & Demirbas 2007, Ghadge & Raheman 2005, Jain & Sharma 2010b, Karmakar et al. 2010, Mahanta & Shrivastava 2004, Meher et al. 2006c, Özcanlı et al. 2011, Sharma et al. 2008, Singh & Singh 2010, Srivastava & Prasad 2000, Yusuf et al. 2011). The comparison of different biodiesel preparation technologies (Atabani et al. 2012, Lin et al. 2011a) is shown in Table 2.5.

Table 2.5: Comparison of main biodiesel preparation technologies (Atabani et al. 2012, Lin et al. 2011a)

Technologies	Advantages	Disadvantages
Dilution or micro-emulsion (Krishna & Mallikarjuna 2009, Namasivayam et al. 2010)	Simple process	1. High viscosity 2. Low volatility 3. Bad stability
Pyrolysis (Balat & Demirbas 2009, Maher & Bressler 2007)	1. Simple process 2. Non-polluting	1.High temperature is required 2. Equipment is expensive 3. Low purity
Transesterification (Leung et al. 2010, Patil & Deng 2009)	1. Fuel properties is closer to diesel	1. Low free fatty acid and water content are required (for base catalyst)

	2. High conversion efficiency	2. Pollutants will be produced because products must be neutralised and washed
	3. Low cost	
	4. Suitable for industrialised production	3. Accompanied by side reactions
		4. Difficult reaction products separation
Supercritical methanol (Demirbas 2009a, Xin et al. 2008)	1. No catalyst	1. High temperature and pressure are required
	2. Short reaction time	2. Equipment cost is high
	3. High conversion	3. High energy consumption
	4. Good adaptability	

Numerous pieces of research have been published focusing on the specific issues related to production process (Balat 2009, Fjerbaek et al. 2009, Hanna & Isom 2009, Rashid et al. 2016, Verma et al. 2016), feedstock (Fjerbaek et al. 2009, Meher et al. 2009, Murugesan et al. 2009), and social, economy and policy (Azad et al. 2016b, Pinzi et al. 2009, Sharma & Singh 2009).

2.5.1 Pyrolysis (Thermal cracking)

The aim of pyrolysis is the optimisation of high-value fuel products from biomass by thermal and catalytic means (Balat & Demirbas 2009). Pyrolysis is the method of thermal conversion of the organic matters without the presence of oxygen and in the presence of a catalyst. The available paralysed materials are vegetable oils, animal fats, bio-waste, natural fatty acids or methyl esters of fatty acids. Pyrolysis of the vegetable oil can produce a product with high cetane number, low viscosity, low water content and smaller proportions of sediments, and reasonable amounts of sulphur and copper corrosion values. However, unacceptable amounts of ash contents, carbon residues and pour points can be produced (Agarwal 2007, Atabani et al. 2013b, Demirbas 2009c, Jain & Sharma 2010b, Koh & Mohd. Ghazi 2011, Mahanta & Shrivastava 2004, Özcanlı et al. 2011, Sharma et al. 2008, Singh & Singh 2010, Srivastava & Prasad 2000, Yusuf et al. 2011). The advantages of this process are simple, waste less, pollution-free as well as cost effective when compared with other cracking processes (Atabani et al. 2012, Singh & Singh 2010).

2.5.2 Dilution

Vegetable oils can be used as an alternative diesel fuel with dilution modification technique (Ozaktas 2000). The direct use of vegetable oils in diesel engines creates problems and has many inherent failings. Mainly, vegetable oils are blended with diesel fuel in order to reduce the viscosity and to improve the performance of the engine. This method does not require any chemical process (Atabani et al. 2012, Balat & Balat 2010, Chauhan et al. 2010). It has been observed that blending of 20-25% vegetable oil with diesel fuel has been considered to give good results for diesel engine (Agarwal 2007, Balat & Balat 2008, Koh & Mohd. Ghazi 2011, Ma & Hanna 1999, Singh & Singh 2010).

2.5.3 Micro-emulsification

Micro-emulsification is the formation of micro-emulsions (co-solvency) which can be made of vegetable oils with an ester and dispersant, or of vegetable oils, and immiscible liquids such as methanol, ethanol, butanol, hexanol and ionic or non-ionic amphiphiles, and is a potential solution for solving the problem of high viscosity vegetable oils (Abbaszaadeh et al. 2012, Atabani et al. 2013b, Balat & Balat 2010, Demirbas 2009c). Furthermore, micro-emulsification technique has been taken into account as a reliable approach to solve the problem of the high viscosity of vegetable oils (Agarwal 2007, Atabani et al. 2013b, Balat & Balat 2008, Balat & Balat 2010, Demirbas 2009c, Jain & Sharma 2010b, Koh & Mohd. Ghazi 2011, Ma & Hanna 1999, Mahanta & Shrivastava 2004, Neuma de Castro Dantas et al. 2001, Özcanlı et al. 2011, Singh & Singh 2010, Srivastava & Prasad 2000, Yusuf et al. 2011).

2.5.4 Transesterification

Transesterification is regarded as one of the most attractive and widely accepted technologies for biodiesel production (de Almeida et al. 2015, Dharma et al. 2016, Gerpen 2005, Saydut et al. 2016, Verdugo et al. 2011, Yatish et al. 2016). It is regarded as the best technique and the most promising solution to the high viscosity problem among other approaches due to its low cost and simplicity (Atabani et al. 2012, Balat & Balat 2010, Jain & Sharma 2010a, Parawira 2010, Shahid & Jamal 2011, Sharma & Singh 2009). Moreover, this technique has been identified as a widely available technique for industrialised biodiesel production due to its high conversion efficiency and low cost (Lin et al. 2011a). Furthermore, this technology has been

adopted by several researchers (Dharma et al. 2016, Ong et al. 2014a, Patil & Deng 2009, Ragit et al. 2011, Verma et al. 2016) to optimise the biodiesel production from various 2nd generation feedstocks. Furthermore, it can be noted that there are many companies around the world that use this technology commercially because of its relatively lower energy consumption, high conversion efficiency and cost effective reactants and catalysts (Canakci & Sanli 2008, Karmakar et al. 2010, Ma & Hanna 1999, Mahanta & Shrivastava 2004, Marchetti et al. 2007, Meher et al. 2006c, Singh & Singh 2010). The basic transesterification reaction is shown in Figure 2.2 (Shahid & Jamal 2011, p. 2).

The technology of biodiesel production includes transesterification of oils (triglycerides) with alcohol which gives biodiesel FAME (fatty acid methyl esters) as the main product and glycerol as the by-product. Transesterification reaction of triglycerides with alcohol is shown in Figure 2.3 (Abbaszaadeh et al. 2012, p. 4; Ma & Hanna 1999, p. 7). There are many factors which affect the transesterification process such as, mixing intensity, the nature of the feedstock, reaction temperature, reaction time, reaction pressure, alcohol/oil molar ratio, type and concentration of catalyst, free fatty acids, moisture and water content, rate and mode of stirring, effect of using organic co-solvents, specific gravity as well as purity of reactants (Abbaszaadeh et al. 2012, Agarwal 2007, Atabani et al. 2012, Balat & Balat 2010, Ehimen et al. 2010, Ijaz et al. 2016, Jain & Sharma 2010b, Khan & el Dessouky 2009, Marchetti et al. 2007, Meher et al. 2006c, Murugesan et al. 2009, Rashid et al. 2016, Shahid & Jamal 2011, Sharma & Singh 2009, Sharma et al. 2008, Verdugo et al. 2011, Verma & Sharma 2016, Wan Ghazali et al. 2015).
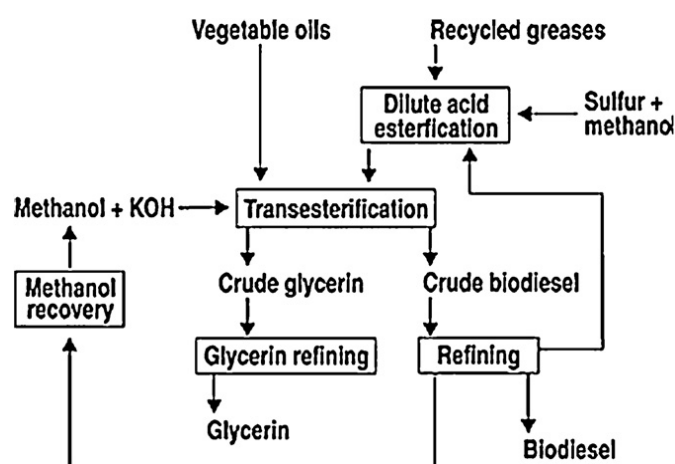
Figure 2.2: Basic Transesterification technology (Shahid & Jamal 2011, p. 2).

$$
\begin{array}{ccccc}
\text{CH}_2\text{-COO-R}_1 & & & \text{CH}_2\text{-OH} & \text{R}_1\text{-COO-R}' \\
| & & \text{Catalyst} & | & \\
\text{CH-COO-R}_2 & + \ 3\text{R}'\text{OH} & \leftrightarrow & \text{CH-OH} & + \ \text{R}_2\text{-COO-R}' \\
| & & & | & \\
\text{CH}_2\text{-COO-R}_3 & & & \text{CH}_2\text{-OH} & \text{R}_3\text{-COO-R}' \\
\text{Triglycerides} & \text{Alcohol} & & \text{Glycerol} & \text{Esters}
\end{array}
$$
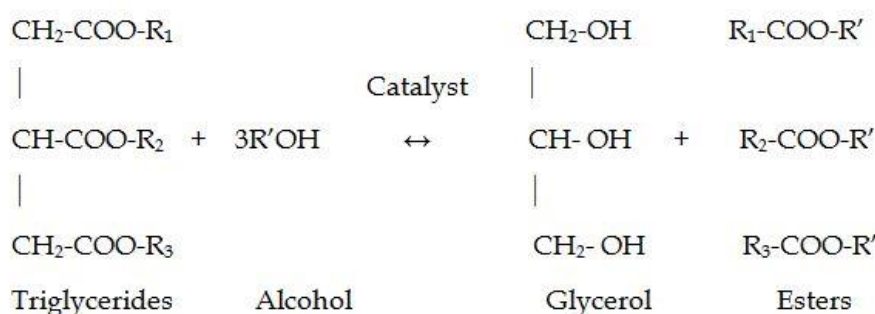
Figure 2.3: Transesterification reaction of triglycerides with alcohol (Abbaszaadeh et al. 2012, p. 4; Ma & Hanna 1999, p.7).

In general, a catalyst is used to initiate the esterification reaction for producing biodiesel. The catalyst increases the reaction rate and enhances the solubility of alcohol. The alcohols used in the transesterification process are short chain alcohols, such as methanol, ethanol, propanol, and butanol (Balat & Balat 2010, Ijaz et al. 2016, Rashid et al. 2016, Speight 2008). However, methanol and ethanol are used commercially among the other alcohols because of their low cost and physical and chemical advantages. It has been reported that an FFA value of lower than 3% is required for completing the reaction and the other materials should be substantially anhydrous (Abdullah et al. 2007, Balat & Balat 2010). Ideally, the FFA value should be kept below 1% to obtain biodiesel. Refaat et al. (2008) reported that the presence of water gives rise to hydrolysis of some of the produced ester with consequent soap formation whereas, the soap formation reduces catalyst efficiency, causes an increase in viscosity, leads to gel formation and makes the separation of glycerol difficult.

There are two mostly used methods for transesterification reaction, such as catalytic and non-catalytic transesterification (Agarwal 2007, Atabani et al. 2013b, Balat & Balat 2008, Balat & Balat 2010, Demirbas 2009c, Jain & Sharma 2010b, Koh & Mohd. Ghazi 2011, Mahanta & Shrivastava 2004, Murugesan et al. 2009, Singh & Singh 2010, Srivastava & Prasad 2000, Yusuf et al. 2011). Catalytic transesterification method includes base-catalysis, acid catalysis as well as enzyme catalysis. On the other hand, non-catalytic transesterification process includes supercritical alcohol and BIOX-co-solvent. The summary of biodiesel conversion technologies and reaction conditions for BL oil is shown in Table 2.6 (Azad et al. 2016c).

Table 2.6: Summary of biodiesel conversion technologies and reaction conditions for BL oil (Azad et al. 2016c)

Used Technique	Catalysts	Catalyst concentration	Alcohol	Temp (°C)	Time	Yield %	References
4 stage transesterification	H_2SO_4, KOH	1.5% KOH	Methanol	65	4 hour	85	(Pinzi et al. 2011)
Modified 4 stage transesterification	KOH	-	-	-	-	85-96	(Ashwath 2010)
3 stage transesterification	H_2SO_4, KOH	1.25% KOH	Methanol	60	2 hour	89	(Venkanna & Venkataramana Reddy 2009)
3 stage transesterification	H_2SO_4, KOH	0.5-1.5% KOH	Methanol	-	4 hour	85	(Ong et al. 2011, Sahoo & Das 2009b)
2 stage transesterification	β-zeolite KOH	0.75-1.5% KOH	-	45-65	2.5 hour	89	(Venkanna & Venkataramana Reddy 2009)

2.5.4.1 Catalytic Transesterification Methods

The transesterification reaction can be catalysed by alkalis (Anwar et al. 2010, Leung et al. 2010), acids (Gao et al. 2010, Li et al. 2010) and enzymes (Chen et al. 2009, Liu et al. 2009b). Acid or base catalysed transesterification is the most general technique used nowadays to produce biodiesel. In the catalytic method, the suitable selection of the catalyst is an important factor to lower the biodiesel production cost. Generally, sodium or potassium hydroxide or sodium or potassium methoxide is used as a catalyst as they are relatively cheap and quite active for this reaction (Macedo et al. 2006).

Transesterification reaction can be catalysed by both homogeneous (alkalis and acids) and heterogeneous catalysts. The transesterification process for biodiesel production is conventionally achieved using homogeneous and heterogeneous alkali or acid catalysts

(Borugadda & Goud 2012, Ma & Hanna 1999, Ranganathan et al. 2008). Several studies (Dossin et al. 2006, Marchetti et al. 2007) have been conducted using different types of oils as raw materials, various alcohols (methanol, ethanol, butanol), as well as various catalysts, including homogeneous ones, such as sodium hydroxide, potassium hydroxide, and sulphuric acid, and heterogeneous ones, such as lipases, CaO and MgO.

It has been realised that the conventional method for biodiesel production involves the use of homogeneous base catalysts under mild heating (50 °C-60 °C), albeit there are many other methodologies available (Verdugo et al. 2011). The process consists of some consecutive, reversible reactions. In case of homogeneous catalysts, greater performance is obtained toward transesterification to yield biodiesel when the free fatty acid content is < 1% (Karmakar et al. 2010). It has many advantages than the other processes, for example, it is achieved under normal conditions and it returns good yield of better quality biodiesel (Azad et al. 2012a, Lin et al. 2011a, Shahid & Jamal 2011, Yan et al. 2009). There are some disadvantages in homogeneous catalysts such as, expensive separation of the homogeneous catalyst from the reaction mixture, production of large amount of waste water during separation and cleaning up of catalyst and the products, and formation of unwanted by-product (that is, soap) by reaction of the FFA (Borugadda & Goud 2012, Kumar et al. 2013).

The drawbacks encountered in the homogeneous catalysts can be overcome by using the heterogeneous catalysts. Heterogeneous catalysts are significant for the transesterification reaction of vegetable oils while the free fatty acid content is > 1% and can be separated more easily from reaction products (Borugadda & Goud 2012). The undesired saponification reactions could be avoided and the transesterification of vegetable oils or animal fats with high contents of FFAs could be facilitated by using these catalysts. These catalysts are environmentally benign, less corrosive in nature, could be operated in continuous processes and they can be reused and regenerated (Borugadda & Goud 2012). The detailed advantages and disadvantages of homogeneous catalysts are listed in Table 2.7. In case of enzyme catalysed transesterification, the enzymatic reactions are insensitive to FFA and water content in oil. Hence, enzymatic reactions can be used in the transesterification of used cooking oil.

Table 2.7: Advantages and disadvantages of homogeneous catalysts (Dias et al. 2008, Tariq et al. 2012)

Advantages	Disadvantages
Alkaline catalysts	
Low cost	Requirement of low FFA
Favorable kinetics	Anhydrous conditions
High catalytic activity, very fast reaction rate, 4000 times faster than acid-catalysts	Saponification, if the FFA contents are more than 2 (wt.%)
Mild reaction condition and less energy intensive	Homogeneous catalysts are stable only in relatively mild conditions which limit their applicability.
Easier to control and manipulate the process parameters	Sometimes low biodiesel yield which is due to the formation of emulsion
Good contact with the reactants and that is why a much greater effective concentration of catalyst	More wastewater from purification
The catalysts are molecularly dispersed within the fluid.	The reactant, products and solvents, and the separation at the end of the process are difficult and expensive since the catalysts are molecularly dispersed. Non-reusable
Acidic catalysts	
Intensive for high FFA and water contents in the oil	Very slow reaction rate
The performance of the catalyst is not strongly affected by the presence of the FFAs in the feedstock	Equipment corrosion
Catalyse esterification and transesterification simultaneously	More waste from neutralisation
No soap formation	Recycling of catalyst is problematic
Preferred for low-grade oil	Weak catalytic activity
Reaction occurs under mild conditions and less energy intensive	Higher reaction temperature

2.5.4.1.1 Alkali-Catalysed Transesterification

The transesterification process is catalysed by alkaline metal alkoxides, hydroxides, as well as sodium or potassium carbonates. The common base catalysts used in biodiesel production are sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide ($NaOCH_3$) (Kulkarni & Dalai 2006). However, it has been observed that the sodium methoxide is the most widely used biodiesel catalyst and over 60% of industrial plants use this catalyst (Huber et al. 2006, Ong et al. 2014b). Alkaline catalysts require short reaction time and relatively low temperature and little or no darkening of the colour of the oil (Singh & Padhi 2009). The alkali-catalysed transesterification of vegetable oils goes on faster than the acid-catalysed reaction. The mechanism of alkali-catalysed transesterification is shown in Figure 2.4 (Balat & Balat 2010, p. 12; Demirbas 2005, p. 13; Koh & Mohd. Ghazi 2011, p. 5; Schuchardt et al. 1998, p. 3).
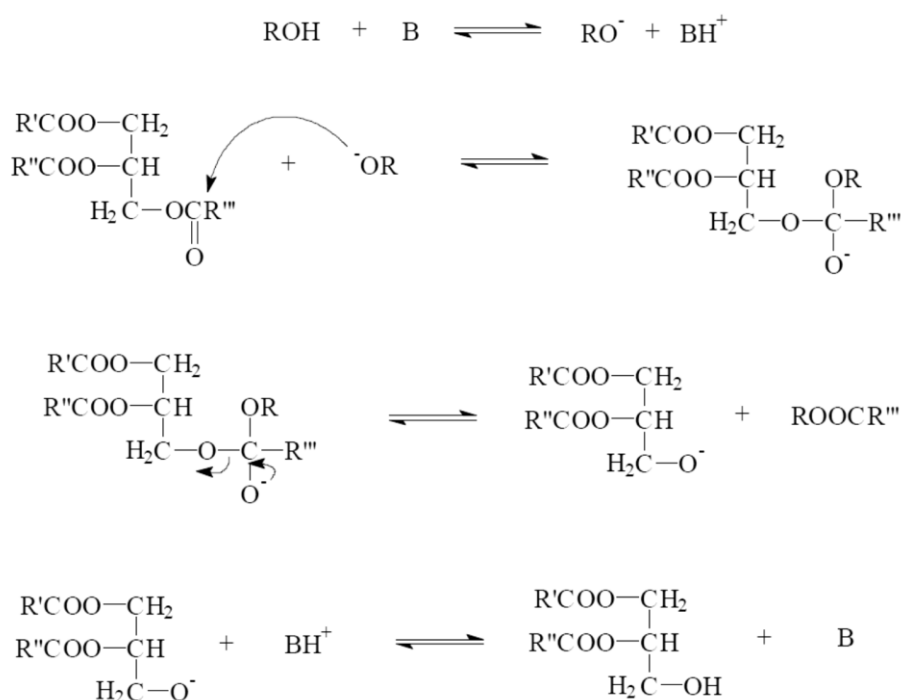
Figure 2.4: Mechanism of alkali-catalysed transesterification of vegetable oils (B: base) (Balat & Balat 2010, p. 12; Demirbas 2005, p. 13; Koh & Mohd. Ghazi 2011, p. 5; Schuchardt et al. 1998, p. 3).

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts as they give very high yields (>98%) in short reaction times (30 min) even if they are applied at

low molar concentrations (0.5 mole %). Although Singh & Padhi (2009) showed high performance for obtaining vegetable oils with high quality, the oils contain a significant amount of FFAs which cannot be converted into biodiesels. It was also reported by Ghadge & Raheman (2005) that the conversion of feedstocks into biodiesel via alkaline catalyst is difficult with oil having huge quantities of FFAs (41% (wt.%)). However, due to the presence of high quantities of FFAs the problem is raised with processing low-cost fats and oils and the results are that they cannot be easily transformed to biodiesel by conventional alkali-catalysed transesterification (Canakci & Van Gerpen 2001, Demirbaş 2003).

2.5.4.1.2 Acid-Catalysed Transesterification

The main acid-catalysed transesterification methods for biodiesel production are methanolic sulphuric acid (Ghadge & Raheman 2005, Kumar Tiwari et al. 2007, Ramadhas et al. 2005, Sahoo et al. 2007, Veljković et al. 2006), ferric sulphate (Wang et al. 2007), sulfonic acid, methanolic hydrogen chloride, and methanolic boron trifluoride (Ghadge & Raheman 2005). Currently, the mostly used catalysts in biodiesel production are the organic acids, such as the derivatives of toluene sulfonic acid and, more often, mineral acids such as sulphuric acids, hydrochloric acid (Balat & Balat 2010, Cardoso et al. 2008, Demirbas 2009c). There are some advantages of acid-catalysed transesterification process: it directly produces biodiesel from low-cost lipid feedstocks, such as used cooking oil and greases, which commonly have FFAs levels of >6% and insensitive to the FFAs content in the feedstock (Borugadda & Goud 2012, Meher et al. 2006b). Liquid acid-catalysts are considered to overcome the abridgements of liquid base-catalysts as the liquid base-catalysed transesterification process poses a lot of problems especially for oil or fat with high FFAs concentrations (Borugadda & Goud 2012). However, the performance of the acid-catalysts is not strongly affected by the presence of FFAs in the feedstock.

Although the transesterification process using acid-catalysts is much slower than that obtained from the alkali-catalysis which is typically 4000 times, due to the presence of high contents of water and FFAs in the vegetable oil, acid-catalysed transesterification method is considered to provide better results (Balat & Balat 2010, Juan et al. 2011). These catalysts give very high yields in alkyl esters in the transesterification process. The mechanism of acid-catalysed transesterification of vegetable oil (for a monoglyceride) is presented in Figure 2.5 (Balat &

Balat 2010, p. 11; Koh & Mohd. Ghazi 2011, p. 8; Meher et al. 2006c, p. 7; Schuchardt et al. 1998, p. 3; Singh & Singh 2010, p. 8).

R" = $\begin{array}{l}\text{—OH} \\ \text{—OH}\end{array}$; glyceride

R' = carbon chain of fatty acid

R = alkyl group of the alcohol
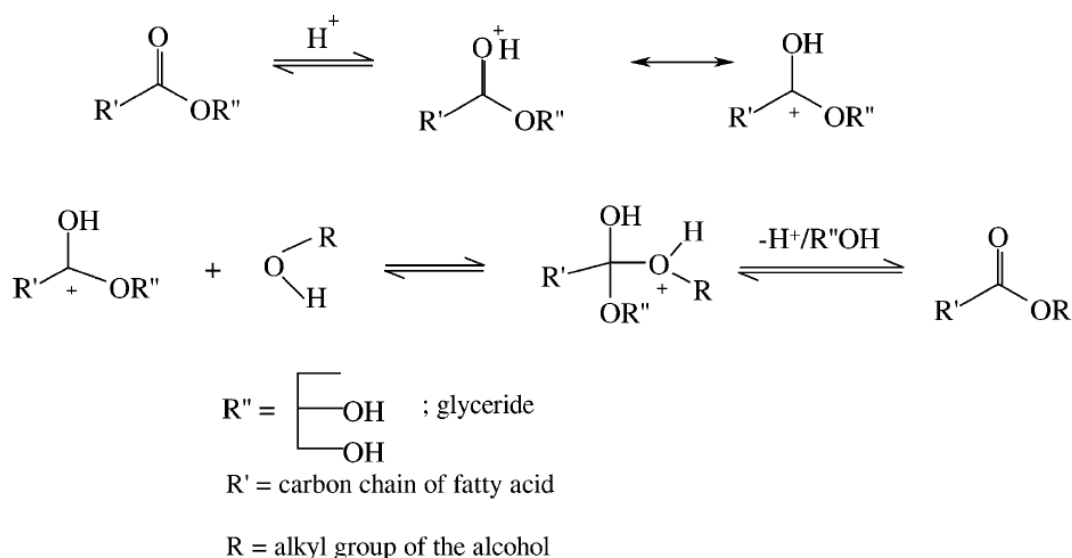
Figure 2.5: Mechanism of acid-catalysed transesterification (Balat & Balat 2010, p. 11; Koh & Mohd. Ghazi 2011, p. 8; Meher et al. 2006c, p. 7; Schuchardt et al. 1998, p. 3; Singh & Singh 2010, p. 8).

It has been obtained that the alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification process (Demirbas 2009c). However, acid-catalysed reactions require the use of high alcohol to oil molar ratios in order to obtain good product yields in practical situations. An excess of the alcohol favours the formation of alkyl esters.

2.5.4.1.3 Enzyme-Catalysed Transesterification

Enzymatic transesterification using a lipase catalyst looks attractive because it is less energy intensive, it does not promote side reactions, it has easy product separation, minimal waste water treatment is needed, it offers easy glycerol recovery and is more environmentally friendly (Borugadda & Goud 2012, Koh & Mohd. Ghazi 2011, Meher et al. 2006b, Meher et al. 2006c). Therefore, the enzyme-catalysed (lipase) transesterification has continued to draw the attention of researchers in last 10 years. Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems (Balat & Balat 2010, Fukuda et al. 2001, Helwani et al. 2009, Meher et al. 2006c). However, an enzyme-catalysed system requires a much longer reaction time than the alkali and acid catalysed systems. In addition, the reaction yields as well as the reaction times from enzyme-catalysed transesterification are still unfavourable compared to the base-catalysed reaction systems and

thus render the process impractical and uneconomical (Bala 2005, Demirbas 2005, Miao et al. 2009).

The optimization is done on biodiesel production process to obtain the maximum yield of methyl ester (biodiesel). The optimization process is conducted with the aim of obtaining the final optimal reaction parameters. The reaction parameters that involved in the optimisation process are the methanol to oil ratio, catalysts concentration, reaction temperature and time. The available literatures on optimisation of biodiesel production reaction parameters and biodiesel yields are listed in Table 2.8.

Table 2.8: Optimisation of biodiesel production reaction parameters and biodiesel yields

Samples	Methanol to oil ratio		Catalyst concentration		Reaction temperature (°C)		Reaction time (min)		Biodiesel yield (%)		References
	Range	Optimum	Range	Optimum	Range	Optimum	Range	Optimum	Range	Optimum	
Ricinus communis	4:1-8:1 (M/M)	6:1	0.25-0.40 g	0.32	45-80	60	60-80	70	46-90	90	(Ijaz et al. 2016)
Jatropha	6:1-20:1 (v/v. %)	11:1	0.5-1.5 (w/v. %)	1.1	-	-	0-250	120	-	-	
Karanja	6:1-20:1 (v/v. %)	11.5:1	0.5-1.5 (w/v. %)	1	-	-	0-250	120	-	-	(Sahoo & Das 2009b)
Polanga	6:1-20:1 (v/v. %)	12:1	0.5-1.5 (w/v. %)	0.9	-	-	0-250	120	-	-	
Callophyllum inophyllum	4:1-10:1 (M/M)	8:1	0.75-1.5 (wt. %)	1.25	45-65	60	30-150	120	61-89	89	(Venkanna & Venkataramana Reddy 2009)
Moringa Oleifera	10-50 (wt/wt. %)	30	0.5-1.5 (wt. %)	1.0	30-60	60	30-90	60	20-82	82	(Kafuku & Mbarawa 2010a)
Hazelnut (*Corylu*	-	6:1		0.7		60 ± 0.5		120		97.5	

s avellana) oil							(Saydut et al. 2016)
Sunflower (*Helianthus annuus*) oil	-	6:1 (M/M)	0.7	60 ± 0.5	120	97.3	
Hybrid (hazelnut and sunflower (50:50 v/v)	-	6:1 (M/M)	0.7	60 ± 0.5	120	97.9	

2.5.4.2 Non-Catalytic Transesterification Methods

As in catalytic reaction process, the production of biodiesel through the conventional transesterification system renders the process complicated, thus it gives a reason to investigate the production of biodiesel from triglycerides via non-catalytic reactions. Besides catalytic methods, there are two non-catalytic transesterification processes, namely: (i) the supercritical alcohol process and (ii) BIOX co-solvent process.

2.5.4.2.1 Supercritical Alcohol Transesterification

The transesterification of triglycerides by supercritical methanol, ethanol, propanol and butanol has been proven to be the promising option (Balat & Balat 2010). Supercritical methanol transesterification is the process in which solvent is subjected to temperature and pressure above its critical point. The problems associated with the two-phase nature of normal methanol/oil mixtures can be solved by using supercritical methanol technique by forming a single phase as a result of the lower value of the dielectric constant of methanol (Demirbas 2009c). Furthermore, the process at higher temperature and pressure conditions provides improved phase solubility, decreases mass transfer limitations, provides higher reaction rates, makes easier separation, has simpler purification steps, has a lower reaction time, is more environmentally friendly, as well as requires lower energy consumption (Abbaszaadeh et al. 2012, Demirbas 2009c). However, the reaction is fast and conversion raises 50%-95% for the first 10 minutes (Abbaszaadeh et al. 2012) but it requires temperatures and pressures of 525 K-675 K and 35 MPa-60 MPa, respectively (Demirbaş 2003, Kusdiana & Saka 2001). However,

the limitations of the supercritical transesterification process are due to the high temperature and pressure that result in the high cost of the apparatus (Koh & Mohd. Ghazi 2011). Additionally, due to severe reaction conditions, high operational cost and high methanol to oil ratios (usually 42), production of biodiesel by supercritical methanol is not a viable option for large scale practice in the industry (Abbaszaadeh et al. 2012, Borugadda & Goud 2012).

2.5.4.2.2 BIOX Co-solvent Process

The BIOX (co-solvent) process is a new Canadian process developed originally by Professor David Boocock of the University of Toronto that has drawn considerable attention. Dr Boocock has metamorphosed the production process through the selection of co-solvents that generate an oil-rich one-phase system (Demirbas 2009c). BIOX's patented production process is performed by two steps: (i) converts the FFAs through acid esterification up to 10% FFA content and (ii) then the triglycerides by the way of transesterification, through the addition of a co-solvent, in a two-step, single phase, continuous process at atmospheric pressures and near-ambient temperatures within 90 min (Abbaszaadeh et al. 2012, Demirbas 2009c). The co-solvent is reused continuously in the process after recycling. This process uses either tetrahydrofuran (THF) or methyl tertiary butyl ether (MTBE) as a co-solvent to generate a one-phase system. Furthermore, this system requires rather low operating temperatures of 303 K (Abbaszaadeh et al. 2012, Helwani et al. 2009). Finally, the use of co-solvents such as THF or MTBE speeds up methanolysis considerably.

It has been reported that oils containing high free fatty acid (FFA) level are not a good source for biodiesel production (SathyaSelvabala et al. 2011) because of the presence of high FFA (>2 (wt. %), soap formation may occur in transesterification when alkali catalysed is used (Kansedo et al. 2009a). Therefore, several researchers proposed a combination of two-step processes, which consists of pre-treatment, that is, esterification (using acid catalyst) and then transesterification (using base catalyst) can be used to overcome this problem (Dhar et al. 2012, Jena et al. 2010, Sahoo & Das 2009b, Silitonga et al. 2013c). During esterification most of the FFAs are converted into its corresponding fatty acid methyl ester (FAME). Generally, sulphuric, hydrochloric, ferric sulphate, phosphoric and organic sulfuric acid are used to reduce acid value in containing high FFAs vegetable oils (Atabani et al. 2012, Silitonga et al. 2013a). The remaining triglycerides in the pre-treated product are converted into methyl ester (biodiesel) by transesterification reaction. In this reaction, methanol or ethanol are the most commonly

used as alcohols, and KOH and NaOH are used as catalysts because of their low cost and availability (Atabani et al. 2013b).

Biodiesel produced by catalysed transesterification contains several impurities which include unreacted alcohol (methanol or ethanol), unreacted triglycerides, mono and diglycerides, residual catalyst, FFA, free glycerine, water and other impurities. It can be noted that one of the main reasons leading to biodiesel production is the costs involved in the biodiesel separation and purification stage. The produced biodiesel should be purified according to the ASTM and EN standards. The above mentioned impurities present in the biodiesel should be removed as these have negative effect on the engine performance, emission and natural environment. For example, the burning of glycerine which is one of the most important impurities leads to the production of acrolein that is a toxic compound. Moreover, content of high free glycerol in biodiesel can cause separation during storage, form gum-like deposits around injector trips and valve heads which cause problems in the fuel system (Saleh et al. 2010). To overcome these limitations, there are several separation and purification techniques, such as gravitational settling, distillation, evaporation, washing with water, acid, absorbent to produce a highly purified and quality biodiesel (Atadashi et al. 2010). Gomes et al. (2010) separated biodiesel and glycerine using ceramic membrane and glycerol retention of 99.6% was achieved.

In conventional method, the access methanol, glycerol and impurities contained in the high-density biodiesel is removed from the bottom layer in the separatory funnel. Secondly, the crude methyl ester is poured into the rotary evaporator to remove any methanol residues, and then washed with distilled water several times to remove entrained glycerol and impurities (Dharma et al. 2016). de Almeida et al. (2015) mentioned the purpose of the separation and purification of crude biodiesel is to remove impurities, such as unreacted catalyst, soap, glycerol and unreacted methanol. The purification is done by washing 3 times with distillated water at 50 °C (García-Moreno et al. 2014).

2.6 Performance, Combustion and Emission Characteristics

Biodiesel also offers improved lubricity over certain low-sulphur petro-diesels (Graboski & McCormick 1998) and thus can help to reduce wear of engine components (Knothe et al. 2005). Diesel engines run by biodiesel can be beneficial in terms of environmental impact and energy security. Several researches were performed to evaluate engine performance, combustion and

emission characteristics in CI engines using biodiesel as well as biodiesel-diesel blend as a substitution for diesel (Aksoy 2011a, Ong et al. 2014b, Sakthivel 2016, Wan Ghazali et al. 2015, Yadav et al. 2016). The biodiesel can be blended with diesel in different proportions and directly used in existing diesel engines without any modification (Azad et al. 2012b, Can 2014, Di et al. 2009). However, biodiesel has poor low-temperature properties and its chemical nature makes it more susceptible to oxidation or autoxidation during long-term storage in comparison to petroleum diesel fuel (Knothe 2007). The technical specifications of biodiesel fuels should be within the limits of ASTM D6751 and EN 14214 biodiesel standards. Ensuring compliance with standards of biodiesel fuel is an important issue for providing the emissions limits and engine durability in long-term use. The variation in physico-chemical properties of the biodiesel-diesel blend has been discussed by several researchers (Ashraful et al. 2014, Azad et al. 2012a, Ribeiro et al. 2007).

The following factors, such as biodiesel feedstocks (sources), contents in biodiesel, cetane number, advance injection timing and combustion, oxygen contents, engine load, engine speed, density and viscosity, and so on affect both the regulated and unregulated emissions (Mofijur et al. 2013a). A summary of different reports regarding the factors which influence engine emissions such as NO_x, CO, PM and HC have been presented in Table 2.9 (Mofijur et al. 2013a). It was reported that the low temperature combustion strategy can significantly reduce the PM and NO_x emission, whereas, CO and HC emission increases which is due to the higher rate of exhaust gas recirculation (Azad et al. 2016a). The effect of using blended non-edible biodiesel with petroleum diesel can be evaluated by determining the engine power/torque, BTE, BSFC and emissions generation (Atabani et al. 2013b, Harch et al. 2014). Extensive research has been conducted worldwide to utilise non-edible biodiesel as a possible substitute diesel fuel for use in a diesel engine (Atabani et al. 2013b, Knothe & Steidley 2009, Ong et al. 2013).

Table 2.9: Factors affecting the engine emissions (Mofijur et al. 2013a)

Factors	References for NO_x emissions	References for CO emissions	References for PM emissions	References for HC emissions
Biodiesel feedstock	(Özgünay et al. 2007)	(Baiju et al. 2009)	(Banapurmath et al. 2008)	(Lin & Li 2009)
Contents of biodiesel	(Nabi et al. 2009)	(Aydin & Bayindir 2010,	(Korres et al. 2008)	(Mahanta et al. 2006)

	Meng et al. 2008)			
Higher cetane number	(Lapuerta et al. 2008b, Özgünay et al. 2007)	-	(Korres et al. 2008)	(Monyem et al. 2001)
Advance injection timing	(Ozsezen et al. 2009)	(Banapurmath et al. 2009)	(Lapuerta et al. 2008b, Ozsezen et al. 2009)	(Ozsezen et al. 2009)
Higher oxygen contents	-	(Godiganur et al. 2010, Usta 2005a)	(Frijters & Baert 2006)	(Puhan et al. 2005)
Engine load	(Gumus & Kasifoglu 2010, Lapuerta et al. 2008b, Murillo et al. 2007)	(Gumus & Kasifoglu 2010, Usta 2005a)	(Nabi et al. 2009)	(Lapuerta et al. 2008b)
Engine speed	(Lin & Li 2009)	(Lin & Li 2009)	-	-

Ong et al. (2014b) conducted an experiment using biodiesel–diesel blends of 10%, 20% and 30% for *Jatropha curcas*, *Ceiba pentandra* and *Calophyllum inophyllum* (beauty leaf) to evaluate engine performance and emission characteristics. The highest results were obtained for 10% blend in terms of engine power, torque, fuel consumption and BTE. The results also showed that the significant reductions in CO_2 and CO were observed with a slight increase in NO_x. It was also noted that 100% biodiesel improved the thermal efficiency of the engine by 0.1% whereas the optimum engine operating condition was observed at 100% load for pure biodiesel (Ameer Uddin et al. 2013). Moreover, about 4% decrease in NO_x emissions was observed for B100 biodiesel at full load due to the decrease in the exhaust temperature of the biodiesel-fuelled engine. However, BSEC as well as the exhaust emissions were reduced remarkably. Sahoo et al. (2007) also studied the polanga oil methyl ester (POME) with high-speed diesel (HSD) in a single cylinder engine. HSD and POME with different fuel blends such as, 20%, 40%, 60%, 80%, and 100% were used for conducting the engine performance tests at varying load conditions (0%, 20%, 40%, 60%, 80% and 100%).

Several researchers (Devan & Mahalakshmi 2009b, Dhar et al. 2012, Sahoo & Das 2009a, Vallinayagam et al. 2013) studied the engine combustion performance characteristic and

showed that the CP is higher in biodiesel blend than the diesel. Numerous researches have been reported in terms of HRR, and the results showed that the HRR is lower than the diesel. (Buyukkaya 2010, Chauhan et al. 2012, Gattamaneni et al. 2008, Imdadul et al. 2016, Jaichandar & Annamalai 2012, Jaichandar et al. 2012, Muralidharan & Vasudevan 2011, Sayin et al. 2012). The HRR is higher at lower blend compared to the higher blend as reported by several researchers (Buyukkaya 2010, Devan & Mahalakshmi 2009d).

No (2011) reviewed the use of different non-edible vegetable oils such as jatropha, karanja, mahua, linseed, rubber seed, cotton seed and neem, and their subsequent blends with diesel fuel. It was found that a diesel engine would run successfully with a blend of 40% biodiesel without any modification or any damage to engine parts. Furthermore, it is also possible to run the common rail direct injection system CI engine using up to 10% blends by volume without any durability problems. It was also pointed out that the emission characteristics, such as HC, CO and PM were reduced remarkably through the use of biodiesel and its blends when compared to diesel fuel. However, an increase in NO_x emissions was also reported for using biodiesel and its blends in a CI engine.

It has been reported that there were unexpected increases in power or torque of engine for pure biodiesel (Al-Widyan et al. 2002a). Most of the researchers (Aydin & Bayindir 2010, Buyukkaya 2010, Chauhan et al. 2012, Gumus & Kasifoglu 2010, Ruhul et al. 2016b, Wood et al. 2015) reported that the biodiesel-diesel blend decreases in BP and increases in BSFC when the engine is fuelled with biodiesel-diesel blend because of the need to compensate for the loss of heating value of biodiesel. In addition, engine power decreases with increase in content in biodiesel (Hull et al. 2006, Meng et al. 2008). For instance, Carraretto et al. (2004) observed that the increase in biodiesel percentage in the blends resulted in a slight decrease in both power and torque over the entire range of engine speed for different biodiesel-diesel blends (B20, B30, B50, B70, B80, B100) on a 6-cylinder direct injection (DI) diesel engine. Aydin & Bayindir (2010) reported that the torque was decreased with the increase in cottonseed oil methyl ester in the blends (B5, B20, B50, B75, and B100) due to higher viscosity and lower heating value of cotton seed methyl ester. In terms of torque, the higher torque has been found in diesel than the biodiesel blend (Ong et al. 2014b, Utlu & Koçak 2008).

Murillo et al. (2007) observed that increasing the amount of biodiesel in the blend decreases the engine power on a single-cylinder, 4-stroke direct injection (DI) and naturally aspirated

(NA) diesel engine. Devan & Mahalakshmi (2009c) reported that at lower biodiesel blend (B40) the BTE was higher than the higher blend (B100) for the poon oil methyl ester. The lower BTE has been observed for all biodiesel–diesel blends in comparison to diesel except B10 for jatropha curcas (Ong et al. 2014b). In addition, several researchers (An et al. 2013, Chauhan et al. 2012, Misra & Murthy 2011, Murayama et al. 1984) reported that biodiesel blend has the lower BTE compared to diesel. The BTE decreases with increase in biodiesel blend as supported by researchers (Campos-Fernández et al. 2012, Muralidharan et al. 2011, Ong et al. 2014a, Ong et al. 2014b).

Several researchers (Çelikten et al. 2012, Kumar et al. 2013, Ong et al. 2014a, Ong et al. 2014b, Sakthivel 2016) showed that biodiesel-diesel blend has the higher EGT than the diesel. The use of biodiesel-diesel blend significantly reduces the emission characteristics, such as CO, HC and PM compared to diesel (Abedin et al. 2014, Mosarof et al. 2015, Rizwanul et al. 2014, Ruhul et al. 2016a). It is overwhelmingly obvious that the use of biodiesel instead of diesel causes the reduction in PM emissions (Gumus & Kasifoglu 2010, Ulusoy et al. 2004). According to several researchers (Godiganur et al. 2010, Raheman & Ghadge 2007, Sharma et al. 2009), it is a common trend that the CO emission is reduced when diesel is replaced by biodiesel. It is also established that HC emission will be reduced when biodiesel is fuelled instead of diesel (Ozsezen et al. 2009, Sharma et al. 2009). It was also reported by some researchers (Ozsezen et al. 2009, Utlu & Koçak 2008) that the biodiesel resulted in lower CO_2 emission than diesel during complete combustion due to the lower carbon to hydrogen ratio. On the contrary, several researchers (An et al. 2013, Fontaras et al. 2009, Gumus et al. 2012, Mofijur et al. 2014b, Muralidharan & Vasudevan 2011, Rahman et al. 2014, Rajaraman et al. 2009, Ruhul et al. 2016b) reported that the CO_2 emission is higher in biodiesel-diesel blend than the diesel.

Lapuerta et al. (2008b) carried out an extensive review on the effect of biodiesel on diesel engine emissions. They found that in most investigations, HC, CO, smoke and PM emissions are low as compared to petroleum diesel. However, biodiesel has a slight increase in NO_x emission. Furthermore, several studies have reported that the use of biodiesel has been shown to be effective at reducing most regulated exhaust emissions, such as PM, unburnt UHCs and CO (Di et al. 2009, Szybist et al. 2007). The emission of aromatic and polyaromatic compounds as well as their toxic and mutagenic effect has been generally considered to be reduced with

biodiesel. However, there is no conclusive trend in the emissions of oxygenated compounds, such as aldehydes and ketones.

Almost all the researchers (Çelikten et al. 2012, Fontaras et al. 2009, Kim & Choi 2010, Monirul et al. 2016, Ong et al. 2014b, Zhu et al. 2010b) reported that the use of biodiesel-diesel blend increases the NO_x emission in comparison to diesel. Generally, it has been observed that the emissions associated with 100% pure biodiesel (B100) are lower than conventional diesel except for NO_x. The average NO_x emissions obtained from pure biodiesel increase by 10% depending on the condition of combustion characteristics of the engine and the testing procedure whereas, the sulphur emissions are essentially eliminated with pure biodiesel as compared to diesel. Additionally, the exhaust emissions of total HCs, CO and PM are lower on average by 67%, 48% and 47%, respectively, for using biodiesel when compared to diesel fuel (Koh & Mohd. Ghazi 2011). In addition, the PAHs also shows a decrease in emission by 80% for using (Ozsezen et al. 2008, Valente et al. 2012) biodiesel.

Numerous researchers (Ozsezen et al. 2008, Valente et al. 2012) have reported that the use of WCO biodiesel instead of petroleum diesel decreases harmful exhaust emissions with equivalent engine performance. Kulkarni & Dalai (2006) concluded that the engine performance of biodiesel obtained from WCO is better than that of diesel fuel while the emissions produced by the use of biodiesel are less than those of diesel fuels except that there is an increase in NO_x. Muralidharan & Vasudevan (2011) evaluated the performance, emission and combustion characteristics of a single cylinder DI diesel engine fuelled by WCO biodiesel and its 20%, 40%, 60% and 80% (vol./vol.) blends with diesel fuel. The results showed longer ignition delay, higher maximum rate of pressure rise, lower heat release rate and higher mass fraction burnt for the WCO biodiesel compared to those of diesel fuel. The effects of biodiesel fuel produced from WCO on combustion, performance and emissions were investigated by An et al. (2013) at different engine speeds (idle speed and 1200 rpm-3600 rpm by 1200 interval) and loads (25%, 50% and 100% load) on a Euro IV diesel engine. It was reported that the biodiesel fuel significantly increased CO emissions and resulted in lower CO_2, HC and NOx emissions in low engine loads. However, opposite trends were observed at lower engine speeds and higher engine loads. In general, biodiesel additions to No. 2 diesel fuel result in considerable reductions in HC, PM, SO_2 (sulphur dioxide), and CO emissions while there is a slightly increase in NO_x emissions. Furthermore, several studies were conducted related to the

usage of WCO biodiesels in diesel engines which are mostly focused on the engine performance and emissions (Kalam et al. 2011, Lin et al. 2011b, Ozsezen & Canakci 2010).

2.7 Summary of the Literature Review

- Biodiesel, produced from renewable and often domestic sources, represents a more prospective source of energy and will therefore play a significant role in providing the energy requirements for transportation in the near future. However, biodiesels available in the market today are unlikely to be sustainable due to production from edible oil feedstock creating the "Food versus Fuel" debate.

- The wide range of available feedstocks for biodiesel production indicates one of the most important advantages of producing biodiesel. It can be noted that feedstock alone represents more than 75% of overall biodiesel production cost. Therefore, selecting the best feedstock is significant to ensure low production cost of biodiesel.

- To explore those types of feedstocks which are not compete with food crops, nor lead to land-clearing and reduce GHGs significantly.

- The solvent extraction technique using n-hexane results in the highest oil yield which makes it the most general method. The chemical oil extraction technique was found to be very effective because of high oil yield and for its consistence performance. However, the n-hexane solvent extraction has a negative environmental impact because of the wastewater generation, higher specific energy consumption and higher emissions of volatile organic compounds and human health impacts.

- The 2nd generation biodiesel produced from non-edible feedstock has not being established yet due to unavailability of feedstock supply, production cost and lack of knowledge of its fuel quality.

- Australia has the potential to become a major source of 2nd generation biofuel having vast land area and diverse naturally grown non-edible oilseed plants bearing large quantities of fruits and seeds that could serve as biodiesel feedstock.

- Raw vegetable oils are not suitable for use directly in diesel engines due to high viscosity. Transesterification is found to be the most suitable process to reduce the viscosity and produce high quality biodiesel from raw vegetable oil. However, yield of ester largely depends on the reaction condition and physio-chemical properties of feedstock and it

varies from one feedstock to another. Therefore, optimisation of production process is an important issue before stating industrial scale production of biodiesel from new feedstock.

- Transesterification is regarded as the best method among other approaches due to its low cost, high conversion yield and simplicity. Most of the researchers suggested that biodiesel production optimisation can be conducted by changing different affecting parameters in transesterification reaction. Thus, this technique could be considered for commercial biodiesel production.

- Depending on feedstock availability and climate conditions, several 2nd generation biodiesels are utilizing in different regions of the world. Although chemically all those biodiesels are fatty acid methyl ester (FAME), but clear differences in chemical structure are apparent from one feedstock to the next in terms of chain length, degree of unsaturation, number of double bond and double bond configuration. Although numerous number of fatty acid, ranging chain length from 6-24, has been found in different biodiesels, but the compositional profiles of common vegetable oils are dominated by five fatty acid species: palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3). However some biodiesels are significantly different such as coconut oil containing large fractions of lighter fatty acid species–especially lauric (12:0) and myristic (14:0).

- Important physico-chemical properties of biodiesel which include kinetic viscosity, density, cetane number, calorific value, flash point, oxidation stability, cold temperature properties and iodine value have a great influence on engine performance, combustion and emission features. Therefore, different levels of combustion performance and emission have been observed in literature while being used as diesel engine fuel.

- According to the vast majority of authors, the fuel consumption increases when using biodiesel-diesel blend and the higher the biodiesel-diesel blend the higher the fuel consumption and vice versa.

- The vast majority of authors reported that NO_x emissions will increase when using biodiesel-diesel blend which is mainly due to the high oxygen content. The higher the engine loads the higher the level of NO_x emissions for biodiesel.

- It is certain that the physico-chemical properties of biodiesel and the fatty acid profile of biodiesel influence the overall engine performance, combustion, emission characteristics, and suitability as a diesel engine fuel.

- Especially, 2nd generation biodiesels which are BL, poppy, PWC and jojoba could be a prospective feedstock due to its availability, potentiality, low prices and meeting the

ASTM and EN specifications of biodiesel standards which could meet the transport energy demand to a great extent.

CHAPTER 3

BEAUTY LEAF (*CALOPHYLLUM INOPHYLLUM* L.) OIL EXTRACTION TECHNIQUE

This chapter presents and discusses beauty leaf (BL) oil extraction techniques with an aim to produce maximum oil yield. The experiments were conducted to determine the effects of fruit cracking, seed (kernel) preparation, kernel drying, moisture content and the kernel size on oil yield. Mechanical and chemical methods were used to extract oil from the BL kernel using a screw press expeller and n-hexane as an oil solvent, respectively. Both whole kernel (WK) and grated kernel (GK) were used in screw press technique, whereas, only GK was used in n-hexane extraction technique. The study indicated that the kernels prepared to 14.4% moisture content produced the highest oil yields in both methods. Oil recovery, residual oil, and oil cake and sediment content were measured at different moisture contents for both techniques. The highest oil recovery of 54% was obtained in n-hexane method with the GK. On the other hand, oil recovery of 45% and 35% were achieved using screw press technique for GK and WK, respectively. The study also revealed that residual oil, and the cake and sediment recovery of 12% and 60%, respectively, was obtained in screw press technique for the WK. The physico-chemical properties of the crude BL oil that were extracted by screw press and n-hexane technique were evaluated. A comparison of the fossil energy ratios (FER) between the two techniques was made and the results indicated that the n-hexane technique is more efficient than the screw press technique. This study provides an understanding of the basis of selecting an appropriate oil extraction technique for commercial applications.

3.1 Introduction

The use of non-edible oils can bring down the price and meet the world energy demand to a large extent by reducing the dependency on edible oils (Ong et al. 2013). Therefore, the non-edible vegetable oils can be taken into account as a prospective feedstock over edible vegetable oils due to the former's low feedstock cost (Azad & Uddin 2013, Bhuiya et al. 2014a, Gui et al. 2008, Leung et al. 2010). Among different non-edible oils, BL oil is regarded as one of the prospective feedstocks for biodiesel production due to its higher oil content in the kernels. Potential of abundant production of this fruit is one of the precursors to consider BL (*Calophyllum inophyllum* L.) as a raw material in Australian context. BL fruits are produced

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twice a year, and seed kernels contain up to 65% of non-edible oil (Friday & Okano 2006a, Hathurusingha & Ashwath 2007), higher than most of the general oilseed harvests such as *Jatropha curcas* – 40%, *Pongamia pinnata* – 30%, and oil palm – 60% (Azam et al. 2005).

Mechanical screw pressing and solvent extraction with organic solvents are commonly applied to extract vegetable oils. Mechanical extraction by using a screw press is regarded as one of the oldest and widespread processes in the world for extracting vegetable oils from seed kernels (Khan & Hanna 1983, Mrema & McNulty 1985). Screw press is generally used for pre-pressing seeds with high oil contents (Matthäus 2012). This technique has relatively low initial and operational costs, and produces uncontaminated oil (Fasina & Ajibola 1989). Mechanical pressing oil extraction is technically less expensive and labour intensive in comparison to the solvent extraction technique (Uquiche et al. 2008). The principal reasons for the appeal of mechanical oil expellers in some developing countries are the simplicity of the equipment, and the ease of maintenance due to its strong construction, as well as the fact that only semi-skilled supervisors are required to operate this machine (Pradhan et al. 2011).

Moreover, the adaptation of this technique for different kinds of oilseeds is quick, and the extraction process is continuous with the product obtained within a few minutes after starting the machine. Furthermore, mechanical screw pressing produces a chemical free protein rich cake, unlike the chemical technique (Haumann 1997, Singh & Bargale 2000). It has been noted that the screw press performance for a given oilseed depends on the preparation of raw material (Singh et al. 2002). However, the mechanical screw press technique is not considered adequately as its oil extraction efficiency is quite low (Bargale et al. 1999, Willems et al. 2008). Mechanical screw presses are relatively inefficient, leaving about 8-14% of available oil in the de-oiled cake (Ali & Watson 2014). It has also been found in mechanical screw pressing that pre-treatment of seeds and the heating of the press head of the oil expeller improved oil yield, which was also moisture dependent (Mrema & McNulty 1985, Zheng et al. 2003) and applied pressure (Jacobsen & Backer 1986).

On the other hand, solid-liquid extraction is a general and effective method of extracting oil for biodiesel production (Forson et al. 2004). The solvent or chemical extraction has become the widespread process of oil extraction due to the high percentage of oil recovery. The solvent or chemical extraction technique recovers almost all oils, with just 0.5% to 0.7% oil remaining in the raw material (Topare et al. 2011). In addition, this process applies to any low oil content

sources. This technique can also be applied for pre-pressed oil cakes which are obtained from high oil content sources. Furthermore, this technique is used in large-scale food industry for the production of vegetable oil (Matthäus 2012). A system integrating the extraction and transesterification of oil from jatropha seeds for the production of biodiesel has been investigated with hexane (Lian et al. 2012).

There are usually various parameters that affect the solid-liquid extraction technique, including nature of the solvent and oil, reaction time between solvent and kernels, the size of kernels, processing temperature of the method, the particle size of the feedstock and the solid /solvent ratio (Sayyar et al. 2009). It has been observed that the optimum conditions for oil extraction for vegetable seed kernels are 8 hours reaction time, reaction temperature up to the boiling point of the solvent and the solid/liquid ratio of 1:6 g/mL (Sayyar et al. 2009). More advanced liquid solvent techniques showed that oil extraction from seed kernels with the solvent at high temperatures improved solubility due to a decrease in viscosity and increase in mass transfer rate.

The oil output in chemical extraction depends on different factors, including the type of solvent, extraction temperature and agitation intensity (Atabani et al. 2013a, Kostić et al. 2013), the solvent: seed ratio and the extraction time (Kostić et al. 2013, Stanisavljević et al. 2007). Due to the larger interfacial area between the solid and liquid, a small particle size is preferable. The liquid has to be chosen in such a way that it would be a good elective solvent, and its viscosity would be sufficiently low to circulate easily. However, it has also been found that the chemical extraction has an adverse environmental impact because of wastewater generation, higher specific energy consumption, higher emissions from volatile organic compounds as well as human health influences (working with hazardous and inflammable chemicals) (Atabani et al. 2013b, Kostić et al. 2014). However, solvent extraction is the most efficient technique in spite of having some industrial disadvantages such as plant security problems, emissions of volatile organic compounds into atmosphere and high operation costs (Uquiche et al. 2008).

Prior to seed pressing or oil extraction, the seeds (kernels) must undergo several pre-treatment processes such as drying, removal of husk (decorticating), cracking, flaking, crushing, cooking, extruding, as well as drying the seeds to expedite oil extraction and increase oil recovery (Chapuis et al. 2014, Zheng et al. 2003). The oil yield is increased by heating or cooking of oilseeds which induce the breakdown of oil cells, coagulation of protein, coordination of

moisture amount to the optimal value for pressing, and reduce the oil viscosity to allow the oil to flow more readily (Ward 1976). It has been found that the moisture content, as well as the temperature of kernels, are the dependent variables to estimate the efficiency of oil extraction technique (Ali & Watson 2014). The moisture content, seed preparation and cracking, kernel sizes and kernel treating conditions has a significant influence on oil yield. The significance of moisture content in the screw press technique has been discussed for a wide range of oilseeds in different studies (Ajibola et al. 1990, Mpagalile & Clarke 2005, Singh & Bargale 1990, Singh & Bargale 2000, Singh et al. 2002, Wiesenborn et al. 2001). Moisture content has a significant influence on screw pressing, and it has been found that seed kernels were softened by increasing the moisture content whereas the friction was increased by lowering the moisture content (Zheng et al. 2005). It has been found that moisture content has a significant effect on oil yield in n-hexane technique (Jahirul et al. 2013).

In order to reap full benefits from Australian BL kernel, it is first necessary to ascertain the appropriate oil extraction technique and then its optimisation. Although several studies have been conducted on oil extraction and optimisation from different feedstocks, very few studies have been conducted on oil extraction and optimisation from BL kernel using different kernel size (WK or GK) with different moisture contents. Therefore, the purpose of this study was to optimise extraction process from BL kernel using different kernel sizes with different moisture contents using both mechanical (screw press) and solvent (n-hexane) extraction techniques. In addition, several optimising parameters, such as fruit cracking, kernel separation, and kernel treatment (drying) were also considered in this study. Furthermore, different kernel to solvent ratios was also considered in the case of solvent extraction.

3.2 Materials and Methods

3.2.1 Fruit Collection

The BL grows in tropical as well as sub-tropical climates. The BL cultivation does not compromise cultivable lands, and it can be grown in degraded and less fertile soils (Little Jr & Skolmen 1989). Furthermore, the BL grows in free draining, less fertile soils in different regions of southern and central Asia such as Sri Lanka, India and Australia. Approximately 140 kg of mature fruits that were fallen on the ground were collected from the wild plants from

Queensland, Australia. These fruits were air dried in a garden shed before extracting the kernels.

3.2.2 Seed Preparation and Cracking

The pre-requisite for oil extraction is seed preparation. Two methods were used for seed extraction: the use of stompers or rubber mallets. By using a large stomper, fruits can be cracked at once by placing the fruits on a hard surface, and separating the kernels manually from the husk. It was possible to crack several fruits at a time by using the stompers (Jahirul et al. 2013). In mallet cracking, the individual fruit was manually cracked open.

3.2.3 Kernel Extraction

The kernels are contained in a semi-hard shell, as shown in Figures 3.1 (a) and (b). The kernels and the husk were detached after cracking of fruits as shown in Figures 3.2 (a) and (b). The first stage of preparation of seeds for oil extraction was removing the outer layers of the fruit (husk) to expose the kernel. The kernels were extracted by cracking open the fruits using stompers or mallets as mentioned before. The kernels which were extracted from the fruits each had a dry weight of about 5 g. The separated kernels were stored at room temperature.

About 51 kg of usable kernels were obtained from 140 kg of air-dried fruits. This translates to a seed content of approximately 36%. Often rubber-headed mallets were selected rather than the wooden or steel-headed mallets. The effectiveness of the stomper was not uniform between batches as the stomper only hits the larger fruits.

a   b

Figure 3.1: (a) BL Fruit with the shell (husk), and (b) BL kernel.

Overall, it was observed that kernel extraction is a time-consuming as well as labour-intensive process. Mechanical methods that are being employed in macadamia industry are therefore needed. It was calculated that around 2-3 kg of seeds were cracked per operator per hour. Hence, the cracking process should be automated to make this process economically viable.

a   b

Figure 3.2: (a) BL fruit cracking and (b) kernel separation.

3.2.4 Kernel Grating

In this study, both WK and GK were used to perform the experiment. The kernels were grated using a grinder to achieve a fine consistency (particle size 0.5 mm-0.8 mm) to maximise the particle surface area.

3.2.5 Kernel Drying

The kernel has to be prepared in such a way that it contains optimum moisture for maximum oil extraction. The kernels were dried at a desired temperature prior to oil extraction. Ashwath (2010) dried the kernels at 60 °C for 3 days in an oven to extract BL oil by using screw press and *n*-hexane. Jahirul et al. (2013) dried the kernels at 50 °C–70 °C for up to 5 days to extract oil by using both screw press and n-hexane techniques. *Hodgsonia macrocarpa* seed kernels have been dried at 80 °C for 8 hours to extract oil from this species (Cao & Zhang 2015). The drying process was conducted using a laboratory scale Clayson electric oven with a temperature controller. There were 12 samples (4 of WK and 8 of GK) of the kernel which were placed in aluminium trays, and each tray contained 1 kg of kernels and were distributed evenly as shown

in Figures 3.3 (a) and (b). One further sample was dried at 65 °C for 3days-5 days as a representative sample to determine the total moisture content.

<div align="center">

a   b

Figure 3.3: Kernel drying in the oven: (a) WK and (b) GK

</div>

Kernels (WK and GK) that were used in the current study were obtained from several trees were dried at 50 °C–65 °C for 2 days–3 days in an oven to determine the effect of mulching as well as temperature on drying rate. The drying process was performed very carefully by weighing the trays several times in a day, and the samples were also mixed up to ensure uniform drying. For drying rate comparison, the percentage weight loss of the WK and GK used for screw press extraction are displayed against drying time as shown in Figures 3.4 (a) and (b), respectively. The percentage weight losses of GK used in n-hexane extraction are plotted against drying time in Figure 3.5. After reaching the desired dryness (moisture content), the trays were removed from the oven and stored in a refrigerated room. The representative sample was dried completely until no moisture loss occurred to determine the total moisture content of the kernel. The absolute moisture content of this sample was used to determine the relative moisture content of the other samples. The standard error (SE) was calculated from the SD. The SD for all the samples was calculated using the following equation:

$$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})} \tag{3.1}$$

Where, s is the SD, N is the total number of samples, x_i is the sample value (i = 1, 2, 3, 4----- n), and $\bar{x}$ bar is the sample mean value. The SE values have been included as shown in Figures 3.4, 3.5, 3.9, 3.11 and 3.12.
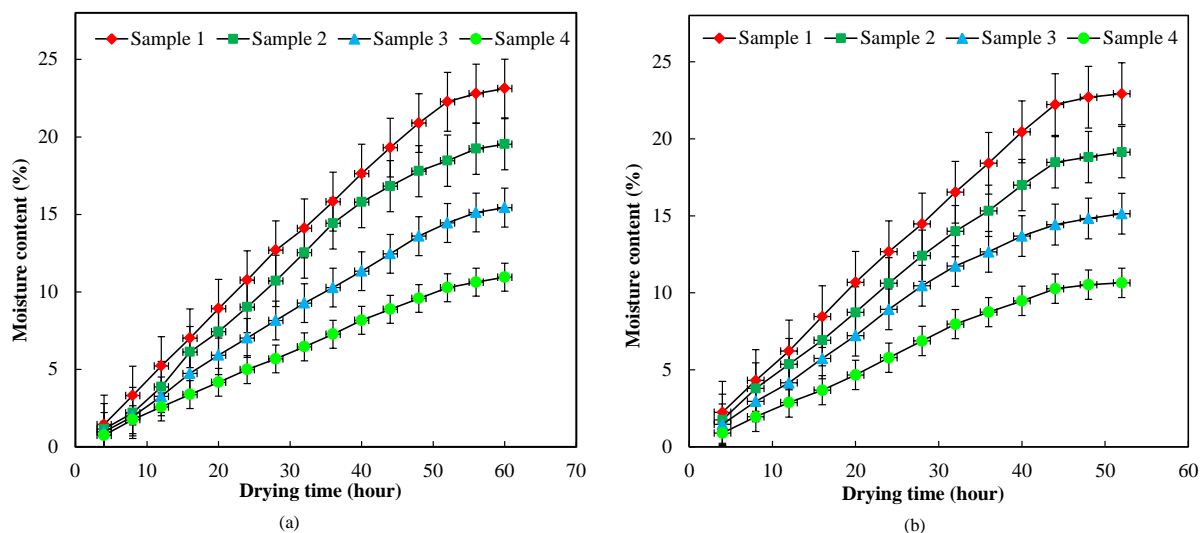
Figure 3.4: Kernel drying to extract oil using screw press technique: (a) WK and (b) GK (Error bars represent the standard error (SE))
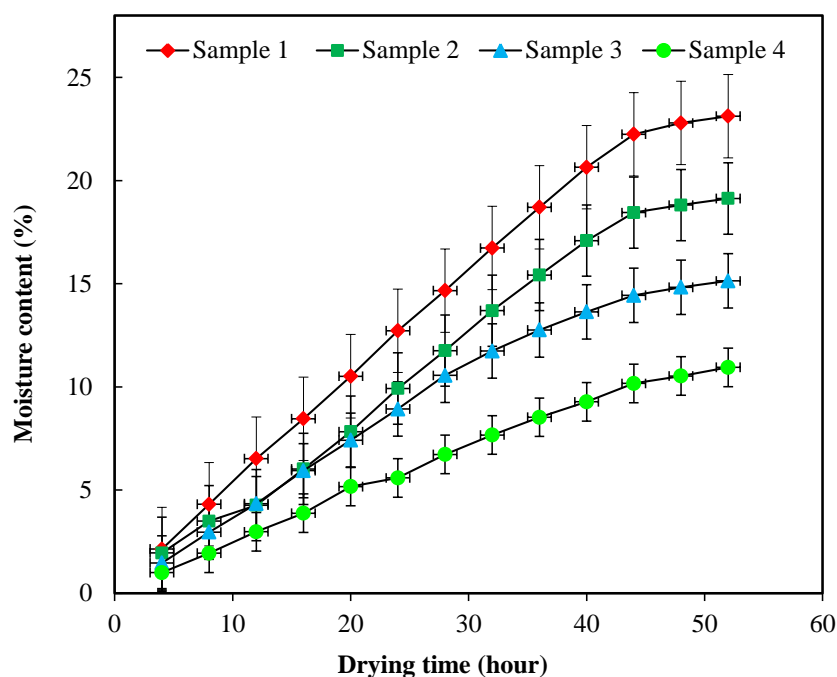
Figure 3.5: Kernel drying to extract oil using n-hexane technique (GK) (Error bars represent the SE)

It can be seen from Figures 3.4 (a) and (b) that the moisture content for samples 1, 2, 3 and 4 (both WK and GK) were estimated as 10.2%, 14.4%, 18.5% and 22.3% after properly treating the kernel samples, that is, after percentage weight loss of the kernel samples which were dried at varying temperature settings, respectively. In terms of GK in n-hexane technique, it can be seen from Figure 3.5 that the moisture contents of 10.2%, 14.4%, 18.5% and 22.3% were observed for samples 1, 2, 3 and 4, respectively. It has been found from the literature that

kernels prepared to 15% moisture content gave the highest oil yields in both mechanical and solvent extraction techniques (Jahirul et al. 2013). These kernel samples were used to optimise the oil extraction for both screw press and n-hexane techniques.

3.2.6 Extraction of Oil

Two methods, namely mechanical oil extraction using an electric powered screw press and chemical (solvent) extraction using n-hexane as a solvent were used for oil extraction from the ready seed kernels. In both techniques, experiments were performed to determine the optimum moisture content for achieving maximum oil extraction. The flowchart of the full oil extraction protocols for both whole and GK is shown in Figure 3.6.

3.2.6.1 Mechanical Extraction or Screw Press Extraction

The oil extraction method by mechanical presses is the most orthodox method amongst the other methods. Either a manual ram press or an engine driven screw press is generally used in this technique. It has been found that the engine driven screw press can extract 68%-80% of oil as shown in Table 3.1 (Achten et al. 2008, Atabani et al. 2013b, Beerens 2007, Rabé 2006, Tewari 2007).

This higher range is due to the fact that seeds can be subjected to some extractions through the expeller (Achten et al. 2008, Atabani et al. 2012, Atabani et al. 2013b, Mahanta & Shrivastava 2004). The mechanical oil extraction technique was conducted using a mini 40 screw press as shown in Figure 3.7. Oil extraction was achieved due to the axial pressure generated by volumetric compression along the screw press as well as the rotating worm shaft applied force inside a pressing cylinder, which results in the squeezing of the oil from the kernels.
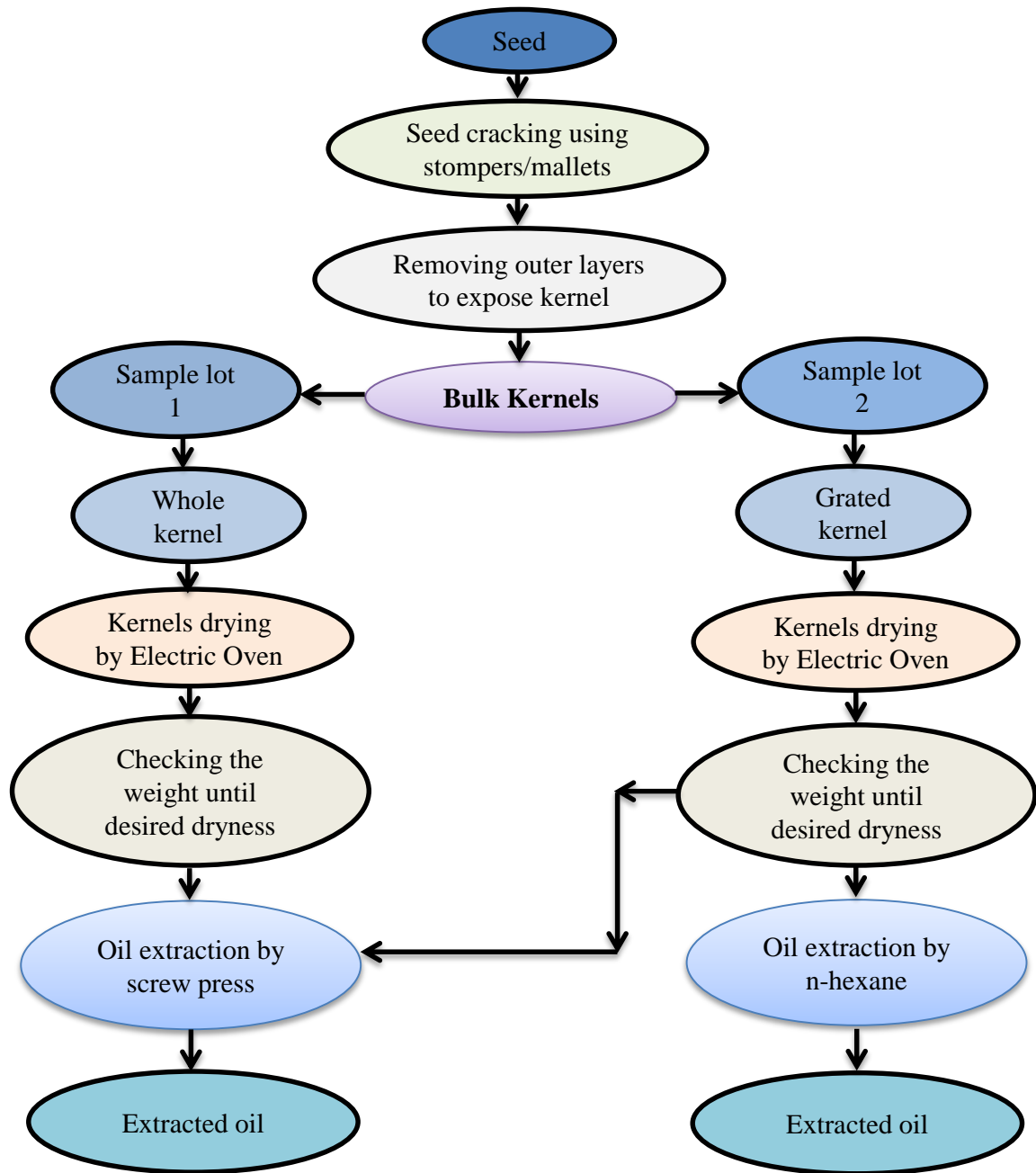
Figure 3.6: Flowchart of full oil extraction protocol, for both WK and GK

Table 3.1: Calculated oil yields (%) obtained by mechanical extraction methods (Achten et al. 2008, Atabani et al. 2013b, Beerens 2007, Forson et al. 2004, Rabé 2006, Tewari 2007).

Press	Oil yield (%)	Necessary treatment
Engine driven screw press	68.0	Filtration and degumming
	80.0	
	79.0	

Some authors reported that heat is generated inside the expeller due to friction between the oil bearing material and the device (Singh & Bargale 2000, Zheng et al. 2005). Properly dried and treated BL kernel samples were used to extract oil using this method. Pre-treatment of the seeds by a cooking process can increase the oil yield of screw pressing up to 89% after a single pass and 91% after dual passes (Achten et al. 2008, Atabani et al. 2012, Mahanta & Shrivastava 2004). Four replications of WK and 4 samples of GK were used to conduct the experiment in screw press method. The kernel samples were ground using a heavy duty blender. The operator was required to attend constantly and operate the machine. WK samples were passed 2-3 times, and GK samples were passed 2 times into the screw press to increase the oil yield and to recapture the oil from the residual and cake and sediment materials. It was observed that the rate of oil production was slow as it was a mini screw press. It could be noted that the GK provided the higher oil yields than the WK. However, a noticeable increase in workability was achieved with the dried samples and resulted in earlier oil extraction.

The dried samples made the process less laborious. The design of the mechanical extractor is very important in conventional mechanical pressing techniques since the oil yield is affected by the type of mechanical extractor used. As the screw press used in this experiment was not designed for BL kernel, it faced a few difficulties during oil extraction. Therefore, some adjustments were made to appropriately control the operation of the press during the experiment.

Figure 3.7: Mechanical oil extraction: (a) electric powered screw press, (b) oil extraction through screw press and (c) oil separation from cake

For instance, cling wrap as well as a plastic container were used around the barrel to capture any spilt material for the specific purpose of keeping mass control as precise as possible to give the most valid oil yield results. During the extraction process, a lot of cake materials were produced in this technique. The cake materials were collected and stored

for further analysis. It can be noted that oil extraction by a screw press needs extra treatment for filtering as well as degumming process (Atabani et al. 2013b).

3.2.6.2 Chemical or Solvent Extraction (n-hexane Extraction)

Solid-liquid extraction, occasionally called leaching, includes the removal of a soluble fraction (the solute or leachant) from a solid material to a liquid solvent. The solute diffuses from the solid into the surrounding solvent. Four replications of GK were used in n-hexane technique to perform the oil extraction. Then n-hexane was added at a ratio of 2:1 (ml hexane: grammes kernel) into conical flasks in which ground kernels were placed. The kernel n-hexane mixture was mixed initially to ensure that all the kernels were soaked in n-hexane. Aluminium foil was used to cover the conical flask openings, and then the flasks were placed on the orbital mixture shaker to agitate the samples. The kernel and n-hexane mixture samples were left to run at least 8 hours in this condition. Then the oil-hexane solutions were collected, vacuum filtered and decanted into aluminium containers for evaporating the solvent by placing the trays in a fume hood as shown in Figures 3.8 (a) and (b) for 8 hours-12 hours. Ashwath (2010) and Jahirul et al. (2013) conducted the solvent extraction technique using n-hexane to extract oil from BL kernels (*Calophyllum inophyllum*).

| a | b |
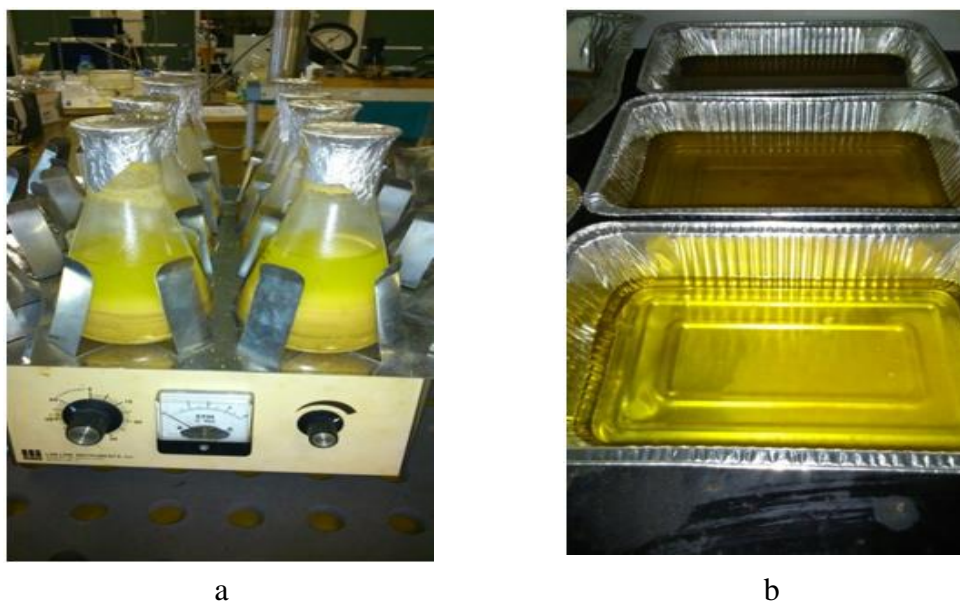
Figure 3.8: n-hexane oil extraction showing: (a) conical flasks with oil content in the shaker, and (b) oil yield in the trays

For the second extraction, n-hexane was added at a ratio of 1:1 to the conical flasks which contained the kernels. This way, up to a fifth extraction was completed by following a similar procedure to extract the last trace of the oil. After ascertaining the full evaporation of n-hexane, the oil was transferred into containers for additional analysis. After extraction of oil, the cake and sediment materials were collected, weighed and stored for further analysis.

3.3 Results and Discussion

3.3.1 Oil, Cake and Sediment Recovery

The properly treated WK and GK were used in both screw press and n-hexane techniques for oil extraction and optimisation. Figure 3.9 presents the oil recovery of dried kernel samples with different kernel types (WK and GK) at different moisture contents (10.2%, 14.4%, 18.5% and 22.3%) for those techniques. It can be noted that the kernel size and moisture content has a significant influence on oil yield. At lower moisture content the oil yield was higher; however, the oil recovery decreased with increase in moisture content for the WK and GKs in both screw press and n-hexane techniques. The highest oil recovery was observed at 14.4% for the WK and GK. It can be seen from Figure 3.9, the oil yield varied in terms of kernel types (WK or GK) in both screw press and n-hexane extraction techniques. The GK (particle size 0.5 mm-0.8 mm) showed the higher yield than the WK. The results indicated that the highest oil recovery found 54% for the GK for sample 2 at 14.4% moisture content in n-hexane technique. On the other hand, in screw press method the highest oil yield of 45% was obtained for the GK for sample 2 at 14.4% moisture content.
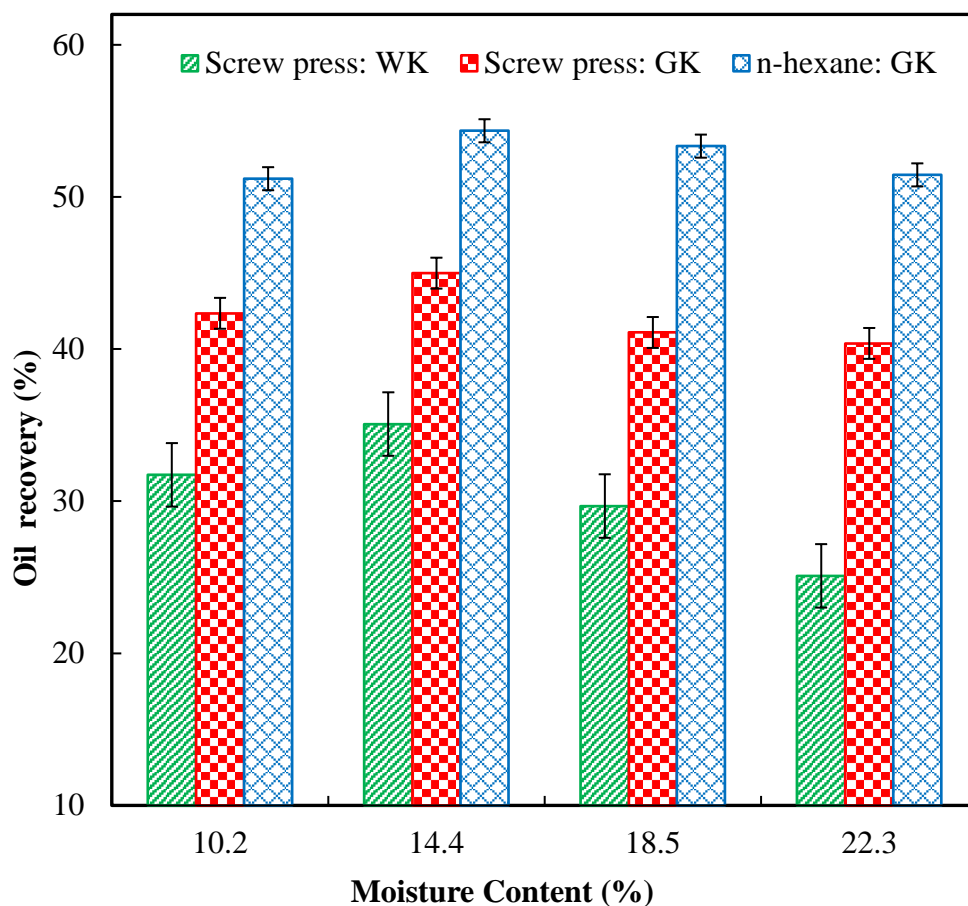
Figure 3.9: Oil recovery with moisture content at different kernel types for both screw press and n-hexane techniques (Error bars represent the SE)

In terms of GKs, 20% higher oil yield was observed in n-hexane technique in comparison to the screw press technique. In screw press method, the highest oil yield of 35% was obtained for the WKs for sample 2 at 14.4% moisture content. The lowest oil yield was observed for sample 4 at 22.3% moisture content in all cases. It can also be noted that drying makes the kernel tissues soft and lowers the viscosity. The cellular structure tended to weaken and was made highly susceptible due to the softening of tissues, whereas the oil flow rate was increased because of low viscosity and as a result, the oil recovery was enhanced (Indrasari et al. 2001). It is necessary to dry the kernel sufficiently for adequate coagulation of protein, the breakdown of oil cells and reduction in viscosity (Pradhan et al. 2011).

The enhanced oil recovery efficiency could be attributed to reduced viscosity of the oil in the capillaries of the kernel tissues (Fasina & Ajibola 1989). Furthermore, the increases in moisture content resulted in a decrease in oil recovery. This can be attributed to mucilage development on oil cells (Vaughan 1970). It could be illustrated that at higher moisture content swelling of

mucilage produced a cushioning effect on the kernel. There might have been an impediment to oil flow in the swollen mucilage during expression while the cushioning effect on the kernel reduced the breaking up of the particles and internal tissues when the pressure was applied. It could also be illustrated that higher moisture content increases plasticity and thus reduces the level of compression, and this could contribute to poor oil recovery (Singh & Bargale 1990). It is believed that the presence of water in the kernels made a significant difference to oil yield (Lim & Lee 2013). Furthermore, higher moisture content is due to the presence of higher amount of water particles inside the seeds which creates an immiscible interlayer boundary between the lipid and the miscella. Subsequently, this reduces the diffusion velocity of the lipid particles into the solvent and thus decreases the overall extraction rate (Franco et al. 2009, Karlovic et al. 1992, Nagy & Simándi 2008).

On the other hand, low moisture content (14.4%) was particularly important, but further reduction in moisture content (10.2%) was not beneficial and resulted in more cake and sediment in the oil (Vargas-Lopez et al. 1999). A comparison of oil recovery between screw press and n-hexane techniques illustrates that oil yields obtained from solvent extraction using n-hexane was higher than that of the mechanical technique using screw press. This is because n-hexane reacts with the kernels and n-hexane had sufficient time to extract the oil from inside the kernels. On the other hand, in screw press method, the kernels were just squeezed by the applied force of the worm shaft for a shorter period and, therefore, the oil comes out from the kernels readily. It has been found that the oil yield obtained by mechanical (screw) pressing was lower than that of the solvent extraction technique (Bargale et al. 1999, Willems et al. 2008).

Figure 3.10 shows the relation between oil recovery and kernel throughput with respect to kernel preparation on the basis of dry (treated) weight of the kernel. From Figure 3.10, it can be noted that the oil recovery tends to decrease with increasing material throughput except n-hexane technique. It is apparent that the increase in material throughput consumes a lower residence time and hence, lowers the oil recovery efficiency. However, in hexane technique, the oil recovery with respect to kernel throughput is always constant for a particular replication, but it varies with varying the replication numbers. It can be noted from Figure 10 that the highest (48.6%) and lowest (22.4%) oil recovery was obtained for the GK and WK kernel in screw press technique for the moisture content of 14.4 and 22.3%, respectively.
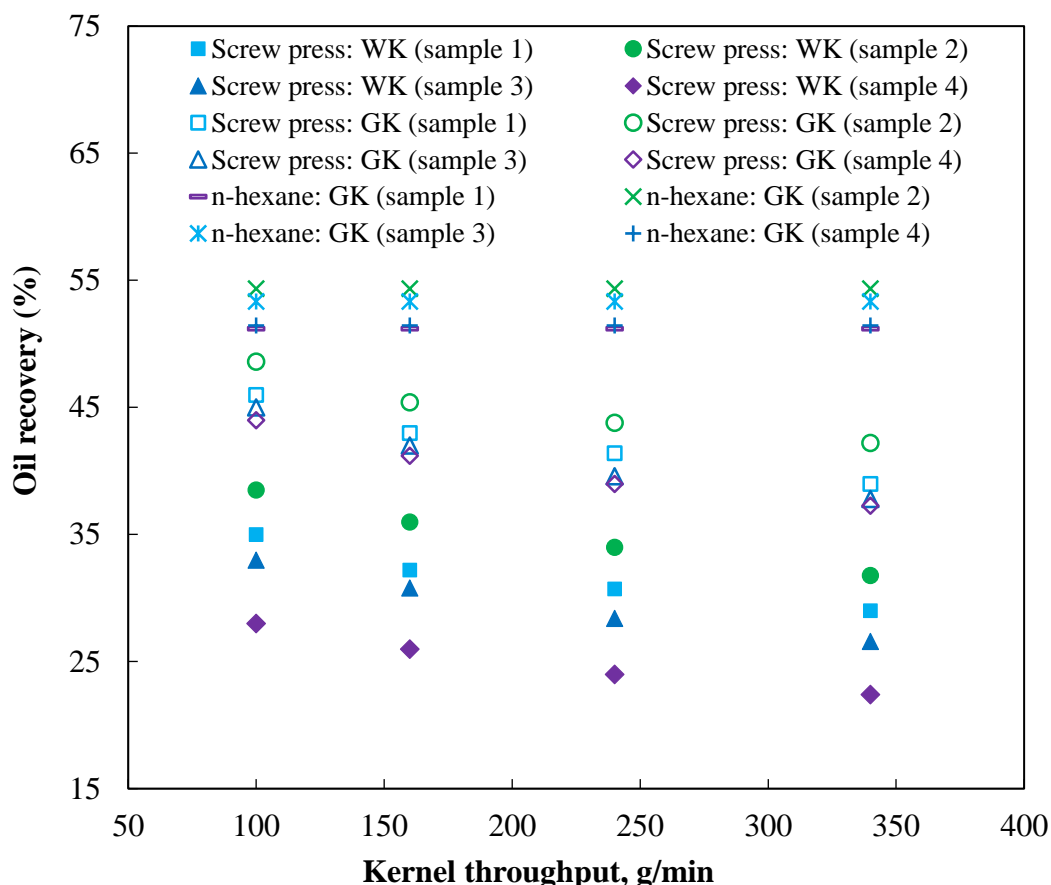
Figure 3.10: Relation between oil recovery and kernel throughput for the WK and GK

The dry matter, that is, cake and sediment that was obtained in both screw press and n-hexane techniques for different moisture contents and kernel sizes is shown in Figure 3.11. The highest cake and sediment recovery was observed for the WK than the GK as shown in Figure 3.11. The highest cake and sediment recovery of 60% was observed in screw press technique for the WK at 22.3% moisture content for sample 4. On the other hand, in n-hexane method the highest cake and sediment recovery of 39% was found for the GK at 22.3% moisture content for sample 4 which is 18% lower than the screw press method. As expected, the lowest cake and sediment recovery was observed for sample 2 in all extraction techniques for WK and GKs.
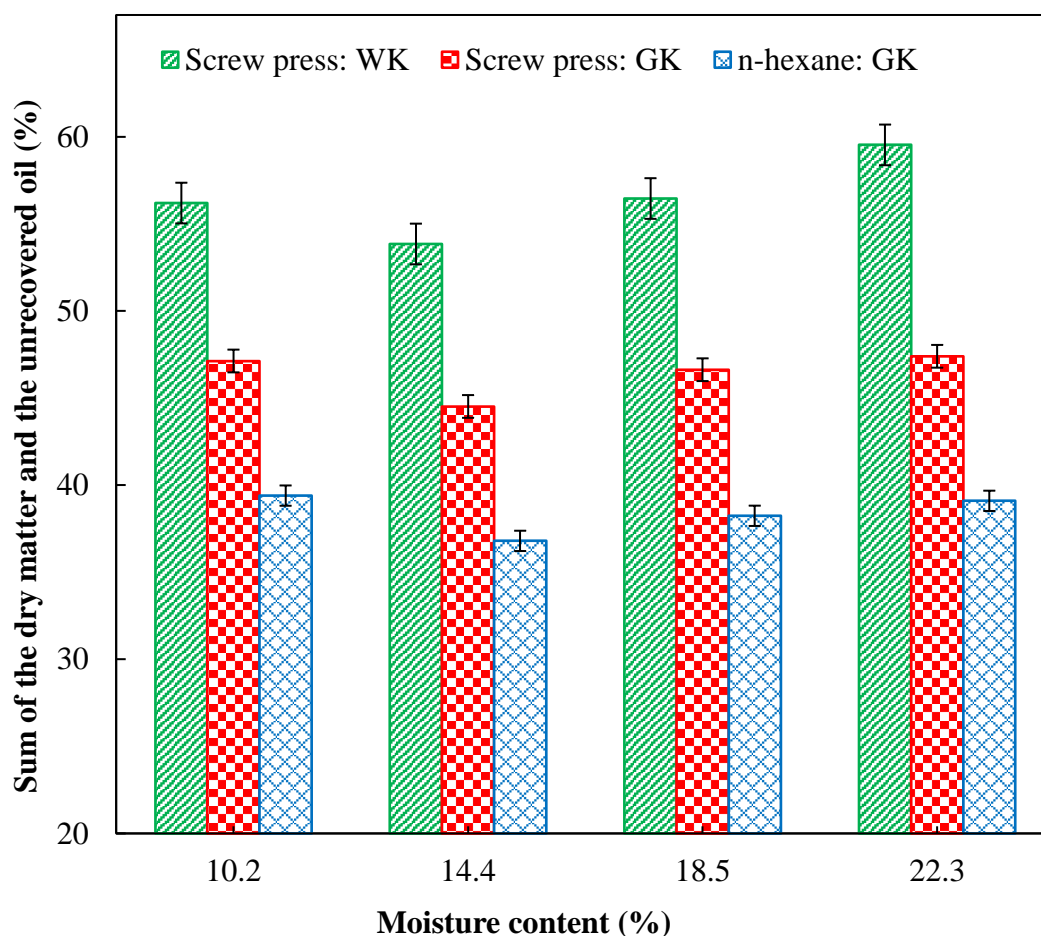
Figure 3.11: Sum of the dry matter and the unrecovered oil with moisture content for different techniques and kernels (Error bars represent the SE)

Figure 3.12 shows the recovery of all components (oil, residual oil, cake and sediment) with different methods and kernel types at 14.4% moisture. From Figure 3.12, the maximum oil, residual oil, cake and sediment recovery of 54%, 8% and 54% was observed for n-hexane GK, screw press WK and screw press WK, respectively. The screw press method is a comparatively low-cost after initial investments.

Although the oil extraction using the screw press technique was obtained at a low cost, this is ineffective due to relatively lower oil recovery. Mahanta & Shrivastava (2004) reported that the mechanical presses are not efficient for extraction of oils because of the problems associated with non-edible seeds. Furthermore, this process is labour intensive. However, optimising the key design factors of the oil expeller, including pressure, compression ratio, speed as well as hot pressing, the BL oil extraction using this technique can be increased. On the contrary, the n-hexane technique was found to be very effective because of high oil recovery efficiency and for its consistent performance.
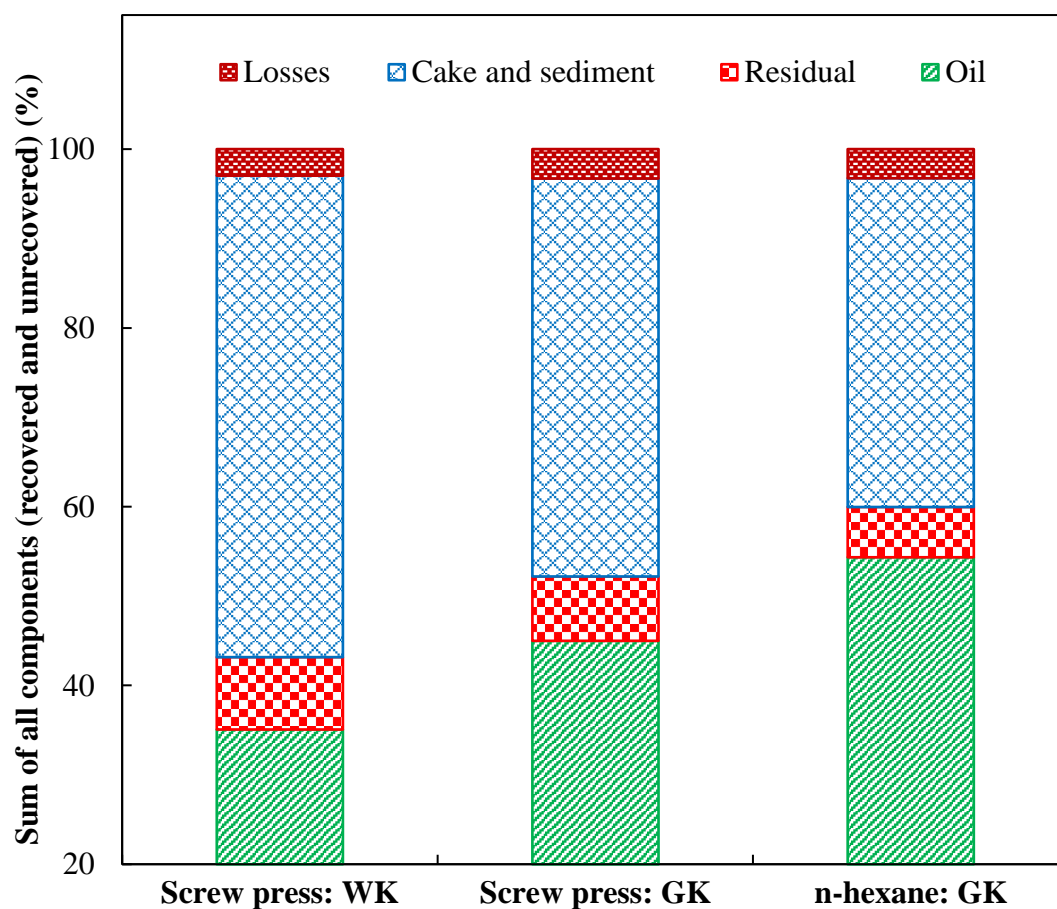
Figure 3.12: Sum of all components with different methods and kernel types at 14.4% moisture content

Overall, this technique is simple with comparatively easy processing arrangements, no extensive training requirement, and reproducible results. The details of relative advantages and disadvantages of both techniques are given in Table 3.2.

Table 3.2: Advantages and disadvantages of oil extraction between screw press and n-hexane techniques (Ali & Watson 2014, Jahirul et al. 2013).

Methods	Advantages	Disadvantages
	Virgin oil is more sought after	Generally ineffective for processing BL kernel
	No potential for solvent contamination	Labour intensive
	Relatively inexpensive after initial capital costs	Relatively low oil yield

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Screw press	Minor consumable costs	Operators require skill to attain best outcomes
	Whole seeds or kernels can be processed	Significant dependency on kernel treatment, i.e., moisture quantity
	No environmental concerns about the use of screw press	Comparatively dirty technique
		Filtration or degumming process for oil is required
		Low and inconsistent oil production
		High oil loss
n-Hexane	Repeatable and reproducible results and process	Less sought after than virgin oil
	High oil yields	High potential for solvent contamination
	Relatively simple and easy	Safety issues and environmental concerns
	Suitable for bulk oil extraction	Very costly if the hexane cannot be recovered
	Low capital investment	High hexane requirement
	No special equipment required	Only kernels can be processed
	Decrease cost considerably if n-hexane can be recaptured and reused	

Comparison of fossil energy ratio (FER) ratio which is the energy output from the products to the energy input to the system, between these two methods has been included in Table 3.3.

Table 3.3: Fossil Energy Ratio (FER) between screw press and n-hexane methods

Actions/Treatments	Screw press technique	n-hexane technique	Energy factor [source]
Energy input for BL crude oil extraction/production			
Kernel preparation	√	√	
Kernel grating	√	√	
Kernel Treatment	√	√	
Oil extraction	28.8 MJ	18 MJ	

Chemicals (n-hexane)	-	2.67 MJ	0.164 MJ/L (Gas Heating Value 2016)
Crude Oil Refining	√	√	
Degumming	√	√	
Neutralizing	√	√	
Dewaxing	√	√	
Energy input for biodiesel production			
Biodiesel production	√	√	
Methanol	√	√	
Sodium hydroxide	√	√	
Sulphuric acid	√	√	
Power for completion of reaction	√	√	
Energy output from produced biodiesel and by-products			
BL biodiesel	**34.18 MJ**	**48.76 MJ**	**37.38 MJ/kg for n-hexane and 37.58 for screw press technique**
Glycerol	1.77 MJ	2.17 MJ	19 MJ/kg(Prueksakorn & Gheewala 2008)
Cake and sediment	40.24 MJ	33.28 MJ	25.9 MJ/ kg
FER	3.70	4.10	

It can be noted from Table 3.3 that net FER in n-hexane technique (4.10) is higher than the screw press technique (3.70). In a comparison of both (screw press and n-hexane) methods, the results revealed that the n-hexane technique is better in regards to producing higher oil recovery as well as fossil energy ratio.

The full benefit of n-hexane technique could not be achieved because of the absence of an n-hexane retrieval system in this study. The main barrier for the n-hexane extraction process is the cost of solvent as well as time requirement. Therefore, it is strongly suggested to use an n-hexane retrieval system to reduce the cost of oil extraction through this process.

3.3.2 Physico-Chemical Properties of Crude Beauty Leaf Oil (CBOL)

The physico-chemical properties of crude BL oil that were extracted using both screw press and n-hexane techniques were evaluated according to the ASTM standard. The average value of the replications for each property has been set out both in screw press and n-hexane techniques. It can be seen from Table 3.4 that the density, viscosity, acid value and free fatty acid (FFA) are higher in oil of screw press technique in comparison to n-hexane technique. On the contrary, the calorific value, cetane number, pH and oxidation stability are higher in oil of n-hexane technique compared to screw press technique. The higher calorific vale, cetane number, pH and oxidation stability indicates the good quality of oil. These results are supported by several researchers (Atabani & César 2014, Atabani et al. 2013a).

Table 3.4: Physico-chemical properties of crude beauty leaf oil (CBLO)

Properties	Units	Test method	CBLO		
			Extraction by screw press	Extraction by n-hexane	SD value of n-hexane technique
Density at 15 °C	kg/m^3	ASTM D4052	941	937	±0.133
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	53.18	52.67	±0.060
Viscosity index	-	-	163.6	163	±0.160
Acid value	mg KOH/g	ASTM D664	40.24	38.86	±0.040
Calorific value	MJ/kg	ASTM D240	37.582	37.83	±0.051
Flash point	°C	ASTM D93	226	223	±0.130

Pour point	°C	ASTM D2500	7	6	±0.060
Cloud point	°C	ASTM D2500	8	8	±0.090
Cold filter plugging point	°C	ASTM D6371	23	22	±0.100
Cetane number	-	ASTM D6890	51	52.2	±0.071
Iodine value	g I$_2$/100 g	EN 14111	87.3	85	±0.130
Saponification value	mg/g	-	194	192	±0.110
pH at 26 °C	-	-	4.46	4.58	±0.050
Free fatty acid (FFA)	(wt.%)	-	20.23	19.54	±0.090
Oxidation stability	hour	EN 14112	0.26	0.28	±0.010

3.3.3 Accuracy and Uncertainty Analysis

The accuracy of the measuring equipment and the uncertainty analysis of the measured values are significant to validate the accuracy of the experimental results. The accuracy and uncertainty analyses were also performed by the measured values to validate the experimental results. Uncertainties occur under different experimental conditions, selection and calibration of the instruments, observation, data input, test assembly and so on (Imdadul et al. 2016, Sajjad et al. 2015). The uncertainty of different measured quantities, such as density, kinematic viscosity, acid value, calorific value, flash point, pour point, cloud point, cold filter plugging point, cetane number, iodine value, pH and oxidation stability were calculated using the percentage uncertainties of the various instruments used. A sample calculation of uncertainty analysis for crude oil properties was done and provided in Appendix A (Table A.1). Table A.2 (Appendix A) shows the measurement accuracy values and uncertainty of the measured quantities.

3.4 Conclusions

The study indicated that seed preparation, seed cracking, kernel sizes, seed kernel treatment (drying) and moisture content have a significant influence on oil recovery for both screw press and n-hexane extraction techniques. The highest oil recovery of 54% was obtained in n-hexane technique with GK at 14.4% moisture. Oil recovery from screw press technique for both whole and GK was lower than the n-hexane technique. It was also found that oil yields from GK were 10% higher than the WK using screw press method. The residual oil as well as cake and sediment recovery was found higher in screw press technique for the GK than the n-hexane technique which is 12% and 60%, respectively. The physico-chemical properties of the crude BL oil were characterised and the results indicated that the calorific value, cetane number, pH and oxidation stability are higher in oil of n-hexane technique than the screw press technique whereas, density, viscosity, acid value and FFA are higher in oil of screw press method in comparison to n-hexane technique. A comparison of FER between those two techniques was made and the results indicated that the n-hexane technique is more effective than the screw press technique. The FER of 4.10 and 3.70 was obtained for n-hexane and screw press technique, respectively.

Although oil extraction using screw press technique was attained at a cheaper cost, this technique is ineffective due to relatively lower oil yields compared to n-hexane technique. On the contrary, n-hexane technique was found to be a very efficient process for oil extraction because of its consistent performance and high oil yield. In spite of having solvent cost for the production of oil in n-hexane technique, a solvent recycling system can reduce the cost of solvent to extract oil from BL kernel. Therefore, it is strongly recommended to use n-hexane recovery systems to get the full benefits and to reduce the production cost of oil in this process.

CHAPTER 4

REFINING OF CRUDE BEAUTY LEAF
(*CALOPHYLLUM INOPHYLLUM* L.) OIL

The refining processes, such as degumming, neutralisation and dewaxing were carried out to remove gums (phospholipid compounds), free fatty acids and waxes, respectively, from the beauty leaf (BL) crude oil before the oil was converted into biodiesel. The crude oils used were obtained from solvent (n-hexane) or mechanical (screw press) extraction techniques. Five replications each of 25 g of crude oil from screw press and n-hexane extraction, respectively, were used in the refining process. The oil recovery efficiencies were calculated in terms of mass and energy from the crude oil extracted from the n-hexane and screw press techniques. The measured physico-chemical properties of the refined oil were evaluated according to the ASTM standard.

4.1 Introduction

Crude oil refining, prior to biodiesel production, is important as it can remove the chemicals that would hinder the transesterification process, and produce poor quality biodiesel. Fat and oil refining process involves a series of steps, such as degumming, chemical neutralisation and bleaching during which the oil is treated either chemically or physically (Marrakchi et al. 2015). The crude oils are generally refined by chemical methods to remove the undesirable constituents with minor losses of oil (Suliman et al. 2013). The refining of crude oil is a purification process which aims to remove all substances that contribute to undesirable flavour, odour and appearance (Akoh & Min 2008). It has been noted that the waste fats and oils, as well as crude vegetable oils and animal fats, contain noticeable quantities of accompanying substances (impurities) apart from free fatty acids (FFAs). The important undesirable compounds are phosphatides, gums, waxes, colour bodies, trace metals, pesticide residues, oxidation products, water and volatiles containing objectionable odours (Chew et al. 2016, de Moura et al. 2005, Ghazani et al. 2013, Shahidi 2005, Wei et al. 2015). These impurities must be removed, or their content must be significantly reduced to make the feedstock appropriate for biodiesel production by transesterification process. The chemical refining process generally includes degumming, neutralisation, bleaching and deodorisation (Farhoosh et al. 2009). However, the use of crude oil, without degumming, neutralisation and dewaxing, can create

difficulties such as emulsification in the transesterification process. The quality of refined oil, as well as the resulting biodiesel, depends on whether the above process is followed, and the extent to which treatments have been effective (O'Brien 2000).

Degumming is the first stage in refining process. The aim is to reduce phospholipid content of the oil to below 5 mg/kg of phosphorous (by using a physical or chemical techniques) (Šánek et al. 2015). In this process, the hydratable phospholipids are eliminated and the content of non-hydratable phospholipids, that is, the calcium or magnesium salts of phospatidyl ethanolamine and phosphatidic acid can also be reduced (Čmolík & Pokorný 2000). Degumming is generally performed by means of one of the following techniques: degumming with water, acid (phosphoric or citric acid) or enzymes (phospholipases), as well as using semi-permeable membranes (Carr 1978, Čmolík & Pokorný 2000, Jiang et al. 2011, O'brien 2008).

Chemical or alkali refining is the most commonly used industrial method for neutralisation or deacidification of fats and oils (Santori et al. 2012). This process allows the removal not only of the FFAs, but also of slime components, phospholipids and pigments (Larsson et al. 1994). Neutralization process is carried out after the degumming process via the addition of alkali to the oil or fat, thus the precipitation of the FFAs occurs, and this results in the formation of alkali soaps which are subsequently removed by centrifugation. The most widely accepted and used alkali for deacidification is sodium hydroxide (NaOH) as it is a strong alkali and is easily capable of neutralizing the FFAs (Bhosle & Subramanian 2005). However, the chemical neutralization of fats and oils will result in significant losses of neutral oil as a result of hydrolysis or the formation of occlusions in the soap. The resulting soaps are able to hold up to 50% of the neutral oil which significantly reduces the outcome of treated fat and oil (Gingras 2000). Subsequent esterification can be easily adjusted to ensure complete removal of the FFAs.

The vegetable oil also contains large amounts of waxes which appear as a cloud when the oil is refrigerated, or subjected below room temperatures. This could also be due to solidification of some fatty acids such as lauric acid. Therefore, these waxes have to be removed prior to biodiesel production. In this Chapter, BL crude oil was refined by degumming, neutralisation and dewaxing processes to produce refined oil.

4.2 Materials and Methods

4.2.1 Materials

The BL crude oils that were extracted by both n-hexane and screw press techniques were used in the refining process. Details of the oil extraction procedures have been described in chapter 3.

4.2.2 Reagents

The reagents, such as phosphoric acid (20% of H_3PO_4) and sodium hydroxide (NaOH) solution were used in this study. These chemicals were the Laboratory supplies. De-ionised water was used in all solution preparations, and tap water was used for washing purposes.

4.2.3 Apparatus

The 50 ml centrifuge tubes (Model: SARSTEDT) were used to perform the experiment. A hot plate magnetic stirrer (Model: IKA C-MAG HS7) was used in a Chemical and Biomedical Engineering Laboratory that was fitted with a fume hood. The laboratory was equipped with an essential equipment, such as centrifuge (Model: ThermoFisher D-37520), a balance (Model: TE1502S), thermometers (temperature range: 0 to 110 °C) and other glasses and plastic wares.

4.2.4 Oil Refining Processes

The BL oil contains large proportion of unsaturated fatty acids (oleic and linoleic) than saturated fatty acids (palmitic and stearic) (Ong et al. 2014a) and is also enriched with free fatty acids (FFA). Hence, it is necessary to remove the unwanted FFAs as they interfere with biodiesel conversion process by forming soap. In addition, the crude BL oil contains gums, phosphate, protein, carbohydrate, and resin. Therefore, refining of BL crude oil is necessary to obtain good quality biodiesel.

The BL crude oil refining was carried out using a series of steps, such as degumming, neutralising and dewaxing to remove undesirable constituents present in the oil (Bhuiya et al. 2015a, Bhuiya et al. 2015b) in accordance with various other researchers (Verleyen et al. 2002, Wang & Johnson 2001). The phospholipids and mucilaginous gums were removed by degumming process, the free fatty acids (FFAs) were removed through chemical neutralisation

process, and finally, the waxes were removed by dewaxing process (Marrakchi et al. 2015). The details of oil refining process are summarised in the flowchart (Figure 4.1).
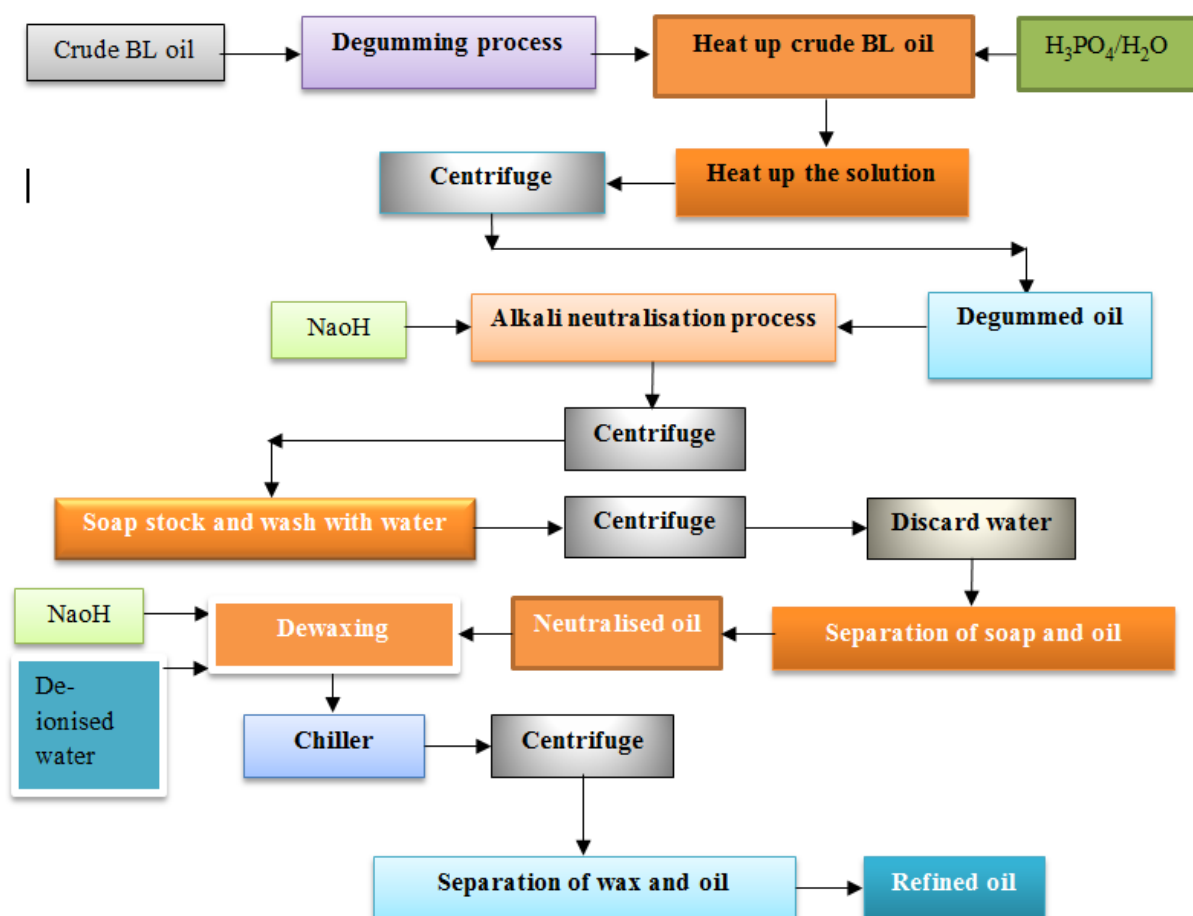
Figure 4.1: Process flowchart for oil refining

If the FFAs were not removed, they would convert into soap during transesterification process. It is also known that the presence of FFAs in the oil will reduce biodiesel conversion efficiency as the saponification process (FFAs reaction with NaOH) will utilise some of the catalysts used in transesterification (Capareda 2013). A summary of the treatments used in different stages of the refining process is shown in Tables 4.1 and 4.2, respectively.

4.2.4.1 Degumming

The degumming process was carried out to remove the gums from the BL oil, that is, to separate oil from the gum in order to improve oxidation stability of the oil (Ong et al. 2014a). Gums are phosphorous-based compounds, primarily lecithins and cephalins that are extracted from the fresh crude oil. Ten sets of crude oil samples (5 from n-hexane extraction and 5 from screw press extraction), each of 25 g were degummed in test tubes. First, the filtered oil was heated

up to 60 °C for about 2 hours and then hot (60 °C) deionised water (DI) was added. It has been found that a large proportion of water-soluble, and a smaller proportion of water-insoluble phospholipids can be removed from the oil during hydration by degumming process through adding hot water at certain temperature (Wei et al. 2015). It has also been found that degumming at 25 °C was insufficient to hydrate the gums, as only 66.1% of phospholipids were removed at this temperature.

Increasing the temperature above 25 °C (35 °C, 55 °C and 75 °C) led to significantly proportions of phospholipids (90.2%, 91% and 93%), respectively, were removed from the tea seed oil (Wei et al. 2015). The mixture was agitated for 1 hour by maintaining the temperature at 55 °C-60 °C. Acid degumming was carried out using 4 BL samples from n-hexane extraction and 4 from screw press extraction). Water degumming was performed for 2 of the 10 replications (1 from n-hexane extraction and 1 from screw press extraction). Acid degumming was performed by adding 4% (wt.%) H_3PO_4 solution. Liu et al. (2012) have shown that the optimum operating conditions for degumming process was 65 °C, 4% (wt.%) H_3PO_4 and 1600 rpm of centrifugation. It was also mentioned that under these conditions, the phospholipid content of the jatropha oil decreased significantly from 1200 ppm (parts per million) to 60 ppm. The solution was heated up to 65 °C and kept at this temperature for 30 min. After centrifugation, the hydrated gums could not be separated from the oil at this stage. The overall oil refining process is illustrated in Figure 4.2. The hydrated gums were separated at the next stage, that is, neutralisation stage. The details of degumming process for both techniques are presented in Tables 4.1 and 4.2, respectively (section 4.3).
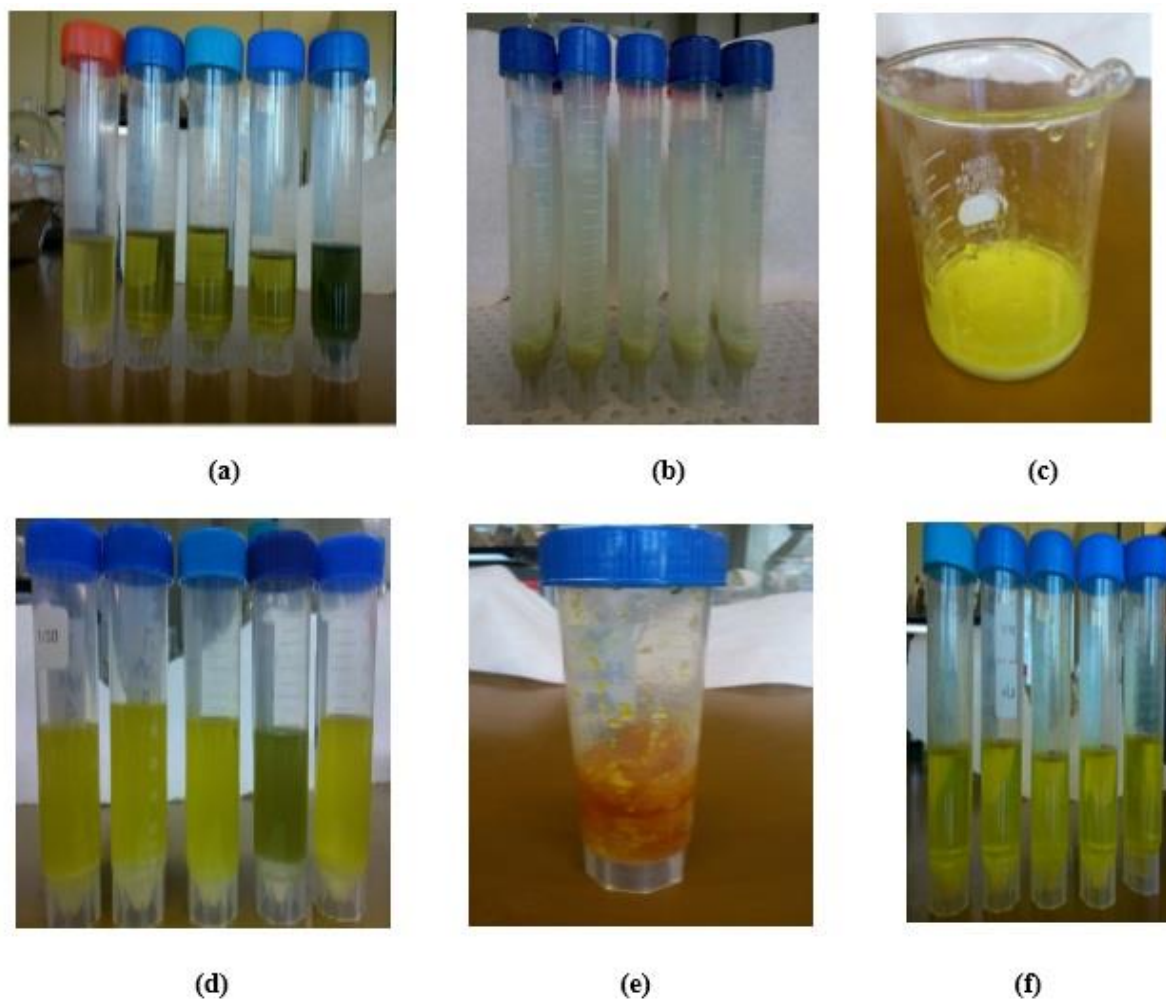
Figure 4.2: Overall oil refining process: (a) oil sample after degumming, (b) gum obtained at neutralisation process, (d) oil sample after neutralisation, (e) wax collected at dewaxing process, (f) oil sample after dewaxing.

4.2.4.2 Neutralisation

Neutralisation process removes undesirable substances in the degummed oil while also neutralising FFAs. Ten sets of tubes (5 samples from n-hexane extraction and 5 samples from screw press extraction) containing degummed oil (25 g each) were neutralised by adding aqueous solution (8% (wt.%)) of sodium hydroxide to each of the 10 tubes. After adding NaOH, the solution was mixed slowly and allowed to form soap. Then the mixture was separated by centrifugation. The top fraction of oil was washed twice with warm tap water (35 °C) to make sure that the traces of soap were removed. Finally, the oil, gum and the soap solution were separated by centrifugation. The proportion of the oil recovered and the resulting gum and soap were quantified. The details of the neutralisation process for both methods are presented in Tables 4.1 and 4.2, respectively.

4.2.4.3 Dewaxing

Wax in the BL oil was removed by cooling the neutralised oil to temperatures between 1 °C and 9 °C, as the condensation point of wax is much higher than that of the oil (Wei et al. 2015). Ten sets of BL neutralised oil samples (5 samples extracted by n-hexane and 5 samples extracted by screw press technique) were dewaxed by adding 5% (wt.%) of sodium hydroxide aqueous solution (concentration 8% (wt.%)) and 5% (wt.%) of de-ionised (DI) water. The tubes were placed in a refrigerator at 5 °C for about 4 hours. The soapy water wetted the waxes and helped the waxes to move from the oil into the water phase. Finally, the oil and the wax were separated by centrifugation and their weights were recorded. The details of dewaxing for both processes are shown in Tables 4.1 and 4.2, respectively.

4.3 Mass and Energy Balance

The mass balance for a refining process was evaluated based on the weights of the initial crude oil used and the products obtained at each step. The mass and energy balances for refining of crude oil extracted by n-hexane and screw press extraction techniques are shown in Figures 4.3 and 4.5, and 4.4 and 4.6, respectively. The efficiency of BL crude oil conversion into refined oil, namely "% Mass Conversion" was calculated using the Eqs. (4.1) and (4.2).

$$\% \ Mass \ conversion = \frac{W_{prod}}{W_{crude \ oil}} \times 100\% \tag{4.1}$$

$$\% \ Mass \ losses = 100\% - \sum(\% \ Mass \ conversion \ of \ all \ products) \tag{4.2}$$

Where, W_{prod} is the weight of products, kg

$W_{crude \ oil}$ is the initial weight of BL crude oil, kg

The energy balance of the refining processes was also determined by energy input and energy output. Energy input to the system was calculated based on the crude oil gross calorific value. Energy output is the summation of energy from the refined oil as well as from the by-products, such as gum, soap and wax in terms of gross calorific value. The energy recovery and energy losses were calculated in terms of percentage using Eqs. (4.3) and (4.4).

$$\% \ Energy \ recovery = \frac{W_{prod} \times HV_{prod}}{W_{crude \ oil} \times HV_{crude \ oil}} \times 100\% \tag{4.3}$$

$$\% \ Energy \ losses = 100\% - \sum(\% \ Energy \ recovery \ of \ all \ products) \tag{4.4}$$

where, W_{prod} is the weight of products, kg

$W_{crude\ oil}$ is the initial weight of BL crude oil, kg

HV_{prod} is the gross heating value of the products, MJ/kg

$HV_{crude\ oil}$ is the gross heating value of the crude oil, MJ/kg

Table 4.1: Oil refining process (oil from n-hexane technique)

Protocol	Replication 1	Replication 2	Replication 3	Replication 4	Replication 5
Amount of test (oil) samples (g)	25	25	25	25	25
Degumming Process	Acid Degumming	Acid Degumming	Acid Degumming	Acid Degumming	Water degumming
1. Heat the oil sample up to 60 °C for 2 hours	√	√	√	√	√
2. Add de-ionised (DI) and heated (60 °C) water (4% (wt.%)) (g)	1	1	1	1	1
3. Add phosphoric (H_3PO_4) acid solution (4% (wt.%)) (g)	1	1	1	1	-
4. Heat the solution at about 65 °C for about 30 min.	√	√	√	√	√
5. Centrifuge, if necessary to separate the gum and oil	√	√	√	√	√
Neutralization Process	Degummed oil	Degummed oil	Degummed oil	Degummed oil	Degummed oil
1. Add NaOH solution (8% (wt.%)) (g)	2	2	2	2	2
2. Mix slowly and allow 30 min for soap formation	√	√	√	√	√
3. Wash with 35 °C warm tap water	√	√	√	√	√
4. Centrifuge to separate the mixture	√	√	√	√	√

5. Wash with 35 °C warm tap water	√	√	√	√	√
6. Centrifuge	√	√	√	√	√
7. Discard water (containing soap)	√	√	√	√	√
8. Separate gum, soap and oil	√	√	√	√	√
9. Amount of soap formed (g)	1.1	1.26	1.11	1.14	1.21
10. Amount of gum formed (g)	2.23	2.31	2.21	2.19	2.14
	Neutralised oil	Neutralised oil	Neutralised oil	Neutralised oil	Neutralised oil
Dewaxing process					
1. Add NaOH solution (5% (wt.%)) (g)	1.25	1.25	1.25	1.25	1.25
2. Add de-ionised (DI) water (5% (wt.%)) and mix slowly (g)	1.25	1.25	1.25	1.25	1.25
3. Place in a chiller at 5 °C for 4 hours	√	√	√	√	√
4. Centrifuge (5 °C)	√	√	√	√	√
5. Separate soap, wax and oil	√	√	√	√	√
6. Wax weight (g)	0.83	1.07	0.79	0.89	1.02
Recovered soap (g)	1.1	1.26	1.11	1.14	1.21
Recovered gum (g)	2.23	2.31	2.21	2.19	2.14

Recovered wax (g)	0.83	1.07	0.79	0.89	1.02
Oil yield (gm)	20.46	20.32	20.13	20.93	19.21
% of oil recovery	81.8	81.3	80.5	83.7	76.8
Average % oil recovery	80.8				

Table 4.2: Oil Refining Processes (oil from screw press technique)

Protocol	Replication 1	Replication 2	Replication 3	Replication 4	Replication 5
Amount of test (oil) samples (g)	25	25	25	25	25
Degumming Process	Acid Degumming	Acid Degumming	Acid Degumming	Acid Degumming	Water Degumming
1. Heat the oil sample up to 60℃ for 2 hours	√	√	√	√	√
2. Add de-ionised (DI) and heated (60℃) water (4% (wt.%) (g)	1	1	1	1	1
3. Add phosphoric (H_3PO_4) acid solution (4% (wt.%) (g)	1	1	1	1	-
4. Heat the solution at about 65 °C for about 30 min.	√	√	√	√	√
5. Centrifuge, if necessary to separate the gum and oil	√	√	√	√	√
Neutralisation Process	Degummed oil	Degummed oil	Degummed oil	Degummed oil	Degummed oil
1. Add NaOH solution (8% (wt.%)) (g)	2	2	2	2	2
2. Mix slowly and allow 30 min for soap formation	√	√	√	√	√
3. Wash with 35 °C warm tap water	√	√	√	√	√

4. Centrifuge to separate the mixture	√	√	√	√	√
5. Wash with 35 °C warm tap water	√	√	√	√	√
6. Centrifuge	√	√	√	√	√
7. Discard water (containing soap)	√	√	√	√	√
8. Separate gum, soap and oil	√	√	√	√	√
9. Amount of soap formed (g)	2.33	2.89	2.73	2.62	2.56
10. Amount of gum formed (g)	2.23	2.13	2.55	2.19	1.88
	Neutralised oil	Neutralised oil	Neutralised oil	Neutralised oil	Neutralised oil
Dewaxing process					
1. Add NaOH solution (5% (wt.%)) (g)	15.625	15.625	15.625	15.625	15.625
2. Add de-ionised (DI) water (5% (wt.)) and mix slowly (g)	2	2	2	2	2
3. Place in a chiller at 5 °C for 4 hours	√	√	√	√	√
4. Centrifuge (5 °C)	√	√	√	√	√
5. Separate soap, wax and oil	√	√	√	√	√
6. Wax weight (g)	0.98	0.92	1.13	1.28	1.35
Recovered soap (g)	2.33	2.89	2.73	2.62	2.56
Recovered gum (g)	2.23	2.13	2.55	2.19	1.88

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Recovered wax (g)	0.98	0.92	1.13	1.28	1.35
Oil yield (gm)	18.23	19.24	18.39	18.51	17.13
% of oil recovery	72.90	76.95	73.55	74.05	68.50
Average % oil recovery	73.2				

4.4 Results and Discussion

4.4.1 Oil Recovery Efficiency

The BL oil that was extracted by n-hexane and screw press techniques was refined through degumming, neutralisation and dewaxing processes. The degumming process was conducted for both acid degumming and water degumming. The results indicated that acid degumming was more effective than water degumming. Phospholipids and some by-products which were formed during transesterification (for example, soaps, mono-and diacylglycerol) can act as surfactants (Rinaldi et al. 2007) and deter the phase separation from stabilisation of emulsions, and hence contributing to a reduction in biodiesel yield. On the other hand, degumming process with water does not allow complete removal of phospholipids, as only a few of these are soluble in water and possibly a large amount of these compounds remained in the reaction medium contributing to reduce yields of BL oil (Vicente et al. 2007). The highest oil recovery in h-hexane technique among 5 samples was obtained at 84% and 77% for acid and water degumming processes, respectively (see Table 4.1). In addition, on an average, 80.8% and 81.8% of oil recovery was achieved via acid degumming, in terms of mass and energy as shown in Figures 4.3 and 4.5, respectively.
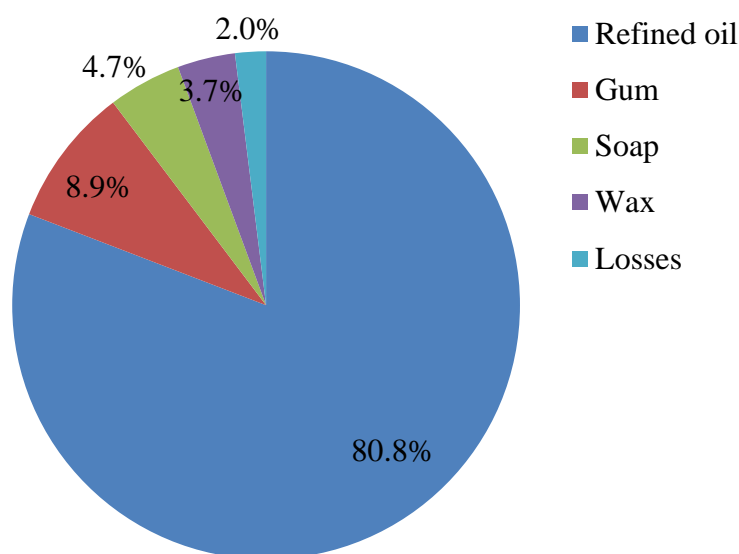
Figure 4.3: Mass balance for refined oil (n-hexane technique)
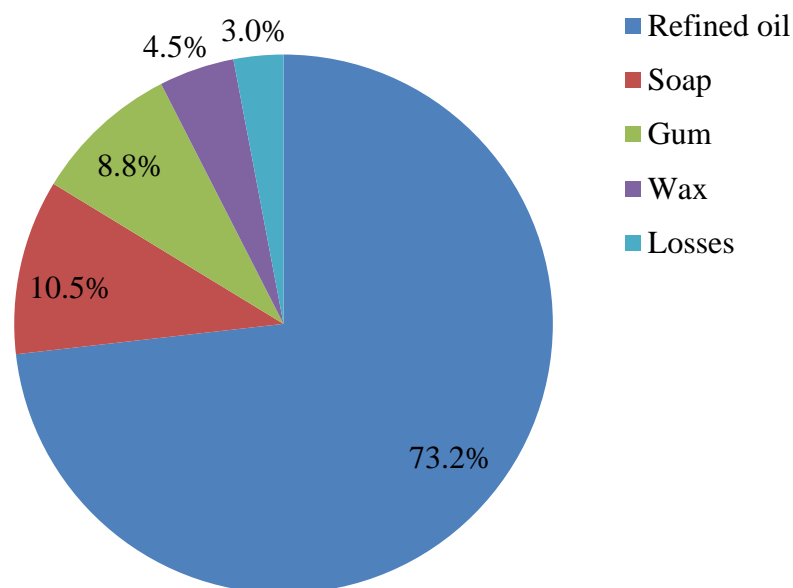
Figure 4.4: Mass balance for refined oil (screw press technique)
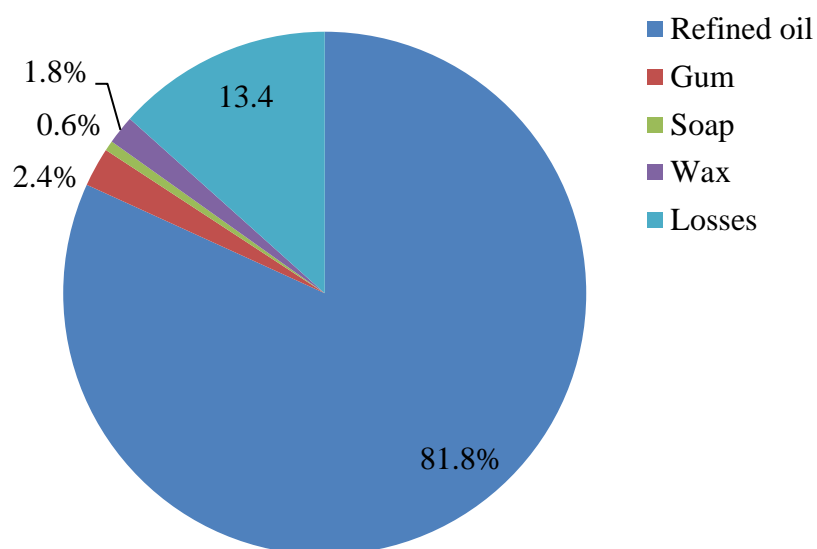
Figure 4.5: Energy balance for refined oil (n-hexane technique)

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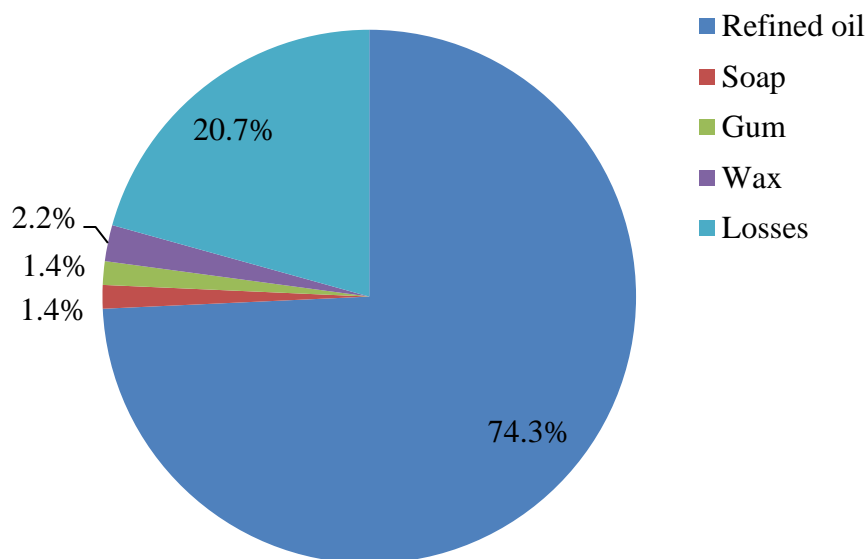
Figure 4.6: Energy balance for refined oil (screw press technique)

On the basis of mass, 8.9% gum, 4.7% soap, 3.7% wax and 2% other losses were removed as shown in Figure 4.3. In the case of energy, gum, soap, wax, and other losses contributed to 2.4%, 0.6%, 1.8% and 13.4% as presented in Figure 4.5, respectively. On the other hand, the maximum oil recovery in screw press technique among 5 replications was achieved at 77% and 69% for acid and water degumming processes, respectively, as shown in Table 4.2. From Figures 4.4 and 4.6, it could be shown that an average of 73% and 74.3% of oil recovery was achieved in screw press technique for mass and energy, respectively, from the acid degumming process. The gross heating value of crude beauty leaf oil (CBLO), refined beauty leaf oil (RBLO) and by-products is shown in Table 4.3.

Table 4.3: Gross heating value of CBLO, RBLO and by-products

Product	n-hexane technique: Heating value (MJ/kg)	Screw press technique: Heating value (MJ/kg)
CBLO	37.826	37.582
Gum	10.3	10.2
Soap	5.1	5.4
Wax	18.2	17.95
RBLO	38.278	38.132

On mass basis, the other impurities such as soap, gum, wax and other products of 10.5%, 8.8%, 4.5% and 3.0%, respectively, were obtained (see Figure 4.4). In terms of energy, gum, soap, wax and other losses accounted for 1.4%, 1.4%, 2.2% and 20.7%, respectively as shown in Figure 4.6. Large amounts of soap or by-product were also produced after neutralisation process indicating that the BL oil has high FFA composition, leading to a reduction in the yield of biodiesel (Koh & Mohd. Ghazi 2011).

4.4.2 Characterisation of Refined BL Oil

The physico-chemical properties of refined BL oil were determined according to the ASTM standards, and the results are presented in Table 4.4. It can be seen from Table 4.4 that the properties, such as density, viscosity, acid value and free fatty acid (FFA) of the refined oil were reduced significantly in comparison with those of crude oil. In addition, the results indicated that the calorific value, cetane number, pH and oxidation stability were found to be higher for refined oil in n-hexane technique compared to the screw press technique. In contrast, the density, viscosity, acid value and FFA were higher in the oil extracted from screw press technique (Table 4.4). It has been reported that the density, viscosity, acid value and FFA decrease considerably after degumming process (Ong et al. 2014a). Adhvaryu et al. (2002) reported that the deposition of waxy substances in the oil leads to increased viscosity. Therefore, it is necessary to remove the waxy materials to maintain desirable viscosity of the refined oil. The refined oil was found to be clearer and light yellow in colour as compared to the crude oil. This is likely to be due to removal of some unwanted chemical components through refining.

Table 4.4: Physico-chemical properties of RBLO

Properties	Units	Standards	RBLO	
			Oil from screw press technique	Oil from n-hexane technique
Density at 15 °C	kg/m^3	ASTM D4052	928	918
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	40.77	39.16
Viscosity index	-		153	154.2
Acid value	mg KOH/g	ASTM D664	16.14	15.2
Flash point	°C	ASTM D93	203	199
Pour point	°C	ASTM D2500	5	4
Cloud point	°C	ASTM D2500	6	5
Cold filter plugging point	°C	ASTM D6371	18	16
Cetane number	-	ASTM D6890	52.3	53.6
Iodine value	g I$_2$/100 g	EN 14111	82.2	80.3
Saponification value	mg/g		168	165.3
pH at 26 °C	-		4.92	5.26
Free fatty acid	(wt.%)		8.07	7.64
Oxidation stability	hour	EN 14112	2.29	2.32

4.5 Conclusion

The aim of this chapter was to develop pre-treatment procedures for BL crude oil prior to converting it into biodiesel. In this study, the BL crude oil was refined (degumming, neutralising and dewaxing) prior to producing biodiesel. It was found that acid degumming was more effective than water degumming, as higher amounts of phospholipids were removed in this process. During alkali neutralisation and dewaxing, the BL oil was de-acidified and dewaxed by removing the FFAs, waxes and undesirable constituents. During refining process, 80.8% and 81.8% of oil recoveries were obtained for n-hexane derived BL oil on mass and energy basis, respectively, along with 8.9% and 2.4% for gum, 4.7% and 0.6% for soap, 3.7% and 1.8% for wax and 2% and 13.4% for other losses.

For screw press derived BL oil, the respective recovery on the basis of mass and energy were 73.2% and 74.3%, respectively, with 10.5% and 1.4% for soap, 8.8% and 1.4% for gum, 4.5% and 2.2% for wax and 3% and 20.7% for other losses. The physico-chemical properties of the refined oil were also evaluated. The results indicated that after refining, calorific value, cetane number, pH and oxidation stability are higher in n-hexane derived BL oil compared to that obtained from screw press method. In contrast, the screw press derived BL oil shows higher density, viscosity, acid value and FFA than that derived from n-hexane extraction. The current study also indicated that the refining process significantly improved the quality of BL oil. The effects of this improvement on the quality of the biodiesel are discussed in chapter 5.

CHAPTER 5

BIODIESEL PRODUCTION, OPTIMISATION AND CHARACTERISATION

Biodiesel production and its optimisation was conducted for three feedstocks namely, BL, poppy and jojoba oil. The crude BL oil (CBLO), refined BL oil (RBLO), refined poppy oil (RPO) and crude jojoba oil (CJO) were used in this investigation. The biodiesel production was done in single stage (base catalysed transesterification) and 2 stage processes which consisted of acid–catalysed esterification and base-catalysed transesterification. The optimisation was done on the basis of different influencing parameters on yield of biodiesel, such as methanol to oil molar ratio, catalyst concentration, reaction temperature and time. The raw biodiesel was purified and dried properly to obtain the desired fatty acid methyl ester (FAME). The gas chromatography (GC) analysis was conducted to evaluate the FAME compositions of poppy, BL, PWC and jojoba biodiesel. In addition, the physico-chemical properties of produced biodiesel were characterised on the basis of ASTM and EN biodiesel standards.

5.1 Introduction

The most important input needed for biodiesel production is the feedstock. Non-edible oil resources are gaining worldwide attention because they are easily available in many parts of the world and can be grown in degraded lands that are not suitable for raising food crops, are more efficient, more environmentally favourable, produce useful by-products and are likely to be more economical compared to edible oils (Atabani et al. 2012, Ong et al. 2014a, Ong et al. 2014b). In addition, non-edible plant oils can be used as promising crude oils for biodiesel production. Among various non-edible oil feedstocks, BL (*calophyllum inophyllum*), poppy (*Papaver somniferum*) and jojoba (*simmondsia chinensis)* are being used as a source for raw material for biodiesel production as they are sufficiently available and comparatively cheaper. In addition, the poppy seed and BL kernel have high oil content (Aksoy 2011b, Venkanna & Venkataramana Reddy 2009).

Biodiesel is produced from vegetable oils via the most efficient technology called transesterification process (de Almeida et al. 2015, Dharma et al. 2016, Gerpen 2005, Saydut

et al. 2016, Verdugo et al. 2011, Yatish et al. 2016). Transesterification process is commonly used in biodiesel production due to its simplicity, low cost, viability and economic process (Atabani et al. 2012, Balat & Balat 2010, Jain & Sharma 2010a, Kumar & Sharma 2011, Parawira 2010, Shahid & Jamal 2011, Sharma & Singh 2009). Transesterification is the reaction in which vegetable oils are reacted with alcohol in presence of a catalyst. Alkali (KOH, NaOH and NaOCH$_3$ and so on) or acid catalyst (H$_2$SO$_4$) transesterification is the most general technique used nowadays to produce biodiesel from oils.

Most of the researchers used both esterification and transesterification processes to produce biodiesel from crude oils with high FFAs (de Almeida et al. 2015, Dhar et al. 2012, Jena et al. 2010, Sahoo & Das 2009b). Several researchers (Dharma et al. 2016, Ong et al. 2014a, Patil & Deng 2009, Ragit et al. 2011, Verma et al. 2016) also studied the optimisation of biodiesel production using transesterification technology. The purpose of these technologies is to reduce the FFAs and viscosity, and produce a quality biodiesel to use in the compression ignition (CI) engine. Although many studies have been conducted regarding optimisation of biodiesel production process parameters from different feedstocks, very few studies have been conducted on optimisation of biodiesel production from poppy, BL (CBLO and RBLO) and jojoba oil. Therefore, the purpose of this chapter is to produce biodiesel from poppy, BL and jojoba oil which will give the maximum yield of biodiesel and optimise the production process parameters based on different affecting factors.

5.2 Materials and Method

5.2.1 Materials

CBLO, RBLO, RPO and CJO were used to perform the biodiesel production and optimisation. The details of oil extraction processes and properties were presented in chapter 3. The refining of CBLO was explained in detail in chapter 4. RPO was collected from Macquarie Oil Company which is located in the northern midlands of Tasmania, Australia. In addition, it could be noted that poppy seed oil is a by-product of the alkaloid extraction process which was processed in that company. This oil is not suitable for human or stock consumption as it contains residual alkaloid (Macquarie Oil Company 2016). Jojoba oil was collected from Aussie Soap Supplies which is located in Kardinya, Western Australia, Australia. The equipment used for testing of biodiesel properties, such as density, viscosity, acid value and

idonie value, calorific value, flash point, pour point and cloud point, cold filter plugging point, cetane number, oxidation stability, copper strip corrosion, carbon residue, sulphur content and sulphated ash content are presented in Table 5.1. The measured physico-chemical properties of RPO and CJO are shown in Table 5.2.

Table 5.1: List of equipment used for testing of biodiesel properties

Property	Equipment	Accuracy
Density	DM40 LiquiPhysics™ density meter (Mettler Toledo, Columbia, MD, USA)	±0.1 kg/m3
Viscosity	NVB classic (Norma lab, Valliquerville, France)	±0.01 mm2/s
Acid value and iodine value	Automation titration rondo 20 (Mettler Toledo)	±0.001 mg KOH/g (Acid value) and ±0.1 g I$_2$/100 g (Iodine value)
Calorific value	6100EF Semi auto bomb calorimeter (Parr, Moline, IL, USA)	±0.001 MJ/kg
Flash point	NPM 440 Pensky-martens flash point tester (Norma lab)	±0.1°C
Pour point and Cloud point	NTE 450 Cloud and pour point tester (Norma lab)	±0.1°C
Cold filter plugging point	Cold filter plugging point tester –automatic NTL 450 (Normalab, France)	±0.1°C
Cetane number	92000-3 Ignition quality tester (IQT^{TM}) (Stanhope-Seta, UK)	±0.1
Oxidation stability at 110 °C	873 Rancimat (Metrohm, Herisau, Switzerland)	±0.01 hour
Copper strip corrosion (3 hours at 50 °C)	Seta copper corrosion bath 11300-0 (Stanhope-Seta, UK)	−
Carbon residue (10% res)	NMC 440 micro-carbon canradson residue tester (Normalab, France)	±0.01%
Ester content	---	

Sulphur content	Multi EA 5000 (Analytical jena, Germany)		± 0.001 ppm
(Sulphated) Ash content	Professional laboratory furnace Model L40 /11 (Nabertherm, Germany)		$\pm 0.001\%$

Table 5.2: Properties of refined poppy oil (RPO) and crude jojoba oil (CJO)

Properties	Units	RPO	CJO
Density at 15 °C	kg/m^3	919	863
Kinematic viscosity at 40 °C	mm^2/s	4.7	24.28
Viscosity index	-		
Acid value	mg KOH/g	4.4	2.25
Calorific value	MJ/kg	39.6	35.44
Flash point	°C	234	228
Pour point	°C	-14	8
Cloud point	°C	-12	3
Cold filter plugging point	°C	-8	10
Cetane number	-	53	59
Iodine value	g I_2/100 g	126	88
pH at 26 °C	-	5.8	7.6
Free fatty acid	(%)	2.2	1.13
Oxidation stability	hour	3.36	36.75

5.2.2 Reagents

All reagents, such as methanol (99.9% purity), anhydrous sulphuric acid (H_2SO_4, purity > 98.9%), potassium hydroxide (KOH) pellet (purity 99%), Na_2SO_4 anhydrous (purity 98%) were used in this study to perform the experiment. The methanol was collected from Chem-supply in South Australia. The sulphuric acid ($H_2SO_{4)}$, catalyst, potassium hydroxide (KOH) pellet, Na_2SO_4 was laboratory supplies.

5.2.3 Apparatus

The experiments were conducted using two 250 ml, three-necked round bottom reactor flasks (Model: FR1L/3s/22A, capacity 500 ml). The three-necked reactor flask was placed on a flat bottom water bath (capacity 1 L) which was placed on a hot plate magnetic stirrer (Model: IKA C-MAG HS7) in an automatic controlled fume hood in the Chemical and Biomedical Engineering Laboratory at Central Queensland University, Australia to complete the reaction. A thermometer (temperature range 0 °C-150 °C) was inserted in one neck of the reactor by using a rubber stand. A centrifuge machine (Model: ThermoFisher D-37520) was also used in this study.

5.3 Biodiesel Production

Generally, the non-edible vegetable oils have high viscosity, low volatility and these consisted of a large amount of polyunsaturated free fatty acids (FFAs) which caused undesired soap formation, and as a result, it reduces the yield of methyl ester during the transesterification reaction (Ong et al. 2014b). In addition, biodiesel production using alkaline catalysed transesterification with high FFAs feedstocks is extremely difficult as the alkaline catalysts react with FFAs to form soap which prevents the separation of glycerine and ester (Dhar et al. 2012, Ramadhas et al. 2005, Sahoo & Das 2009b).

In order to overcome these difficulties, several techniques have been successfully adopted to reduce the FFAs, such as, pre-treatment of crude oil which includes: refining and acid catalyst esterification (Chattopadhyay & Sen 2013). Therefore, a pre-treatment process, that is, esterification using acid-catalysed is necessary to reduce the FFA content (less than 1%) in oil before the transesterification process is carried out (Dharma et al. 2016, Ong et al. 2014a). Researcher (de Almeida et al. 2015) reported that the acid value of the methyl ester after esterification should be less than 2 mg KOH/g oil. Then the transesterification reaction using base catalyst was conducted to remove the remaining glycerides and produce the methyl ester. It could be noted that quality of biodiesel is an important factor as this is related to the power output of the engine. The quality of oil was checked by measuring the acid value. In this investigation, single stage for RBLO and 2 stage processes for CBLO, RBLO, RPO and CJO were conducted to produce biodiesel. The biodiesel production process flow diagram is shown in Figure 5.1.
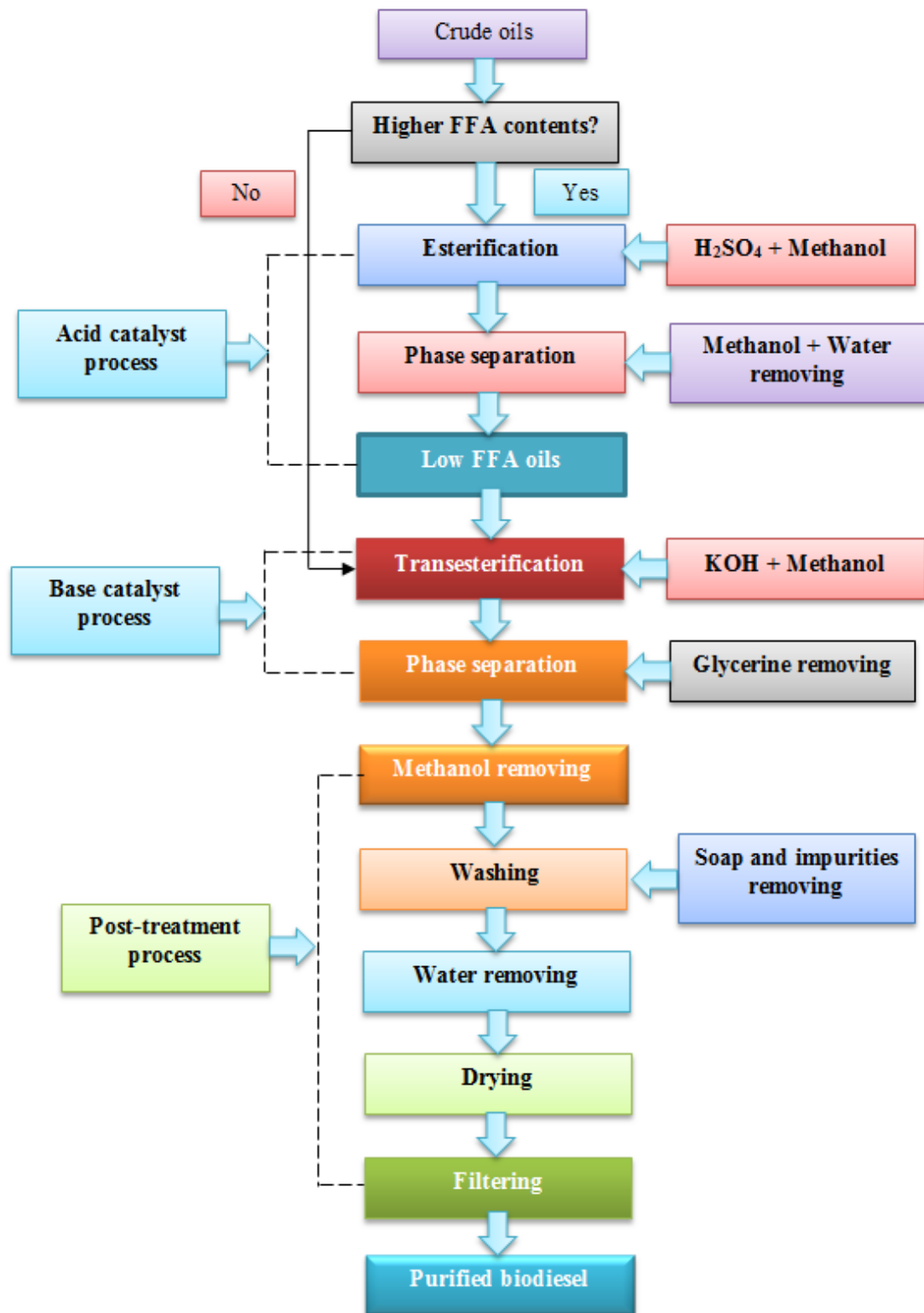
Figure 5.1: Biodiesel production process flow diagram

5.3.1 Pre-Treatment Process (Acid-Catalysed Esterification)

In esterification, two 250 m1, three-necked round-bottom reactors, each with a flat bottom water bath (capacity 500 ml) equipped with a hot plate magnetic stirrer, one thermometer and a reflux condenser were used to avoid alcohol evaporation and to complete the reaction. For each experiment, 100 ml of CBLO, RBLO, RPO and CJO was used for acid-catalysed esterification. The oil samples were filtered through filter paper to remove any undesirable components present in the oil before starting the reaction.

The reactor containing the oil sample was placed in a water bath heated by a magnetic hot plate. All oil samples were pre-heated in a reactor at 60 °C for 30 min to remove the undesirable components and water particles (if any) before starting the reaction. Stirring was applied to enhance the reaction with the help of a mechanical stirrer. Anhydrous sulphuric acid (H_2SO_4) was used as a catalyst in this process. Pre-heated methanol (molar ratio methanol to oil of 12:1) and then H_2SO_4 was mixed to the oil sample drop by drop using one-neck of the reactor at a ratio of 1% (vol./vol.) (Sahoo & Das 2009b, Silitonga et al. 2013d). During the reaction, the mixture was stirred at a temperature of 60 °C and at a speed of 750 rpm for all the experiments. The reaction time was maintained for 2 hours for all the experiments. After completing the reaction, the product was transferred to a separatory funnel to separate the excess methanol with FFAs and impurities, and the esterified product for 4 hours (Dharma et al. 2016). The top layer which contains excess methanol, H_2SO_4 and FFAs was separated from the bottom layer. The bottom layer was the low FFA content esterified product. The esterified product was then used for alkali transesterification.

5.3.2 Transesterification (Alkali-Catalysed Transesterification)

The transesterification reaction was carried out in the same reactors as the esterification reaction and using the same experimental facility for biodiesel production. The overall biodiesel production process with pictures is shown in Figure 5.2. The transesterification reaction was conducted for crude esterified beauty leaf oil (CEBLO), refined esterified beauty leaf oil (REBLO), refined without esterified beauty leaf oil (RWEBLO), refined esterified poppy oil (REPO), and crude esterified jojoba oil (CEJO). After esterification, the
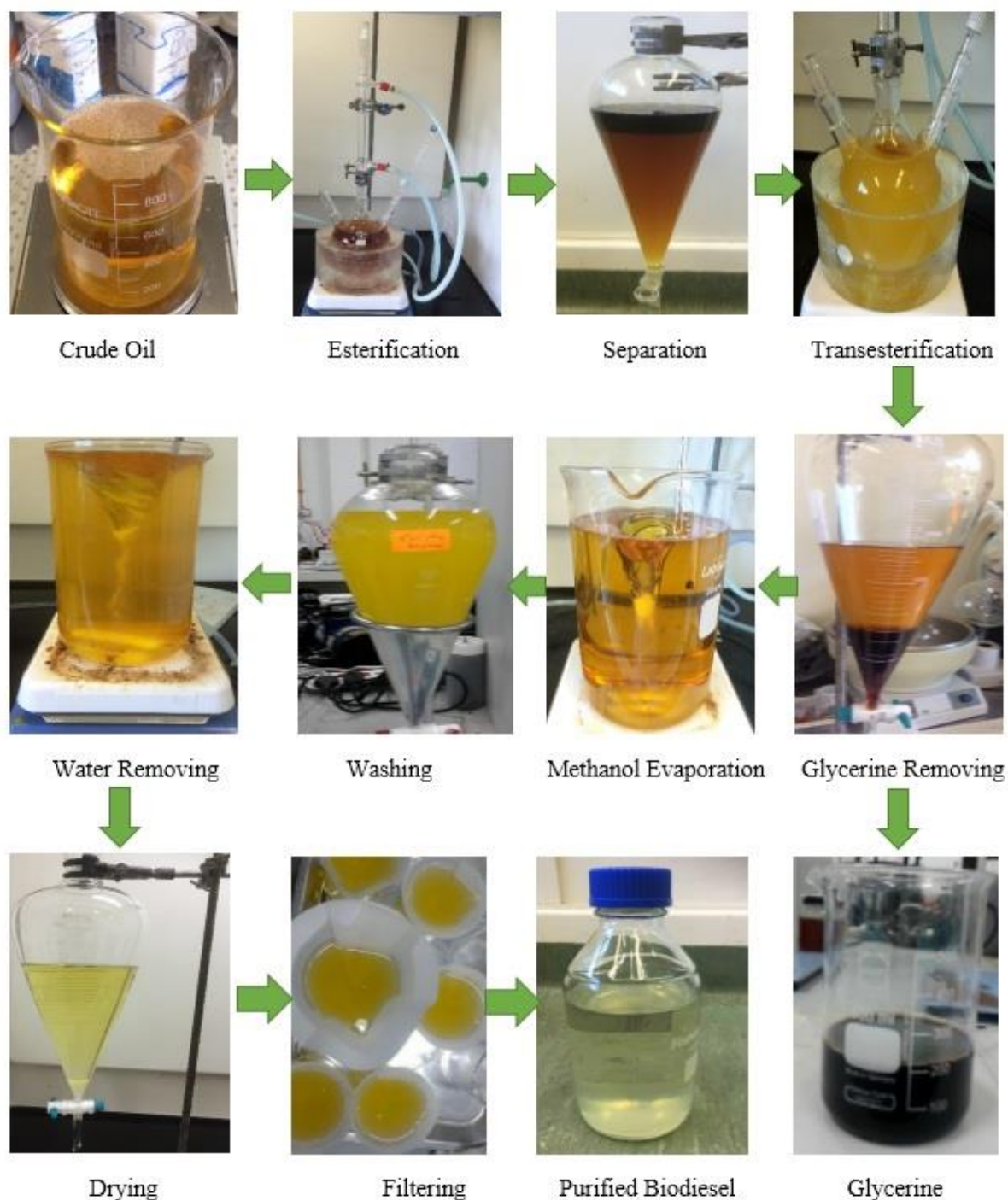
Figure 5.2: Overall biodiesel production process showing pictures (both esterification and transesterification)

FFA contents of CEBLO, REBLO, RWEBLO, REPO and CEJO were 1.72%, 1.52%, 7.64%, 1.42% and 0.76%, respectively. For each experiment, 50 ml of CEBLO, REBLO, RWEBLO, REPO and CEJO was used for base-catalysed transesterification. The KOH was used as a catalyst in the transesterification process. The reactors containing oil sample were placed in water baths heated by magnetic hot plates. The process flowchart for transesterification

reaction is shown in Figure 5.3. The esterified product was first heated up to the desired temperature of 60 °C for 30 min before adding the potassium methoxide solution (CH$_3$OK) in it (Ijaz et al. 2016, Kostić et al. 2016, Venkanna & Venkataramana Reddy 2009).
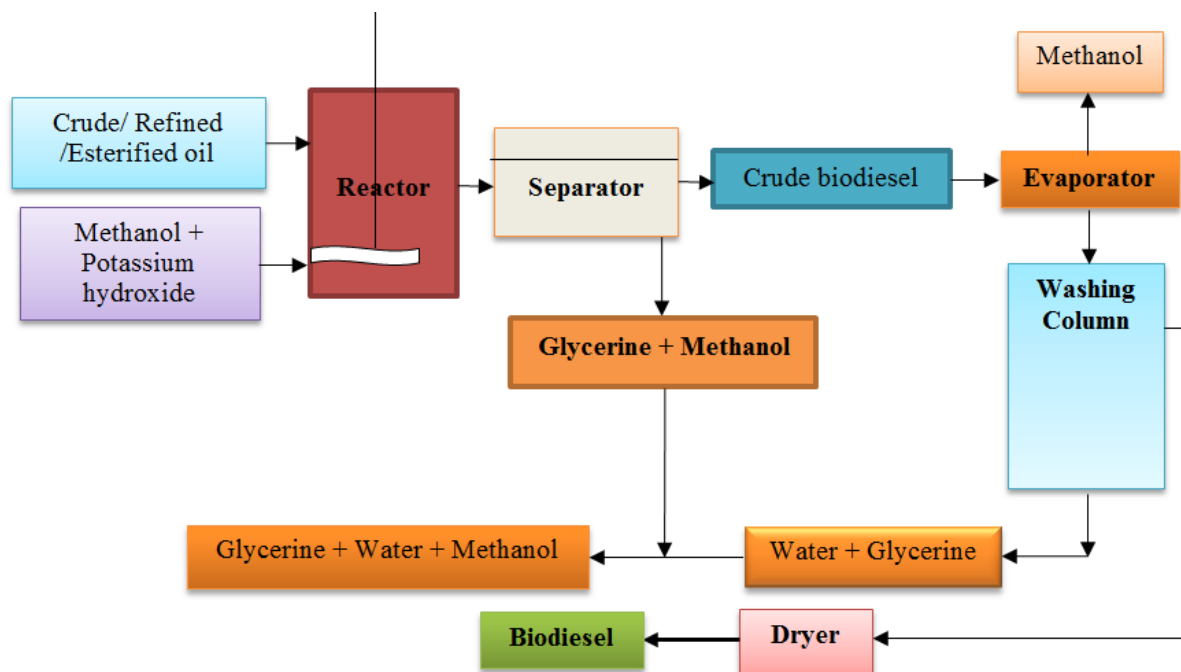
Figure 5.3: The process flowchart of transesterification reaction for biodiesel production

The CH$_3$OK solution was prepared first by adding NaOH pellets into a conical flask containing methanol, and the mixture was stirred until the NaOH was dissolved. The heated CH$_3$OK solution was added to the pre-heated esterified product to complete the reaction for biodiesel production. The CH$_3$OK was mixed with different proportions to the esterified sample to obtain the maximum FAME. The mixture was stirred at a constant speed of 750 rpm for different methanol to oil molar ratios, catalysts concentrations, temperature and time range (Venkanna & Venkataramana Reddy 2009). It was observed that methanol to oil ratio, catalyst concentration, temperature, as well as reaction time had a direct effect on ester yields. The effect of different methanol to oil ratios, catalyst amounts, temperature and time ranges are shown in Figures 5.4-5.7, respectively. These are discussed in section 5.4 under results and discussion. It has been observed that molar ratio (methanol to oil) of 6:1 (Ragit et al. 2011, Usta 2005b) and catalyst (KOH) concentration of 1 (wt.%) are the most often used in transesterification reaction (Berchmans et al. 2013, Parlak et al. 2009, SathyaSelvabala et al. 2011).

All the transesterification reactions were conducted 5 times in order to get the variation in results and to achieve the highest yield of biodiesel. The experiments were repeated for various affecting variables, such as methanol to oil molar ratio (5.0:1 to 8.0:1), catalyst concentration (0.25 (wt.%) to 1.5 (wt.%)), reaction temperature (40 °C to 80 °C) and reaction time (50 min to 130 min). Later, the biodiesel production process was carried out on the basis of optimum condition from BL, poppy and jojoba oil. In addition, the REBLO product was used for biodiesel production as significant variations in yield of biodiesel and improved fuel properties were observed in comparison to CEBLE and RWEBLO.

5.4 Results and Discussion

The influence of reaction parameters, such as methanol to oil ratio, the amount of catalyst, reaction temperature, reaction time and reaction speed on the yield of BL, poppy and jojoba oil methyl esters were performed via transesterification.

5.4.1 Effect of Methanol to Oil Ratio on Biodiesel Yield

The amount of methanol adding to the vegetable oil for biodiesel production is one of the most significant parameters that affect conversion efficiency of methyl ester (Sahoo & Das 2009b). A sufficient amount of methanol is required to drive the reaction to completion at a faster rate. During the reaction, it is observed that yield of methyl ester is depended on methanol to oil ratios.

The methanol to oil ratio is varied within the range of 5.5:1 to 7.5:1, 5.0:1 to 7.0:1 and 6.0:1 to 8.0:1 for BL, poppy and jojoba oil, respectively. The yield of biodiesel increases with increase in methanol to oil ratio but when adding excessive amounts of methanol to oil ratio (over 7.0:1, 6.0:1, 6.5:1, 6.0:1 and 7.5:1 for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively) the opposite trend is observed as shown in Figure 5.4. This could be explained as, a less amount of methanol is not enough to complete the reaction successfully, and an excessive amount of methanol indicates unreacted methyl ester oil (Sahoo & Das 2009b).
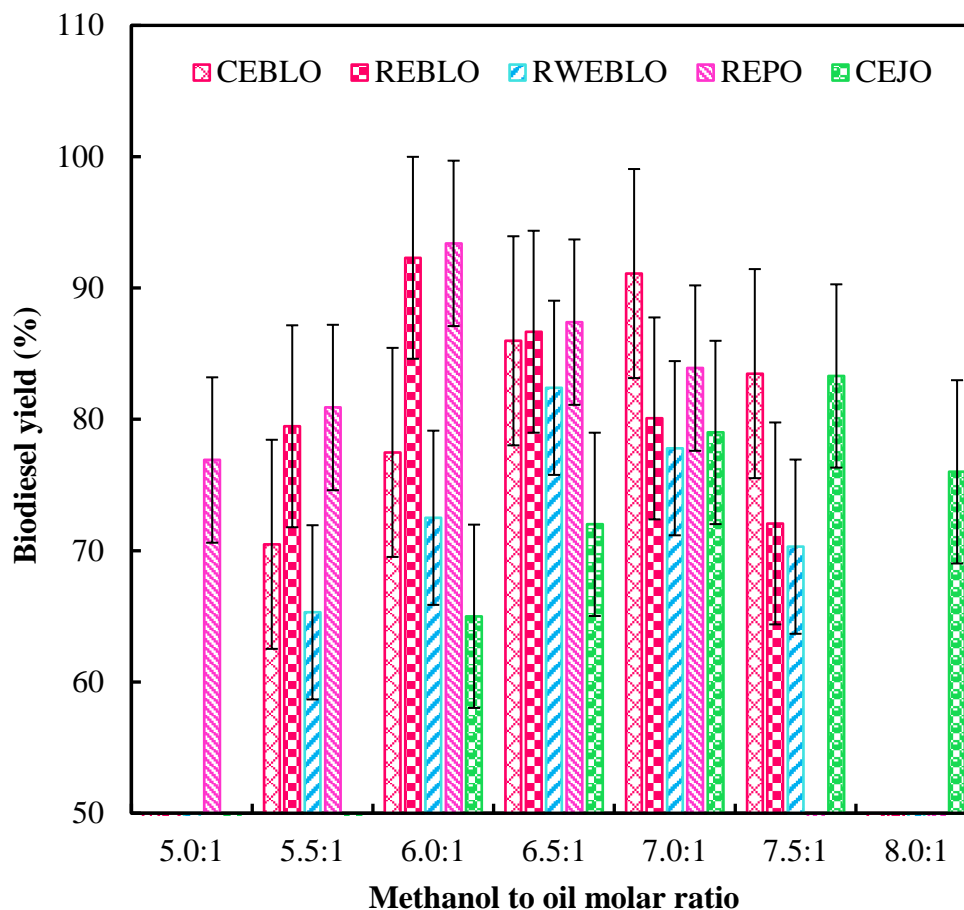
Figure 5.4: Effect of molar ratio (methanol to oil) on biodiesel yield (Error bars represent the SD)

The ester recovery increases with increase in molar ratio from 6:1 to 8:1, however, at lower molar ratio the ester recovery decreases as reported by Ragit et al. (2011). It has been observed that a lower amount of methanol requires a longer reaction time to complete the reaction (Sahoo & Das 2009b). Several researchers (Berchmans & Hirata 2008, da Costa Barbosa et al. 2010, Kafuku & Mbarawa 2010a, Karmee & Chadha 2005, Parlak et al. 2009, Ragit et al. 2011) agreed that with increase in the molar ratio (methanol to oil) the yield of methyl ester increases. With further increase in methanol to oil ratio from 7.0:1, 6.0:1, 6.5:1, 6.0:1 and 7.5:1 for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively, no improvement in the conversion efficiency is observed (Figure 5.4). This is due to the fact that adding an excess amount of methanol increases the solubility of glycerol, and this causes a part of the glycerol to go to ester phase; therefore, the glycerol which is in ester phase lead to more foam formation with the lower biodiesel yield (Dwivedi & Sharma 2015, Kafuku & Mbarawa 2010a, Predojević 2008, Uzun et al. 2012).

Amongst three different types of BL oils (CEBLO, REBLO and RWEBLO), the highest biodiesel yield of 92.3% is obtained for REBLO which is synthesised by both esterification and transesterification processes. In addition, CEBLO (synthesised both by esterification and transesterification) shows the higher methyl ester yield than the RWEBLO. The lower conversion efficiency of RWEBLO is possibly due to the presence of gums, FFAs, waxes, entrained impurities as well as the presence of glycerol. The highest methyl ester yield of 91.1%, 92.3%, 82.4%, 93.4% and 83.3% is obtained at methanol to oil ratio of 7.0:1, 6.0:1, 6.5:1, 6.0:1 and 7.5:1 for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively.

5.4.2 Effect of Catalyst Loading on Methyl Ester Yield

The catalyst concentration is a significant factor in transesterification for biodiesel production and optimisation. The effect of catalyst loading on conversion of oil into biodiesel is investigated with different concentrations, such as 0.50 (wt.%), 0.75 (wt.%), 1.0 (wt.%), 1.25 (wt.%) and 1.5% (wt.%), at an interval of 0.25 (wt.%) to obtain the highest yield of methyl ester. Figure 5.5 presents the variation in biodiesel yield with catalyst concentration for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively. It can be seen from Figure 5.5, that biodiesel yield increases with increase in catalyst concentration up to 1.0 (wt.%), 0.75 (wt.%), 1.0 (wt.%), 1.0 (wt.%), and 1.25 (wt.%), for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively. However, a further increase in the concentration of a catalyst the biodiesel yield decreases gradually. Several researchers reported that catalyst loading has an effect on yield of methyl ester (Meher et al. 2006c, Ong et al. 2014a).

It has been reported that the ester recovery increases with a decrease in catalyst concentration from 3 (wt.%) to 1 (wt.%) (Ragit et al. 2011). The optimal amount of the base catalyst was observed at 1 (wt.%) by Banković-Ilić et al. (2012) although some researchers have mentioned that lower concentrations of catalyst, such as 0.5 (wt.%) (Parlak et al. 2009), 0.7 (wt.%) (Nabi et al. 2008) or 0.8 (wt.%) (Tapanes et al. 2008) have the optimal value.
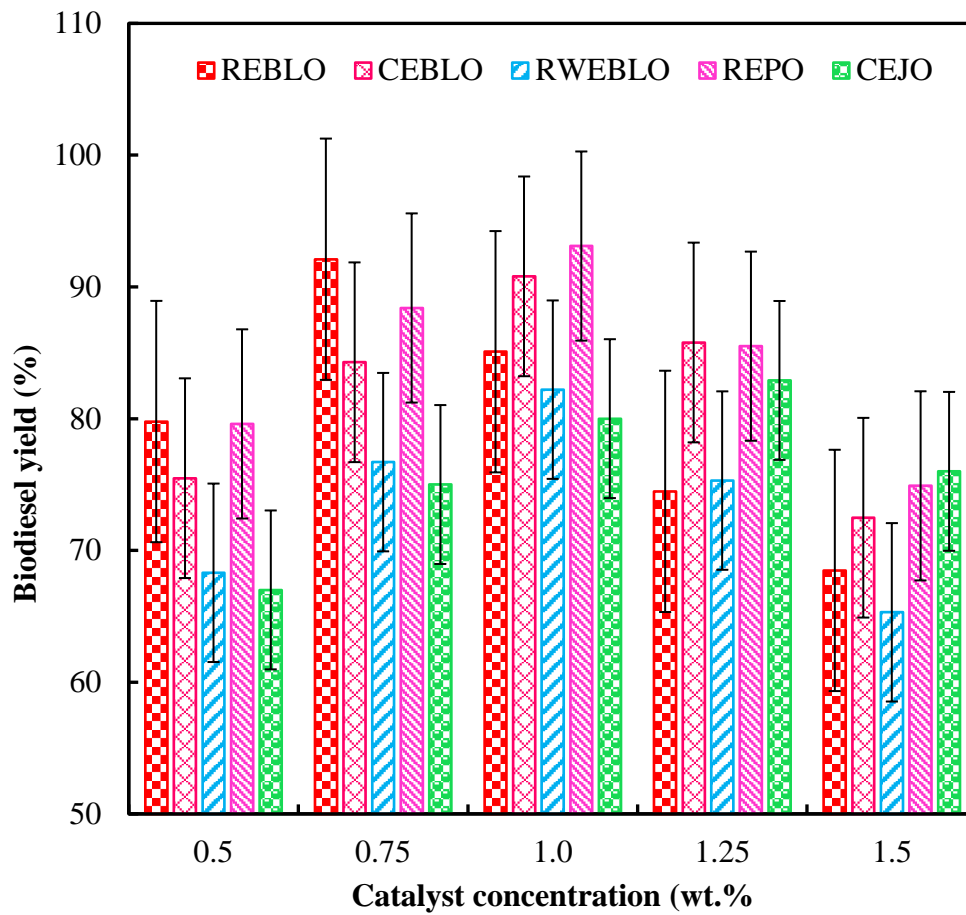
Figure 5.5: Effect of catalyst concentration on biodiesel yield (Error bars represent the SD)

It can be shown from Figure 5.5 that a lower amount of catalyst concentration is insignificant to catalyse the reaction because the lower amount of catalyst is not able to complete the reaction successfully (Ong et al. 2014a). In addition, the decrease in yield of methyl ester is due to the formation of emulsion, increasing viscosity and saponification to the gel formation (Venkanna & Venkataramana Reddy 2009). In contrast, increasing catalyst loading causes insolubility to oil. Furthermore, adding more amount of catalyst causes more triglycerides as well as the formation of soap (Uzun et al. 2012). The same results have also been reported by several researchers (Bhatti et al. 2008, Encinar et al. 2005, Leung & Guo 2006, Leung et al. 2010, Phan & Phan 2008, Society & Firestone 1994).

In terms of effect of catalyst loading, REBLO shows the highest biodiesel yield of 92.1%, amongst three samples of CEBLO and RWEBLO. In addition, CEBLO shows the higher methyl ester yield in comparison to RWEBLO. The results indicate that the optimum biodiesel yield of 90.8%, 92.1%, 82.2%, 93.1% and 82.9% are obtained at catalyst concentration of 1.0

(wt.%), 0.75% (wt.%), 1.0 (wt.%), 1.0 (wt.%) and 1.25% (wt.%) for CEBLO, REBLO, RWEBLO, REPO and CEJO during transesterification, respectively.

5.4.3 Effect of Reaction Temperature (°C)

Reaction temperature has a significant role in transesterification when the reaction is performed by the alkali catalyst. The experiments were conducted at different reaction temperatures, such as 40 °C, 50 °C, 60 °C, 70 °C and 80 °C to find the effect on yield of biodiesel. The effect of reaction temperatures on biodiesel yield of CEBLO, REBLO, RWEBLO, REPO and CEJO is presented in Figure 5.6. It has been reported that temperature had a positive influence on biodiesel yield during transesterification reaction (Aksoy 2011b, Encinar et al. 1999, Meher et al. 2006b, Venkanna & Venkataramana Reddy 2009).
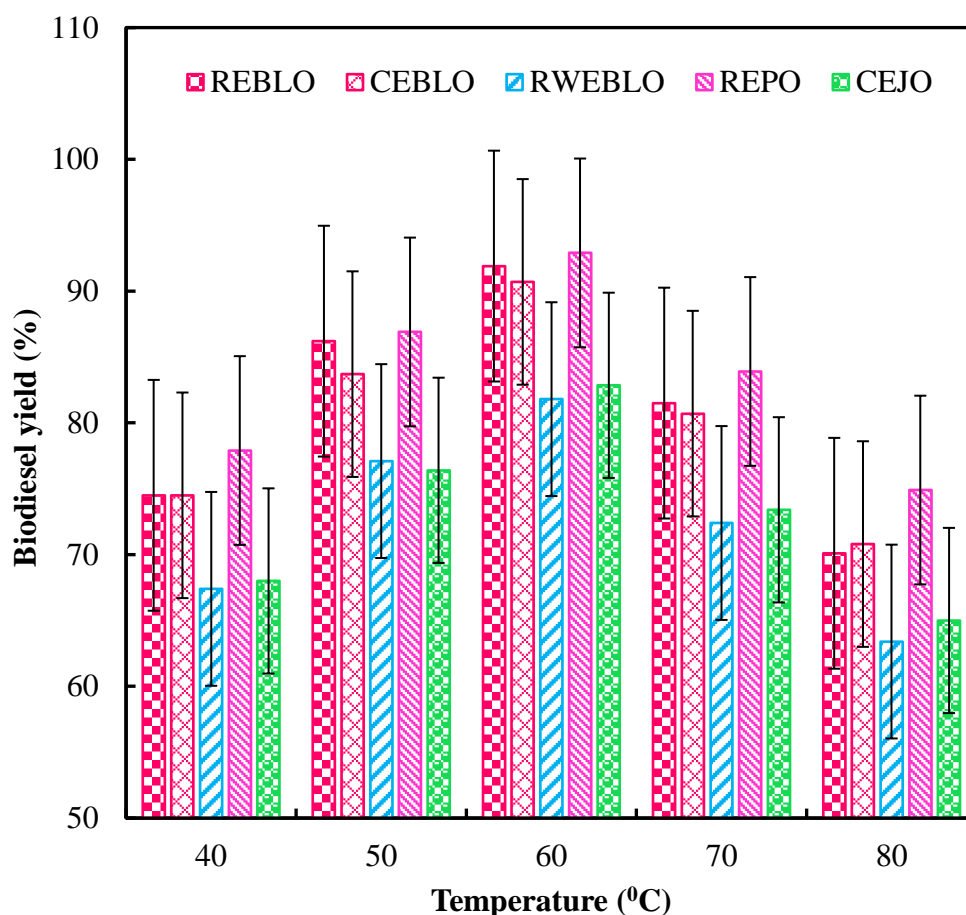
Figure 5.6: Effect of reaction temperature on biodiesel yield (Error bars represent the SD)

At lower temperature (40 °C), no significant effect is observed on yield of methyl ester for CEBLO, REBLO, RWEBLO, REPO and CEJO. The similar results have been reported by several researchers for different vegetable oils (Sinha et al. 2008, Srivastava & Prasad 2000).

At lower temperature (30 °C-40 °C), the formation of phase changes is slow which indicates a longer time is required to complete the reaction (Kafuku & Mbarawa 2010a). However, the author has indicated that at a higher temperature (60 °C) bubbles were formed and observed due to the formation of faster phase changes and the reaction was completed quickly. In this investigation, the biodiesel yield increases with increase in reaction temperature up to 60 °C for all the experiments. This is due to the fact that higher reaction temperature assists to increase in reaction speed (Aksoy 2011b) and consequently, the methyl ester is formed easily.

The faster settlement of glycerol obtained with increase in reaction speed (Venkanna & Venkataramana Reddy 2009). The viscosity of oil decreases with increase in temperature and hence, the yield of methyl ester increases. On the contrary, the biodiesel yield decreases beyond a reaction temperature of 60 °C. This could be attributed due to the formation of saponification of triglycerides before the completion of transesterification reaction (Meher et al. 2006a, Patil & Deng 2009, Sinha et al. 2008). Furthermore, it has been reported that higher temperature is not favourable for synthesising of biodiesel as it helps to evaporate the methanol and ultimately causes a reduction in yield of methyl ester (Ma & Hanna 1999, Ong et al. 2014a).

Amongst 3 different samples of BLO, the maximum biodiesel yield is obtained for REBLO on the basis of influence of recation temperature. Moreover, the higher biodiesel yield is found for CEBLO in comparison to RWEBLO. The optimum methyl ester yield of 90.7%, 91.9%, 81.8%, 92.9% and 82.85% is obtained at a temperature of 60 °C for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively.

5.4.4 Effect of Reaction Time

In order to obtain an effective interaction during transesterification the reaction time is significant (Sahoo & Das 2009b). The effect of reaction time, such as 50 min to130 min, 50 min to 130 min, 50 min to 130 min, 60 min to 120 min and 60 min to 120 min on yield of biodiesel for CEBLO, REBLO, RWEBLO, REPO and CEJO is shown in Figure 5.7, respectively. The methyl ester yield is insignificant at a lower reaction time for all the samples.
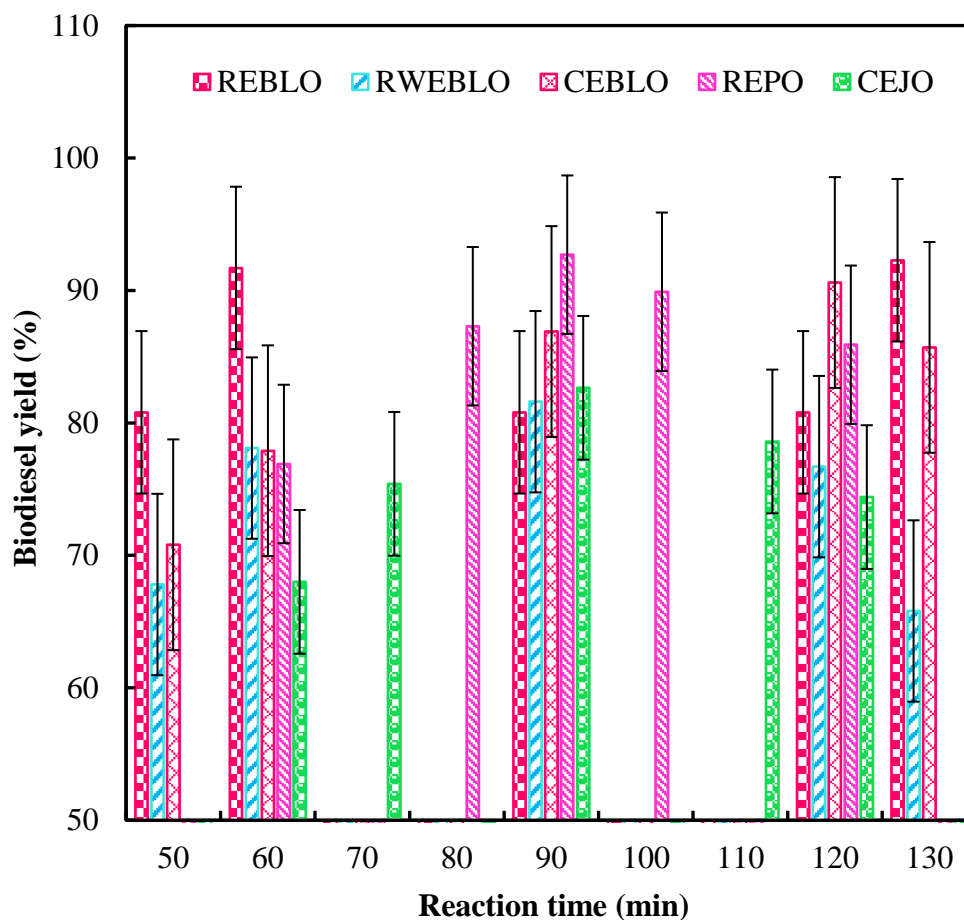
Figure 5.7: Effect of reaction time on biodiesel yield (Error bars represent the SD)

It is observed from Figure 5.7 that biodiesel yield increases with increase in reaction time up to 120 min, 60 min, 90 min, 90 min and 90 min for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively, and a further increase in reaction time the biodiesel yield decreased.

It has been reported that the stirred time varied from 30 min to 150 min for biodiesel production especially for non-edible oils is beneficial, but further increase in duration decreased the biodiesel yield (Ijaz et al. 2016). Longer reaction time leads to form hydrolysis of esters and ultimately produces more fatty acids which help to produce soap (Leung & Guo 2006, Uzun et al. 2012). In addition, the biodiesel yield decreases with increase in reaction time because of the reversible reaction.

REBLO shows the highest biodiesel yield which is 91.7% compared to CEBLO and RWEBLO. In addition, CEBLO shows the higher yield compared to RWEBLO. The optimum biodiesel yield of 90.6%, 91.7%, 81.6%, 92.7% and 82.65% is observed for CEBLO, REBLO, RWEBLO, REPO and CEJO at a reaction time of 120 min, 60 min, 90 min, 90 min and 90 min, respectively.

5.5 Optimisation

The optimisation is done by changing the different operating parameters which influence the yield of biodiesel in transesterification. The optimisation is done to obtain the maximum yield of biodiesel for all the oil samples. The parameters considered in the optimisation process are methanol to oil molar ratio, catalyst concentration, reaction temperature and time. The impact of these affecting variables on the yield of methyl ester is observed for all the experiments. The range of optimal variables for methanol to oil ratio, catalyst concentration, reaction temperature and reaction time that is selected for optimisation is shown in Table 5.3.

Table 5.3: Range of optimal variables for biodiesel production

Samples	Methanol to oil ratio		Catalyst concentration (wt. %)		Reaction temperature (°C)		Reaction time (min)		Biodiesel yield (%)	
	Range	Optimum	Range	Optimum	Range	Optimum	Range	Optimum	Range	Optimum
CEBLO	5.5:1-7.5:1	7.0:1	0.5-1.5	1.0	40-80	60	50-130	120	90.6-91.1	91.1
REBLO	5.5:1-7.5:1	6.0:1	0.5-1.5	0.75	40-80	60	50-130	60	91.9-92.3	92.3
RWEBLO	5.5:1-7.5:1	6.5:1	0.5-1.5	1.0	40-80	60	50-130	90	81.6-82.8	82.8
REPO	5.0:1-7.0:1	6.0:1	0.5-1.5	1.0	40-80	60	60-120	90	92.7-93.4	93.4
CEJO	6.0:1-8.0:1	7.5:1	0.5-1.5	1.25	40-80	60	60-120	90	82.7-83.3	83.3

The optimal value is evaluated by varying each of the parameters. The maximum yield of biodiesel is obtained using the optimal value of each parameter. Biodiesel production from CEBLO, REBLO, RWEBLO, REPO and CEJO in transesterification under optimum conditions is observed at methanol to oil molar ratio of 7.0:1, 6.0:1, 6.5:1, 6.0:1 and 7.5:1, catalyst concentration of 1.0 (wt.%), 0.75 (wt.%), 1.0 (wt.%), 1.0 (wt.%) and 1.25% (wt.%), reaction time of 120 min, 60 min, 90 min, 90 min and 90 min, respectively. The optimum reaction temperature is found at 60 °C for all cases.

5.6 Purification and Drying

After completing the transesterification reaction, the mixture of the reacted product was poured into a separatory funnel and allowed to settle down the methyl ester and glycerol at room temperature for 8 hours. The product of the alkali transesterification results in the formation of two layers: the upper layer containing small quantities of excess methanol and transesterified products (esters) and the lower layer containing glycerol and other impurities (Venkanna & Venkataramana Reddy 2009). The methyl ester was obtained from the top of the separatory funnel after separating the glycerine and impurities on the bottom part of the funnel. The residual methanol and the water present in the biodiesel were removed by evaporation (Cao & Zhang 2015).

Glycerol is the by-product which was drained off from the bottom layer of the separatory funnel. After phase separation of crude biodiesel and glycerine, the obtained product was purified and washed carefully (Ong et al. 2014a). The transesterified product was separated from the top layer of the funnel and washed with 50% (vol./vol.) hot distilled water at 40 °C to purify the product, that is to remove traces of glycerine and impurities (Atapour et al. 2014). The successive washing process was utilised several (3-4) times to remove the impurities, such as residual catalyst, methanol, glycerol and soaps. In order to neutralise soap and residual catalyst, washing was done up to pH of 4.5 (Du et al. 2004). The lower layer was discarded and the upper layer was poured into a flask. The upper layer that contained biodiesel was centrifuged and subsequently dried to obtain high quality biodiesel. Finally, the washed methyl ester was dried over anhydrous sodium sulphate (Na_2SO_4) and filtered under vacuum conditions.

5.7 Gas Chromatrography (GC) Analysis and Fatty Acid Methyl Ester (FAME) Composition of Fuel

Gas chromatography (GC) analysis was performed to obtain the FAME composition of the produced biodiesel according to the European Standard (EN 14103 Standards). The details specifications of the GC analysis equipment and operating conditions are shown in Table 5.4. The FAME composition of the produced biodiesels is exhibited in Table 5.5. The FAME composition of poppy and waste cooking (PWC) biodiesel which is a binary mixture of poppy (80%) and waste cooking (20%) biodiesel is also included in Table 5.5. The results indicate that the crude esterified transesterified beauty leaf mehtyl ester (CETBLME), refined esterified transesterified beauty leaf methyl ester (RETBLME), refined transesterified beauty leaf methyl

ester (RTBLME), poppy methyl ester (PME), poppy waste cooking methyl ester (PWCME), and jojoba methyl ester (JME) contain 30.7%, 31.2%, 22.6%, 13.5%, 20.5% and 2.8% total saturated methyl ester, 41.8%, 41.1%, 45.3%, 17.3%, 46.4% and 83.9% of mono-unsaturated methyl ester, and 27.5%, 27.7%, 32.1%, 70.2%, 33.3% and 13.3% of poly-unsaturated methyl esters, respectively.

The FAME compositions of CETBL, RETBL, RTBL, poppy and jojoba methyl esters are agreed on the data available in the literature (Aksoy 2011b, Larkin 2007, Mosarof et al. 2016, Ong et al. 2014a, Rashid et al. 2016, Sajjad et al. 2015, Shah et al. 2010), respectively. The higher saturated fatty acid composition is observed in BL methyl ester, whereas, the higher unsaturated fatty acid composition is found in jojoba methyl ester. The most abundant FA of oleic (40.4%), oleic (40.1%), oleic (42.2%), linoleic (68.6%), oleic (45.3%), and eicosanoic (59.2%) is found in CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively.

Table 5.4: Operating conditions of gas chromatography (GC) 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	1µL
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	60 °C for 2 min.
	10 °C per min. to 200 °C
	5 °C per min. to 240 °C
	Hold 240 °C for 7 min.
Split flow	100 mL/min
Detector	250 °C, FID, full EFC control

The biodiesel production yield based on the GC analysis is calculated using Eq. (5.1) as shown below (Hamze et al. 2015, Omar et al. 2009, Wan Omar & Saidina Amin 2011):

$$Biodiesel\ yield = FAME\ percentage\ from\ GC\ analysis \times \frac{weight\ of\ biodiesel}{weight\ of\ oil} \qquad (5.1)$$

Table 5.5: Fatty acid composition of beauty leaf (*Calophyllum inophyllum*) methyl ester (BLME), poppy (*Papaver somniferum*) methyl ester (PME), poppy and waste cooking methyl esters (PWCME) and jojoba (*Simmondsia chinensis*) methyl ester (JME)

Fatty acid methyl ester (FAME)	Structure	Molecular formula	Composition (wt. %)					
			CETBLME	RETBLME	RTBLME	PME	PWCME	JME
Methyl Laurate	C12:0	$C_{12}H_{24}O_2$	0	0	0	0	0	0
Methyl Myristate	C14:0	$C_{14}H_{28}O_2$	0.10	0	0	0	0.2	0
Methyl Palmitate	C16:0	$C_{16}H_{32}O_2$	13.4	13.60	8.5	9.4	13.30	2.3
Methyl Palmitoleate	C16:1	$C_{16}H_{30}O_2$	0.3	0.2	0.8	0.2	0.6	0
Methyl Stearate	C18:0	$C_{18}H_{36}O_2$	16.5	16.7	13	3.1	4.3	0.2
Methyl Oleate	C18:1	$C_{18}H_{34}O_2$	40.4	40.1	42.2	16.6	45.3	10.4
Methyl Linoleate	C18:2	$C_{18}H_{32}O_2$	26.2	26.3	29.3	68.6	31.7	0.1
Methyl Linolenate	C18:3	$C_{18}H_{30}O_2$	0.4	0.3	0.8	0.8	0.6	0.5
Methyl Arachidate	C20:0	$C_{20}H_{40}O_2$	0.5	0.7	0.8	0	2.7	0
Methyl Eicosenoate	C20:1	$C_{20}H_{38}O_2$	0.3	0.3	0.7	0	0	58.2
Methyl Arachidonate	C20:4	$C_{20}H_{32}O_2$	0	0	0	0	0	8.2
Methyl Docosanoate	C22:0	$C_{22}H_{44}O_2$	0.2	0.2	0.3	0	0	0.3
Methyl Erucate	C22:1	$C_{22}H_{42}O_2$	0	0	0	0	0	11.4

Methyl Docotetrasenoate	C22:4	$C_{22}H_{36}O_2$	0	0	0	0	0	3.6
Methyl Lignocerate	C24:0	$C_{24}H_{48}O_2$	0	0	0	0	0	0
Methyl Nervonate	C24:1	$C_{24}H_{46}O_2$	0	0	0	0	0	1.4
Saturated fatty acid			30.7	31.2	22.6	13.5	20.5	2.8
Mono-unsaturated fatty acid			41.8	41.1	45.3	17.3	46.4	83.9
Poly-unsaturated fatty acid			27.5	27.7	32.1	70.2	33.3	13.3
Others			1.7	1.6	3.6	1.3	1.5	3.4

5.8 Characterisation of Physico-Chemical Properties of Methyl Esters (Biodiesel)

Several factors influence the quality of biodiesel, such as the quality of feedstock, fatty acid composition of the feedstock, type of production, refining processes and post production parameters (Atabani et al. 2012, Azad & Islam 2012, Azad et al. 2014c). Therefore, a standard has to be established to assess the biodiesel fuel quality. The physico-chemical properties of synthesised poppy, BL and jojoba biodiesel are tested on the basis of the ASTM and EN standards, and the results are shown in Table 5.6. The physico-chemical properties of the PWC methyl ester are also included in Table 5.6. It can be noted that biodiesel fuels should meet the international standard specifications of biodiesel, such as the ASTM and EN standards. The important fuel property parameters that are investigated include: density (ASTM D4052), kinematic viscosity (ASTM D445), acid value (ASTM D664), calorific value (EN 14213), flash point (ASTM D93), pour point (ASTM D2500), cloud point (ASTM D2500), cold filter plugging point (ASTM D6371), cetane number (ASTM D6890), oxidation stability (EN 14112), iodine value (EN 14111), copper strip corrosion (ASTM D130), carbon residue (ASTM D4350), sulphur content (ASTM D6667) and sulphated ash content (ASTM D874). The entire properties test is conducted at Engine Tribology Laboratory, University of Malaya (UM), Malaysia.

It can be seen from Table 5.6 that the CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs fulfil the major international ASTM and EN biodiesel standards. The table shows that the produced biodiesel has a good agreement on fuel properties with those of diesel with few exceptions. It was also observed that the properties of CETBLME, RETBLME, RTBLME, PME, PWCME, and JMEs have a good agreement with other studies (Aksoy 2011b, Ong et al. 2014a, Ong et al. 2014b). The results obtained from fuel properties indicated that the transesterification process improved the fuel qualities of methyl ester with respect to density (kg/m^3), viscosity (mm^2/s), calorific value (MJ/kg), flash point (°C), cloud point (°C) and pour point (°C). The physico-chemical properties of CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs are summarised below:

Table 5.6: Physico-chemical properties of BLME, PME, PWCME and JMEs

Properties	Units	Methods/ Standards	ASTMD6751 (Accept. limit)	EN14214 (Accept. limit)	Diesel	CETBLME	RETBLME	RTBLME	PME	PWCME	JME	SD of Diesel
Density at15 °C	kg/m^3	ASTM D4052	880	860-900	832	879.2	878.2	886.6	874.2	877.3	868.6	±0.12
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	1.9-6.0	3.5-5.0	3.32	4.57	4.44	5.24	4.13	4.33	6.66	±0.09
Acid value	mg KOH/ g	ASTM D664	Max. 0.5	Max. 0.5	0.05	0.45	0.42	0.55	0.37	0.40	0.33	±0.01
Calorific value	MJ/kg	ASTM D240	-	35	45.66	38.527	38.741	38.342	40.365	39.492	36.3	±0.08
Flash point	°C	ASTM D93	Min. 100-170	>120	68	169	166.8	177	172	176	167	±0.06
Pour point	°C	ASTM D2500	-15 to -16	-	0	8	10	5	-13	-9	-7	-
Cloud point	°C	ASTM D2500	-3 to -12	-	8	10	12	6	-5	-3	-3	±0.09
Cold filter plugging point	°C	ASTM D6371	19	Max. +5	5	5	4	8	-5	-4	-6	±0.05
Cetane number	-	ASTM D6890	Min. 47	Min. 51	48	58.3	59.6	53.7	58	56	68	±0.1
Oxidation stability at 110 °C	hour	EN 14112	Min. 3	Min. 6	39	13.27	13.42	13.08	12.26	11	3.1	±0.08
Iodine value	g I$_2$/100 g	EN 14111	-	Max. 120	-	101	98	106	116	96	109	-
Copper strip corrosion (3 hours at 50 °C)	-	ASTM D130	Max. 3	Min. 1	1a	1a	1a	1b	1a	1a	-	-
Carbon residue (10% res)	wt. %	ASTM D 4350	Max. 0.3	-	0.820	0.031	0.03	0.036	-	0.160	-	±0.03

Ester content	wt. %	-	-	Min. 96.5	-	97.1	97.4	86.3	-	97.7	-	-
Sulphur content	wt. %	ASTM D6667	Max. 0.05	10	0.05	4.1	3.97	5.1	0.01	<0.013	-	±0.02
(Sulphated) Ash content	wt. %	ASTM D874	Max. 0.02	Max. 0.02	0.002	0.0012	0.001	0.0014	0.015	0.016	-	±0.001

5.8.1 Density

The density of the fuel is very important for injector nozzle because it effects on engine operation. Moreover, this can influence the efficiency of the fuel atomization for airless combustion systems (Silitonga et al. 2013c, Uriarte 2010). Usually, the biodiesel fuels are denser and less compressible than the diesel fuel (Atabani et al. 2013b, Canakci & Sanli 2008). The presence of an unsaturated acid with more than two double bonds will increase the density of biodiesel (Silitonga et al. 2013c). The density of biodiesel is measured using the ASTM D4052 test method. The densities of 879.2 (kg/m^3), 878.2 (kg/m^3), 886.6 (kg/m^3), 874.2 (kg/m^3), 877.3 (kg/m^3) and 868.6 (kg/m^3) are obtained for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively, which is shown in Table 5.6.

5.8.2 Kinematic Viscosity

Viscosity is the most important parameter of biodiesel as it affects the operation of fuel injection equipment as well as spray atomisation, particularly at low temperatures while increase in viscosity affects the fluidity of the fuel (Atabani et al. 2012, Atabani et al. 2013b, Demirbas 2009c, Shah et al. 2014). In addition, high viscosity may cause the formation of soot and engine deposits due to insufficient fuel atomisation. It has been observed that the viscosity of oil decreased significantly after transesterification (Atabani et al. 2013b). In this study, the kinematic viscosity of methyl ester was determined according to the ASTM D445 standard. The kinematic viscosity of CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs is within the range of ASTM and EN standards of biodiesel. However, these values are higher than the petroleum diesel. As shown in Table 5.6, the viscosities of 4.57 (mm^2/s), 4.44 (mm^2/s), 5.24 (mm^2/s), 4.13 (mm^2/s), 4.33 (mm^2/s) and 6.66 (mm^2/s) are found for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively.

5.8.3 Acid Value (AV)

The AV is a measure of FFAs contained in a fresh fuel sample. Fatty acids vary in carbon chain length and the number of unsaturated bonds (double bonds). However, AV or neutralisation number can be expressed as mg KOH required for neutralising 1 g of fatty acid methyl esters (FAMEs). It has been observed that a higher amount of free fatty acids leads to a higher AV, and consequently, higher acid content can cause severe corrosion in the fuel supply system of

an engine (Atabani et al. 2012). AV can provide an indication of the level of lubricant degradation while the fuel is in service (Fernando et al. 2007). In this study, the AV is evaluated using the ASTM D664 standard and the values are found within the limit of ASTM standard of biodiesel except for RTBLME. The AVs of 0.42 (mg KOH/g), 0.55 (mg KOH/g), 0.37 (mg KOH/g), 0.40 (mg KOH/g), 0.45 (mg KOH/g) and 0.33 (mg KOH/g) are observed for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively, which is exhibited in Table 5.6.

5.8.4 Calorific Value (CV)

The CV or heating value is one of the most important parameters to characterise a fuel because of its energy content. Clearly, higher CV value is desirable for a combustion engine. The CV of all methyl esters were found lower in comparison to diesel due to its higher oxygen content which assists for complete combustion of fuel in the engine (Atabani et al. 2013b, Ramadhas et al. 2005, Sahoo & Das 2009b). The CV is measured according to the EN 14213 standard, and the value fulfilled the requirements of EN biodiesel standard. The CVs of 38.527 (MJ/kg), 38.741 (MJ/kg), 38.342 (MJ/kg), 40.365 (MJ/kg), 39.492 (MJ/kg) and 36.3 (MJ/kg) are observed for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively, as shown in Table 5.6.

5.8.5 Flash Point (FP)

The FP is the temperature at which biodiesel ignites when exposed to a flame or a spark. FP varies inversely with the fuels' volatility. Generally, biodiesel has a higher FP compared to diesel fuel and is usually more than 150 °C, while the conventional diesel has a flash point of 55-66 °C. It has been observed that the relationships between viscosity and FP for vegetable oil methyl esters are irregular (Demirbas 2008c, Demirbas 2009c). It can be shown from Table 5.6, the values of FPs are within the prescribed limit of ASTM specification. The higher FPs of 169 °C, 166.8 °C, 177 °C, 172 °C, 176 °C and 167 °C are observed for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively, which indicates the benefit of higher safety than the petroleum diesel for transport purposes (Atapour et al. 2014). However, higher FP may cause low ability to complete combustion in diesel engines as compared to petro-diesel (Shah et al. 2014).

5.8.6 Cloud Point (CP) and Pour Point (PP)

The CP and PP are two important characteristics of fuel for their use under low-temperature conditions. The CP is the temperature at which a cloud of wax crystals first becomes visible when the fuel is cooled under controlled conditions during a standard test. The PP is defined as the temperature at which the amount of wax form of a solution is enough to get the fuel. Generally, biodiesel has higher CP and PP compared to conventional diesel (Atabani et al. 2013b, Demirbas 2009c). The CP and PP are measured using ASTM D2500 and D2500 procedures, respectively. The CPs and PPs of -10 °C and 8 °C, 12 °C and 10 °C, 6°C and 5 °C, 5 °C and -13 °C, -3 °C and -9 °C, and -3 °C and -7 °C are observed for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively, as shown in Table 5.6. However, the CPs and PPs of CETBLME, RETBLME and RTBLMEs are found to be higher than the petro-diesel except CP of RTBL methyl ester which is due to the higher FFA compositions of the FAMEs (Atabani et al. 2013b, Silitonga et al. 2013c).

5.8.7 Cold Filter Plugging Point (CFPP)

The CFPP is used as an indicator of low-temperature operability of fuels. It indicates the temperature at which the test filter starts to plug due to fuel components that have started to gel or crystallise (Atabani et al. 2012, Atabani et al. 2013b). It also states the fuels limit of filterability, having a better characteristic than CP for biodiesel as well as petro-diesel. Generally, the CFPP value of fuel is lower than its CP. In this analysis, the CFPP is measured using ASTM D6371 standard and the values of CFPP for all methyl esters also fulfilled the ASTM biodiesel standard. Table 5.6 shows the CFPPs of CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs. The CFPPs of -4 °C, 5 °C, 4 °C, 8 °C, 5 °C, -5 °C and -6 °C are observed for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively.

5.8.8 Cetane Number (CN)

The CN is the most significant property of biodiesel that affects the ignition delay. The CN is an indication of the ignition quality or ability of fuel to auto-ignite quickly after being injected. A higher CN indicates shorter ignition delay, that is, shorter time between the ignition and the initiation of fuel injection into the combustion chamber (Atabani et al. 2012, Karmakar et al. 2010, Lapuerta et al. 2008b). The CN increases with increase in chain length and saturation of

fatty acids (Atabani et al. 2012, Ong et al. 2013). The lower CN tends to cause knocking, and increase gaseous and particulate exhaust emissions (PM). However, biodiesel has higher CN than conventional diesel because of its higher oxygen content which resulted in higher combustion efficiency (Atabani et al. 2012, Atabani et al. 2013b). The CN found in this study fulfilled the ASTM and EN specifications. The CN obtained in this analysis is found to be higher than the CN of petro-diesel. The CNs of 58.3, 59.6, 53.7, 58, 56 and 59 are found for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs which is shown in Table 5.6, respectively.

5.8.9 Oxidation Stability

The oxidation of biodiesel fuel is one of the major parameters that help to assess the fuel quality. Oxidation stability is an indication of the degree of oxidation, potential reactivity with air and can determine the need for antioxidants (Atabani et al. 2012). Oxidation occurs due to the presence of heat, traces of metal, peroxides, light, unsaturated fatty acid chains and the double bonds, which react with oxygen as soon as it is being exposed to the air (Hoekman et al. 2012, Ong et al. 2013). The oxidation stability is measured on the basis of EN 14112 standard, and it is found that the value is within the limit of EN 14112 specifications. The oxidation stabilities of CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs are shown in Table 5.6, and the values are found to be 13.27 hours, 13.42 hours, 13.08 hours, 12.26 hours, 11 hours and 3.1 hours, respectively.

5.8.10 Iodine Value (IV)

The IV is an index of the number of double bonds in biodiesel which measures the degree of unsaturation of the biodiesel. The oxidation stability and polymerisation of glycerides are strongly influenced by this property. It helps to cause the formation of deposits in diesel engine injectors (Ong et al. 2013, Sanford et al. 2009). It has been observed that the IV is closely correlated to biodiesel viscosity, CN and cold flow characteristics (cold filter plugging point) (Atabani et al. 2013b). The IV is found within the prescribed limit of EN biodiesel standard. As presented in Table 5.6, the IVs of 101 (g I_2/100 g), 98 (g I_2/100 g), 106 (g I_2/100 g), 116 (g I_2/100 g), 96 (g I_2/100 g) and 109 (g I_2/100 g) are observed for CETBLME, RETBLME, RTBLME, PME, PWCME and JMEs, respectively.

5.8.11 Copper Strip Corrosion

The evaluation of copper strip corrosion property is a qualitative method to determine the corrosion of biodiesel. The corrosion tendency of fuel, when used with copper, brass or bronze parts, is measured by the copper corrosion test. To determine the degree of corrosion, a copper strip is heated up to 50 °C in a fuel bath for 3 hours followed by comparison with a standard strip (Atabani et al. 2012). According to ASTM D130 standard, the copper strip corrosion values of 1a, 1a, 1b, 1a and 1a are found for CETBLME, RETBLME RTBLME, PME and PWCMEs, respectively (Table 5.6).

5.8.12 Carbon Residue

Carbon residue of fuel indicates the extent of carbon deposits resulting from the combustion of fuel. Carbon residue for biodiesel fuel is more important than that of diesel fuel owing to its higher correlation with the presence of FFAs, glycerides, soaps, polymers higher unsaturated fatty acids as well as inorganic impurities (Atabani et al. 2012). However, carbon residue is formed by decomposition and subsequent pyrolysis of the fuel components that can clog the fuel injectors. According to ASTM D4350 standard, the carbon residue values are found at 0.031 (wt.%.), 0.03 (wt.%.), 0.036 (wt.%.) and 0.160 (wt.%.) for CETBLME, RETBLME, RTBLME and PWCMEs, respectively, as shown in Table 5.6.

5.8.13 Sulphur Content

Combustion of fuel containing sulphur causes emissions of sulphur oxides. It has been observed that the biodiesel produced from vegetable oils has very low levels of sulphur content (Atabani et al. 2013b). However, specifying this parameter is significant for engine operability (Balat & Balat 2010). The sulphur contents of 4.1 (wt.%.), 3.97 (wt.%.), 5.1 (wt.%.), 0.01 (wt.%.) and <0.013 (wt.%.) are observed for CETBLME, RETBLME, RTBLME, PME and PWCMEs, respectively (Table 5.6).

5.8.14 Sulphate Ash Content

The inorganic contaminants such as abrasive solids, catalyst residues, and the concentration of soluble metal soaps contained in a fuel sample are the instances of ash content (Fernando et al. 2007). Sulphate ash content is lower compared to petro-diesel. Therefore, biodiesel will not

create any problems when used as a fuel in diesel engines. The sulphate ash contents of 0.0012 (wt.%.), 0.001 (wt.%.), 0.0014(wt.%.), 0.015 (wt.%.) and 0.016 (wt.%.) are found for CETBLME, RETBLME, RTBLME, PME and PWCMEs, as shown in Table 5.6.

5.9 Conclusion

The biodiesel produced from BL, poppy and jojoba could be a future generation product which will fulfil the modern market demand while also resolving environmental concerns. In this study, single stage and 2 stage processes which consisted of esterification and transesterification were conducted while methanol was used as a reagent and H_2SO_4 and KOH as catalysts to synthesise poppy, BL and jojoba oil into respective methyl ester. First, esterification was conducted to reduce the free fatty acids (FFAs) as high FFAs content in oil leads to soap formation and reduce the biodiesel yield significantly and then transesterification was done to produce biodiesel, respectively. This study demonstrates the successful production and optimisation of poppy, BL and jojoba-based FAMEs which are on good agreement to meet the ASTM and EN biodiesel standards.

The results indicate that BLME, PME, PWCME and JMEs fulfilled all the major international specifications of ASTM and EN biodiesel standards with few exceptions. Physico-chemical properties of BLME, PME, PWCME and JMEs were evaluated and characterised according to the ASTM and EN biodiesel standards. It is found that almost all the biodiesel properties are within the acceptable range of the ASTM and EN biodiesel standards with few exceptions. The FAMEs of BL, poppy, PWC and jojoba biodiesel were determined by GC analysis. Biodiesel quality and fuel properties are highly dependent on the presence of fatty acid composition in the fuel blend. Moreover, biodiesel CN, CP, and oxidation stability increases in presence of saturated fatty acid alkyl ester in the fuel blend.

The optimum yield of methyl ester is obtained through methanolysis of oil under various affecting variables which include: methanol to oil ratio, catalyst loading, reaction temperature and reaction time. The results indicate that the maximum conversion efficiencies of 91.1%, 92.3%, 82.8%, 93. 4% and 83.3% are obtained for CEBLO, REBLO, RWEBLO, REPO and CEJO at optimum conditions. During optimisation, optimal variables were achieved as follows: methanol to oil ratio of 7.0:1, 6.0:1, 6.5:1, 6.0:1, and 7.5:1, catalyst concentration of 1.0 (wt.%), 0.75 (wt.%), 1.0 (wt.%), 1.0 (wt.%) and 1.25 (wt.%), and reaction time of 120 min, 60 min, 90

min, 90 min and 90 min for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively. At optimum condition, the reaction temperature was observed at 60 °C for all cases.

Later, the biodiesel production process was carried out under the optimum conditions and similar procedures were used from the poppy, BL and jojoba oil. It can be noted that the REBLO can be used for biodiesel production due to the variation in yield of biodiesel and better fuel properties in comparison to CEBLO and RWEBLO.

CHAPTER 6

ENGINE PERFORMANCE ANALYSIS

In this chapter, the performance of the engine output is presented in terms of brake power (BP), torque, brake specific fuel consumption (BSFC), brake thermal efficiency (BTE) and brake mean effective pressure (BMEP). To achieve these, an experimental study was conducted on a compression ignition (CI) engine using neat diesel and biodiesel-diesel blends. Biodiesel-diesel blends of B5, B10 and B20 for poppy, PWC, BL and jojoba were used in this investigation. The experiment was conducted for different engine speed (1200 rpm-2400 rpm) and load (25%, 50%, 75% and 100%). The speed of the engine was varied from 1200 rpm to 2400 rpm with 200 rpm interval. The results indicate that BP increases with increase in speed up to the maximum speed of 2400 rpm, whereas, BSFC decreases initially up to 1400 rpm and then increases up to the maximum speed of 2400 rpm at full load condition. On the other hand, torque, BTE and BMEP initially increases up to 1400 rpm, and then, decreases with increase in speed up to the maximum speed of 2400 rpm. With increasing load, the performance variables BP, torque, BTE and BMEP increases, whereas, BSFC decreases. The engine performance results with diesel and biodiesel-diesel blends are compared and discussed. The results revealed that BP, torque, BTE, BSFC and BMEP are lower in biodiesel blends in comparison to diesel.

6.1 Introduction

Numerous studies have been conducted to explore alternative renewable fuel resources and measures on how to use the energy in the most efficient way (Ashnani et al. 2014, Mofijur et al. 2015a, Mosarof et al. 2015). One of the principal ways to overcome the dependency on fossil fuel is using the alternative liquid fuel which is so called biodiesel in CI engines. It has the higher flash point, lubricity, cetane number and oxygen content, although it has the higher viscosity, pour point, lower calorific value and volatility, lower oxidation stability in comparison to diesel (Rakopoulos et al. 2011). Also, it has good ignition ability due to its high cetane number in comparison to diesel (Gumus 2010). It is generally accepted that biodiesel-diesel blends up to B20 could be used in existing diesel engines. In terms of engine performance, most of the studies showed that biodiesel-diesel blends decrease in BP and increase in fuel consumption compared to diesel (Aydin & Bayindir 2010, Buyukkaya 2010, Chauhan et al.

2012, Gumus & Kasifoglu 2010, Ruhul et al. 2016b, Wood et al. 2015). Several researchers showed that increase in the percentage of biodiesel in the blend resulted in a decrease in power (Ong et al. 2014b, Ruhul et al. 2016b). A few researchers reported that diesel has higher torque than the biodiesel blend (Ong et al. 2014b, Utlu & Koçak 2008). Overall, biodiesel-diesel blends could be considered as a prospective future transportation fuel. Although many studies have been conducted on engine performance characteristics using different feedstocks, however, very few studies have been conducted using poppy, BL and jojoba biodiesel-diesel blends on engine performance analysis. Furthermore, to the best of the author's knowledge, no study has been conducted using PWC biodiesel-diesel blends in a CI engine. The purpose of this chapter is to analyse the performance characteristics using poppy, PWC, BL and jojoba biodiesel-diesel blends.

6.2 Experimental Setup for Engine Testing

A four-cylinder, four-stroke, liquid-cooled diesel engine was used for the experimental investigation. The experiments were conducted at the thermodynamics laboratory in Central Queensland University, Australia. The engine test bed which was used for the experiment is shown in Figure 6.1. A schematic diagram of the engine test rig is shown in Figure 6.2.
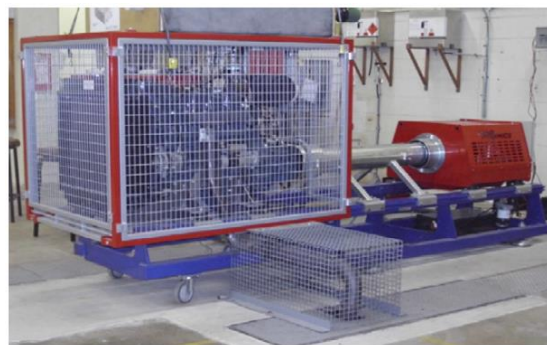
Figure 6.1: Engine test bed for experiment
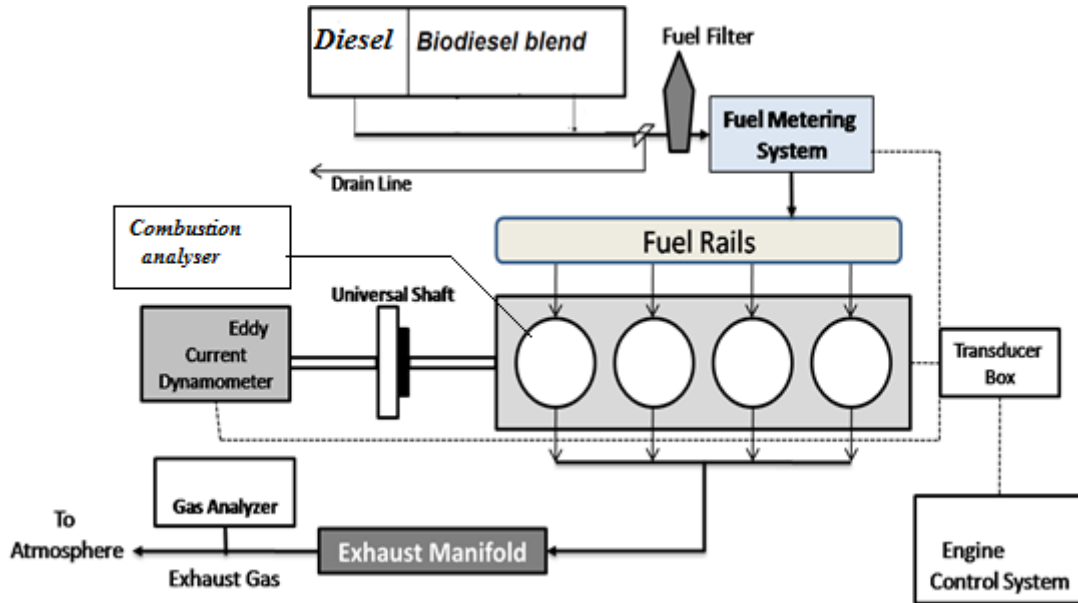
Figure 6.2: Schematic diagram of the engine test rig

The test rig is directly coupled to the eddy current dynamometer. An eddy current dynamometer built in auto controller system was used to determine the engine performances and speed. The detailed specifications of the engine test rig and operating condition is presented in Table 6.1.

Table 6.1: Test engine specifications

Model	Kubota V3300
Type	Vertical, 4 cycle liquid cooled diesel
No. of cylinders	4
Total displacement (L)	3.318
Bore × Stroke (mm)	98 × 110
Combustion system	E-TVCS
Intake system	Natural aspired
Output:	
Gross intermittent (kW/rpm)	54.5/2600
Net intermittent (Rated power output) (kW/rpm)	50.7/2600
Net continuous (kW/rpm)	44.1/2600

Rated Torque (N m/rpm)	230/1400
Compression ratio	22.6
No load high idling speed (rpm)	2800
No load low idling speed (rpm)	700-750
Direction of rotation	Counter clockwise (viewed from flywheel side)
Governing	Centrifugal fly weight high speed governor
Fuel	Diesel fuel No-2-D (ASTM D975)
Starter capacity (V-kW)	12-2.5
Alternator capacity (V-A)	12-60

A Coriolis-type flow meter (Model: CMF025M319NQEIEZZZ) was used to measure the fuel flow rate. The engine fuel system was adjusted by using two different tanks with nozzle systems to the main fuel supply line. An initial engine run was conducted with diesel before starting the test with different biodiesel-diesel blends.

The performance parameters of the engine, such as BP, torque, BTE, BSFC and BMEP. BP, torque and engine speed were measured using Dyno Dynamics (450DS) software which was interfaced with the computer.

BSFC, BTE and BMEP were calculated using the following formulae, respectively:

$$BSFC = \frac{f}{BP} \tag{6.1}$$

where, $BSFC$ is the brake specific fuel consumption (g/kWh), f is the fuel consumption rate (g/hr), and BP is the brake power (kW)

$$BTE = \frac{BP \times 100 \times 3600}{f \times CV} \tag{6.2}$$

where, BTE is the brake thermal efficiency (%), CV is the calorific value of the fuel (kJ/kg)

and

$$BMEP = \frac{4.\pi.T}{D} \tag{6.3}$$

where, *BMEP i*s the brake mean effective pressure (kPa), *T* is the engine torque (N.m) and *D* is the engine displacement volume (m^3).

An exhaust gas analyser (EGA) CODA was used to measure the exhaust emissions, such as nitrogen oxides (NO_x), carbon dioxide (CO_2), carbon monoxide (CO), hydrocarbon (HC) and PM emission. Particulate matter (PM) meter MAHA Emission Viewer was used to measure the PM emission. The EGT was measured by a K-type thermocouple. The detailed specifications of the EGA and PM meter are shown in Table 6.2.

Table 6.2: The detailed specification of the exhaust gas analyser (EGA) and particulate matter (PM)

Measured gas	Measurement		
	Range	Resolution	Accuracy
HC	0–30,000 ppm (n-Hexane)	1 ppm	±4 ppm abs.
CO	0-15%	0.001%	±0.02% abs.
CO_2	0-20%	0.01%	±0.3% abs.
O_2	0-25%	0.01%	±0.1% abs.
NO_x	0-5,000 ppm	1 ppm	±20 ppm abs.
PM	Particle size <100 nm - > 10 microns	Particle concentration range (0.1 - > 700 mg/m^3)	Resolution ±0.1 mg/m^3

A combustion analyser measured the combustion data, such as cylinder pressure (CP) and instantaneous cylinder volume against crank angle (CA). The engine testing conditions for both diesel and biodiesel-diesel blends are given in Table 6.3.

Table 6.3: Engine test setting for diesel and biodiesel-diesel blends

Fuels	Engine speed (rpm)	Engine Load (%)			
		25%	50%	75%	100%
Diesel and Biodiesel-diesel blends: PB5, PB10, PB20, PWCB5, PWCB10, PWCB20, BLB5, BLB10, BLB20, JB5, JB10 and JB20	1200	√	√	√	√
	1400	√	√	√	√
	1600	√	√	√	√
	1800	√	√	√	√
	2000	√	√	√	√
	2200	√	√	√	√
	2400	√	√	√	√

In this chapter, the performance characteristics are discussed, whereas, the emission and combustion characteristics are discussed in chapters 7 and 8, respectively.

6.3 Biodiesel-Diesel Blend

Blending of poppy, PWC (80% poppy and 20% waste cooking), BL and jojoba methyl esters with diesel was first prepared at different ratios (5%-20% by volume) using a magnetic stirrer (IKA C-MAG HS7) and a shaker (IKA KS 130) at 2000 rpm and 600 rpm for 30 min, respectively. Specifically, the biodiesel-diesel blends of B5, B10 and B20 for poppy, PWC, BL and jojoba methyl esters were used to run the experiment, where, B5, B10 and B20 indicates 5% biodiesel and 95% diesel, 10% biodiesel and 90% diesel, and 20% biodiesel and 80% diesel, respectively. Overall, the experimental investigation was conducted using 13 fuel samples: neat diesel, PB5, PB10, PB20, PWCB5, PWCB10, PWCB20, BLB5, BLB10, BLB20, JB5, JB10 and JB20, respectively. All the experimental data of biodiesel blends are compared with that of neat diesel fuel.

6.4 Characterisation of Biodiesel-Diesel Blend

The biodiesel-diesel blends are used to evaluate the effect of blending on physio-chemical properties, performance, emission and combustion characteristics. The physico-chemical properties of poppy (*Papaver somniferum*), PWC, BL (*calophyllum inophyllum)* and jojoba (*simmondsia chinensis*) biodiesel-diesel blends are shown in Table 6.4. It can be seen from

Table 6.4 that most of the properties (density, kinematic viscosity, acid value, flash point and oxidation stability) of biodiesel blends met the ASTM and EN standards. It could be noted that density, kinematic viscosity, acid value, flash point and cetane number increase with an increase in the percentage of biodiesel in the blends. Calorific value and oxidation stability decrease with an increase in the level of the biodiesel blend. The decrease in calorific value is mainly due to the higher oxygen content in biodiesel than diesel. The decrease in oxidation stability in biodiesel blends is because of increase in the percentage of unsaturated fatty acids.

Table 6.4: Physico-chemical properties of poppy (*Papaver somniferum*), poppy and waste cooking, beauty leaf (*calophyllum inophyllum)* and jojoba (*simmondsia chinensis*) biodiesel blends

Properties	Units	Methods/ Standards	Diesel	PB5	PB10	PB20	PWCB5	PWCB10	PWCB20	BLB5	BLB10	BLB20	JB5	JB10	JB20
Density at 15°C	kg/m^3	ASTM D4052	832	833.8	837.4	841.1	835.6	837.8	840.3	836.7	838.6	841.2	833.4	834.5	836.2
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	3.32	3.39	3.47	3.55	3.54	3.60	3.65	3.62	3.69	3.77	3.95	4.02	4.10
Acid value	mg KOH/g	ASTM D664	0.05	0.20	0.22	0.25	0.22	0.24	0.26	0.23	0.25	0.27	0.17	0.18	0.20
Calorific value	MJ/kg	EN 14213	45.66	45.0	44.22	43.6	44.3	43.5	42.8	43.6	42.8	42.0	42.2	41.4	40.5
Flash point	°C	ASTM D93	68	74	77	81	76.5	79.2	83	72.3	75.2	79	72.6	75.6	79.5
Pour point	°C	ASTM D2500	0	1	2	2	1	2	3	1	1	3	1	3	3
Cloud point	°C	ASTM D2500	8	8	8	7	8	7	7	8	8	7	7	7	6
Cold filter plugging point	°C	ASTM D6371	5	6	7	7	6	5	6	7	6	5	5	6	6
Cetane number	-	ASTM D6890	48	50.8	55.9	61.8	50.7	55.3	61.4	51.1	55.9	61.1	53.3	62.6	71.4

Oxidation stability at 110 °C	hour	EN 14112	39	36	33	29	35	32	27.4	37	35	31	27	24	20
Copper strip corrosion (3 hours at 50 °C)	-	ASTM D130	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a

6.5 Accuracy and Uncertainty Analyses

The accuracy and uncertainty analysis of the measured values is significant to validate the accuracy of the experimental results. The accuracy and uncertainty analysis was performed in this study to validate the data obtained from the experimental measurements. Table 6.5 shows the accuracy values and uncertainty of the measured quantities used during this experiment. Uncertainties occur under different experimental conditions, selection and calibration of the instruments, observation, data input, test assembly and so on (Imdadul et al. 2016, Sajjad et al. 2015). The uncertainty of different measured quantities, such as speed, BP, torque, NO_x, CO_2, CO, HC EGT, and PM was calculated using the percentage uncertainties of the various instruments used.

Table 6.5: Measurement accuracy and uncertainty of the instruments

Measurements	Measurement accuracy	Uncertainty (%)
Fuel flow	± 0.03 (L/h)	±0.39
Temperature	± 1 °C	±0.21
Engine speed	± 2 rpm	±0.14
BP	± 0.03 kW	±0.13
Torque	± 5 N/m	±0.05
BSFC	± 4 g/kWh	±2.01
BTE	± 4%	±1.90
BMEP	± 10 kPa	±1.18
NO_x	± 20 ppm	±5.02
CO	± 0.02 (% vol.)	±1.20
CO_2	± 0.3 (% vol.)	±1.4
HC	± 4 ppm	±2.18
PM	± 0.1 mg/m^3	±0.02

The uncertainty of calculated values was determined by using the linearized approximation method of uncertainty (Fattah et al. 2014, Kalam & Masjuki 2011, Mofijur et al. 2014b). A sample calculation of uncertainty analysis for CO emission was done and provided in Appendix

A (Table A.3). To calculate the overall uncertainty in percentage, uncertainties of different variables and propagation of errors were considered. The overall uncertainty was computed as follows:

The overall experimental percentage uncertainty was calculated based on the principle of propagation of errors and was estimated as ±6.53%. The overall uncertainty was calculated as follows:

Overall experimental uncertainty

$$= \sqrt{\begin{pmatrix} (uncertainty\ of\ fuel\ flow)^2 + (uncertainty\ of\ temperature)^2 + (uncertainty\ of\ engine\ speed)^2 \\ + (uncertainty\ of\ CO)^2 + (uncertainty\ of\ CO_2)^2 + (uncertainty\ of\ HC)^2 + \\ + (uncertainty\ of\ PM)^2 + + (uncertainty\ of\ BP)^2 + (uncertainty\ of\ torque)^2 \\ + (uncertainty\ of\ BSFC)^2 + (uncertainty\ of\ BTE)^2 \\ + (uncertainty\ of\ BMEP)^2 + (uncertainty\ of\ NO_x)^2 \end{pmatrix}}$$

$$= \sqrt{\begin{matrix} (0.39)^2 + (0.21)^2 + (0.14)^2 + (1.20)^2 + (1.4)^2 + (2.18)^2 + (0.02)^2 + (0.13)^2 + (0.05)^2 + (2.01)^2 + (1.9)^2 \\ + (1.18)^2 + (5.02)^2 \end{matrix}}$$

$$= \pm 6.53\%$$

6.6 Brake Power (BP)

The relation between BP and engine speed for PB, PWC, BL and JB at biodiesel-diesel blends of B5, B10 and B20 at full load condition is presented in Figures 6.3 (a), (b), (c) and (d), respectively. It shows that the trend of engine BP output for all biodiesel-diesel blends over the entire range of engine speed is similar, that is, the brake power increases with increase in speed for all blending conditions. It can be seen from Figure 6.3 that the BP decreases with increase in biodiesel-diesel blend level at all engine speeds. The maximum BP is obtained at B5 compared to B10 and B20 for all biodiesel-diesel blends as presented in Figure 6.3.
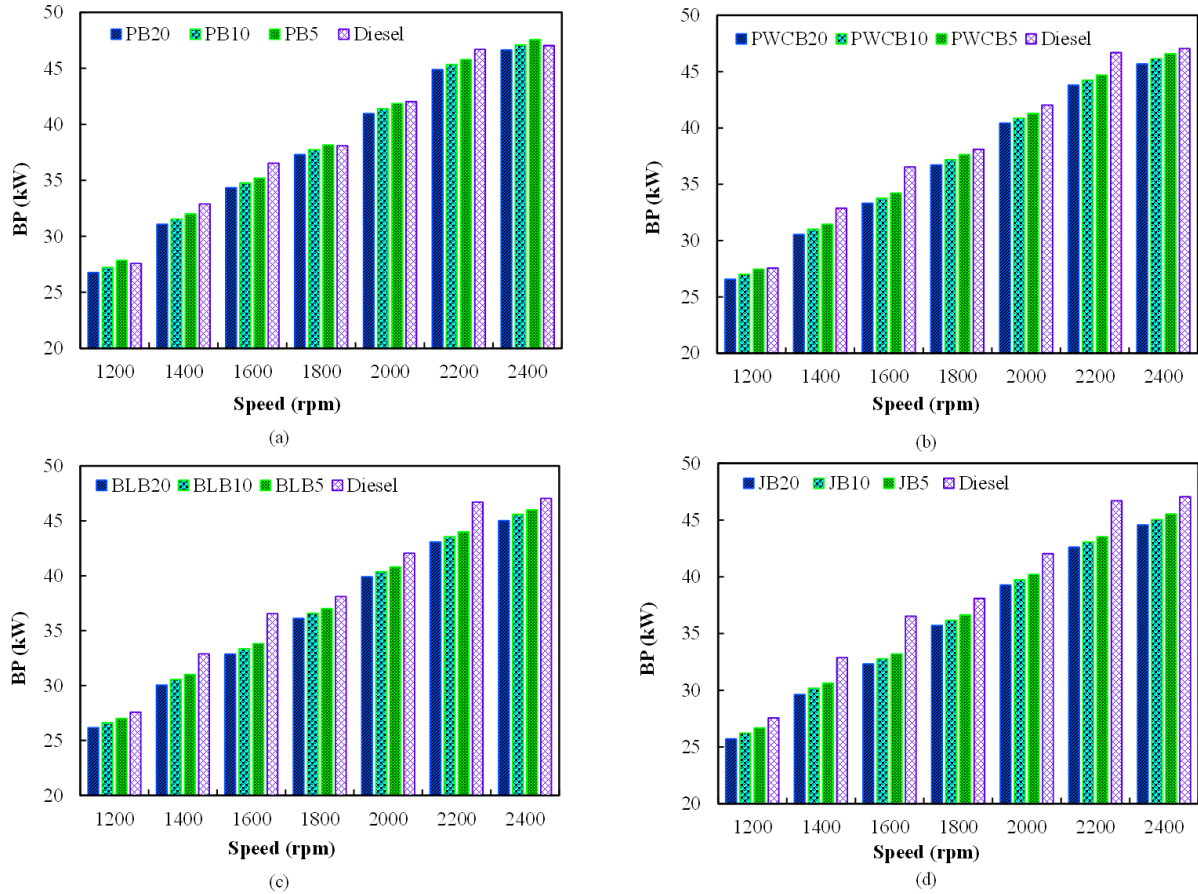
Figure 6.3: Relation between BP and engine speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

This is because of the higher heating value, lower density, as well as the lower viscosity of B5 blended fuel (Mofijur et al. 2014a, Ong et al. 2014b). Similar results were reported by several other researchers (An et al. 2013, Aydin & Bayindir 2010, Buyukkaya 2010, Kalam et al. 2003, Kim & Choi 2010, Ong et al. 2014b, Ozsezen et al. 2009, Usta 2005a). It has been observed that the properties of the blended fuel influence the combustion system.

Furthermore, the higher BP indicates a better combustion in using biodiesel blends. From Figure 6.3, it can be seen that PB has a higher BP in comparison to PWCB, BLB and JB. Also, PB has a positive influence on combustion especially in fuel rich zones due to the higher oxygen content. From Figure 6.3, the average BPs of 38.35 kW, 37.62 kW, 37.09 kW and 36.62 kW are observed for PB5, PWCB5, BLB5 and JB5, which are 1.26%, 1.23%, 1.20% and 1.29% higher than the PB10, PWCB10, BLB10 and JB10 and 2.48%, 2.46%, 2.57% and 2.65% higher than the PB20, PWCB20, BLB20 and JB20, respectively.

Figure 6.3 indicates that the output power for B5 at full load condition is closer to diesel fuel. The lower BP in blended fuels could be attributed to the lower calorific values, higher densities and viscosities. In addition, the lower BP in all biodiesel blends in comparison to diesel is due to the formation of the poor mixture, higher viscosity and density (Lin et al. 2009, Ong et al. 2014a, Usta 2005a). Moreover, the prolonged ignition delay was observed in the blended fuels which are due to their comparatively higher densities and viscosities than the diesel which has caused an improper combustion (Mofijur et al. 2014a). Furthermore, uneven combustion characteristics in blended fuels are responsible for reducing the engine BP (Mofijur et al. 2014a, Mofijur et al. 2014b, Muralidharan et al. 2011). The average percentage (%) reduction in BP at B5, B10 and B20 for all fuels tested over the entire range of engine speed at full load condition compared to diesel is shown in Table 6.6. It can be seen from Table 6.6 that the lowest reduction is observed for PB (0.90%) at B5 and the highest reduction is found for JB (7.8%) at B20 in comparison to diesel.

Figures 6.4 (a), (b), (c) and (d) show the variation in BP with changing load for PB, PWCB, BLB and JB at a particular speed of 1400 rpm, respectively. It could be seen from Figure 6.4 that the BP increases with increase in load for all biodiesel blends. B5 blend shows the highest BP compared to B10 and B20 for all samples tested at all loading conditions. In addition, it could be noted that the maximum power output of B5 at all loading conditions is closer to diesel as expected. The percentage (%) reduction in BP for all biodiesel blends at B5 and at 1400 rpm for different loading conditions compared to diesel is shown in Table 6.7. For PB, the lowest reduction (2.45%) is observed at 75% load, whereas, the highest reduction is found for JB (18.10%) at 25% load in comparison to diesel.

Table 6.6: Average percentage (%) reduction in BP for B5, B10 and B20 for all fuels tested at full load condition compared to diesel

Biodiesel samples	BP (% reduction)		
	Blend level		
	B5	B10	B20
PB	0.90	2.10	3.30
PWCB	2.75	3.95	5.10
BLB	4.15	5.30	6.55

JB	5.35	6.55	7.80

Figure 6.4: Variation in BP with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

Table 6.7: The percentage (%) reduction in BP for all biodiesels at B5 in comparison to diesel for different loading conditions

Biodiesel samples	BP (% reduction)			
	Load (%)			
	25	50	75	100
PB	4.35	3.35	2.45	2.65
PWCB	9.65	6.3	4.85	4.35
BLB	14.1	9.35	7.10	5.70
JB	18.10	13.0	9.25	6.85

The variation in BP with changing speed at B5 for all biodiesels at different loads (25%, 50%, 75% and 100%) is presented in Figures 6.5 (a), (b), (c) and (d), respectively. Figure 6.5 indicates that BP increases with increase in load over the entire range of engine speed (1200 rpm-2400 rpm). The minimum and maximum BP is observed at 1200 rpm and 2400 rpm for all loading conditions, respectively. At B5, the lower BP is observed for PB, PWCB, BLB and JB for all loading conditions in comparison to diesel.

The relationship between BP and biodiesel-diesel blend compositions (B5, B10 and B20) for all samples tested with different speeds and load conditions are exhibited in Figures 6.6 (a) and (b), respectively. As predicted, the highest BP is observed for PB5 amongst all other blends of all fuels tested which are due to the higher heating value and lower density of PB5, respectively.

Figure 6.5: Variation in BP with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions

Figure 6.6: Variation in BP with biodiesel blend composition for: (a) different speeds at full load and (b) different loading conditions at 1400 rpm

6.7 Torque

The variation in engine torque with respect to speed for all tested fuels of PB, PWCB, BLB and JB at full load condition is presented in Figures 6.7 (a), (b), (c) and (d), respectively. It can be seen from Figure 6.7 that the torque increases initially with an increase in speed up to reach the maximum level at 1400 rpm and then decreases continuously until the maximum speed of 2400 rpm for all blending conditions. This could be primarily explained by two reasons, these are: (i) mechanical friction loss and (ii) lower volumetric efficiency of the engine which is because of increase in speed (İlkılıç & Aydın 2011b, Liaquat et al. 2012, Mofijur et al. 2013b).

The torque decreases with increase in biodiesel-diesel blend level for all engine speeds. It could be seen from Figure 6.7 that the highest engine torque is obtained at B5 in comparison to B10 and B20. The higher torque accomplished at B5 is due to the lower density and viscosity, and higher calorific value of the fuel (Mofijur et al. 2013b). Several researchers also reported similar reasons in achieving higher torque at B5 (Dhar & Agarwal 2014, Ong et al. 2014b). Over the entire range of engine speed, the average torques of 208.0 N.m, 206.14 N.m, 4.14 N.m and 201.79 N.m are observed for PB5, PWCB5, BLB5 and JB5, which are 0.94%, 1.0%, 1.1% and 0.91% higher than PB10, PWCB10, BLB10 and JB10 and 1.93%, 2.12%, 2.14% and 2.02% higher than PB20, PWCB20, BLB20 and JB20, respectively. As seen from Figure 6.7, the maximum torque is obtained at PB compared to PWCB, BLB and JB which is because of the higher heating value of the fuel.

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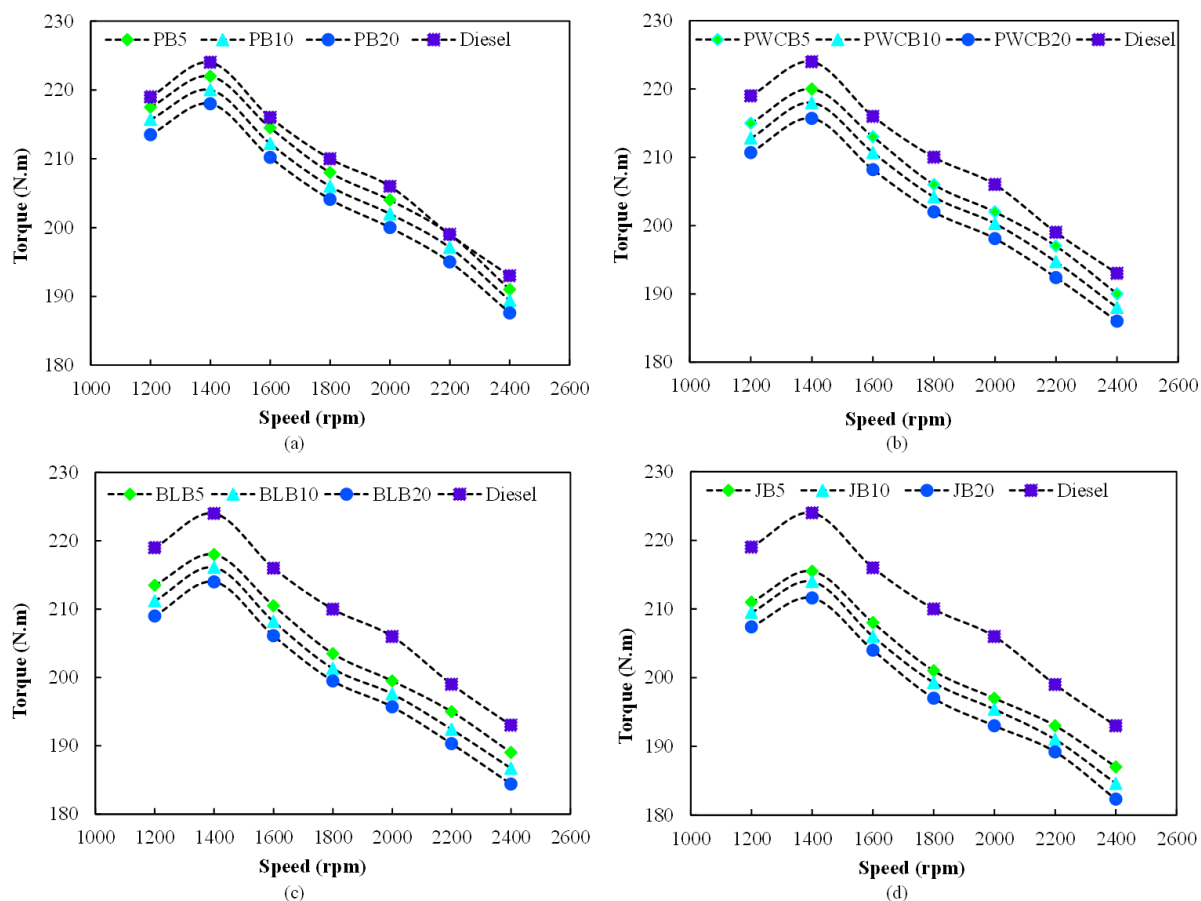
Figure 6.7: Relation between torque and engine speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB and at full load condition

As expected, it can be seen from Figure 6.8 that the engine torque of the diesel is higher than those of B5, B10 and B20 for all samples inspected which are due to the lower density and viscosity, and higher calorific value. The average percentage (%) reduction in torque at B5, B10 and B20 for all samples tested at full load condition in comparison to diesel is shown in Table 6.8. The table shows that the lowest reduction is found for PB (0.75%) at B5 and the highest reduction is observed for JB (5.60%) at B20 in comparison to diesel. Figure 6.8 shows the relationship between torque and load for all tested fuels at a particular speed of 1400 rpm. It can be seen from Figure 6.8 that the torque increases with increase in load for all blending conditions. As expected, B5 shows the maximum torque than other blends of B10 and B20 for all engine loading conditions. It can be seen from Figure 6.8 that the output torque for all samples tested and for all loading conditions at B5 is closer to diesel.

Table 6.8: Average percentage (%) reduction in torque for B5, B10 and B20 for all samples tested at full load condition compared to diesel

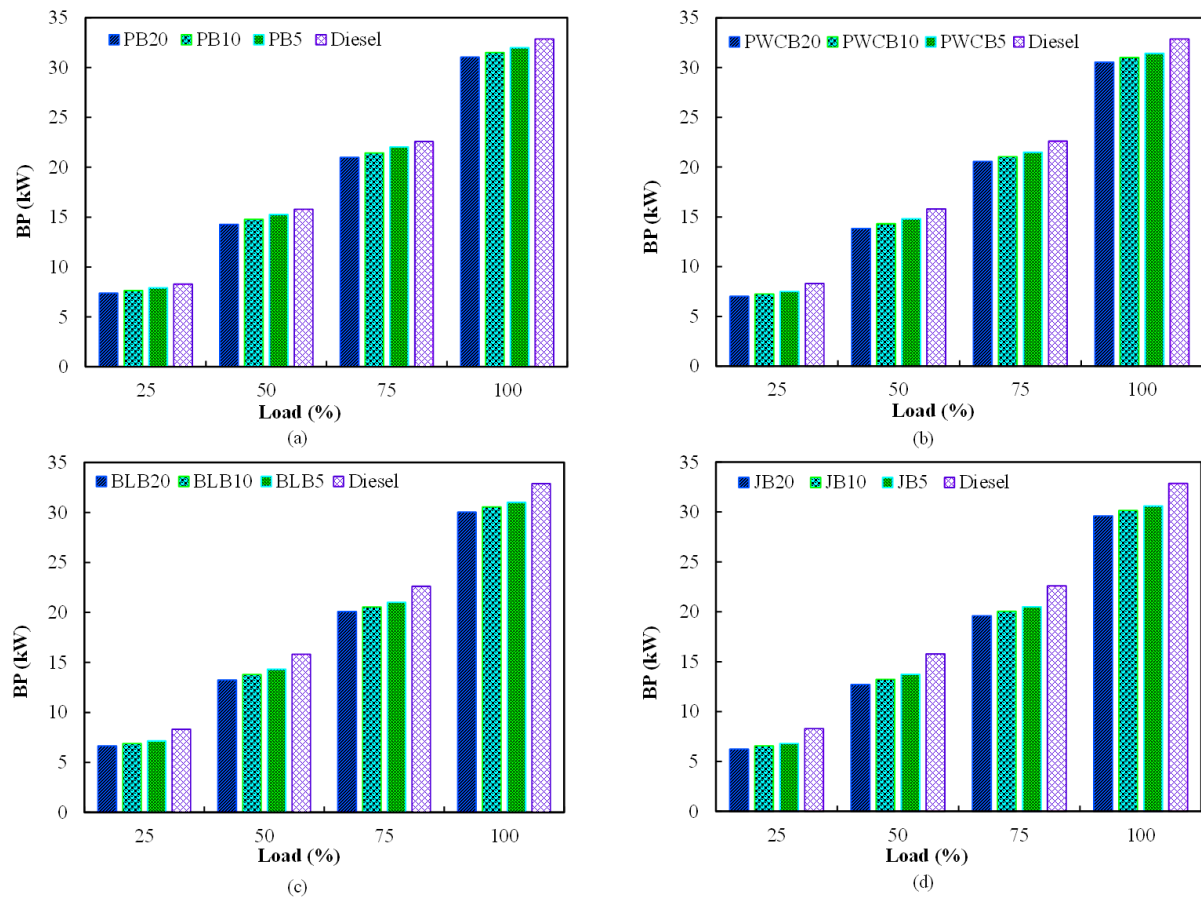| Biodiesel samples	Torque (% reduction)		
	Blend level		
	B5	B10	B20
PB	0.75	1.70	2.65
PWCB	1.65	2.6	3.65
BLB	2.60	3.65	4.65
JB	3.70	4.60	5.60
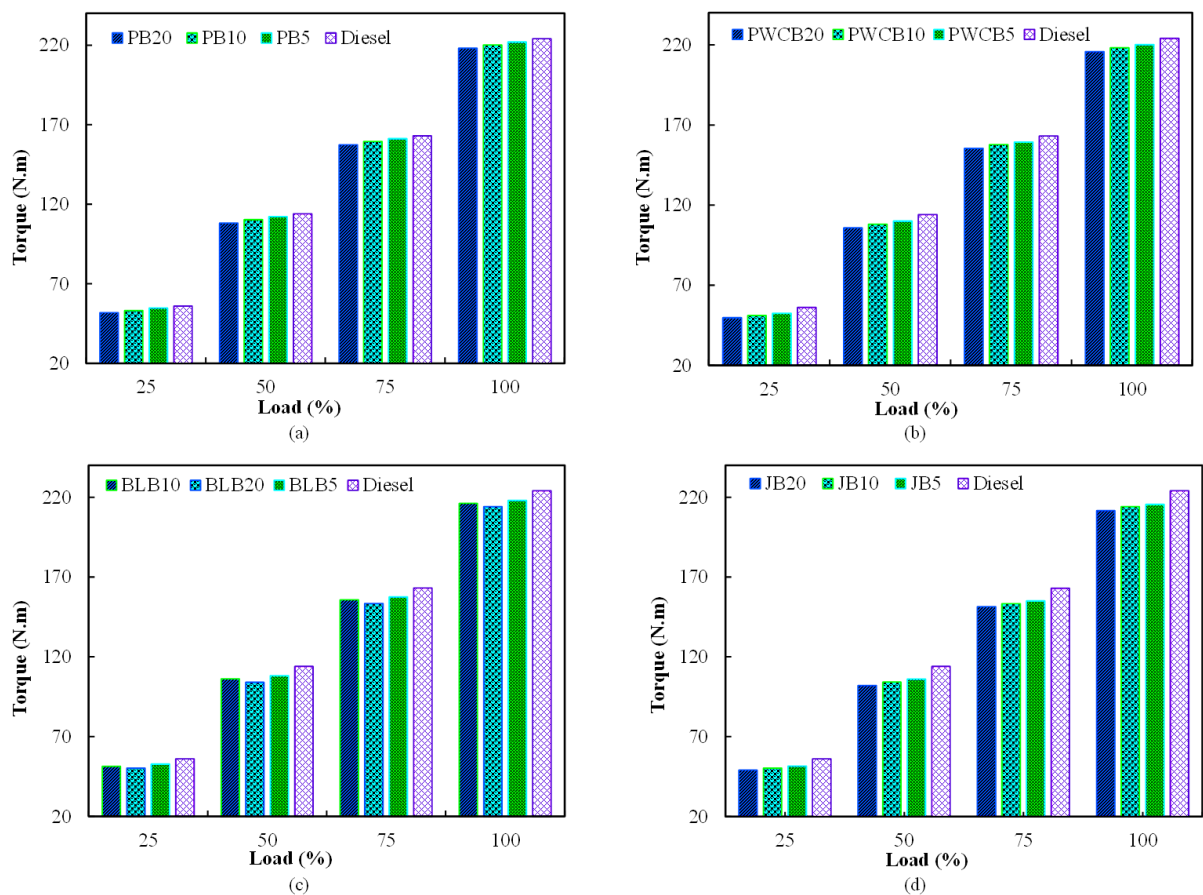
Figure 6.8: Variation in torque with changing load for; (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

The percentage (%) reduction in torque at B5 for all biodiesel samples and different loading conditions compared to diesel is shown in Table 6.9. It can be seen from the Table 6.9 that the

lowest and highest reduction is observed for PB (0.90%) at 100% load and for JB (8.05%) at 25% load compared to diesel, respectively.

Table 6.9: The percentage (%) reduction in torque at B5 for all biodiesel samples in comparison to diesel for different loading conditions

Biodiesel samples	Torque (% reduction)			
	Load (%)			
	25	50	75	100
PB	2.30	1.60	1.10	0.90
PWCB	6.45	3.50	2.25	1.80
BLB	5.90	5.10	3.35	2.70
JB	8.05	7.00	4.90	3.80

Figures 6.9 (a), (b), (c) and (d) show the variation in torque with changing speed for different loading conditions (25%, 50%, 75% and 100%) for PB5, PWCB5, BLB5 and JB5, respectively. The torque increases with increase in load for the entire range of speed (1200 rpm-2400 rpm). For all loading conditions, the maximum and minimum torque is observed at 1400 and 2400 rpm, respectively. The lower engine torque is observed at B5 for all biodiesel samples and for all engine loading conditions compared to diesel. The relation between torque and biodiesel-diesel blend compositions (B5, B10 and B20) for all tested fuels with variation in speed (1400 rpm-2400 rpm) and load (25%-100%) are exhibited in Figures 6.10 (a) and (b), respectively. As expected, the highest torque is observed at PB5 amongst all other blends for all samples tested at 1400 rpm and 100% load.
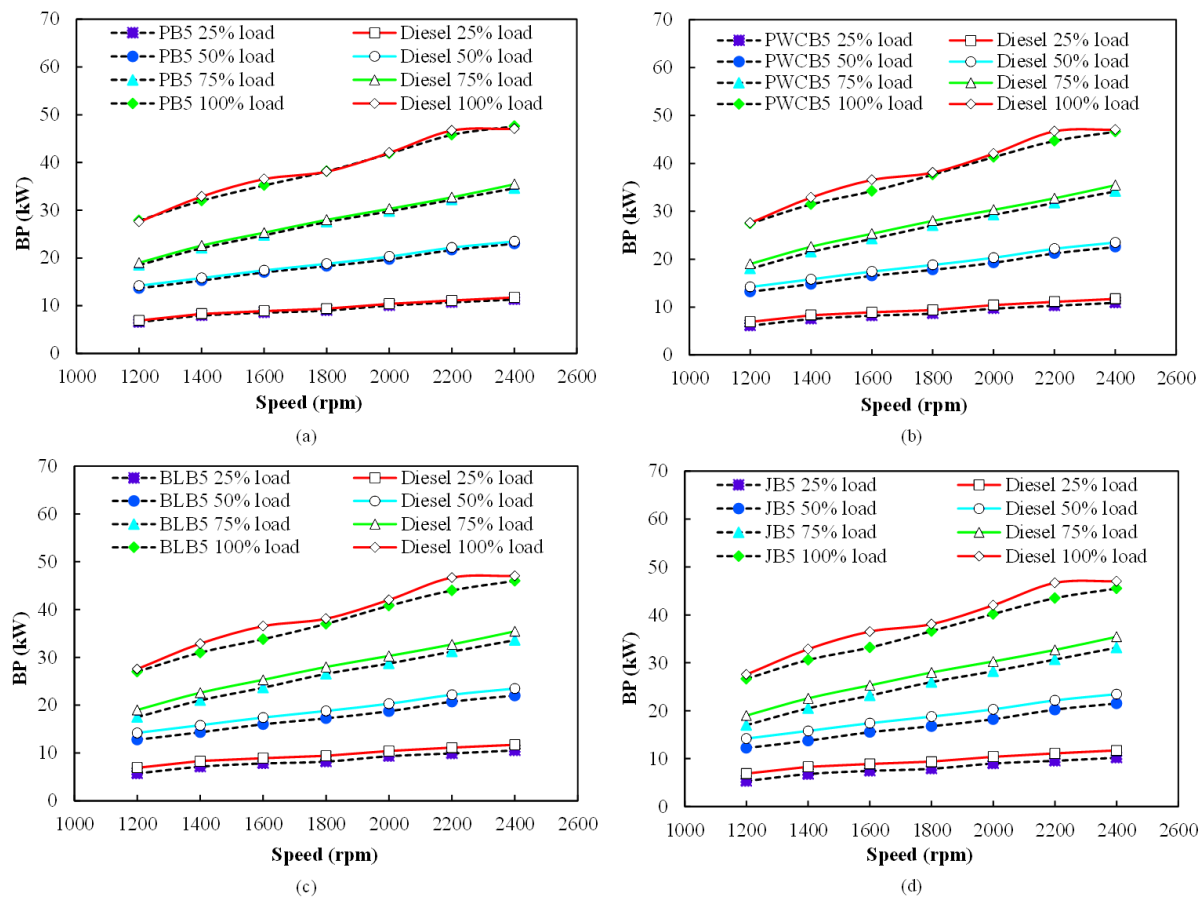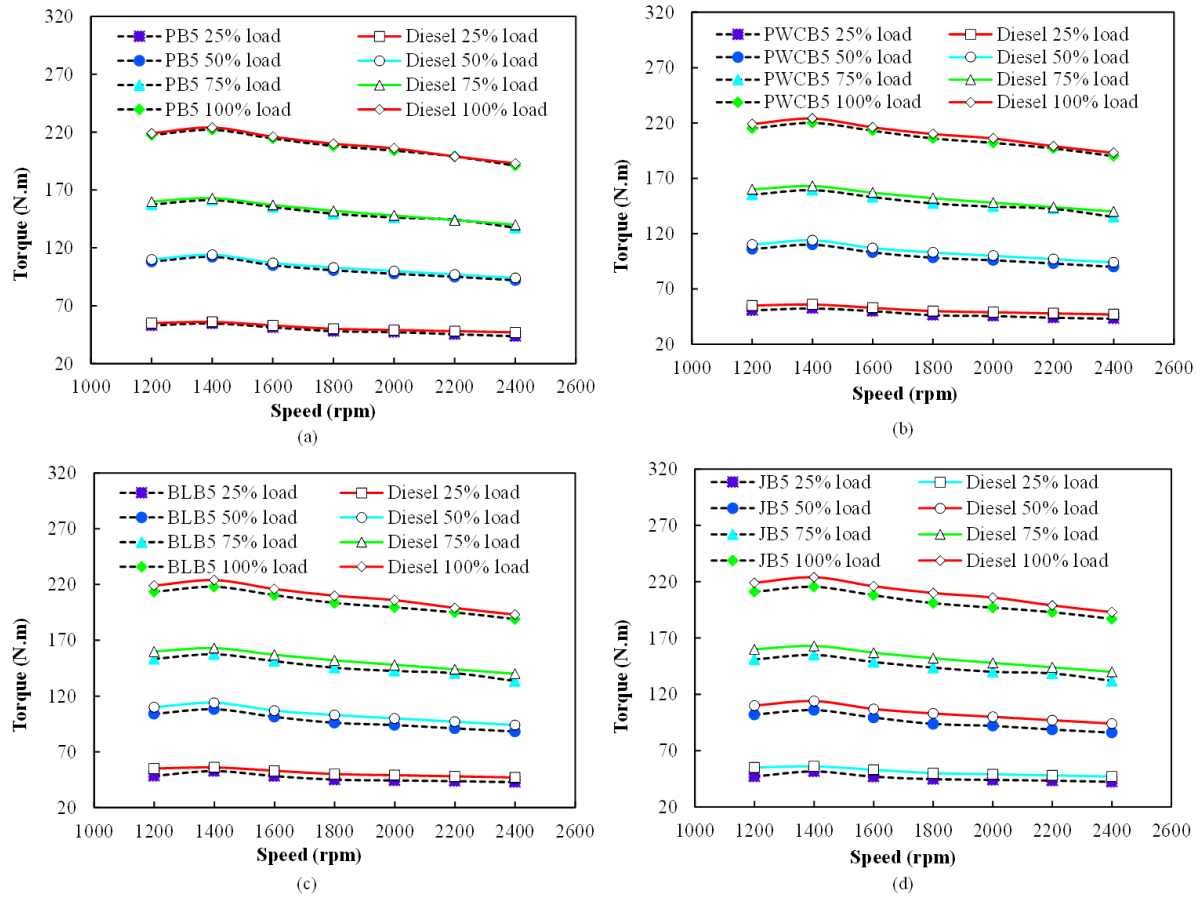
Figure 6.9: Variation in torque with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 and at different loading conditions
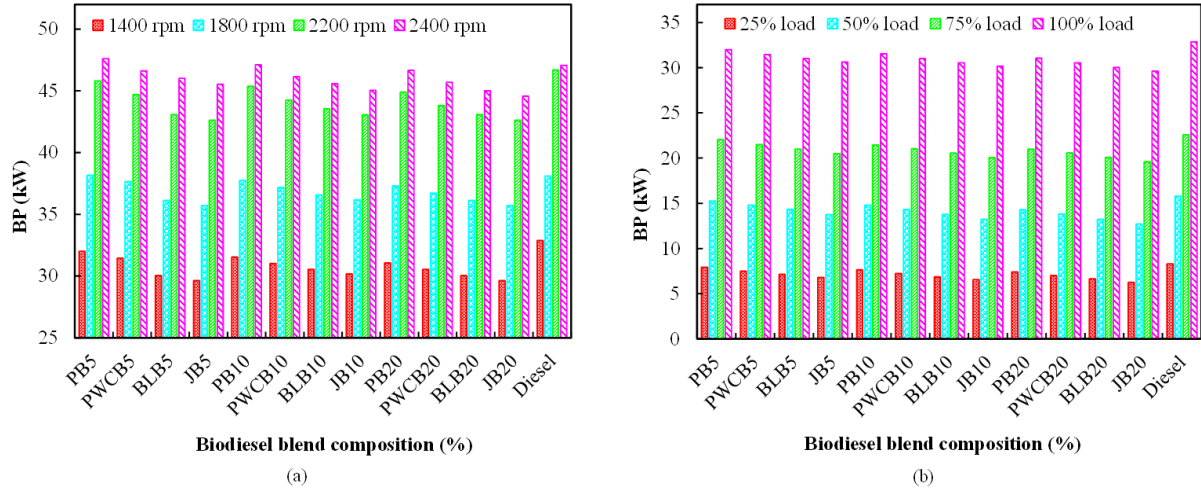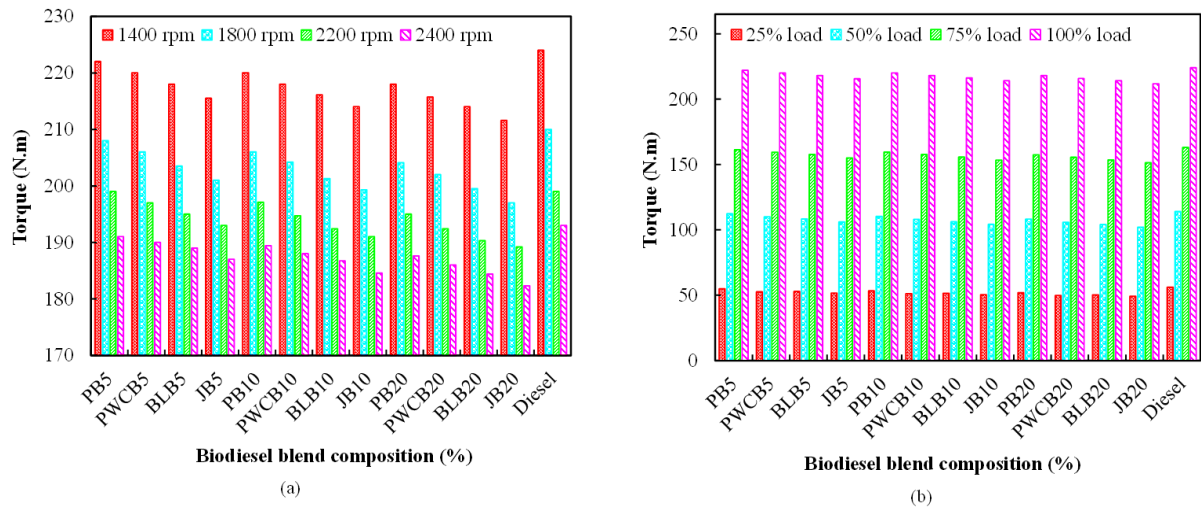

Figure 6.10: Variation in torque with biodiesel blend composition for: (a) different speeds at full load and (b) different loading conditions at 1400 rpm

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6.8 Brake Specific Fuel Consumption (BSFC)

Figures 6.11 (a), (b), (c) and (d) illustrate the changes in BSFC as a function of speed for PB, PWCB, BLB and JB at full load condition. Initially, at full load condition, the BSFC decreases from 1200 rpm to 1400 rpm, afterwards increases with increase in speed up to the maximum speed of 2400 rpm as shown in Figure 6.11. In addition, the decrease in BSFC is due to the better physical and chemical properties of fuel which assisted in improving combustion at low engine speeds (Ong et al. 2014a). On the other hand, at high speeds, the friction heat losses occur and combustion deteriorates which increases the BSFC (Ong et al. 2014b). Due to causing the higher fuel consumption to produce power the lower combustion efficiency is obtained. At higher speeds, the friction power increases at a rapid rate which caused a slower increase in power than in fuel consumption with an increase in BSFC (Ong et al. 2014a, Silitonga et al. 2013b, Tesfa et al. 2013).

Figure 6.11: Relation between BSFC and engine speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

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The BSFC increases with increase in the percentage of biodiesel in the blends, such as B5, B10 and B20 which is presented in Figure 6.11. B5 indicates the lowest fuel consumption compared to B10 and B20 for PB, PWCB, BLB and JB biodiesel. The lowest fuel consumption at B5 is due to the lower viscosity and density, and higher calorific value (Ong et al. 2014b). In addition, the increase in BSFC at B10 and B20 is because of the short ignition delay (Channapattana et al. 2015). Moreover, the higher BSFC of B10 and B20 could be attributed to due to the volumetric effect of constant fuel injection rate and to their higher viscosity values (Sajjad et al. 2015). Furthermore, it could be explained that the higher density of biodiesel blends in B10 and B20 caused higher mass injection for the same volume which resulted in an increase in BSFC. It has been reported that the parameters, such as volumetric fuel injection system, fuel density, viscosity and calorific value affect the BSFC to a great extent (Qi et al. 2010a, Rahman et al. 2014).

The decrease in BSFC for B5 could be illustrated by the combustion criteria and fuel characteristics (Sajjad et al. 2015). Similar results of decrease in BSFC with lower biodiesel blend level have also been reported by several researchers (Buyukkaya 2010, Mofijur et al. 2013b, Ong et al. 2014b, Qi et al. 2009, Qi et al. 2014). The fuel delivering rate into the combustion chamber is on a fixed volumetric basis, and the quantity of fuel injection into a single stroke is the same for all blends (Sajjad et al. 2015). However, as the B5 blend contains a higher calorific value, a smaller amount of fuel is required per stroke to produce the same power in comparison to the other blends (Abu-Jrai et al. 2006, Sajjad et al. 2015, Yehliu et al. 2010). The average BSFCs for PB5, PWCB5, BLB5 and JB5 are observed at 269.98(g/kWh), 277.16 (g/kWh), 283.15 (g/kWh), and 288.74 (g/kWh), which are 2.26%, 2.15%, 2.26% and 7.10% lower than PB10, PWCB10, BLB10 and JB10, and 4.41%, 6.30%, 7.10% and 7.98% lower than the PB20, PWCB20, BLB20 and JB20, respectively. PB shows the lowest BSFC in comparison to PWCB, BLB and JB. In addition, the results indicate that PB5 has quite satisfactory results of BSFC compared to other blends of PWCB5, BLB5 and JB5. This is because of increases in oxygen content and a higher combustion rate at the same engine power for various speeds.

Generally, using biodiesel-diesel blends resulted in higher BSFC than that of diesel, as biodiesel has higher density and lower calorific value compared to diesel. Several researchers reported that high viscosity and density of biodiesel blends are the affecting parameters to increase in BSFC (Chauhan et al. 2012, Kalam et al. 2011, Mofijur et al. 2014b, Rahman et al.

2013, Silitonga et al. 2013c, Wang et al. 2013). The average percentage (%) increase in BSFC at B5, B10 and B20 for all fuels tested at full load condition in comparison to diesel is shown in Table 6.10. The minimum and maximum increases are found for PB (1.15%) at B5 and for JB (17.55%) at B20, respectively, in comparison to diesel (Table 6.10).

Table 6.10: The average percentage (%) increase in BSFC for B5, B10 and B20 for all fuels tested at full load condition compared to diesel

Biodiesel samples	BSFC (% increase)		
	Blend level		
	B5	B10	B20
PB	1.15	3.45	5.80
PWCB	3.85	6.10	10.80
BLB	6.10	8.55	14.20
JB	8.15	10.70	17.55

The relation between BSFC and load for PB, PWCB, BLB and JB at a particular speed of 1400 rpm is exhibited in Figures 6.12 (a), (b), (c) and (d), respectively. It can be clearly explained from Figure 6.12 that at a particular engine speed, BSFC decreases with increase in engine load for all biodiesel blends. Similar results have also been reported by several researchers (An et al. 2013, Godiganur et al. 2010, Godiganur et al. 2009, Meng et al. 2008, Zhu et al. 2011). BSFC consumption decreases with increase in load could be attributed to the higher percentage of increase in BP with the load as compared to fuel consumption. The lowest BSFC is observed for all samples tested at B5 compared to B10 and B20. The percentage (%) increase in BSFC at B5 for all biodiesel blends and 1400 rpm for different loading conditions in comparison to diesel is presented in Table 6.11. The lowest and highest increase is found for PB (1.25%) at 100% load and JB (26.30%) at 25% load, respectively, compared to diesel.
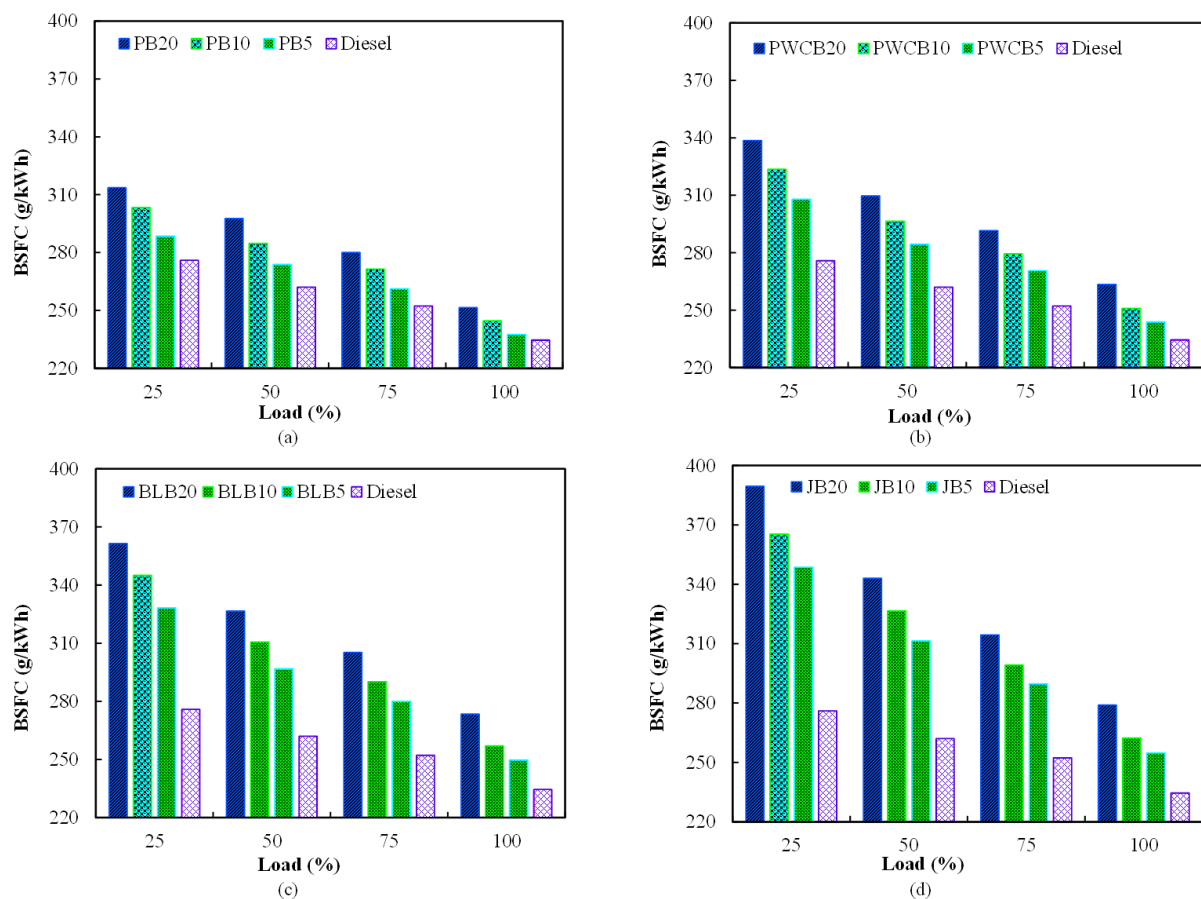
Figure 6.12: Variation in BSFC with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

Table 6.11: The percentage (%) increase in BSFC for all biodiesels at B5 in comparison to diesel for different loading conditions

Biodiesel samples	BSFC (% increase)			
	Load (%)			
	25	50	75	100
PB	4.55	4.45	3.55	1.25
PWCB	11.65	8.55	7.35	4.00
BLB	18.95	13.25	11.00	6.45
JB	26.30	18.8	14.85	8.60

Figures 6.13 (a), (b) , (c) and (d) indicate the variation in BSFC with changing speed at B5 for PB, PWCB, BLB and JB with different load conditions (25%, 50%, 75% and 100%), respectively. As seen from Figure 6.13, BSFC decreases with increase in load varied from 25%-100%. The minimum and maximum BSFC is observed at 1400 rpm and 2400 rpm for all loading conditions, respectively. At B5, the lower BSFC is found for PB, PWCB, BLB and JB for all loading conditions in comparison to diesel.

Figure 6.13: Variation in BSFC with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 and at different loading conditions

The relation between BSFC and biodiesel-diesel blend compositions for PB, PWCB, BLB and JB with different speeds (1400 rpm, 1800 rpm, 2200 rpm and 2400 rpm) and loads (25%, 50%, 75% and 100%) are presented in Figures 6.14 (a) and (b), respectively. As expected, PB5 shows the lowest BSFC amongst all other blends for all feedstocks at 1400 rpm and 100% load (see Figure 6.14).

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Figure 6.14: Variation in BSFC with biodiesel blend for: (a) different speeds at full load and (b) different loading conditions at 1400 rpm

6.9 Brake Thermal Efficiency (BTE)

The variation in BTE with changing speed for PB, PWCB, BLB and JB at full load condition is shown in Figures 6.15 (a), (b), (c) and (d), respectively. The use of biodiesel-diesel blend initially increases BTE up to 1400 rpm and then decreases over the entire range of speed. At higher speeds, the BTE decreased due to lack of sufficient air which caused uneven combustion of fuel (Buyukkaya 2010, Sajjad et al. 2015).

As seen from Figure 6.15, the BTE decreases with increase in the level of biodiesel blends from B5 to B20. As expected, the higher BTE is observed at B5 compared to B10 and B20. The reason for higher BTE is due to the higher calorific value and lower fuel consumption as compared to B10 and B20. In addition, this could be explained due to the lower viscosity and increases volatility which leads to improved air-fuel mixing and resulted in better combustion (Channapattana et al. 2015, Ong et al. 2014a, Sajjad et al. 2015). Moreover, the higher BTE at B5 is attributed to the higher oxygen content, better atomisation and improved ignition quality for combustion (Campos-Fernández et al. 2012, Muralidharan et al. 2011, Ong et al. 2014a, Ong et al. 2014b). Furthermore, it could be explained that the higher BTE is because of the reduction in heat losses with decreasing temperatures at the beginning of combustion (Imdadul et al. 2016). For PB5, PWCB5, BLB5 and JB5, the average BTEs of 29.67%, 29.11%, 28.61% and 28.05% are observed which are 2.80%, 3.07%, 3.43% and 3.43% higher than PB10, PWCB10, BLB10 and JB10, and 3.91%, 5.22%, 5.65% and 6.59% higher than PB20, PWCB20, BLB20 and JB20 over the entire range of engine speed, respectively.

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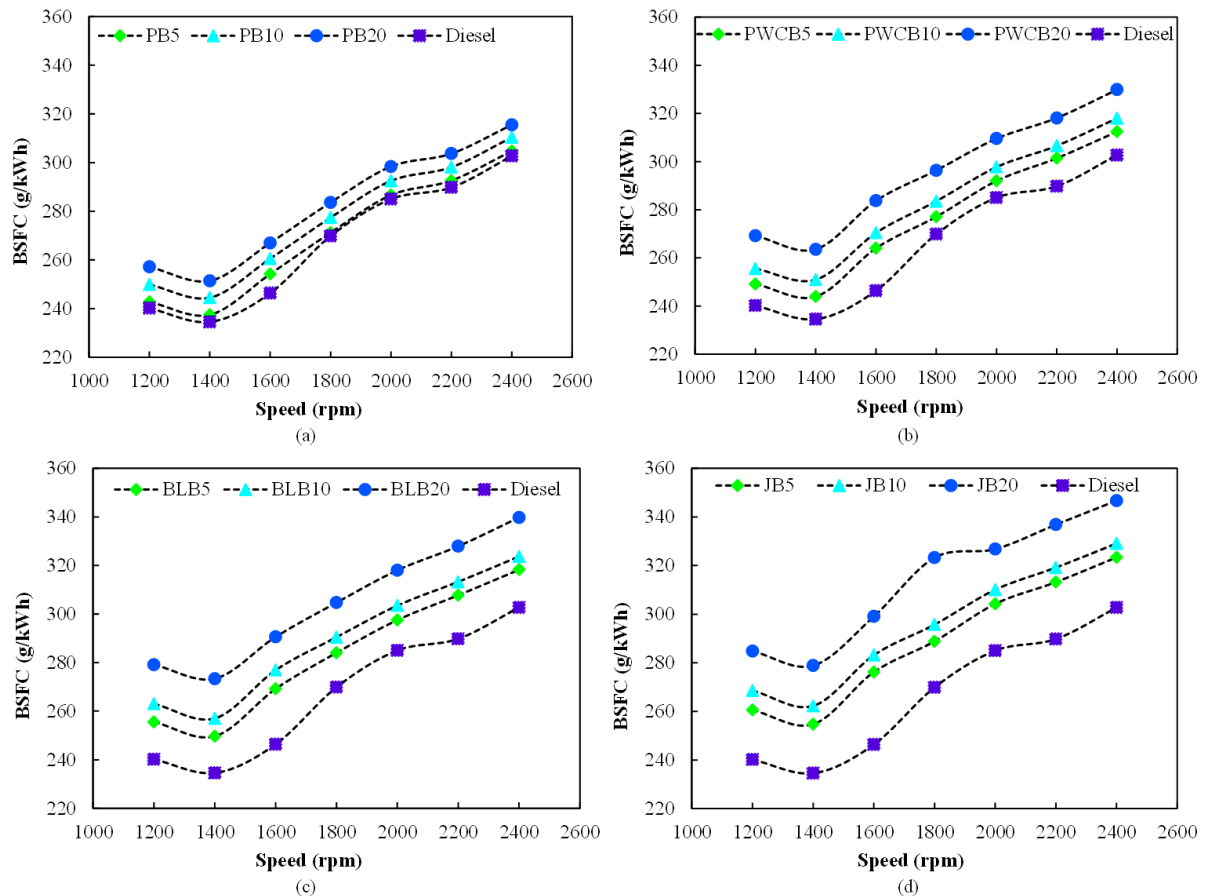
Figure 6.15: Relation between BTE and engine speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

PB shows the highest BTE amongst PWCB, BLB and JB at full load condition. Generally, petro-diesel shows the higher BTE than biodiesel-diesel blend which is because of the higher calorific value, lower density and viscosity. In addition, this could be attributed to the higher fuel consumption of biodiesel-diesel blends compared to diesel (Mosarof et al. 2016). Due to the higher viscosity of the blended fuels, it predominated the fuel atomisation as well as mixing of air which resulted in a poorer combustion and ultimately reduced the BTE (An et al. 2013, Misra & Murthy 2011, Murayama et al. 1984). The average percentage (%) reduction in BTE for B5, B10 and B20 and for all samples tested at full load condition over the entire range of speed in comparison to diesel is shown in Table 6.12. The lowest and highest reduction is observed for PB (0.40%) at B5 and for JB (11.65%) at B20, respectively, compared to diesel. Figures 6.16 (a), (b), (c) and (d) show the variation in BTE with increase in load for PB, PWCB, BLB and JB at a particular speed of 1400 rpm, respectively. At a particular engine speed, BTE increases with increase in load for all samples tested.

Table 6.12: Average percentage (%) reduction in BTE for B5, B10 and B20 for all samples tested compared to diesel at full load condition

Biodiesel samples	BTE (% reduction)		
	Blend level		
	B5	B10	B20
PB	0.40	3.10	4.15
PWCB	2.30	5.20	7.15
BLB	3.95	7.15	9.10
JB	5.85	8.95	11.65

This could be explained due to the reduction in heat loss and an increase in power with a corresponding increase in load (Godiganur et al. 2010). At full load condition, the fuel injection pressure reached a maximum value and caused a negligible effect of viscosity; and therefore, the fuel enabled to cause a better combustion which ultimately increases the BTE (An et al. 2013). In contrast, at partial load (25%-75%), the oxygenated nature of biodiesel is not beneficial as the fuel to air ratios of all tested fuels were very low. The BTE at lower blend (B5) is higher in comparison to B10 and B20 for all samples tested and for all loading conditions (25%, 50%, 75% and 100%). The reduction in BTE for all biodiesels at B5 and 1400 rpm in comparison to diesel for different loads is shown in Table 6.13. The minimum and maximum reduction in BTE is found for PB (0.45%) at 100% load and for JB (19.25%) at 25% load, respectively, compared to diesel.

Table 6.13: The decrease in BTE for all biodiesels at B5 in comparison to diesel for different loading conditions

Biodiesel samples	BTE (% decrease)			
	Load (%)			
	25	50	75	100
PB	3.55	3.50	2.65	0.45
PWCB	9.05	6.45	5.40	2.35
BLB	14.25	9.95	8.10	4.15

JB	19.25	14.15	11.15	6.10
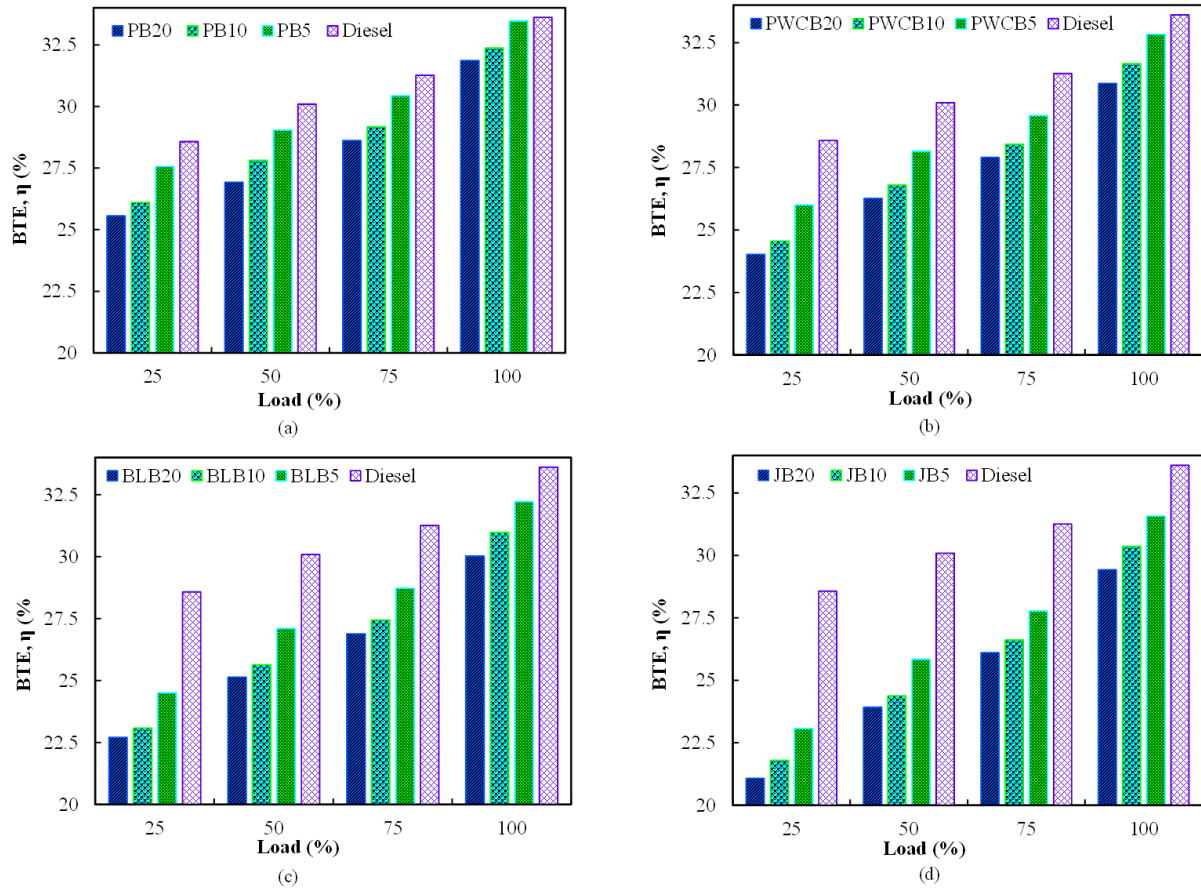
Figure 6.16: Variation in BTE with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

The relation between BTE and speed with different loads for PB5, PWCB5, BLB5 and JB5 is shown in Figures 6.17 (a), (b), (c) and (d), respectively. As expected, the BTE increases with increase in load for the whole range of speed (1200 rpm-2400 rpm). For all engine loading conditions, the highest and lowest BTE is observed at 1400 rpm and 2400 rpm, respectively. The lower BTE is observed at B5 for all biodiesel blends tested and for all loading conditions.

Figures 6.18 (a) and (b) show the variation in BTE with biodiesel blend compositions for PB, PWCB, BLB and JB at different speeds (1400 rpm, 1800 rpm, 2200 rpm and 2400 rpm) and loads (25%, 50%, 75% and 100%), respectively. As expected, PB5 indicates the maximum BTE amongst all other blends of tested samples at 1400 rpm and 100% load, respectively.
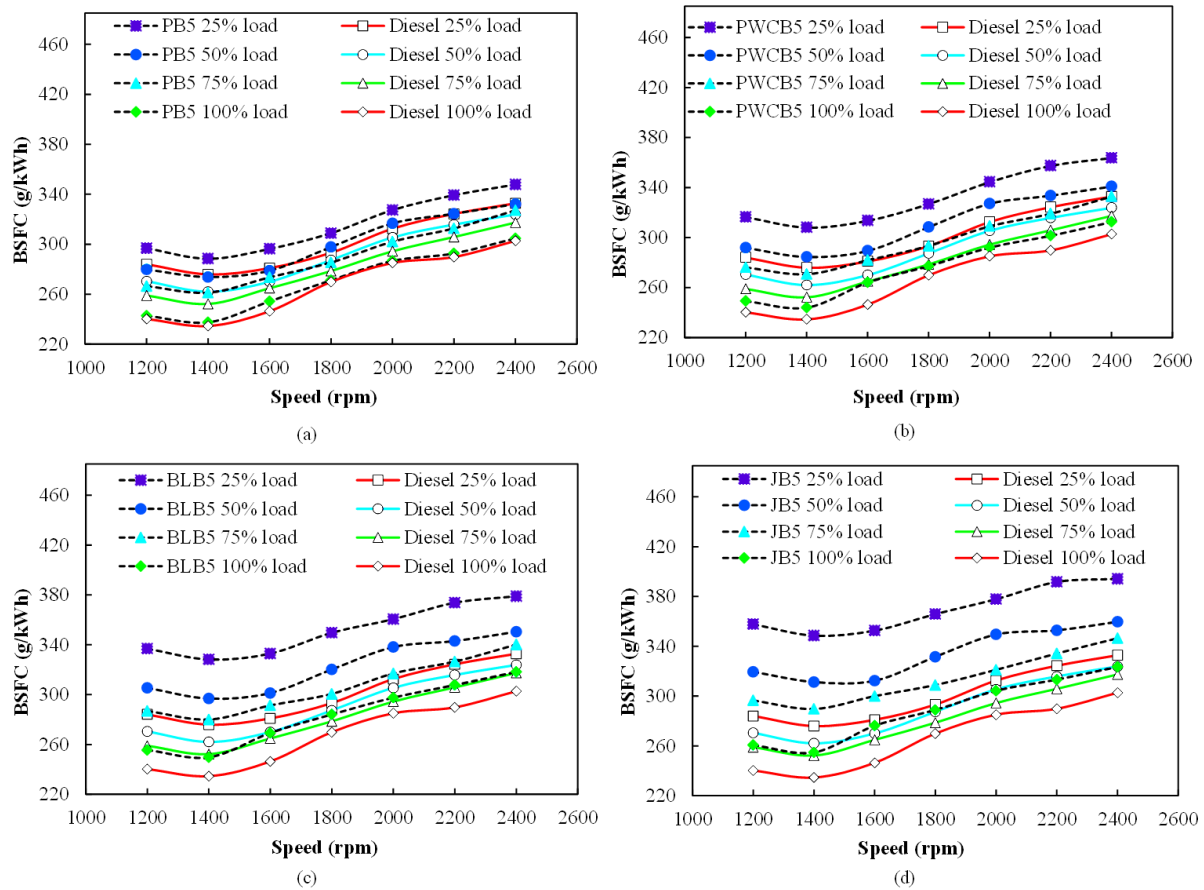
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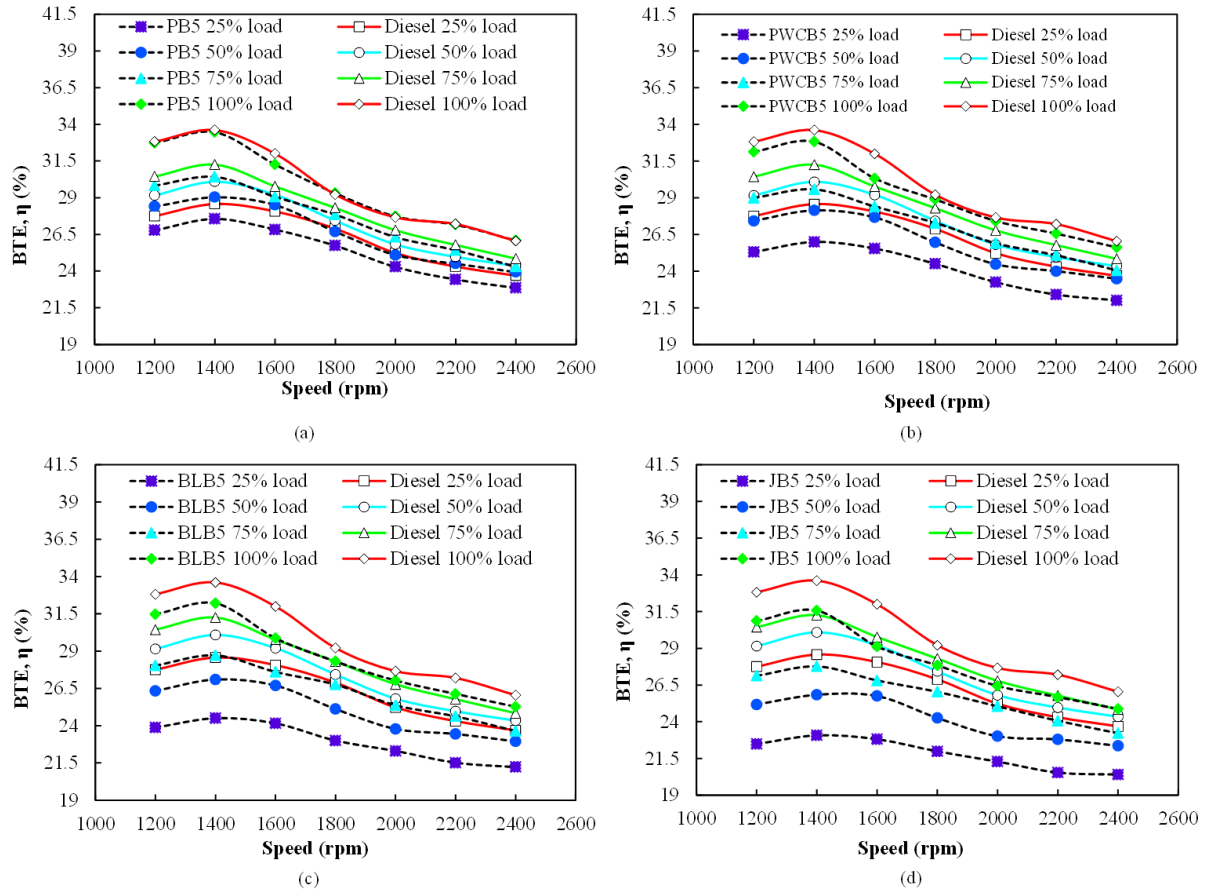
Figure 6.17: Variation in BTE with changing speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at different loading conditions
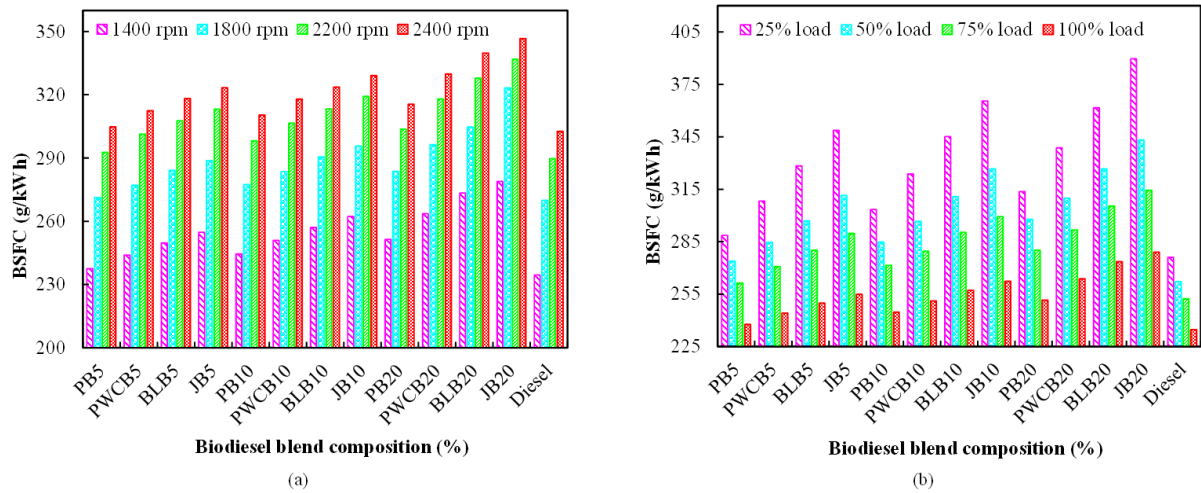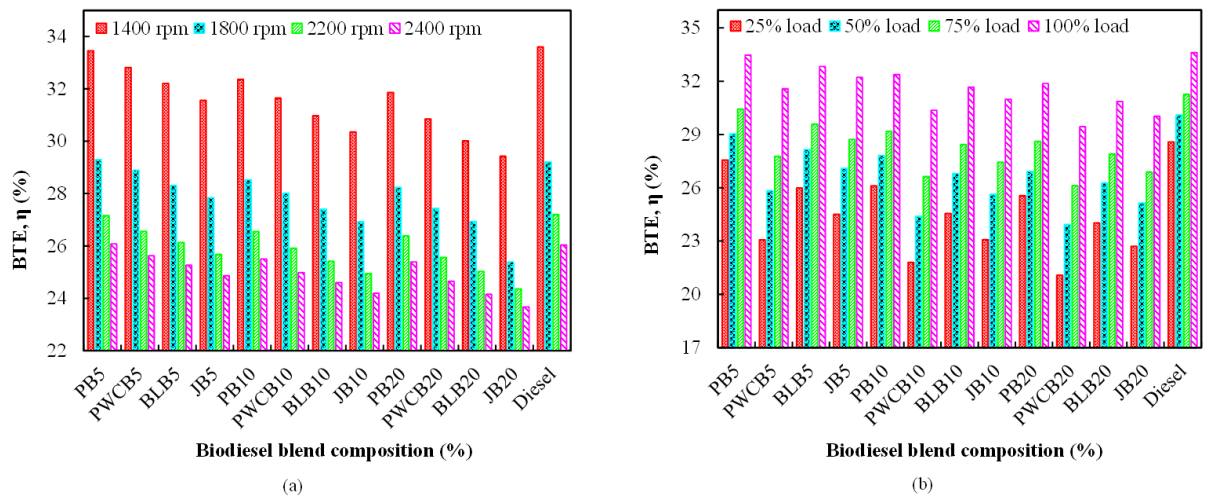

Figure 6.18: Variation in BTE with biodiesel blend for: (a) different speeds at full load and (b) different loading conditions at 1400 rpm

6.10 Brake Mean Effective Pressure (BMEP)

Figures 6.19 (a), (b), (c) and (d) show the relation between BMEP and speed for PB, PWCB, BLB and JB at full load condition. As seen from Figure 6.19, with increase in speed the BMEP increases up to 1400 rpm and afterwards, decreases gradually over the entire range of speed (1400 rpm-2400 rpm).

The BMEP decreases with increase in concentration in biodiesel in the blend for all engine speeds as shown in Figure 6.19. The highest BMEP is obtained at B5 compared to B10 and B20. This could be because of the lower density and viscosity of the fuel. Furthermore, the higher BMEP at B5 could be owing to the higher torque at B5. Regarding biodiesel feedstocks, the maximum BMEP is obtained for PB in comparison to PWCB, BLB and JB because of the higher torque. The average BMEPs of 787.29 kPa, 780.26 kPa, 772.69 kPa and 763.77 kPa are observed for PB5, PWCB5, BLB5 and JB5, which are 0.94%, 1.0%, 1.01% and 0.91% higher than PB10, PWCB10, BLB10 and JB10, and 1.93%, 2.12%, 2.14% and 2.02% higher than PB20, PWCB20, BLB20 and JB20 over the entire range of engine speed, respectively.

As expected, the BMEP for all blends at full load condition is lower than the diesel. The average percentage (%) reduction in BTE at B5, B10 and B20 for all samples tested at full load condition in comparison to diesel is shown in Table 6.14. It can be seen from Table 6.14 that the minimum and maximum reductions are observed at B5 for PB (0.75%) and at B20 for JB (5.60%), respectively, compared to diesel.
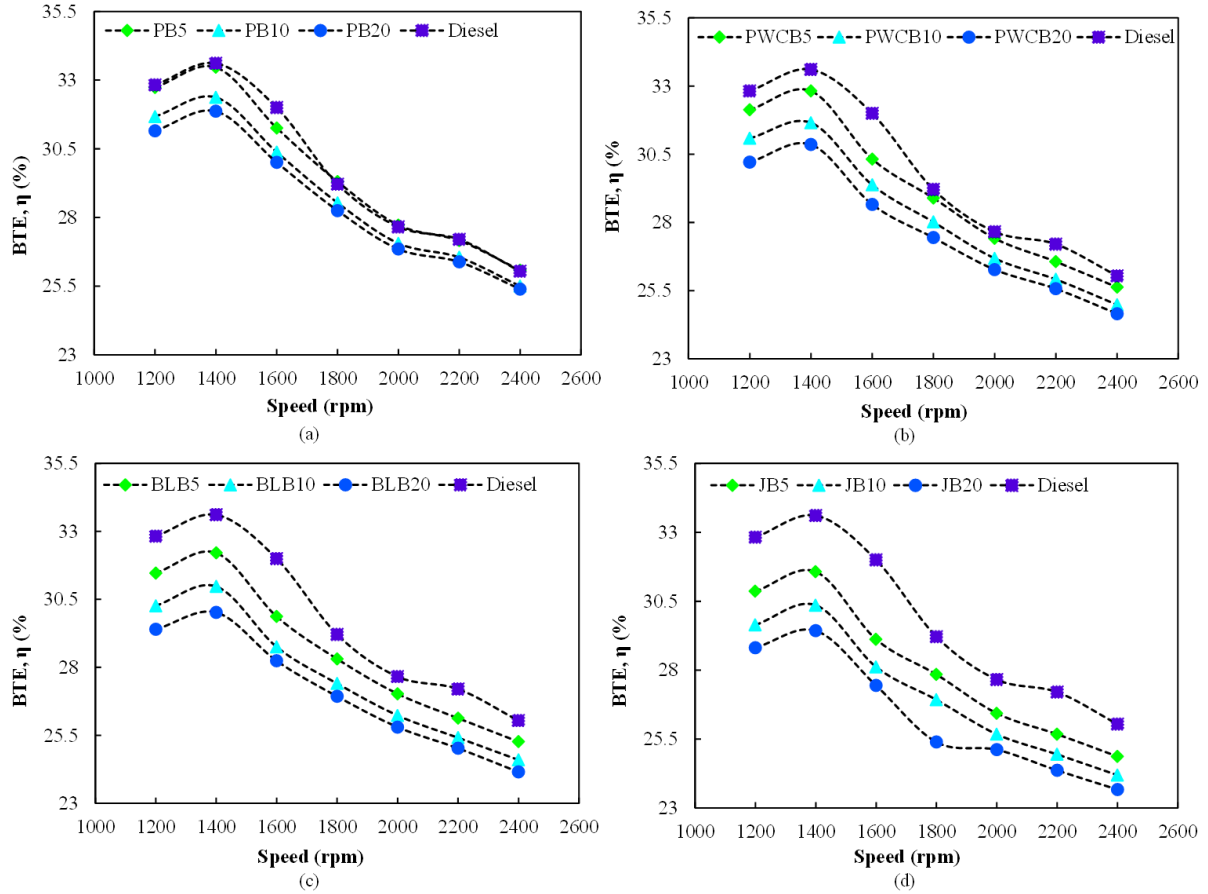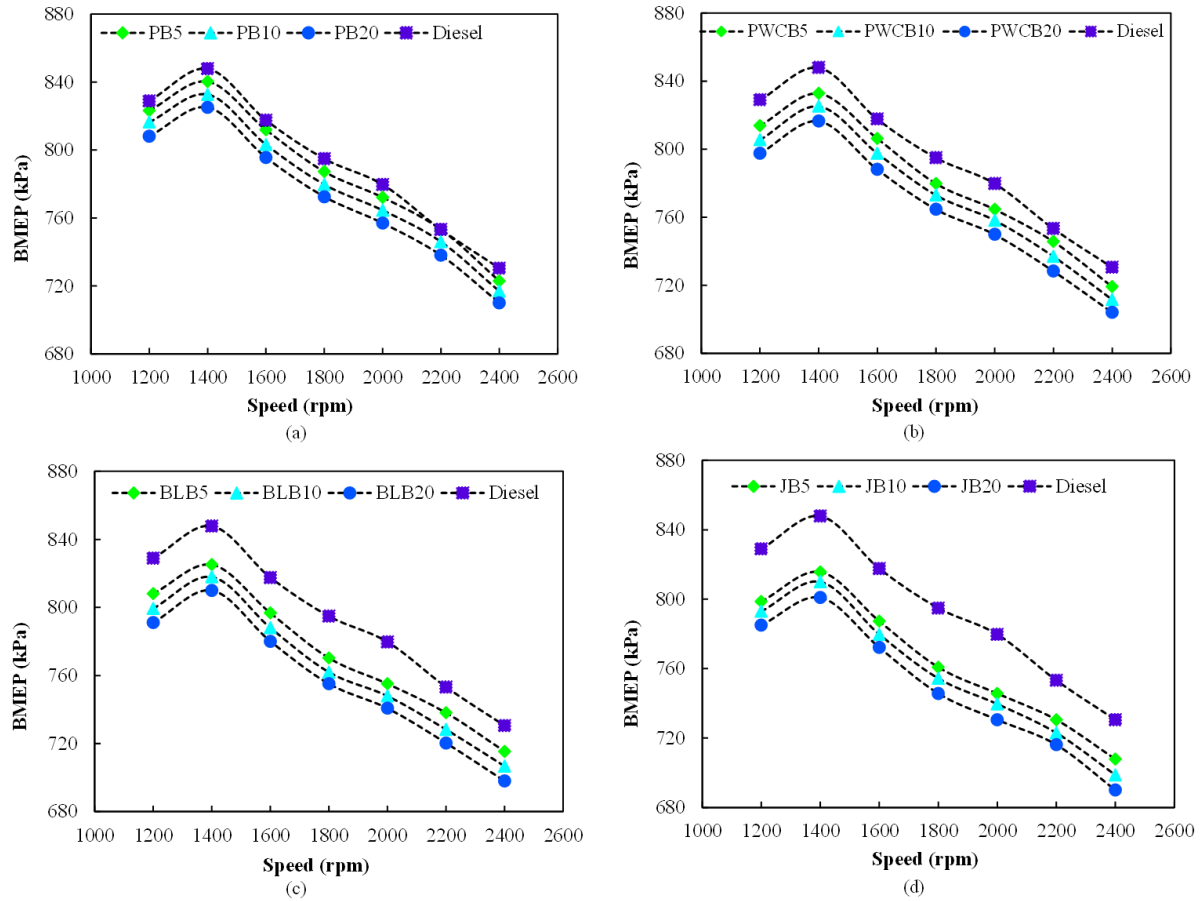
Figure 6.19: Relation between BMEP and engine speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

Table 6.14: Average percentage (%) reduction in BTE for B5, B10 and B20 for all samples tested at full load condition in comparison to diesel

Biodiesel samples	BMEP (% reduction)		
	Blend level		
	B5	B10	B20
PB	0.75	1.70	2.65
PWCB	1.65	2.60	3.70
BLB	2.60	3.65	4.65
JB	3.70	4.60	5.60

The variation in BMEP with changing load for PB, PWCB, BLB and JB at 1400 rpm is shown in Figures 6.20 (a), (b), (c) and (d), respectively. Figure 6.20 shows that the BMEP increases with increase in load varied from 25%-100% for all blends (B5, B10 and B20) of PB, PWCB,

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BLB and JB, respectively. B5 shows the higher BMEP compared to B10 and B20 for all samples tested and loading conditions.
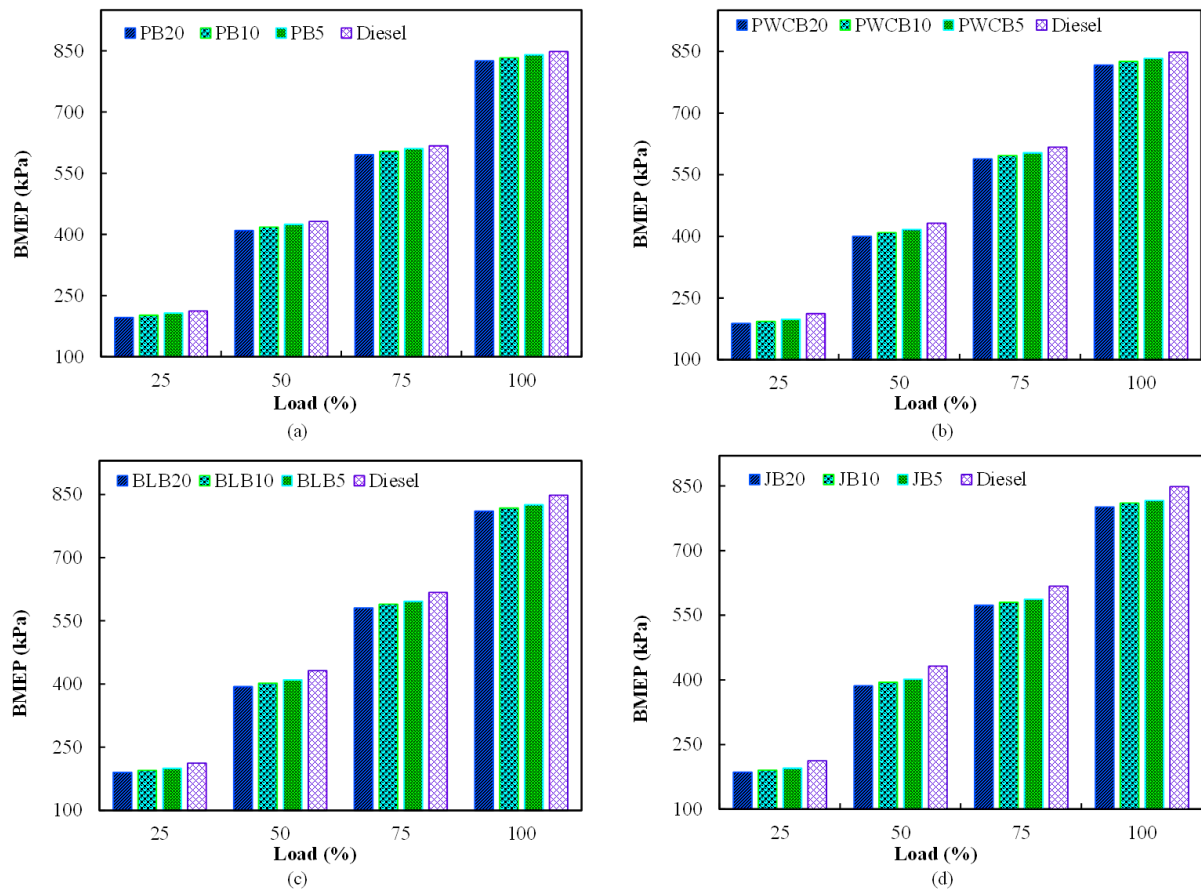
Figure 6.20: Variation in BMEP with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

The percentage (%) reduction in BMEP for all biodiesel fuels tested at B5 and 1400 rpm for different loading conditions in comparison to diesel is shown in Table 6.15. The table shows the minimum and maximum BMEP of (0.90%) for PB at 100% load and (8.05%) for JB at 25% load, respectively, compared to diesel. Figures 6.21 (a). (b), (c) and (d) show the relation between BMEP and speed with different engine loads of 25%, 50%, 75% and 100% for all biodiesels tested, respectively. The BMEP decreases with decrease in load (25%-100%) for all speeds.

Table 6.15: The percentage (%) decrease in BMEP for all biodiesels at B5 for different
loading conditions compared to diesel

Biodiesel samples	BMEP (% decrease)			
	Load (%)			
	25	50	75	100
PB	2.30	1.60	1.10	0.90
PWCB	6.45	3.50	2.25	1.80
BLB	5.90	5.10	3.35	2.70
JB	8.05	7.00	4.90	3.80
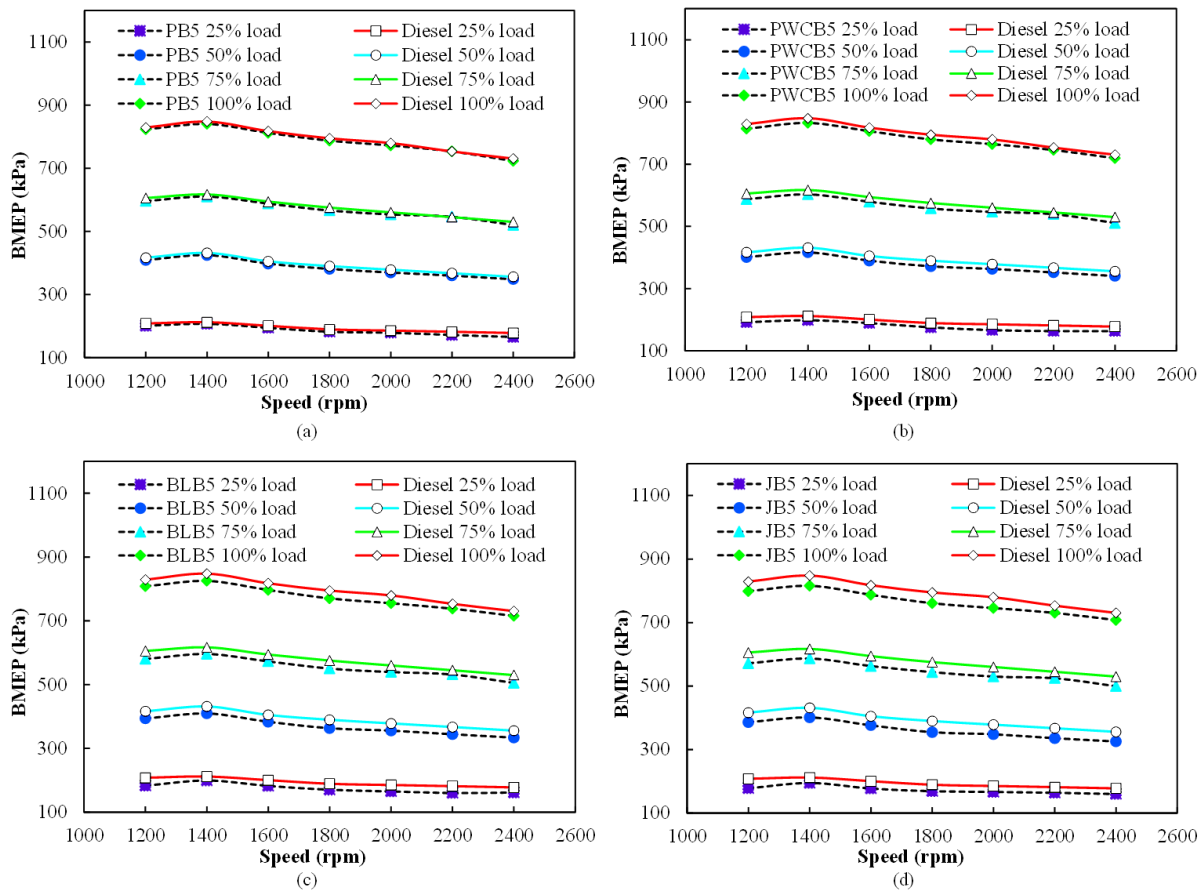
Figure 6.21: Variation in BMEP with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5
and (d) JB5 at different loading conditions

The maximum and minimum BMEP is observed at 1400 rpm and 2400 rpm for all loading conditions, respectively. In addition, the lower BMEP is found at B5 for PB, PWCB, BLB and JB and all loading conditions.

The variation in BMEP with biodiesel-diesel blend compositions for PB, PWCB, BLB and JB at different speeds and loads are exhibited in Figures 6.22 (a) and (b), respectively. PB5 shows the highest BMEP amongst all other blends of tested fuels at 1400 rpm and 100% load.
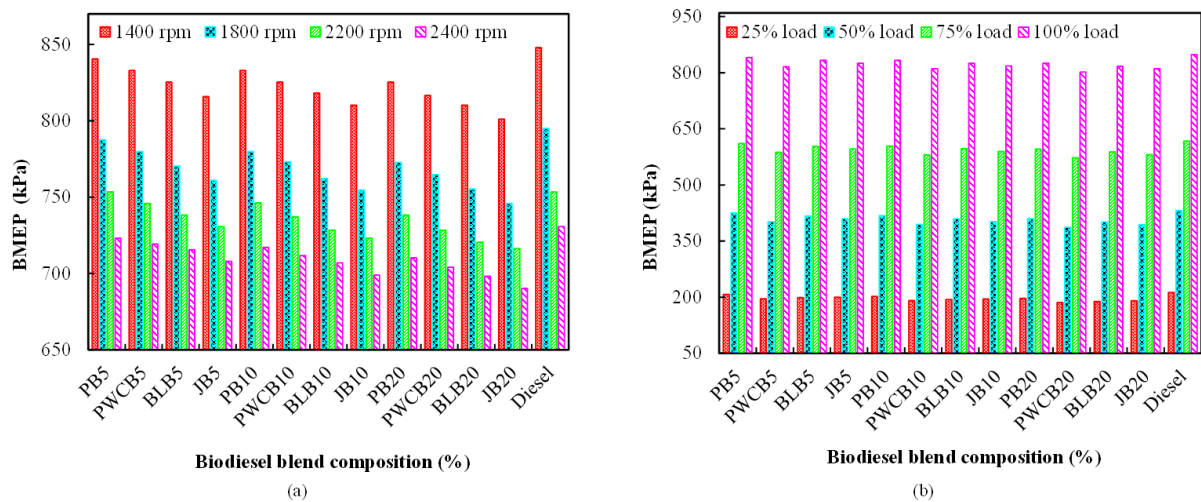
Figure 6.22: Variation in BMEP with biodiesel blend for: (a) different speeds at full load condition and (b) different loading conditions at 1400 rpm

6.11 Conclusion

Biodiesel produced from advanced feedstocks represents a more sustainable source of energy and would therefore, play an increasingly significant role in providing the energy requirements for transportation. Therefore, more and more researchers are focused on the biodiesel's engine performance characteristics, such as BP, torque, BSFC, BTE and BMEP.

- The use of biodiesel led to slightly reducing engine power mainly due to the reduction in heating value of biodiesel compared to diesel over the entire range of engine speeds (1200 rpm-2400 rpm) for PB, PWCB, BLB and JB, but there exists power recovery through increases biodiesel fuel consumption. In addition, the BP reduces as a function of level in biodiesel blends and engine load, that is, with increase in biodiesel blend level from B5 – B20 and decrease in load ranging from 100%-25%, respectively.

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- Engine torque decreases with increase in speed except 1400 rpm when the engine is fuelled with biodiesel-diesel blend instead of diesel for all biodiesel feedstocks. The maximum torque is obtained at 1400 rpm. In addition, it could be noted that reduction in torque is observed with increase in the percentage of biodiesel in the blends and decrease in engine load varying from 100%-25%.

- The BSFC increases with increase in engine speed when using biodiesel-diesel blend instead of diesel for all blends (B5, B10 and B20) of PB, PWCB, BLB and JB. This is due to low heating value, high density and high viscosity of biodiesel, but this could be minimised by reducing the proportion of biodiesel in the blend. Furthermore, increase in BSFC is observed with increase in the concentration of biodiesel in the blends and decrease in engine load (100%-25%).

- BTE decreases when the engine is fuelled with biodiesel-diesel blend instead of diesel over the entire range of engine speeds except 1400 rpm for all blends of PB, PWCB, BLB and JB. In addition, it can also be seen that BTE decreases with increase in the concentration of biodiesel in the blends and decrease in engine load varying from 100%-25%, respectively.

- Over the entire range of engine speeds (1200 rpm-2400 rpm) except 1400 rpm, the BMEP decreases with using biodiesel-diesel blends instead of diesel for all blends (B5, B10 and B20) of biodiesel feedstocks. Furthermore, BMEP reduces with increase in the level of biodiesel blend and decreases in load from B5 to B20 and 100%-25%, respectively.

Overall, it can be concluded from the experimental results that the diesel engine could run on a lower proportion of biodiesel-diesel blends (up to B20) to get satisfactory results.

CHAPTER 7

ENGINE COMBUSTION CHARACTERISTICS

In this chapter, the influence of biodiesel-diesel blend on engine combustion characteristics is explained and discussed. The influencing parameters that are considered for engine combustion characteristics are cylinder pressure (CP), peak pressure and heat release rate (HRR). The average in-CP data of successive cycles with crank angle (CA) ranges from -360°-360° were taken into consideration to estimate the HRR. The CP and HRR achieved using diesel, poppy, BL, PWC and jojoba biodiesel and their blends (B5, B10 and B20) at different engine operating conditions (25%, 50%, 75% and 100% load for CP and 50% and 100% load for HRR) are discussed in detailed. The characteristic results of diesel and biodiesel-diesel blends are displayed in graphs which include CP and HRR with CA at full load condition at 1400 rpm and 2400 rpm. The B20 showed the higher cylinder pressure in comparison to B5, B10 and diesel. On the other hand, B5 showed the higher HRR in comparison to B10 and B20. However, the HRR was lower at B5 than the diesel.

7.1 Introduction

The combustion characteristics (CP and HRR) of biodiesel and its blends have exhibited a similar trend of conventional diesel at different operating conditions (Tarabet et al. 2014). Several researchers reported (Monirul et al. 2016, Ozsezen et al. 2009) that biodiesel blends showed a higher peak pressure than diesel (Devan & Mahalakshmi 2009b, Dhar et al. 2012, Sahoo & Das 2009a). Moreover, it has been observed that at higher biodiesel blend the peak pressure is higher in comparison to lower blend (Dhar et al. 2012). In addition, it could be noted that the peak CP increases with increase in load for both diesel and biodiesel blends as reported by several other researchers (Kivevele et al. 2011, Saravanan et al. 2010b). The CP characterises the ability of fuel to mix with air and to burn. The burnt fuel fraction during the premixed combustion (PC) is responsible for creating the maximum in-CP in CI engines (Imdadul et al. 2016). It has been noted that HRR analysis can provide important information about the effect of engine design changes, fuel injection system, fuel type and engine operating conditions on combustion process and engine analysis (Ghojel & Honnery 2005). In addition, the higher HRR has been found in diesel in comparison to biodiesel blends by several researchers (Buyukkaya 2010, Chauhan et al. 2012, Gattamaneni et al. 2008, Imdadul et al.

2016, Jaichandar et al. 2012, Muralidharan & Vasudevan 2011, Sayin et al. 2012). Several researchers reported that at lower biodiesel blend (B5) the HRR is higher compared to higher blends (Buyukkaya 2010, Devan & Mahalakshmi 2009d). In addition, the HRR increases with increase in load for both diesel and biodiesel blends (Tarabet et al. 2014).

7.2 Cylinder Pressure (CP)

The variation in in-CP against CA for PB, PWCB, BLB and JB at 1400 and 2400 rpm with full load condition is presented in Figures 7.1 (a), (b), (c) and (d), and Figures 7.2 (a), (b), (c) and (d), respectively. The experimental results revealed that the use of biodiesel-diesel blends have an effect on the peak in-CP for both engine speeds. From Figure 7.1 and Figure 7.2, it can be seen that the peak in-CP is slightly higher for all samples tested at B5, B10 and B20 in comparison to diesel at 1400 rpm and 2400 rpm. Also, all the blended fuels show a maximum in-CP within the CA limit between 15° and 35°.

The peak in-CP is found higher at a higher concentration in biodiesel in the blend for PB, PWCB, BLB and JB for both engine speeds. The increase in maximum in-CP at the higher blend (B20) could be explained due to the shorter ignition delay and fast burning of the accumulated fuel as a result of the higher oxygen content in the fuel (Dhar et al. 2012, Sharon et al. 2012). This result is consistent with available literature reported by several researchers (Devan & Mahalakshmi 2009b, Sahoo & Das 2009a).

The CP of a diesel engine mainly depends on the mass of fuel combusted in the PC phase (Sivalakshmi & Balusamy 2013). At higher blends (B20), the peak CP is comparable with diesel. The higher peak CP at B20 compared to diesel could be attributed to the combined effects of higher CN, higher BSFC, boiling point, oxygen content and progression in starting of the injection timings (Imtenan et al. 2014, Ozsezen & Canakci 2011, Ozsezen et al. 2009, Sajjad et al. 2015). Moreover, this could be illustrated to the higher bulk modulus of biodiesel-diesel blends which initiated the advancement of the nozzle opening and as a result caused an earlier injection in comparison to diesel (Palash et al. 2014). Furthermore, the higher CP at B20 could be due to the optimum conditions for combustion displays by a mixture of two fuels (Dhar et al. 2012).

At 1400 rpm, the maximum CPs at B20 for PB, PWCB, BLB and JB are 3.65%, 2.10%, 3.40% and 1.80% higher than the diesel, respectively, whereas, those are 2.10%, 1.80%, 1.55% and 1.45% higher than the diesel at 2400 rpm at full load condition, respectively.
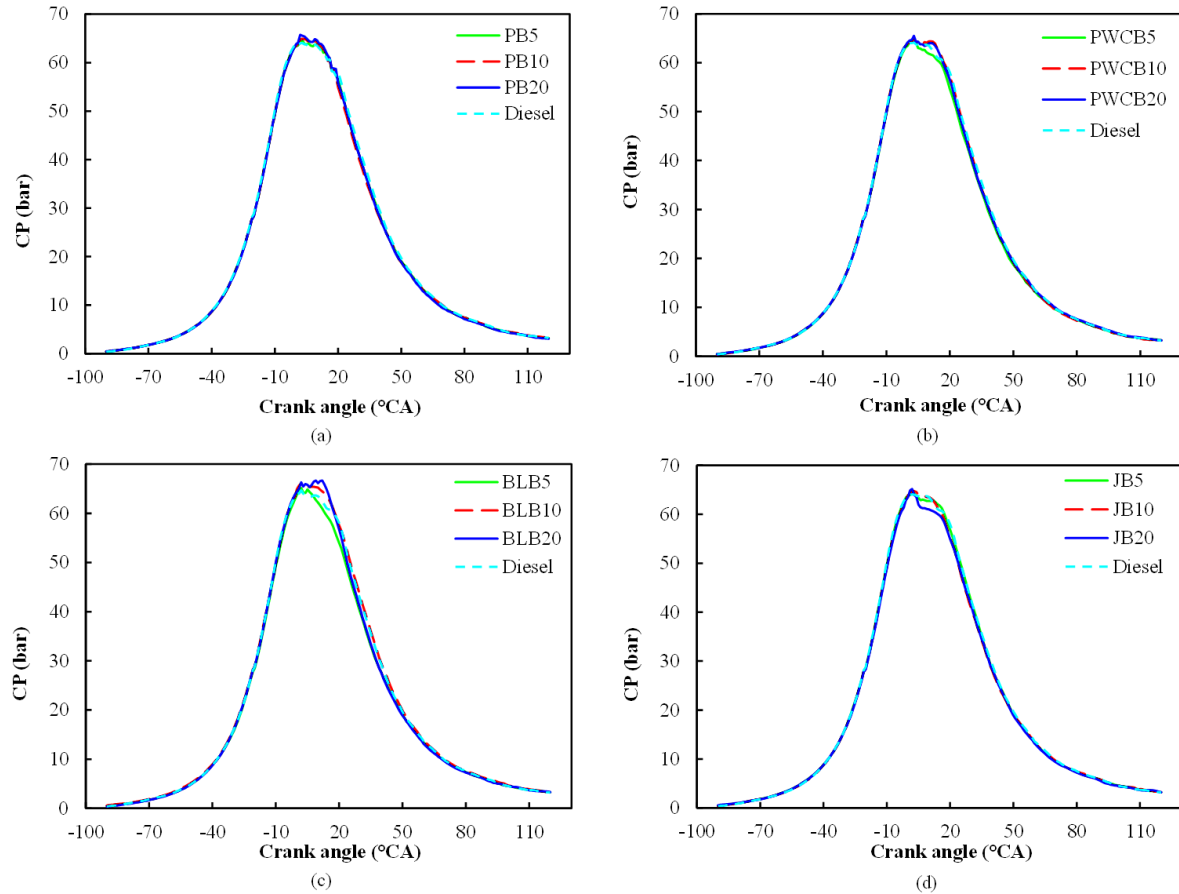
Figure 7.1: Relation between CP and CA for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm and full load condition

It can be noted that the peak CP occurs near TDC (top dead centre) for biodiesel blended fuels due to an earlier start of combustion and as a consequence of their higher cetane number (Dhar et al. 2012). It is clear from Figure 7.1 and Figure 7.2 that after TDC, that is after CA of 20° there is no significant variation in in-CP with increase in CA for all biodiesel blends.
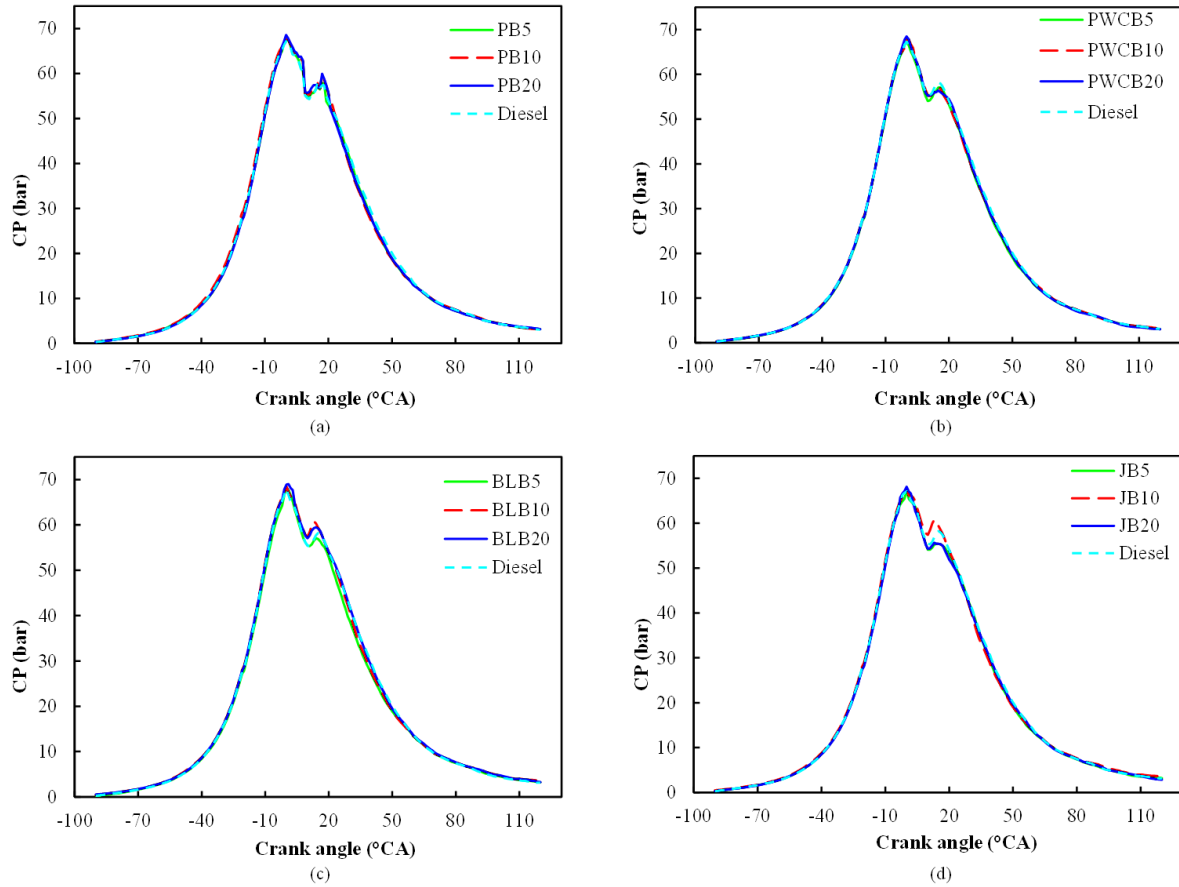
Figure 7.2: Relation between CP and CA for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 2400 rpm and full load condition

The relationship between in-CP and CA with different engine loading conditions (25%, 50%, 75% and 100%) is presented in Figures 7.3-7.6. Figure 7.3 for B5, and Figure 7.4 for B20 at 1400 rpm, whereas, Figure 7.5 for B5 and Figure 7.6 for B20 at 2400 rpm show the variation in CP with CA for PB, PWCB, BLB and JB. The CP results of B10 at 1400 rpm and 2400 rpm for all loading conditions are shown in Appendix B at Figure B.1 and Figure B.2, respectively. From Figures 7.3-7.6, it can be noticed that the CP as a function of CA for all loading conditions are similar for all fuels tested.

Figures 7.3-7.6 indicate that the peak in-CP increases with increase in load (25%-100%) for all blends of all samples inspected. The higher peak in-CP is observed for B20 at 1400 rpm and 2400 rpm for all engine loading conditions. At all engine loads, combustion starts earlier for higher blends whereas, the start of combustion is delayed for lower blends in comparison to diesel. With increase in engine load, ignition delay for all samples tested decreases as the in-cylinder gas temperature increases at high engine loads. As a result, it reduces the physical

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ignition delay period (Dhar et al. 2012). The similar results were also reported by several researchers (Kivevele et al. 2011, Saravanan et al. 2010b). Moreover, the results reveal that biodiesel-diesel blends show different combustion characteristics with the variation in engine load which is because of variation in properties of blended fuels. The peak CP for B5 (Figure 7.3 and Figure 7.5) and B20 (Figure 7.4 and Figure 7.6) is higher in comparison to diesel for all engine loading conditions and speeds. The increase in CP for all fuels tested in comparison to diesel at different engine speeds and loading conditions is shown in Table 7.1.

Table 7.1: Increase in CP for biodiesel blends compared to diesel at different engine speeds and loading conditions

Fuels	Blends	Engine speed (rpm)	Increase in CP (%)			
			Load (%)			
			25	50	75	100
PB	PB5	1400	2.55	2.5	1.20	1.107
	PB20	1400	3.30	2.85	2.15	3.65
	PB5	2400	0.20	0.74	1.32	0.65
	PB20	2400	0.65	0.35	0.45	2.10
PWCB	PWCB5	1400	2.46	1.38	0.89	0.39
	PWCB20	1400	2.65	1.50	1.25	2.10
	PWCB5	2400	0.55	0.20	0.51	0.19
	PWCB20	2400	1.00	0.95	0.95	1.80
BLB	BLB5	1400	2.19	2.03	1.94	0.77
	BLB20	1400	2.25	3.25	2.95	3.40
	BLB5	2400	1.68	0.86	1.09	0.40
	BLB20	2400	0.40	0.80	1.65	1.55
JB	JB5	1400	2.07	2.80	1.19	0.58
	JB20	1400	3.05	3.00	2.65	1.80
	JB5	2400	0.15	0.33	1.05	0.34
	JB20	2400	0.75	1.80	1.25	1.45

It can be seen from Table 7.1 that the highest increase in CP is observed for PB20 at 1400 rpm and 100% load and the lowest increase in CP is found for JB5 at 2400 rpm and 50% load in comparison to diesel.
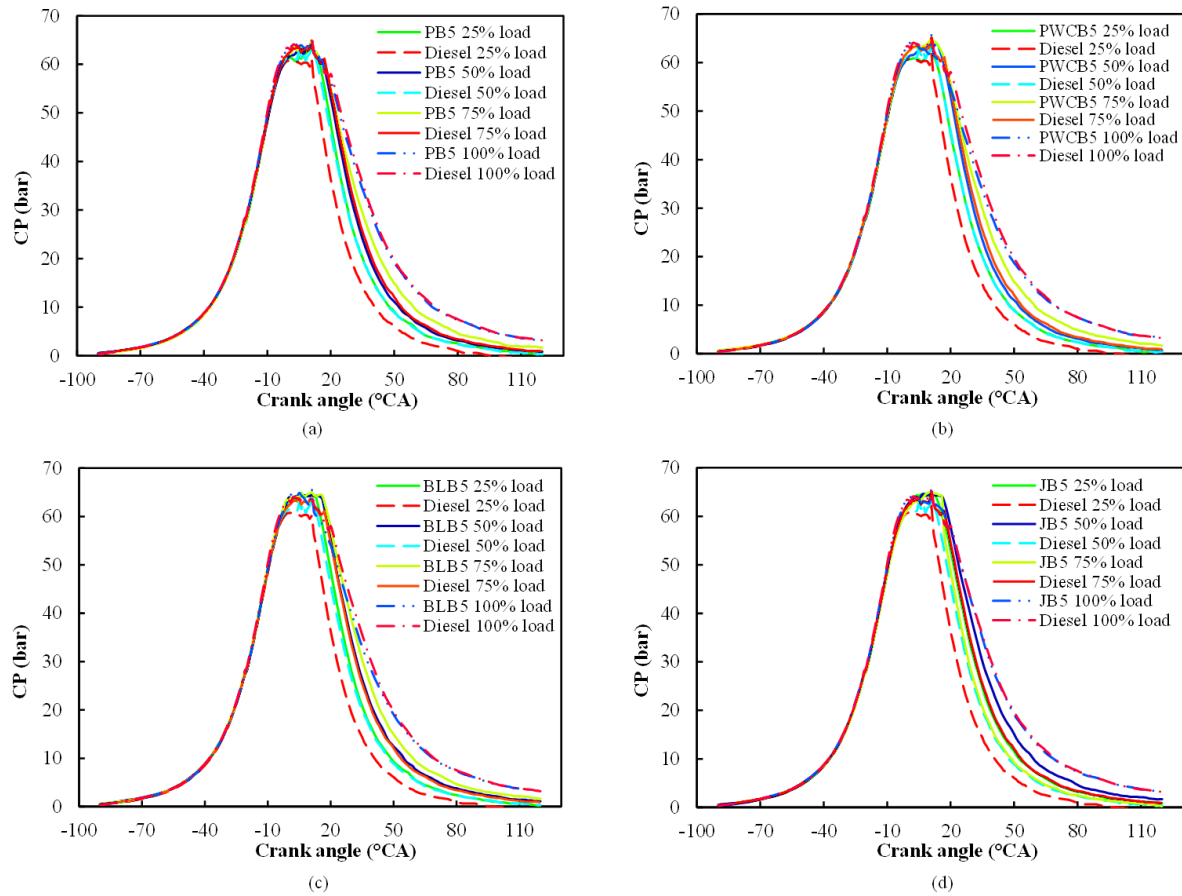
Figure 7.3: Variation in CP with CA for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions and 1400 rpm
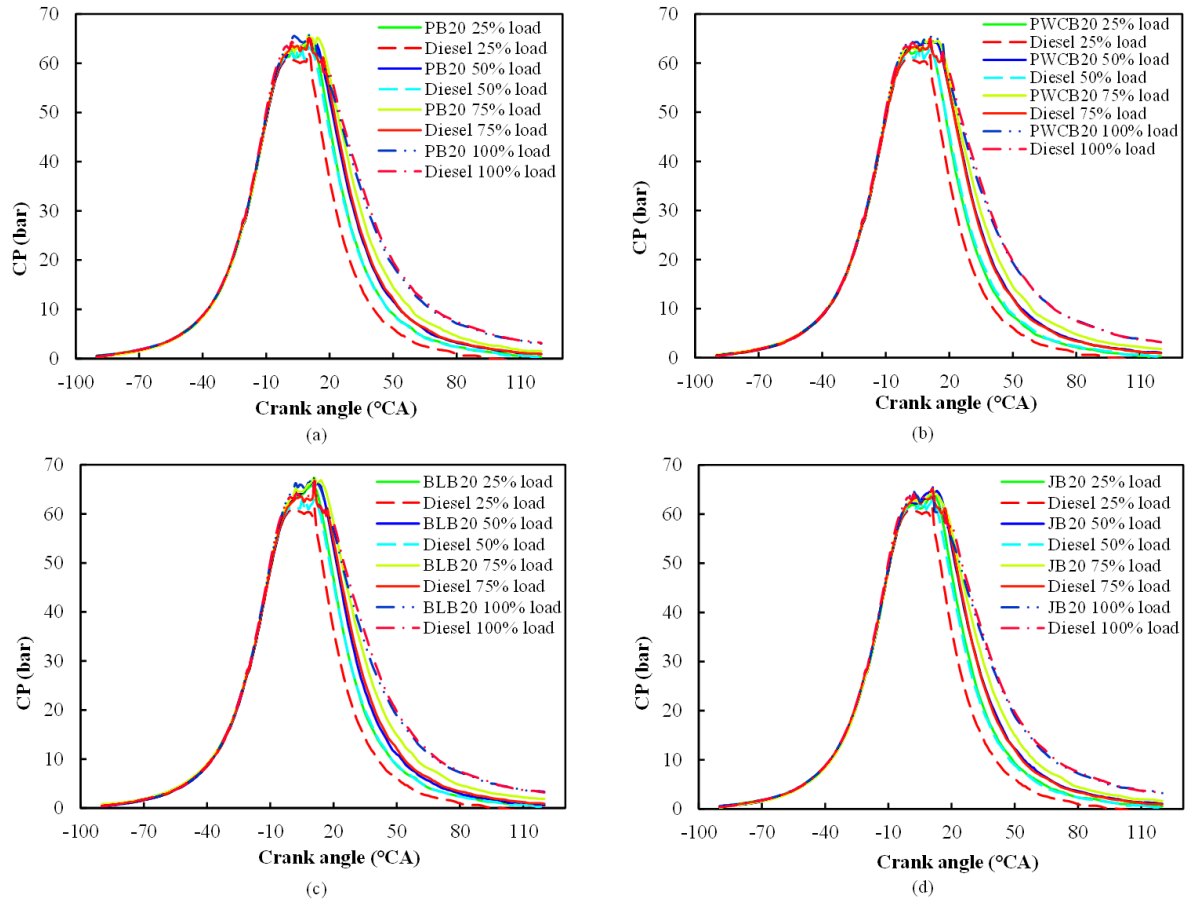
Figure 7.4: Variation in CP with CA for: (a) PB20, (b) PWCB20, (c) BLB20 and (d) JB20 at different loading conditions and 1400 rpm
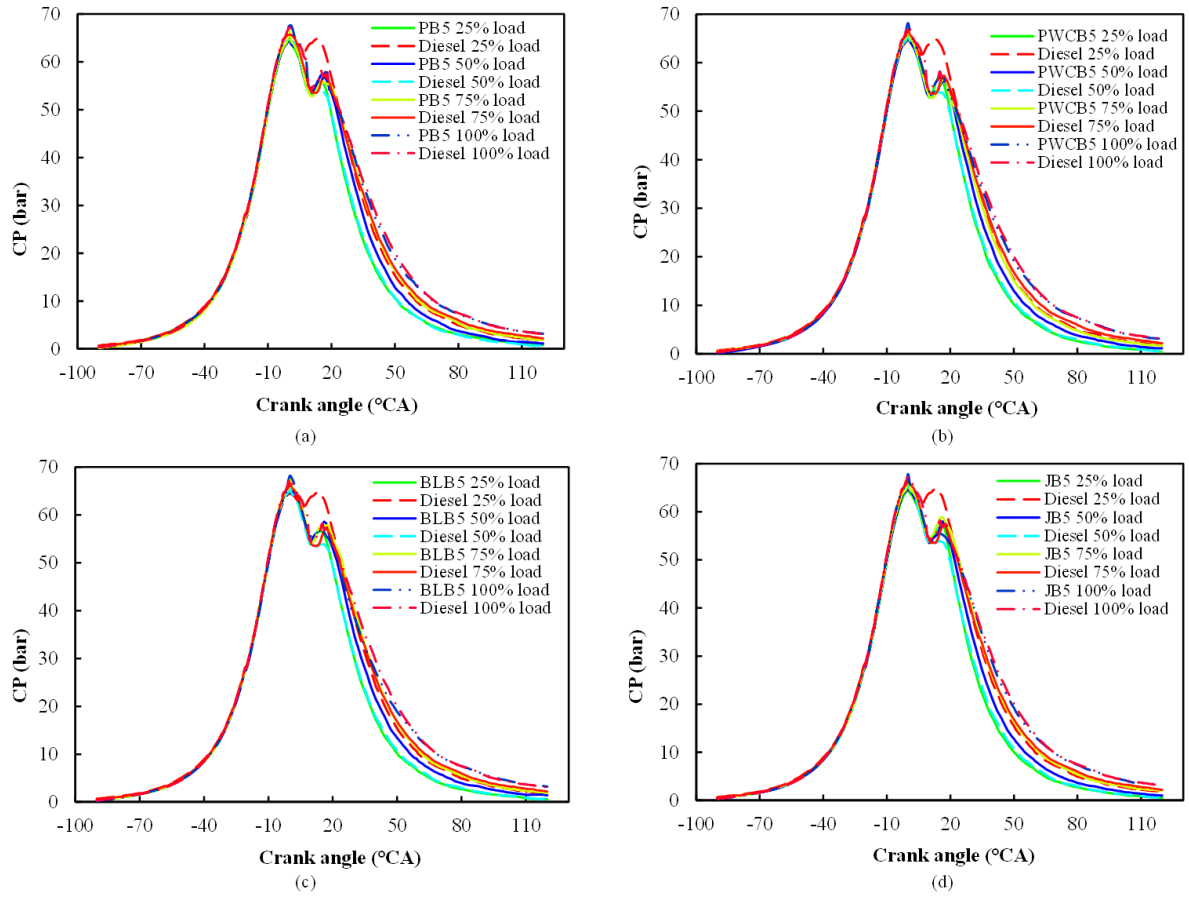
Figure 7.5: Variation in CP with CA for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions and 2400 rpm
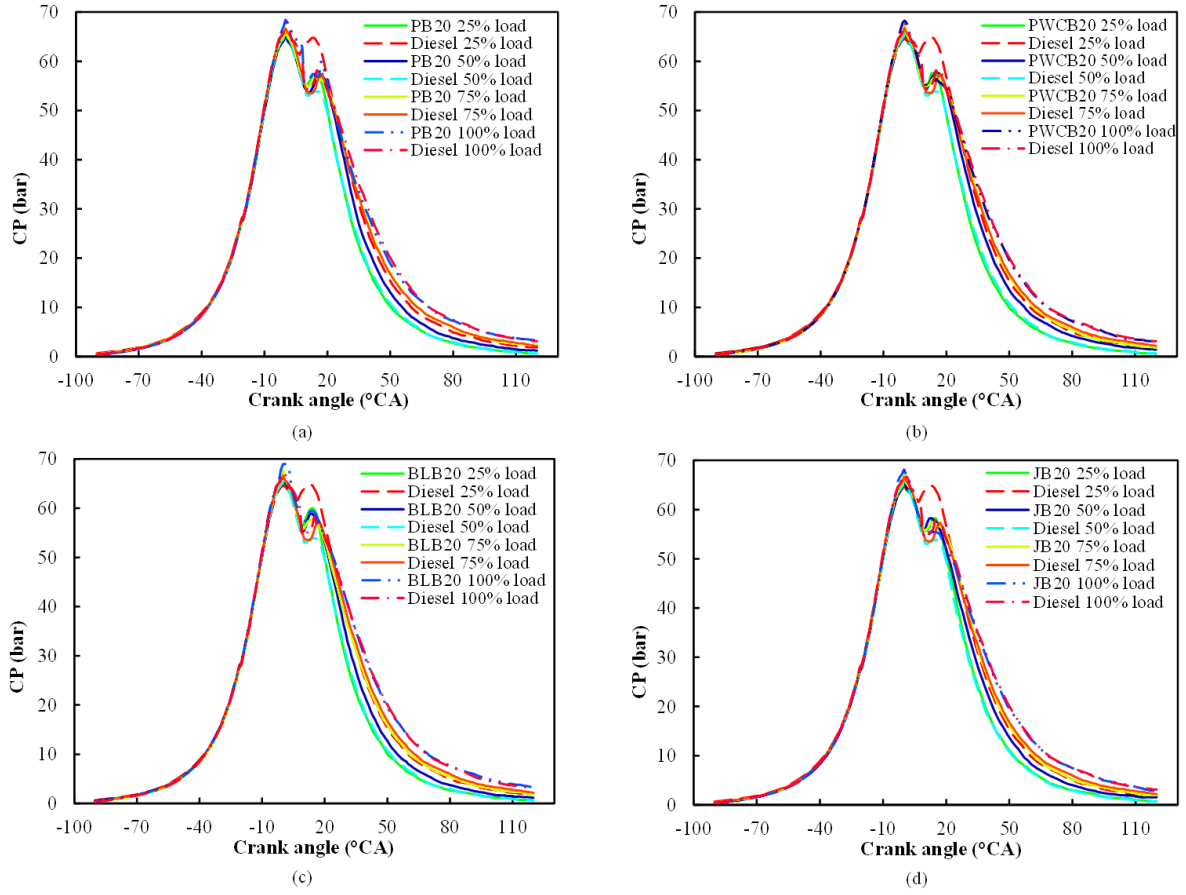
Figure 7.6: Variation in CP with CA for: (a) PB20, (b) PWCB20, (c) BLB20 and (d) JB20 at different loading conditions and 2400 rpm

7.3 Heat Release Rate (HRR)

HRR analysis is one of the most significant matters for better understanding of the combustion mechanism. It is an important constraint for evaluating combustion characteristics of fuel. It is used to identify the ignition delay and combustion duration. HRR was evaluated against CA on the basis of CP and instantaneous cylinder volume. HRR rate was calculated using the following formula:

$$\frac{dQ}{d\theta} = \frac{V\frac{dp}{d\theta} + \gamma P\frac{dv}{d\theta}}{\gamma - 1} \tag{7.1}$$

where, V is the instantaneous cylinder volume (m^3), θ is the crank angle (°CA), P is the instantaneous cylinder pressure (Pa), γ is the specific heat ratio which is considered as 1.35, $\frac{dQ}{d\theta}$ is the rate of heat release (J/°CA).

Figures 7.7 (a), (b), (c) and (d) at 1400 rpm and Figures 7.8 (a), (b), (c) and (d) at 2400 rpm represent the variation in HRR with respect to CA for PB, PWCB, BLB and JB with B5, B10 and B20 at full load condition. At the beginning a negative HRR and after initiated of combustion a positive HRR value is observed which is due to the vaporisation of fuel accumulated during ignition delay (Dhar et al. 2012).

The experimental results indicate that the overall HRR trend for all biodiesel-diesel blends is quite similar to diesel. It can be seen from Figure 7.7 and Figure 7.8 that PB, PWCB, BLB and JB have an influence on HRR for both 1400 rpm and 2400 rpm. From both figures, the higher HRR is observed at B5 in comparison to B10 and B20.
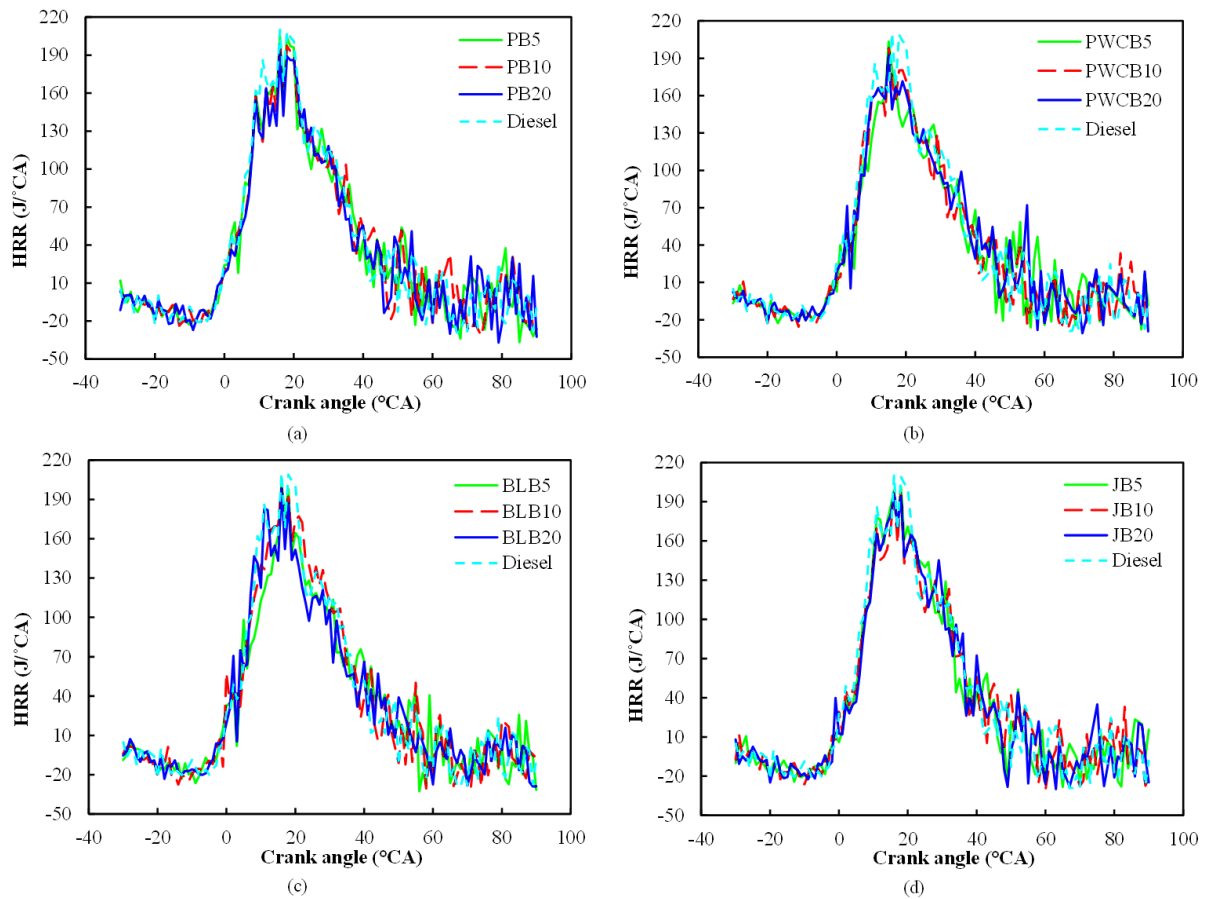
Figure 7.7: Variation in HRR with CA for: (a) PB, (b) PWCB, (c) BLB and (D) JB at 1400 rpm and full load condition

The higher HRR at B5 could be explained due to the good mixing velocity of fuel-air which is the main affecting parameter of HRR (Heywood 1988). In addition, the higher calorific value of lower biodiesel blend (B5) is responsible for higher HRR (Devan & Mahalakshmi 2009d). The start of combustion could occur slightly earlier at B20 compared to B5 which resembled a

shorter ignition delay at full load condition (An et al. 2013). Furthermore, the total combustion duration could be shorter with increase in biodiesel blend level.
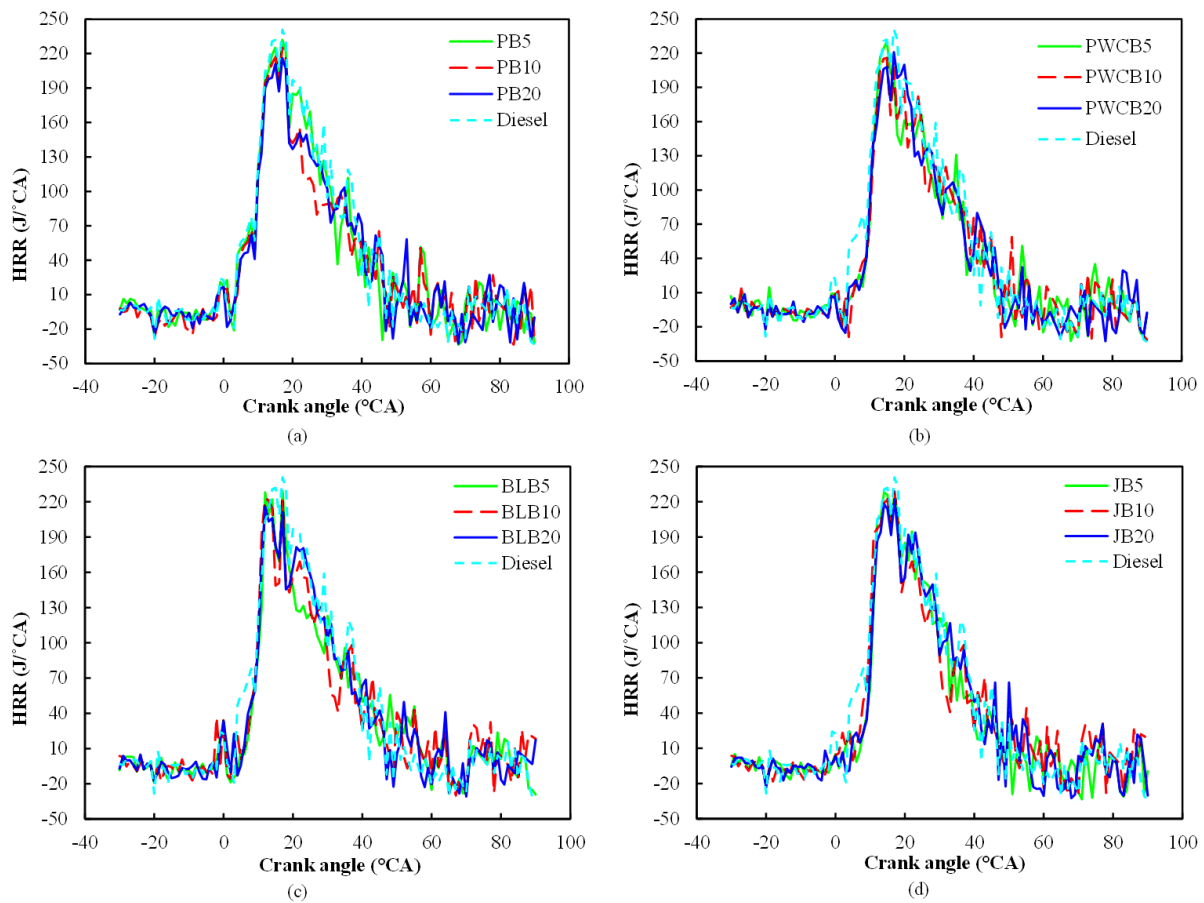
Figure 7.8: Variation in HRR with CA for (a) PB, (b) PWCB, (c) BLB and (d) JB at 2400 rpm and full load condition

As predicted from Figure 7.7 and Figure 7.8, the lower HRR is observed for all biodiesel-diesel blends in comparison to diesel. This result is consistent with other studies (Gattamaneni et al. 2008, Jaichandar et al. 2012, Sayin et al. 2012). The lower HRR in biodiesel blend is because of the decrease in the premixed air-fuel mixture which is due to the poor atomisation and the slow mixing ratio of air-fuel (Imdadul et al. 2016). In addition, the higher density and viscosity of blended fuel are the affecting parameters which lead to increase physical ignition delay and delayed start of combustion in contrast to diesel (Koçak et al. 2007). Moreover, HRR decreases for blended fuels compared to diesel because of its lower energy content and shorter delay period (Anand et al. 2011, Sahoo & Das 2009a, Saravanan et al. 2010b) at full load. The similar results were also reported by several researchers (Buyukkaya 2010, Sahoo & Das 2009a, Yu et al. 2002). In contrast, while the engine is running with diesel, increases accumulation of fuel

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at the time of relatively longer delay period resulted in higher HRR (Agarwal 2007). The same reason has also been supported by several researchers (Buyukkaya 2010, Sahoo & Das 2009a). At 1400 rpm and 2400 rpm, the reductions in HRR for PB, PWCB, BLB and JB at B5 compared to diesel are (2.40%, 3.10%, 3.80% and 4.05%) and (3.70%, 4.45%, 4.95% and 5.35%) at full load condition, respectively. Figure 7.9 and Figure 7.10 show the relation between HRR and CA for different engine loading conditions (50% and 100%) for B5 and B20 at 1400 rpm, respectively.
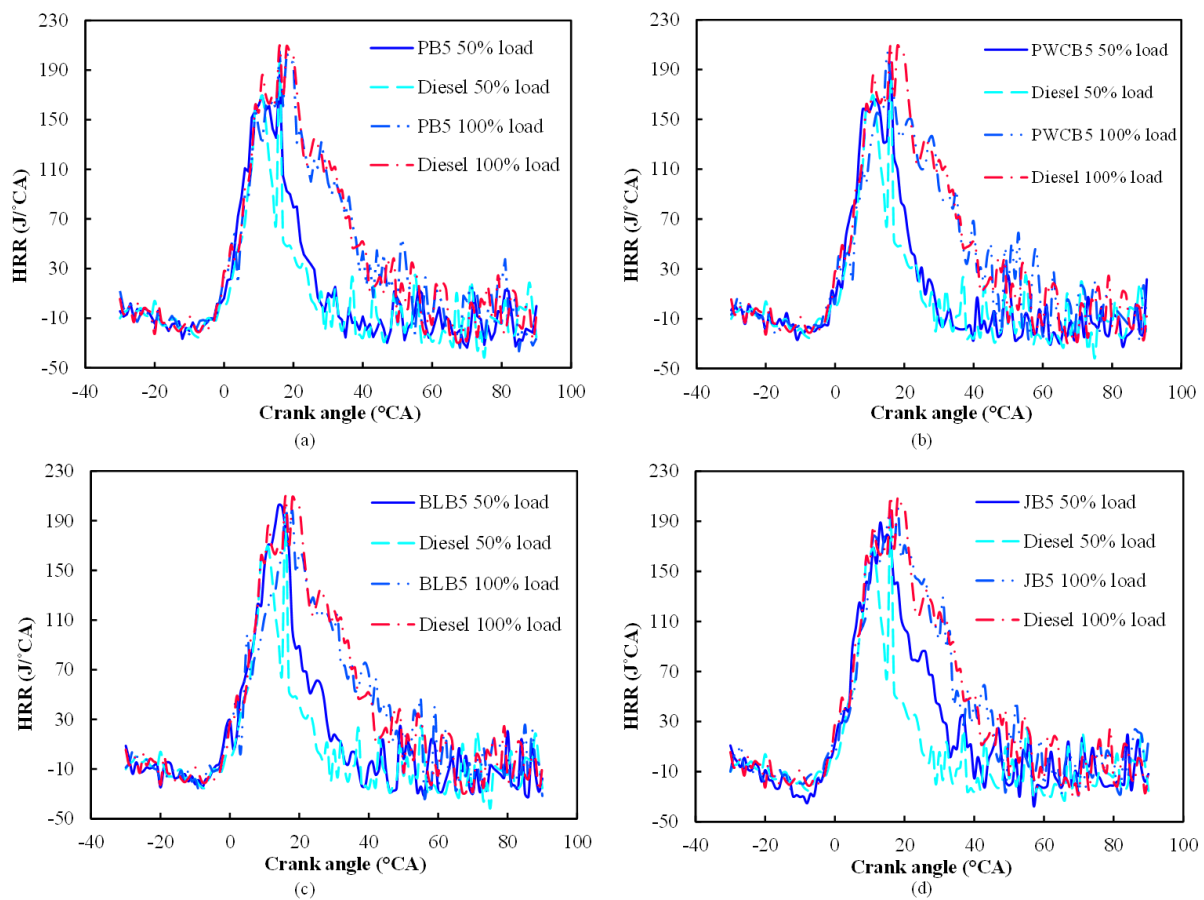
Figure 7.9: Relation between HRR and CA for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions and 1400 rpm

At 2400 rpm, Figure 7.11 and Figure 7.12 show the relation between HRR and CA for different engine loading conditions (50% and 100%) for B5 and B20, respectively. The HRR results of B10 at 1400 rpm and 2400 rpm for all loading conditions are shown in Appendix B at Figure B.3 and Figure B.4, respectively.
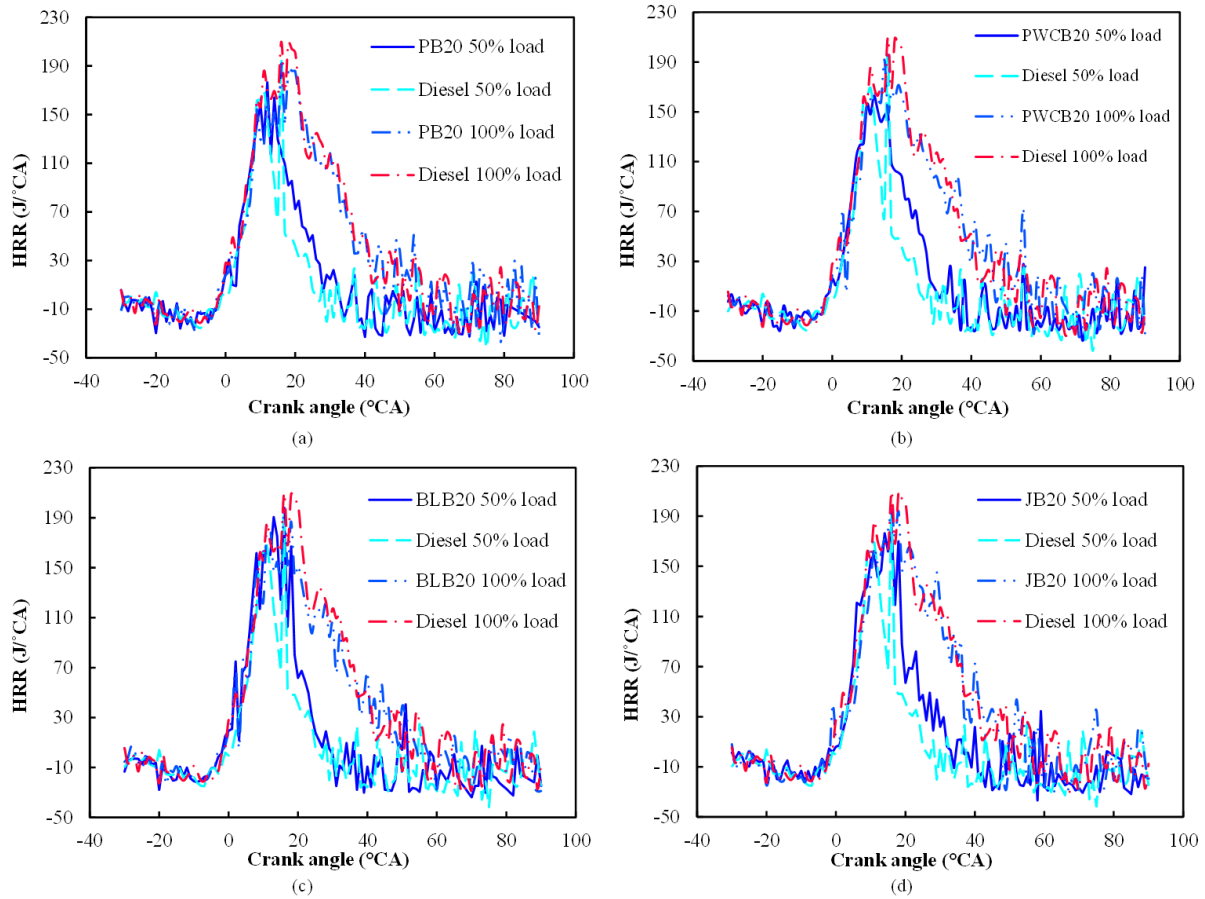
Figure 7.10: Relation between HRR and CA for: (a) PB20, (b) PWCB20, (c) BLB20 and (d) JB20 at different loading conditions and 1400 rpm

It can be noted from Figures 7.9-7.12 that biodiesel blends show a similar trend of HRR as diesel for all loading conditions. The HRR increases with increase in load for all samples tested as shown in Figures 7.9-7.12. At higher loads, HRR rate during combustion increases owing to increasing fuel quantity injected. The higher HRR rate is observed at lower biodiesel blend (B5) in comparison to higher blend (B10 and B20) for all engine loading conditions due to optimum condition for the formation of mixture and better combustibility of the mixture because of oxygen content (Dhar et al. 2012).

At lower load conditions, the HRR decreases as the amount of fuel prepared for burning during the delay period decreases and the contribution of the gaseous fuel to the heat release is not significant during this stage (Tarabet et al. 2014). The decrease in HRR for PB, PWCB, BLB and JB at B5 and B20 compared to diesel for different speeds and engine loading conditions is shown in Table 7.2.

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Table 7.2: Decrease in HRR compared to diesel for all fuels tested at different engine speeds and loading conditions

Fuels	Blends	Engine speed (rpm)	Decrease in HRR (%)			
			Load (%)			
			25	50	75	100
PB	PB5	1400	4.80	5.10	2.45	2.40
	PB20	1400	4.80	5.91	5.45	6.57
	PB5	2400	5.55	1.05	3.45	3.70
	PB20	2400	4.72	5.22	5.39	6.34
PWCB	PWCB5	1400	2.15	3.55	3.95	3.10
	PWCB20	1400	3.33	4.83	5.38	6.57
	PWCB5	2400	4.70	4.35	5.60	4.45
	PWCB20	2400	4.29	4.76	5.19	6.26
BLB	BLB5	1400	5.90	3.35	5.90	3.80
	BLB20	1400	2.67	2.75	3.44	5.71
	BLB5	2400	5.10	3.15	3.90	4.95
	BLB20	2400	1.23	3.07	4.17	5.34
JB	JB5	1400	2.65	3.70	4.75	4.05
	JB20	1400	1.72	3.14	5.39	6.14
	JB5	2400	4.15	5.55	1.90	5.35
	JB20	2400	1.70	3.31	4.90	5.85

It can be noted from Table 7.2 that the highest and lowest decrease in HRR is found for PB20 at 100% load and for PB5 at 50% load for 1400 rpm and 2400 rpm, respectively, compared to diesel. From Figures 7.9 -7.12, the highest HRR is observed within the CA range between 10° and 22° It is clear from Figures 7.9 -7.12 that after TDC, that is, after CA of 22° the trend variations in HRR with increase in CA is similar for all blends (B5, B10 and B20) of PB, PWCB, BLB and JB, respectively.
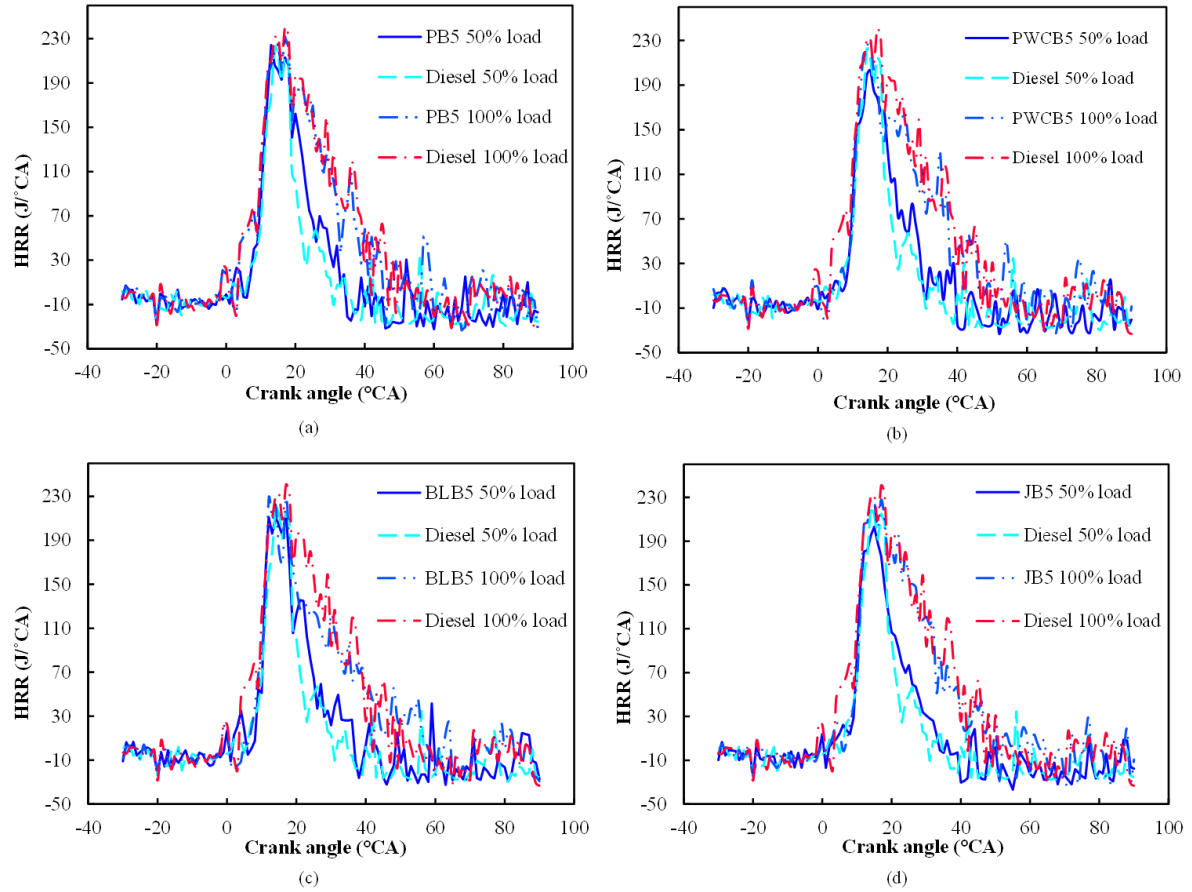
Figure 7.11: Relation between HRR and CA for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions and 2400 rpm

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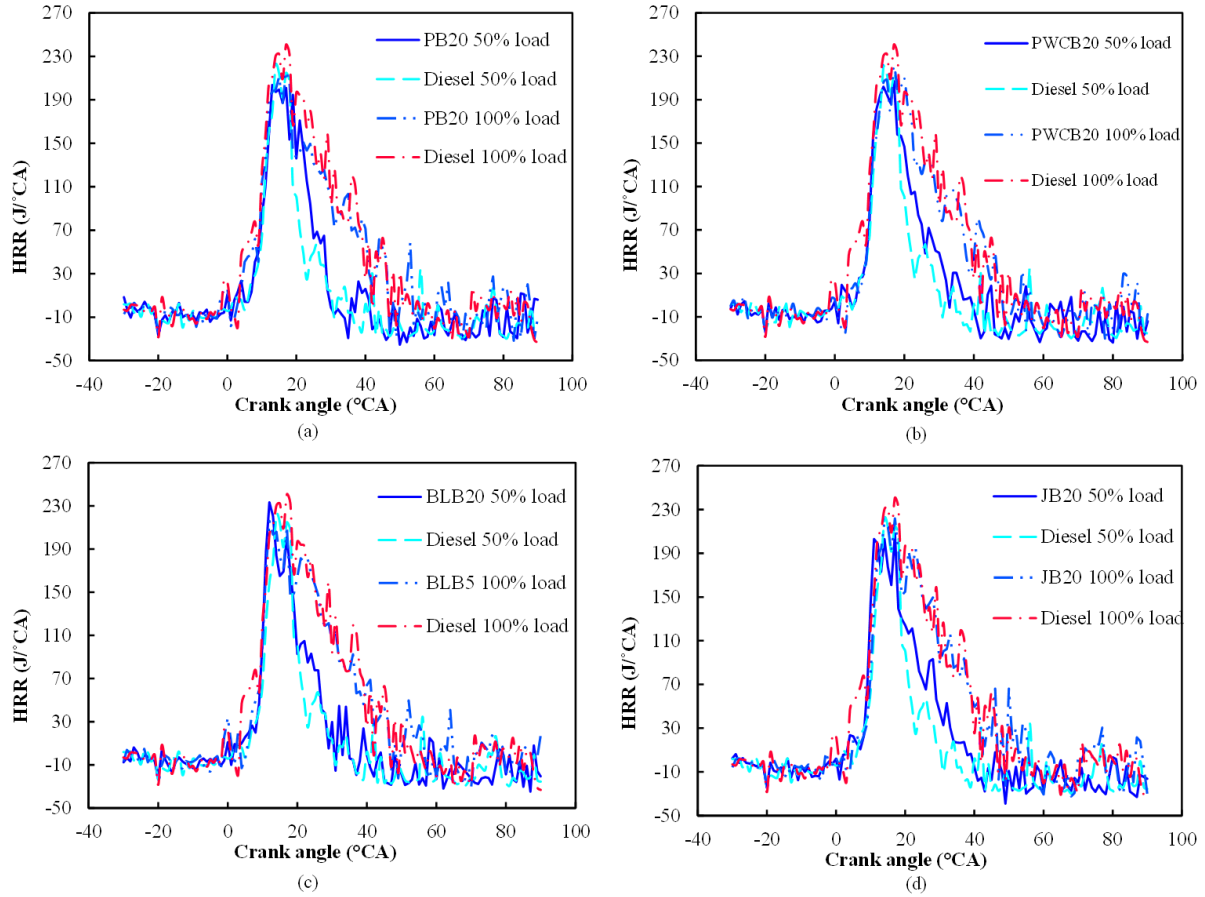
Figure 7.12: Relation between HRR and CA for: (a) PB20, (b) PWCB20, (c) BLB20 and (d) JB20 at different loading conditions and 2400 rpm

7.4 Conclusion

The combustion characteristic result revealed that combustion starts earlier at higher biodiesel-diesel blends; however, start of combustion was slightly delayed at lower blends compared to diesel. The HRR trend for all biodiesel-diesel blends is almost identical, and the values are close to diesel. In addition, combustion duration for all biodiesel–diesel blends is observed to be shorter in comparison to diesel.

The trend in-CP and HRR variation with increase in CA for all biodiesel-diesel blends are similar to diesel, respectively. The peak in-CP is observed higher at higher biodiesel-diesel blend (B20) in comparison to other blends. In addition, the peak CP is found higher for biodiesel blend in comparison to diesel. The higher HRR is found at lower biodiesel-diesel blend (B5) for all samples tested compared to other blends. Moreover, it could be noted that the HRR is observed higher for diesel compared to biodiesel blend. As expected, the CP and

HRR increases with increase in load for all fuels tested. Overall, the results indicate that up to B20 of biodiesel-diesel blends could be used in CI engine as a diesel substitute.

CHAPTER 8

ENGINE EMISSION CHARACTERISTICS

In this chapter, an attempt has been made to discuss the effect of biodiesel-diesel blends on engine emission characteristics. The results revealed that the use of biodiesel-diesel blends led to the significant reduction in carbon monoxide (CO), hydrocarbon (HC) and particulate matter (PM) emissions in comparison to conventional diesel. On the other hand, increase in exhaust gas temperature (EGT), nitrogen oxides (NO_x) and carbon dioxide (CO_2) is observed in using biodiesel blends over the diesel. The experiment was performed for different engine operating conditions which include speed (1200 rpm-2400 rpm) and load (25%, 50%, 75% and 100%). The results indicate that EGT, NO_x and CO_2 increase, whereas, CO, HC and PM decrease with increases in speed at full load condition. It could be noted that all the emission parameters (EGT, NO_x, CO, CO_2, HC and PM) increase with increase in load. The characteristic results are compared with diesel and among the biodiesel blend. The results also indicated that EGT, NO_x and CO_2 are comparatively lower at the lower blend (B5) than the higher blends (B10 and B20), whereas, CO, HC and PM are lower at the higher blend (B20) than the lower blends (B5 and B10).

8.1 Introduction

The use of biodiesel-diesel blends in CI engines leads to the reduction in CO, HC and PM emissions during the combustion process (Tarabet et al. 2014). These results could be explained by low aromatic content and presence of high oxygen content (Yoon et al. 2009). Several researchers showed that using biodiesel-diesel blends in CI engines decreases CO, HC and PM emission significantly in comparison to diesel (Abedin et al. 2014, Mosarof et al. 2015, Rizwanul et al. 2014, Ruhul et al. 2016a). Most of the studies from the available literature reported that biodiesel-diesel blends increase NO_x emission in comparison to diesel (Çelikten et al. 2012, Fontaras et al. 2009, Kim & Choi 2010, Monirul et al. 2016, Ong et al. 2014b, Zhu et al. 2010b). Almost all the researchers showed that EGT was higher in biodiesel-diesel blend compared to diesel (Çelikten et al. 2012, Kumar et al. 2013, Ong et al. 2014a, Ong et al. 2014b, Sakthivel 2016). Several researchers showed that CO_2 emission is higher in biodiesel blends in comparison to diesel (Fontaras et al. 2009, Gumus et al. 2012, Labeckas & Slavinskas 2006, Rahman et al. 2014, Ruhul et al. 2016b).

8.2 Exhaust Gas Temperature (EGT)

Figures 8.1 (a), (b), (c) and (d) show the variation in EGT with speed for PB, PWCB, BLB and JB at full load condition. As seen from Figure 8.1, the EGT increases with increase in speed for all biodiesel blends.
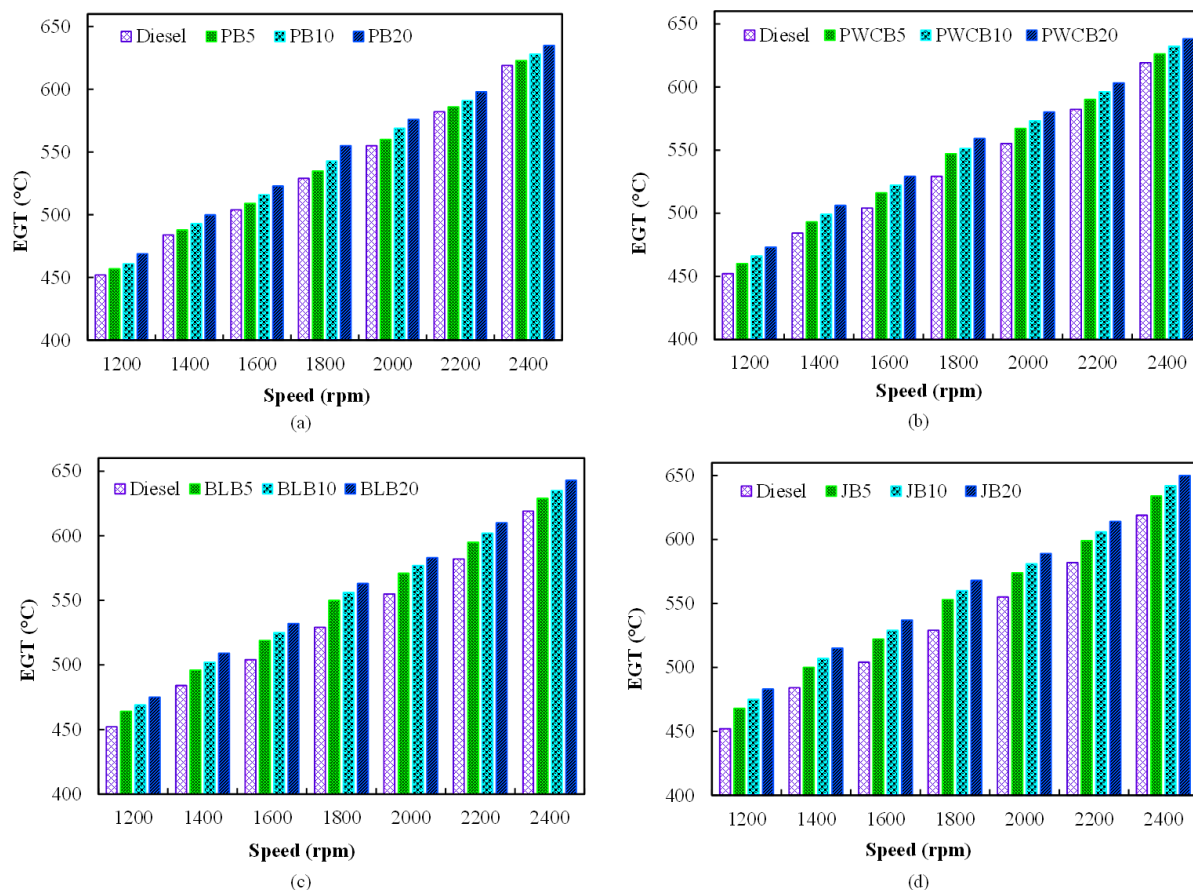
Figure 8.1: Variation in EGT with changing speed for: (A) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

This is due to the increase in fuel quantity in the combustion chamber in a unit time, and therefore, the amount of heat energy produced in the combustion chamber increases (Ong et al. 2014b). The EGT increases with increase in biodiesel blend level from B5 to B20 for all feedstocks. The lower EGT at B5 can be explained due to the fact that B5 has a higher cetane number, produced a good formation of the mixture and it is an oxygenated fuel which assisted in causing better combustion (Ong et al. 2014a). On the contrary, the higher EGT of B10 and B20 might be due to the lower calorific value and higher viscosity which caused the poor atomisation and incomplete combustion in the combustion chamber. In addition, this could be

due to the increase of heat loss for higher blends which is also supported from its lower BTE's as compared to diesel.

The similar results have also been reported by several researchers while testing different biodiesels (Devan & Mahalakshmi 2009a, Godiganur et al. 2010, Raheman & Phadatare 2004, Ramadhas et al. 2004). Moreover, this could be illustrated due to the presence of constituents with higher boiling points in PB, PWCB, BLB and JB in comparison to diesel (Devan & Mahalakshmi 2009a), as those constituents are not evaporated sufficiently during the combustion and sustained to burn in the late combustion phase. This resulted in a slight increase in EGT and the lower BTE. Furthermore, a higher amount of oxygen is required for the higher blend in the air-fuel ratio which caused high activation energy to complete the chemical reaction (Ong et al. 2014b). It could be stated that the lower EGT indicates a better combustion of fuel in the combustion chamber at B5.

Over the entire range of engine speed examined, PB5, PWCB5, BLB5 and JB5 produced average EGTs of 536.86 °C, 542.71 °C, 546.29 °C and 550.0 °C which are 1.13%, 1.04%, 1.09% and 1.28% lower than PB10, PWCB10, BLB10 and JB10, and 2.54%, 2.29%, 2.32% and 2.6 % lower than PB20, PWCB20, BLB20 and JB20, respectively. Generally, diesel has the lower EGT compared to all fuels tested as it has the higher calorific value and shorter combustion phase (Ong et al. 2014b). Biodiesel-diesel blends show the higher EGT than diesel which could be due to low volatility which affected the spray formation in the combustion chamber and therefore, led to slow combustion (Ong et al. 2014b). The poor combustion characteristics of biodiesel-diesel blends were observed by several researchers (Devan & Mahalakshmi 2009c, Ong et al. 2014a, Panwar et al. 2010). They reported that the higher EGT is due to the reason of longer combustion duration for biodiesel-diesel blends as these have high viscosity. In addition, it has been reported by Kumar et al. (2013) that blending of biodiesel-diesel has the higher EGT compared to diesel. Overall, it could be noted that the higher EGT is the indication of lower performance in biodiesel-diesel blends. The average percentage (%) increase in EGT at B5, B10 and B20 for all fuels tested at full load condition in comparison to diesel is shown in Table 8.1. It can be seen from Table 8.1 that the lowest and the highest increase in EGT is observed for PB (0.90%) at B5 and for JB (6.20%) at B20, respectively, compared to diesel.

Table 8.1: Average percentage (%) increase in EGT for B5, B10 and B20 for all fuels tested at full load condition compared to diesel

| Biodiesel samples | EGT (% increase) | | |
| | Blend level | | |
	B5	B10	B20
PB	0.90	2.05	3.50
PWCB	2.00	3.05	4.40
BLB	2.65	3.80	5.10
JB	3.35	4.70	6.20

The variation in EGT with respect to engine load for PB, PWCB, BLB and JB at a particular speed of 1400 rpm is presented in Figures 8.2 (a), (b), (c) and (d), respectively.

Figure 8.2: Variation in EGT with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

As seen from Figure 8.2, the EGT increases with increase in load for all the fuels tested. This is because more quantity of fuel is required in the engine to generate extra power which is essential to take up the additional loading (Godiganur et al. 2010). Over the entire range of load (25%-100%), the EGT at B5 is lower compared to B10 and B20 for all samples tested. The percentage (%) increase in EGT for all biodiesel fuels tested at B5 and 1400 rpm for different loading conditions compared to diesel is shown in Table 8.2. The minimum and maximum increase in EGT is observed for PB (0.40%) at 25% load and for JB (3.55%) at 75% load, respectively, in comparison to diesel.

Table 8.2: The percentage (%) increase in EGT for all biodiesels at B5 for different loading conditions in comparison to diesel

| Biodiesel samples | EGT (% increase) | | | |
| | Load (%) | | | |
	25	50	75	100
PB	0.40	0.65	0.85	0.85
PWCB	1.25	1.70	1.85	1.85
BLB	2.10	2.50	2.90	2.50
JB	2.95	3.35	3.55	3.30

Figures 8.3 (a), (b), (c) and (d) show the relation between EGT and speed with different loading conditions (25%, 50%, 75% and 100%) for PB5, PWCB5, BLB5 and JB5, respectively. Over the whole range of speed (1200 rpm-2400 rpm), the EGT increases with increase in load varied from 25%-100% for all samples tested. The lowest and highest EGT is obtained at 1200 rpm and 2400 rpm for all loading conditions, respectively. For all loading conditions, the lower EGT is observed at diesel compared to biodiesel blend for all fuels tested.

The variation in EGT with respect to change in biodiesel-diesel blend compositions (B5, B10 and B20) for PB, PWCB, BLB and JB for different speeds (1400 rpm, 1800 rpm, 2200 rpm and 2400 rpm) and loads (25%, 50%, 75% and 100%) are shown in Figures 8.4 (a) and (b), respectively. As expected, the lowest EGT temperature is observed for PB5 amongst all other blends of all samples tested at 1400 rpm and full load condition, respectively (Figure 8.4).
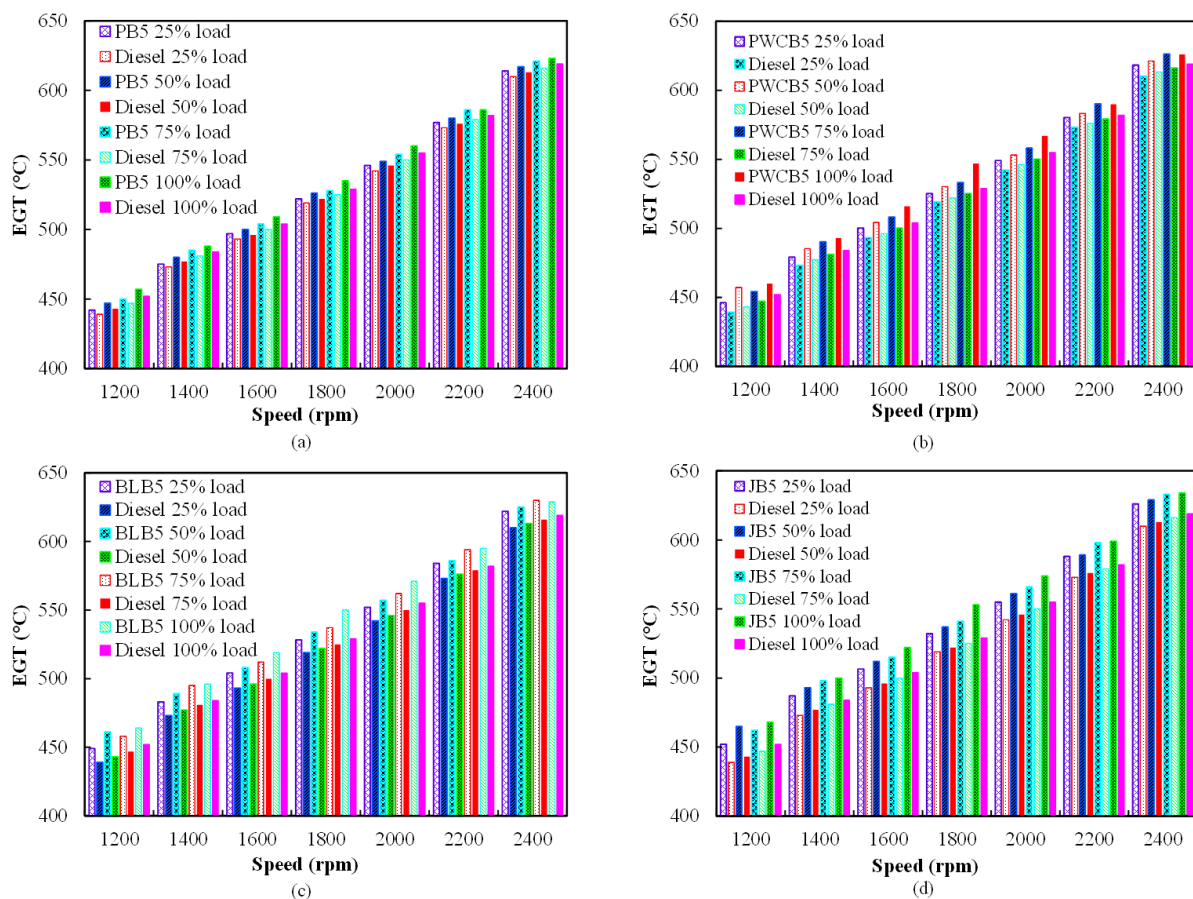
Figure 8.3: Variation in EGT with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions

Figure 8.4: Variation in EGT with biodiesel blend composition for: (a) different speeds at full load and (b) different loading conditions at 1400 rpm

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8.3 Nitrogen Oxides (NO$_x$) Emission

Figures 8.5 (a), (b), (c) and (d) show the variation in NO$_x$ emission with respect to speed for PB, PWCB, BLB and JB at 100% loading condition. The NO$_x$ increases with increase in speed for the entire range of speed (1200 rpm-2400 rpm) as shown in Figure 8.5.
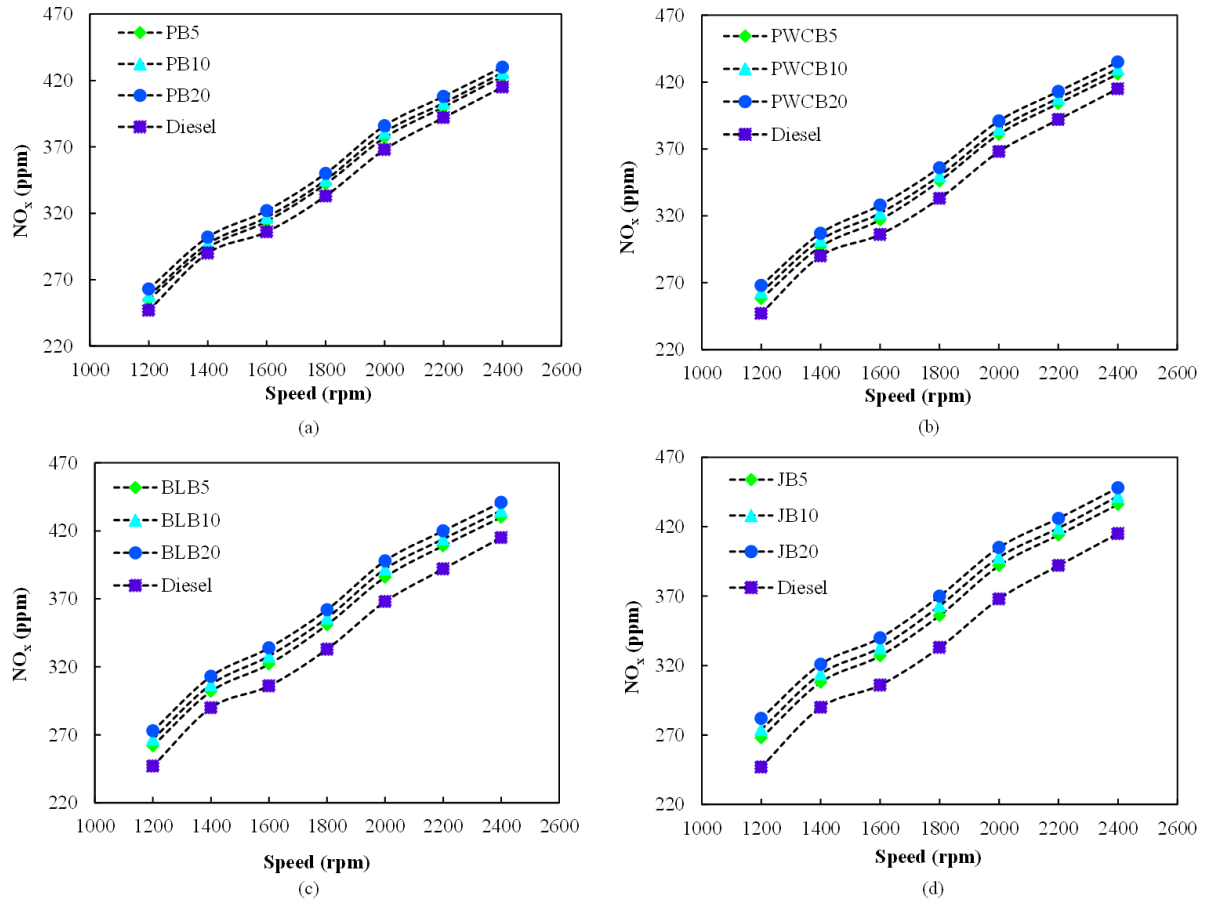
Figure 8.5: Relationship between NOx and speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

In CI engines, the formation of NO$_x$ could be demonstrated by the Zeldovich mechanism (Rizwanul Fattah et al. 2014, Sajjad et al. 2015). The breaking of the molecular bonds of nitrogen is due to the high temperature which is produced in the combustion chamber and therefore, initiated a series of reactions with oxygen for the formation of NO$_x$ (Sajjad et al. 2015). In addition, the variables which affect the formation of NO$_x$ in the flame front and post-flame are the oxygen contents, in-cylinder temperature and the residence time.

The NO$_x$ emission increases with increase in biodiesel blend level from B5 to B20 for all fuels tested as shown in Figure 8.5. The decrease in NO$_x$ emission at B5 could be demonstrated by

the effect of fuel properties on combustion phenomenon and exhaust emission (Sajjad et al. 2015). For instance, the higher CN at B5 initiated a shorter ignition delay, which resulted in lower combustion temperature and pressure and consequently, it led to producing less NO_x formation (Wu et al. 2007, Yongcheng et al. 2006). In addition, the higher NO_x emission could be attributed to the higher oxygen content and a high 'premixed part' at the time of combustion (Rakopoulos 2013). Generally, the higher combustion temperature which is due to the better combustion of fuel assisted in the formation of higher NO_x (Devan & Mahalakshmi 2009b, Mofijur et al. 2013b). Moreover, the increase in NO_x emission could be explained due to the higher and lower heat release rates in the premix and the late combustion phase, respectively, as NO_x emission is greatly influenced by the higher combustion temperature (Masjuki et al. 2000, Mofijur et al. 2013b).

Furthermore, this could be explained due to increasing EGT and presence of oxygen content which assisted in the formation of the higher NO_x emission (Godiganur et al. 2010). Several researchers also agreed that biodiesel with high oxygen content could increase in high exhaust gas temperature and increase the formation rate of NO_x (İlkılıç & Aydın 2011a, Ong et al. 2014a). Other researcher found that only the higher EGT leads to increase in NOx (Lin et al. 2009). PB5, PWCB5, BLB5 and JB5 produced average NO_x emissions of 343.57 (parts per million (ppm)), 347.0 (ppm), 351.71 (ppm) and 357.29 (ppm) which are 0.91%, 1.26%, 1.48% and 1.65% lower than PB10, PWCB10, BLB10 and JB10, and 2.28%, 2.76%, 3.11% and 3.51% lower than PB20, PWCB20, BLB20 and JB20 over the entire range of engine speed, respectively.

It can also be seen that the NO_x emission for PB, PWCB, BLB and JB, respectively, at B5, B10 and B20 are higher than those of diesel. This could be due to the leaner air/fuel ratio of blends as biodiesel is an oxygenated fuel and contains 12% more molecular oxygen which increases in combustion temperature and cause better combustion (Devan & Mahalakshmi 2009b, Rahman et al. 2014). This result is consistent with other studies reported by several researchers (El-Kasaby & Nemit-allah 2013, Rahman et al. 2014). In addition, the higher NO_x emission could be explained because of the higher adiabatic flame temperature of the blends (Rahman et al. 2014). The average percentage (%) increase in NO_x emission at B5, B10 and PB20 for all biodiesel samples tested at full load condition in comparison to diesel over the entire range of engine speed is shown in Table 8.3. From Table 8.3, the lowest and highest increase in NO_x

emission is found for PB (2.30%) at B5 and for JB (10.25%) at B20, respectively, compared to diesel.

Table 8.3: Average percentage (%) increase in NOx emission for B5, B10 and B20 for all biodiesel samples tested at full load condition in comparison to diesel

Biodiesel samples	NO_x (% increase)		
	Blend level		
	B5	B10	B20
PB	2.30	3.25	4.70
PWCB	3.30	4.65	6.25
BLB	4.70	6.30	8.10
JB	6.40	8.15	10.25

The variation in NO_x emission with increase in engine load (25%-100%) for all samples tested (PB, PWCB, BLB and JB) at B5, B10 and B20 is presented in Figures 8.6 (a), (b), (c) and (d), respectively. The NO_x increases with increase in load for all blends of all fuels tested. Similar results also were reported by several researchers (Buyukkaya 2010, Godiganur et al. 2010, Gumus & Kasifoglu 2010, Murillo et al. 2007, Zhu et al. 2010b). The NO_x increases with increase in load are due to the higher combustion temperature and stoichiometry of the mixture as these are the significant factors for the emission of NO_x (Devan & Mahalakshmi 2009a). Furthermore, the overall fuel-air ratio increases with increase in engine load; consequently, increases in average gas temperature in the combustion chamber and therefore, NO_x is formed (Godiganur et al. 2010).
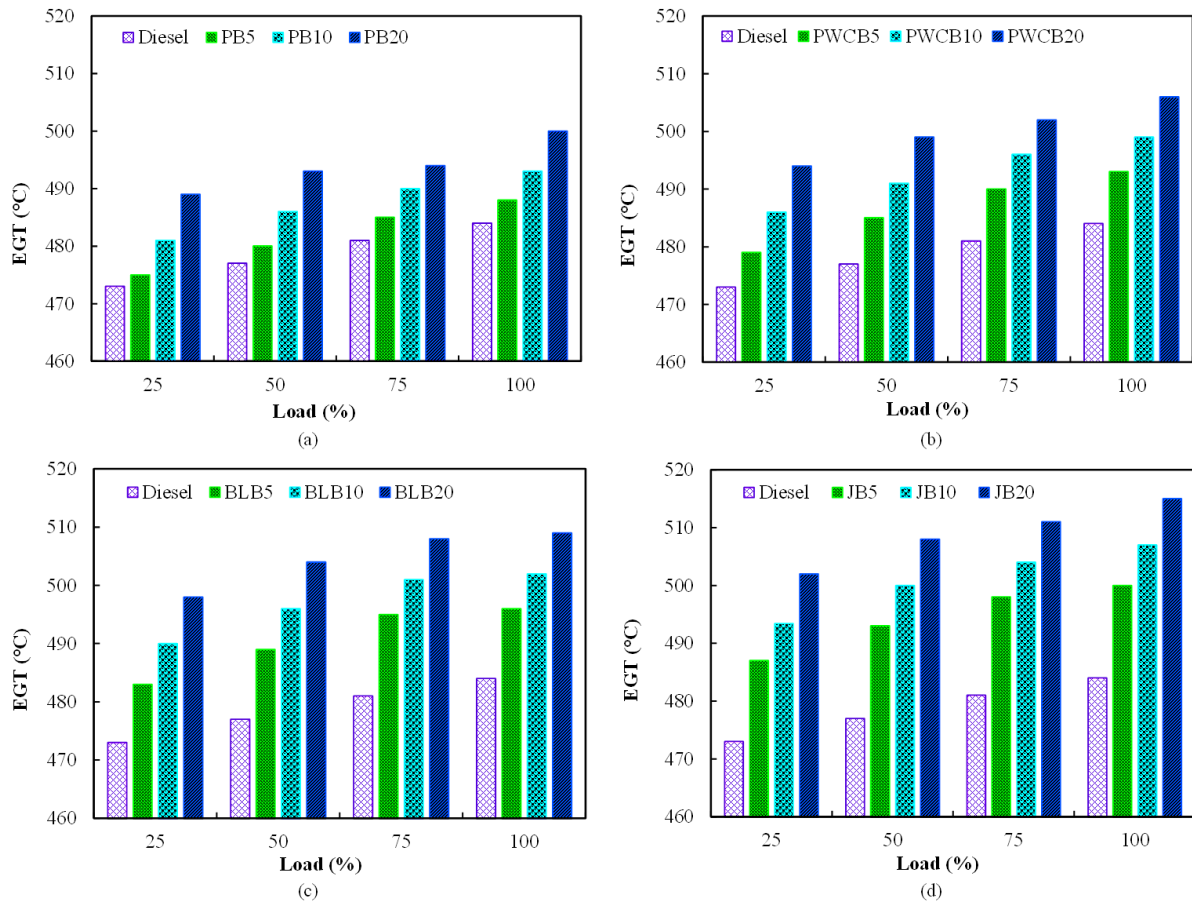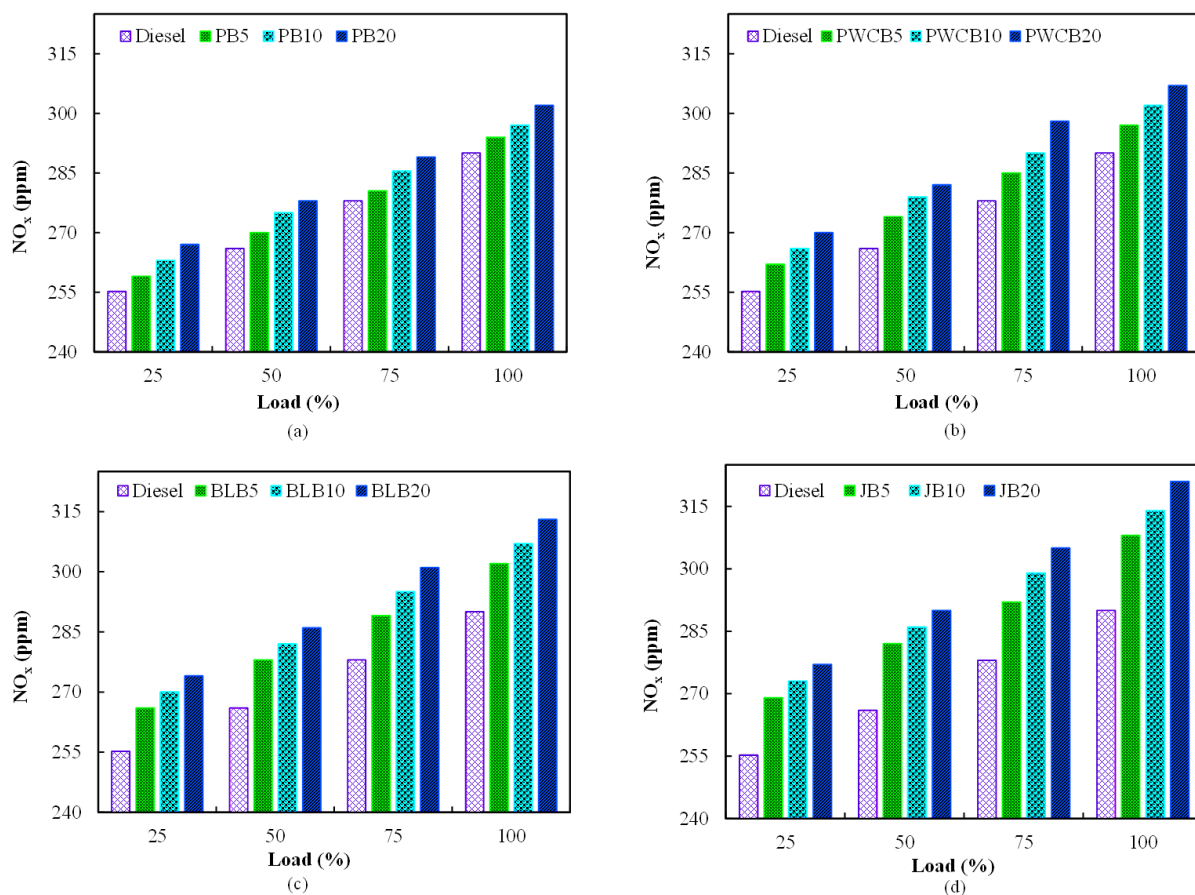
Figure 8.6: Variation in NOx with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

As seen from Figure 8.6, under all loading conditions, the NO_x produced by B5, B10 and B20 for PB, PWCB, BLB and JB are higher in comparison to diesel. The percentage (%) increase in NO_x emission for all biodiesel samples at B5 and 1400 rpm in comparison to diesel for different loads is shown in Table 8.4. The lowest and highest increase in NO_x emission is observed at 100% load for both PB (1.40%) and JB (6.20%), respectively, in comparison to diesel (Table 8.4). The variation in NO_x with changing speed for PB5, PWCB5, BLB5 and JB5 with different engine loads varied from 25%-100% is exhibited in Figures 8.7 (a), (b), (c) and (d), respectively. Over the entire range of engine speed, the NO_x increases with increase in load from 25%-100% for all samples tested (PB5, PWCB5, BLB5 and JB5). At 100% load, the lowest and highest NO_x is observed at 1200 rpm and 2400 rpm, respectively. For all loading conditions, the NO_x emission is found to be lower at diesel in comparison to biodiesel blend for all fuels tested.

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Table 8.4: The percentage (%) increase in NOx emission for all samples at B5 compared to diesel for different loading conditions

| Biodiesel samples	NO$_x$ (% increase)			
	Load (%)			
	25	50	75	100
PB	1.50	1.50	0.90	1.40
PWCB	2.65	3.00	2.50	2.40
BLB	4.25	4.50	3.95	4.15
JB	5.40	6.00	5.05	6.20

Figure 8.7: Variation in NOx with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5at different loading conditions

Figures 8.8 (a) and (b), show the relation between NO$_x$ and biodiesel-diesel blend compositions for PB, PWCB, BLB and JB with different speeds (1400 rpm, 1800 rpm, 2200 rpm and 2400

rpm) and loads (25%, 50%, 75% and 100%), respectively. The lowest NO_x emission is observed at PB5 amongst all other blends of PB, PWCB, BLB and JB at 1400 rpm and full load condition.
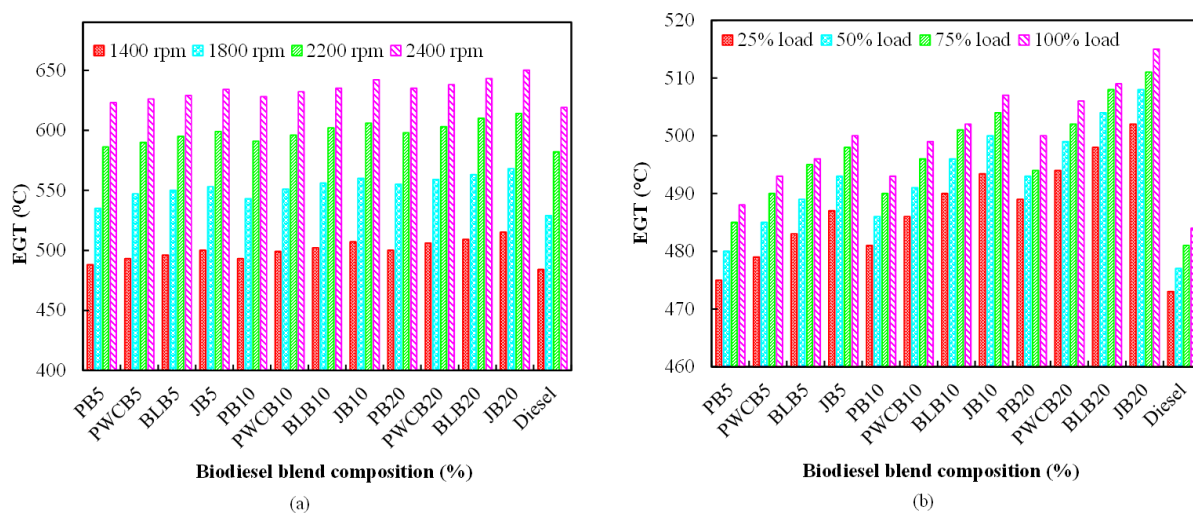

Figure 8.8: Variation in NOx with biodiesel blend composition for: (a) different speeds at full load condition and (b) different loading conditions at 1400 rpm

8.4 Carbon Monoxide (CO) Emission

Incomplete combustion into an engine cylinder is due to the presence of high CO content in exhaust emission. There are two processes that can produce carbon monoxide (CO) into the engine cylinder, these are: (i) an excessively lean blend of air-fuel and (ii) an excessively rich blend of air-fuel. Flame quenching which occurs in the midst of the over-lean and wall impingement zones is the responsible factor to produce CO emission into the engine cylinder (Sajjad et al. 2015). On the other hand, insufficient or low air-fuel proportion in rich combustion mixture is the main reason which causes CO emission into the engine cylinder. In addition, CO forms in rich air-fuel mixture regions due to the unreachability of O_2 to oxidise all CO proportion in the fuel (Ong et al. 2014a). It has been observed that air-fuel ratio, engine speed, injection timing, pressure and fuel types affect CO emissions (Gumus et al. 2012, Mofijur et al. 2014b). Moreover, the CO emission is due to the presence of aromatic hydrocarbons in fuels.

Figures 8.9 (a), (b), (c) and (d) demonstrate the variation in CO with change in engine speed for PB, PWCB, BLB and JB at full load condition, respectively. The CO emission decreases with increase in speed for all biodiesel blends. This could be attributed to the better air-fuel

mixing process and/or the increases of the fuel-air equivalence ratio with the increases in engine speed (Keskin et al. 2008, Lin & Li 2009, Lin & Lin 2006, Qi et al. 2009).
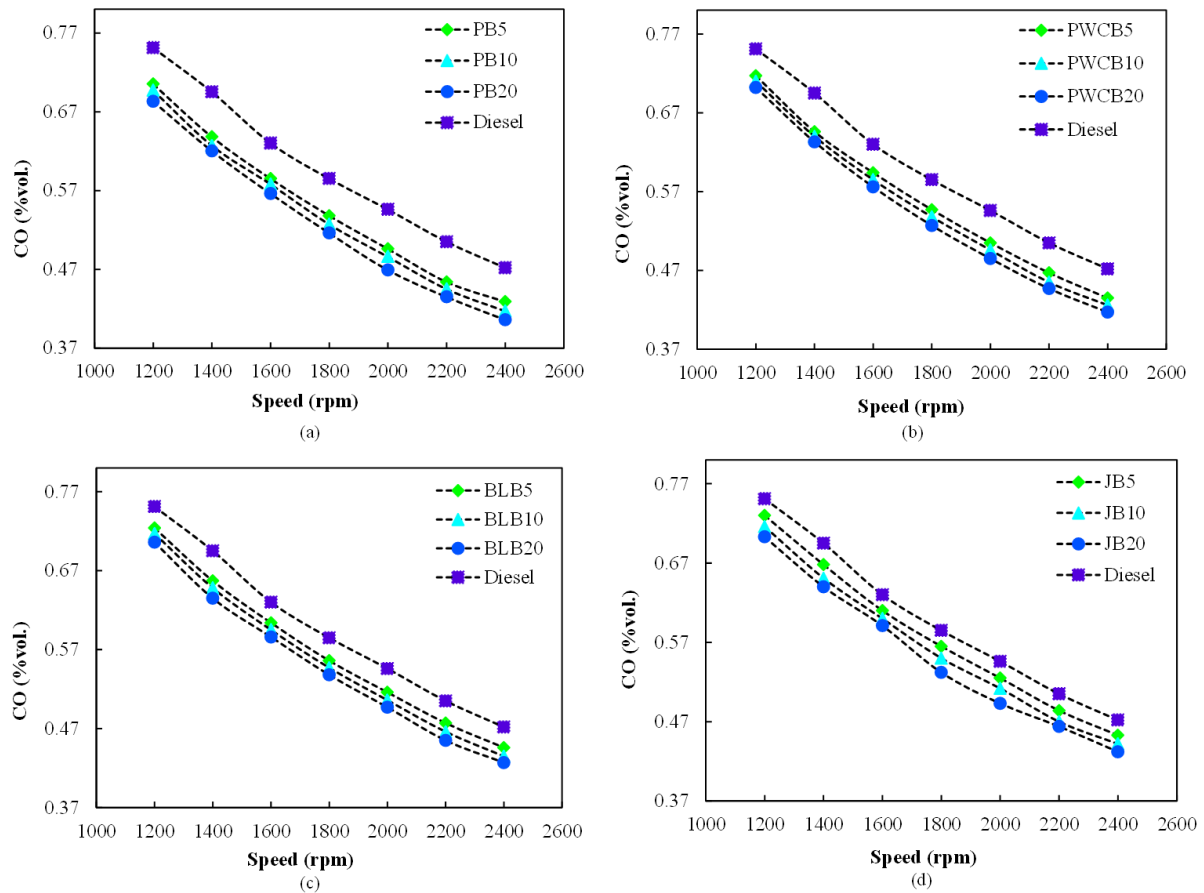
Figure 8.9: Variation in CO with changing speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

The CO emission decreases with an increase in the concentration of biodiesel that is biodiesel blend level from B5 to B20. This is because an increase rate of oxygen content in the air-fuel mixture with an increase in biodiesel blend level assisted in improving combustion (Chauhan et al. 2012, Mofijur et al. 2013b, Rahman et al. 2013, Roy et al. 2013). Generally, biodiesel fuel contains 12% higher oxygen than the diesel (Mofijur et al. 2014a). In addition, the reduction in CO emission for B20 could be demonstrated by the fuel properties and combustion phenomenon (Devan & Mahalakshmi 2009a, Sajjad et al. 2015). Moreover, it can be explained in relation with fuel characteristics, such as, high hydrogen to carbon ratio and higher CN, which B20 contributed to produce a reduction in CO emission (Devan & Mahalakshmi 2009a). Furthermore, the higher CN at B20 initiated the shortening of ignition delay which restricted the formation of less over-lean zones and therefore, improved the combustion process. This

result is supported by several researchers (Hirkude & Padalkar 2012, Kim & Choi 2010, Lapuerta et al. 2008b, Mofijur et al. 2014a, Rajaraman et al. 2009) that indicate that higher biodiesel blend produces lower CO emission in comparison to lower blends. Over the whole range of engine speed, average CO emissions of 0.53 (%vol.), 0.54 (%vol.), 0.56 (%vol.) and 0.55 (%vol.) are produced for PB20, PWCB20, BLB20 and JB20 which are 3.90%, 3.17%, 3.42% and 4.46% lower than PB5, PWCB5, BLB5 and JB5, and 2.17%, 1.64%, 1.79% and 2.18% lower than PB10, PWCB10, BLB10 and JB10 when operating at 100% load, respectively.

The CO emissions for all biodiesel-diesel blends of all fuels tested are lower in comparison to diesel. This is because of the higher O_2 content and cetane number in the biodiesel-diesel blends which directed to complete combustion. In addition, the lower CO emission of biodiesel-diesel blends could be explained due to their more complex oxidation in comparison to diesel (Murillo et al. 2007). This result is consistent with available literature (Kim & Choi 2010, Lapuerta et al. 2008b, Mofijur et al. 2014b, Rajaraman et al. 2009, Sahoo et al. 2009). The average percentage (%) reduction in CO emission at B5, B10 and B20 for all biodiesel samples tested at full load condition compared to diesel is presented in Table 8.5. From this table, the maximum and minimum reduction is observed for PB (11.70%) at B20 and for JB (3.55%) at B5, respectively, in comparison to diesel.

Table 8.5: Average percentage (%) reduction in CO emission for B5, B10 and B20 for all samples tested at full load condition compared to diesel

Biodiesel samples	CO (% reduction)		
	Blend level		
	B5	B10	B20
PB	8.10	9.75	11.70
PWCB	6.50	8.00	9.50
BLB	4.90	6.45	8.15
JB	3.55	5.80	7.85

The relation between CO and engine load (25%-100%) for PB, PWCB, BLB and JB at different blends and 1400 rpm is exhibited in Figures 8.10 (a), (b), (c) and (d), respectively.

Figure 8.10: Variation in CO with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

The CO emission increases with increase in load for all biodiesel blends of all fuels tested. The increase in CO emission with increase in load is because of the decrease in air-fuel ratio. This result is consistent with available studies reported by several researchers (Gumus & Kasifoglu 2010, Lertsathapornsuk et al. 2008, Ulusoy et al. 2009). Under all loading conditions (25%, 50%, 75% and 100%), CO emissions for all samples tested are lower compared to diesel as presented in Figure 8.10. At each load, the lowest CO emission is observed for PB, PWCB, BLB and JB at B20 in comparison to diesel. The percentage (%) decrease in CO emission for all samples tested at B5 and 1400 rpm in comparison to diesel for different loading conditions is shown in Table 8.6. It can be seen from Table 8.6 that the maximum and minimum reduction in CO emission is found at 100% load for PB (8.20%) and at 25% load for JB (2.80%), respectively, comapared to diesel.

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Table 8.6: The percentage (%) decrease in CO emission for all biodiesels tested at B5 in comparison to diesel for different loading conditions

Biodiesel samples	CO (% decrease)			
	Load (%)			
	25	50	75	100
PB	5.75	6.45	6.5	8.20
PWCB	4.80	5.50	5.55	7.05
BLB	3.85	4.55	4.65	5.45
JB	2.80	3.80	3.75	3.90

Figures 8.11 (a), (b), (c) and (d) represent the variation in CO with changing speed at different loads (25%, 50%, 75% and 100%) for PB5, PWCB5, BLB5 and JB5, respectively. Over the whole range of speed (1200 rpm-2400 rpm), CO emission decreases with decrease in load from 100%-25% for B5 of all fuels tested. At full load, the lowest and highest CO is observed at 1200 rpm and 2400 rpm, respectively. The CO emission at B5 for all samples tested is observed lower in comparison to diesel for all loading conditions.

The relation between CO and biodiesel-diesel blend compositions for different speeds (1400 rpm, 1800 rpm, 2200 rpm and 2400 rpm) and loading conditions varied from 25%-100% is presented in Figures 8.12 (a) and (b), respectively. The lowest CO value is found at PB20 amongst all other biodiesel blends for all samples tested at 1400 rpm and 100% load, respectively. This could be attributed to the higher density and viscosity at PWC20, BLB20 and JB20 in comparison to PB20, which caused poor spray characteristics and improper mixing and therefore, led to incomplete combustion during combustion process (Rahman et al. 2013).
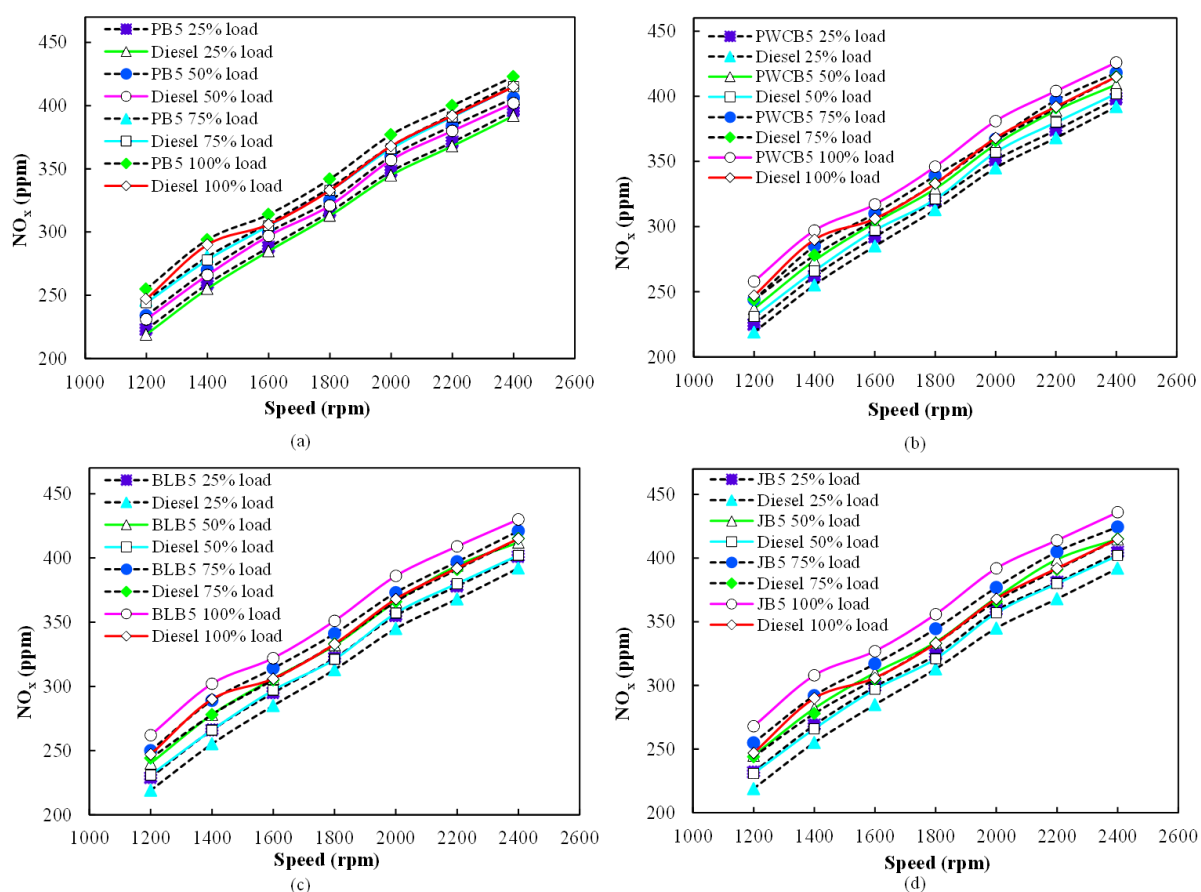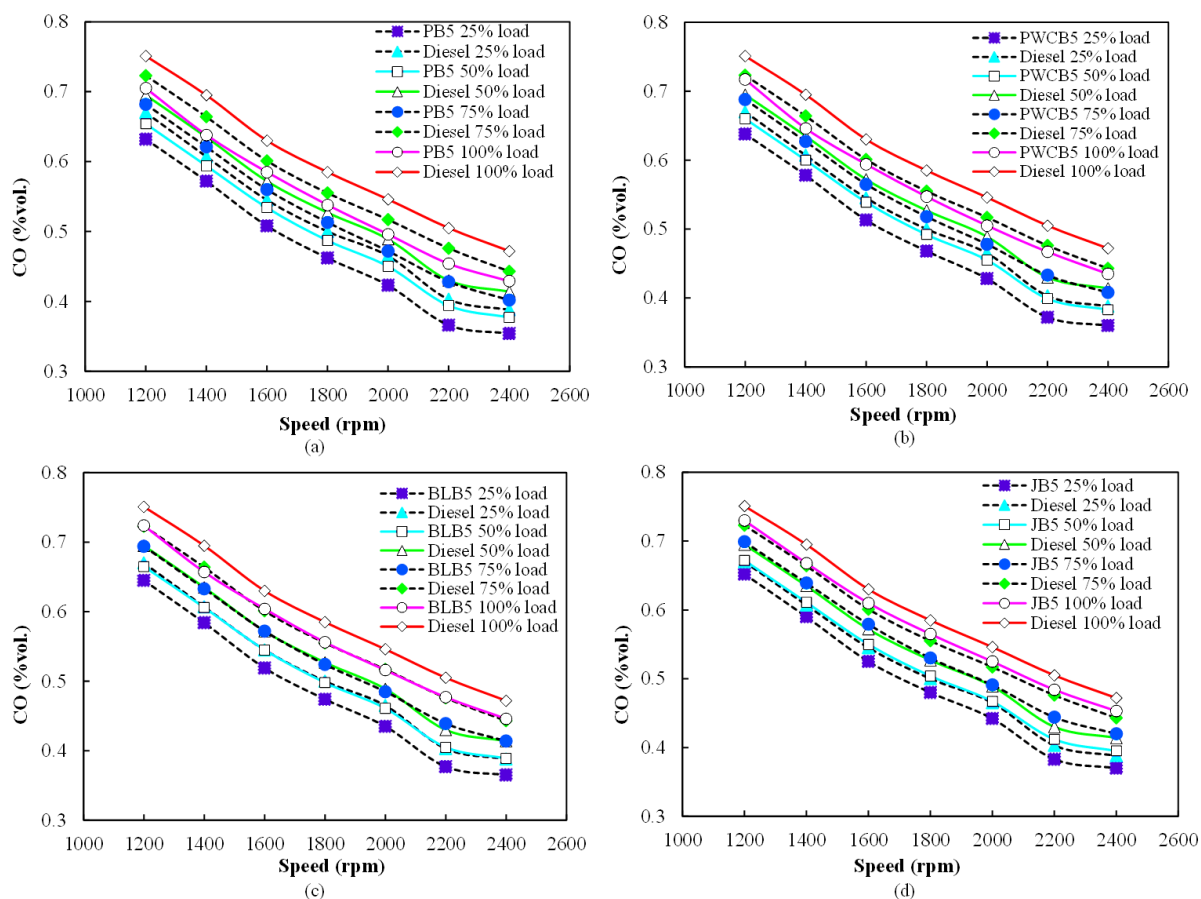
Figure 8.11: Variation in CO with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions
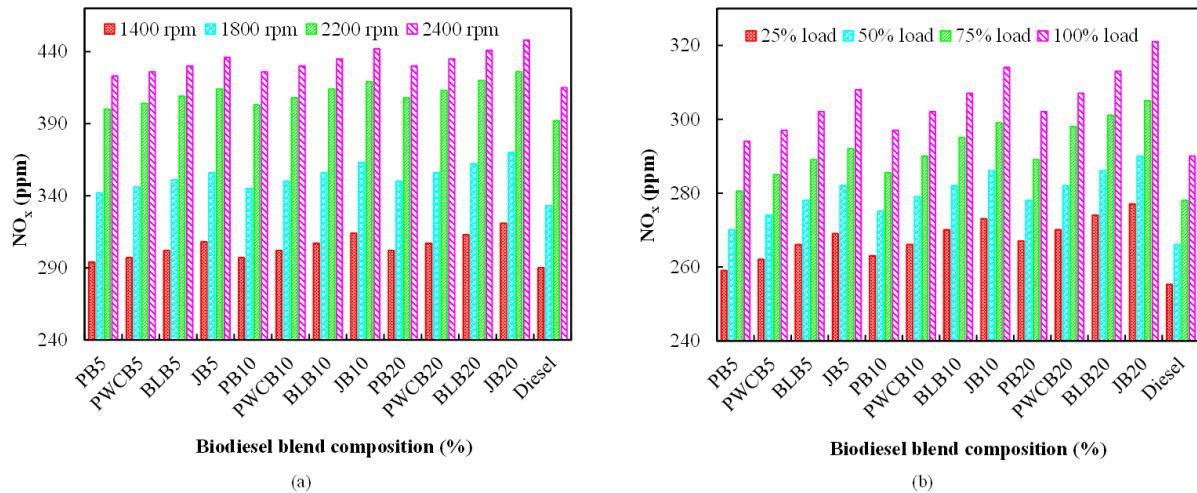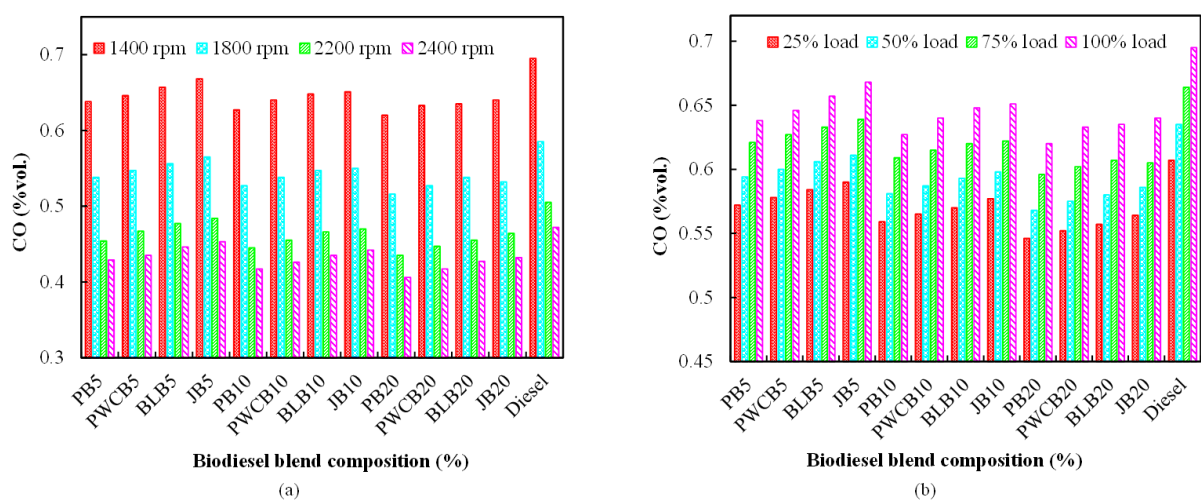

Figure 8.12: Variation in CO with biodiesel blend composition for: (a) different speeds at full load condition and (b) different loading conditions at 1400 rpm

8.5 Carbon Dioxide (CO_2) Emission

Figure 8.13 shows the variation in CO_2 as a function of engine speed. The influence of biodiesel-diesel blends (B5, B10 and B20) for PB, PWCB, BLB and JB on CO_2 emission at full load condition is shown in Figures 8.13 (a), (b), (c) and (d), respectively. CO_2 emission increases with increase in speed up to the maximum speed of 2400 rpm. CO converts into CO_2 with the help of the hydroxyl radical (OH) which is one of the principle oxidising agents when sufficient O_2 is accessible (Imdadul et al. 2016, Qi et al. 2014).

It can be seen from Figure 8.13 that the CO_2 emission increases with increase in percentage of biodiesel, that is biodiesel blend level from B5 to B20 for all samples tested over the entire range of speed (1200 rpm-2400 rpm), respectively. This could be illustrated due to the higher oxygen content and cetane number in the biodiesel blended fuels (Mofijur et al. 2014b).
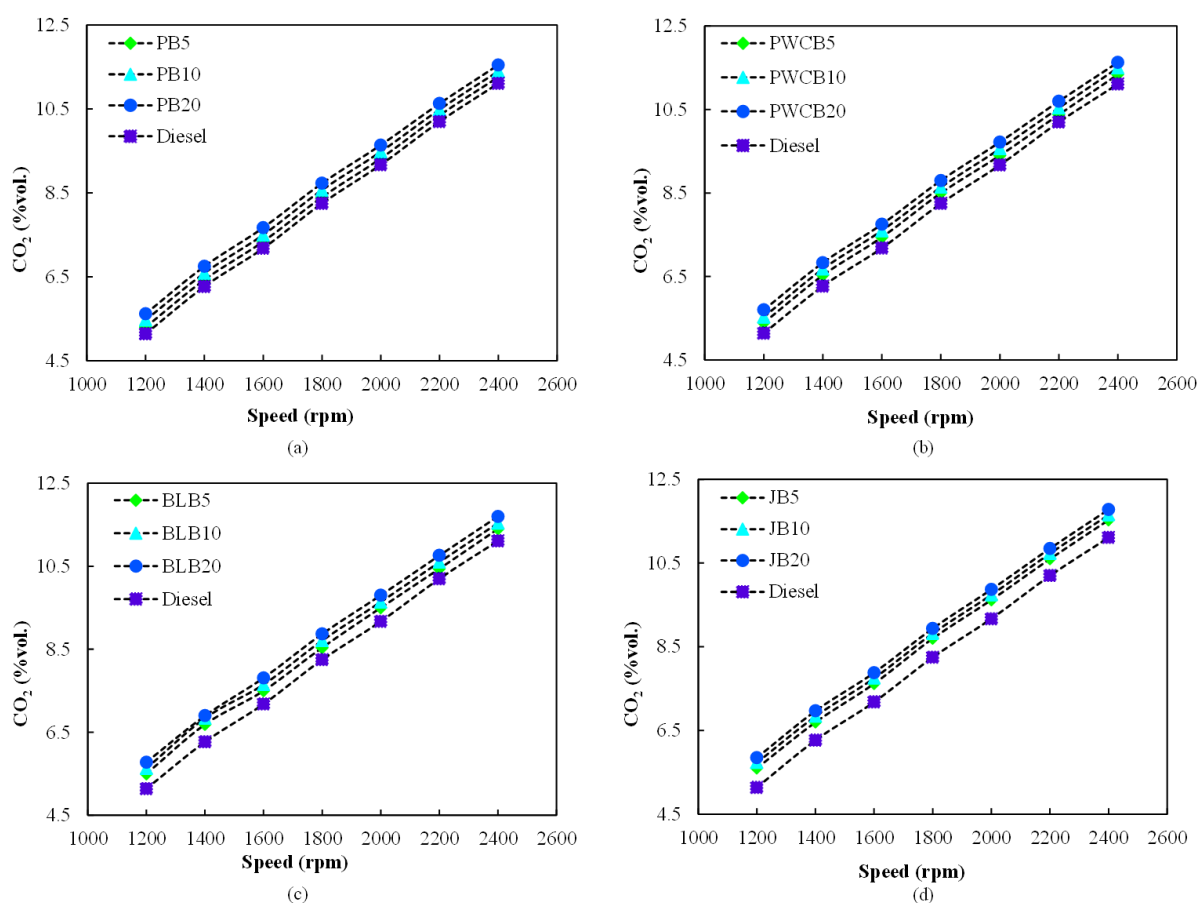
Figure 8.13: Variation in carbon dioxide (CO2) with changing speed for: (a) PB, (b) WCB, (c) BLB and (d) JB at full load condition

Similar results were also reported by several researchers (An et al. 2013, Xue et al. 2011). In addition, B20 shows the highest CO_2 emission compared to B5 and B10 because of the presence of higher O_2 molecules in their chemical structures which assisted in causing complete combustion (Imdadul et al. 2016). Generally, it can be stated that biodiesel blend and oxygenated fuel require fewer O_2 molecules than diesel to cause combustion. The average CO_2 emissions of 8.34 (% vol.), 8.43 (% vol.), 8.51 (% vol.) and 8.62 (% vol.) is observed for PB5, PWCB5, BLB5 and JB5 which are 1.85%, 1.78%, 1.72% and 1.45% lower than PB10, PWCB10, BLB10 and JB10, and 3.61%, 3.52%, 3.33%, and 2.85% lower than PB20, PWCB20, BLB20 and JB20, respectively, over the whole range of engine speed.

As expected, all biodiesel-diesel blends of PB, PWCB, BLB and JB show higher CO_2 emissions compared to diesel for the whole range of engine speed. This result is also supported by several researchers (An et al. 2013, Mofijur et al. 2014b, Muralidharan & Vasudevan 2011, Rahman et al. 2014, Rajaraman et al. 2009, Ruhul et al. 2016b). The average percentage (%) increase in CO_2 emission at B5, B10 and B20 for all biodiesel samples tested at full load condition in comparison to diesel is shown in Table 8.7. The lowest and highest increase in CO_2 emission is observed for PB (1.90%) at B5 and for JB (8.40%) at B20, respectively, in comparison to diesel (see Table 8.7).

Table 8.7: Average percentage (%) increase in CO2 for B5, B10 and B20 for all biodiesel samples tested at full load condition compared to diesel

Biodiesel samples	CO_2 (% increase)		
	Blend level		
	B5	B10	B20
PB	1.90	3.80	5.70
PWCB	2.90	4.75	6.65
BLB	3.95	5.75	7.50
JB	5.30	6.85	8.40

The variation in CO_2 emission as a function of load varied from 25%-100% for all fuels, which is displayed in Figures 8.14 (a), (b), (c) and (d), respectively. CO_2 emission increases with increase in load for all samples tested. At each load, CO_2 emission increases with increase in biodiesel blend level from B5 to B20 for all cases compared to diesel.
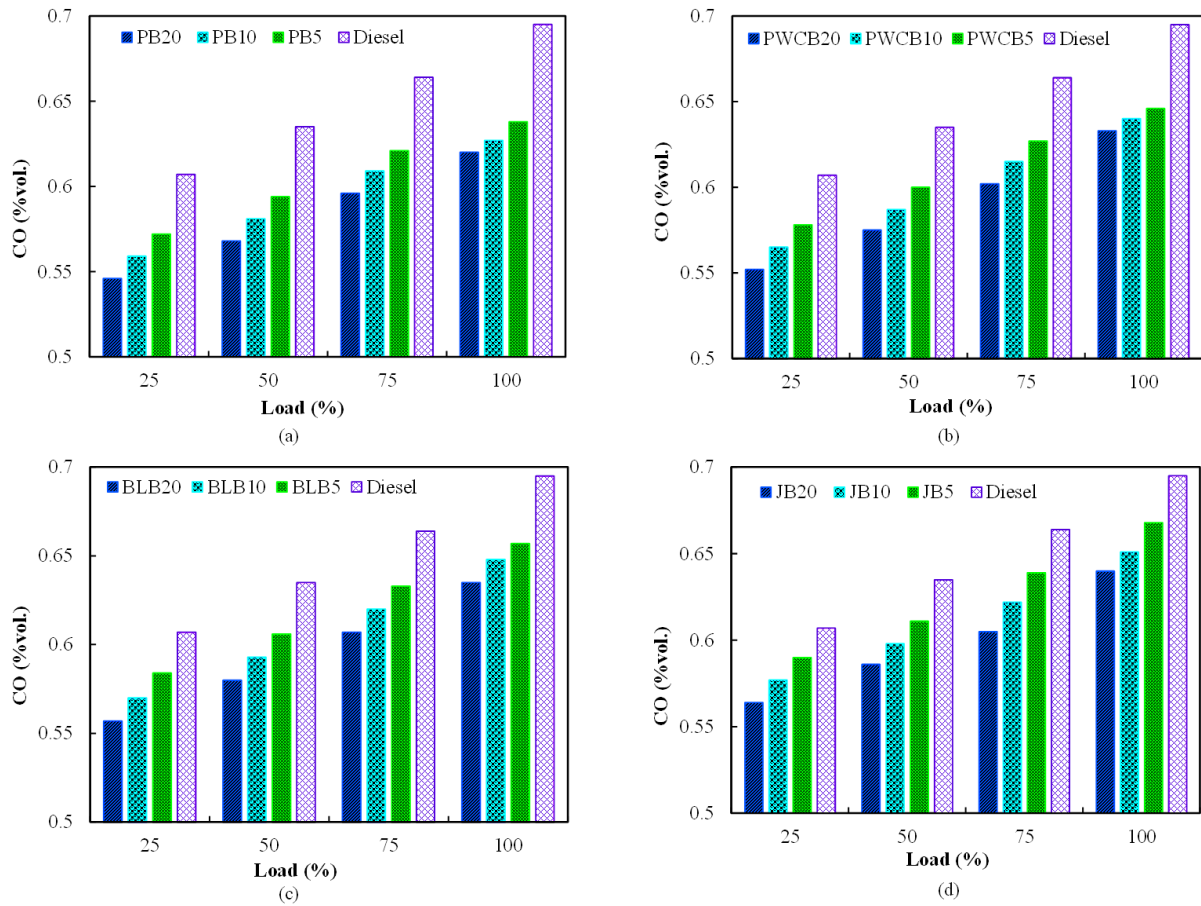
Figure 8.14: Variation in CO2 with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

The percentage (%) increase in CO_2 emission for all samples tested at B5 and 1400 rpm compared to diesel for different loading conditions is presented in Table 8.8. The table indicates that the minimum and maximum increase in CO_2 emission is at 100% load for both PB (2.5%) and JB (6.85%), respectively, compared to diesel.

The relation between CO_2 and speed with different loads (25%, 50%, 75% and 100%) for all fuels tested at B5 is demonstrated in Figures 8.15 (a), (b), (c) and (d), respectively. Over the whole range of engine speed (1200 rpm-2400 rpm), CO_2 emission increases with increase in load (25%-100%) at B5 for all samples tested. The lowest and highest CO_2 is observed at 1200 rpm and 2400 rpm for all loading conditions, respectively. At B5, the higher CO_2 emission is observed for all fuels tested in comparison to diesel for all loading conditions.

Table 8.8: The percentage (%) increase in CO_2 emission for PB, PWCB, BLB and JB at B5 in comparison to diesel for different loading conditions

Biodiesel samples	CO_2 (% increase)			
	Load (%)			
	25	50	75	100
PB	3.15	2.60	2.55	2.50
PWCB	4.50	3.30	3.25	4.15
BLB	5.90	4.80	4.75	6.70
JB	2.75	6.10	5.95	6.85

Figure 8.15: Variation in CO2 with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions

The variation in CO_2 with biodiesel-diesel blends compositions (B5, B10 and B20) for different speeds (1400 rpm, 1800 rpm, 2200 rpm and 2400 rpm) and loading conditions (25%, 50%, 75% and 100%) is demonstrated in Figures 8.16 (a) and (b), respectively. As expected, the lowest CO_2 emission is found at PB5 amongst all other biodiesel-diesel blends of PB, PWCB, BLB and JB at 1400 rpm and 100% loading condition, respectively.

Figure 8.16: Variation in CO2 with biodiesel blend composition for: (a) different speeds at full load condition and (b) different loading conditions at 1400 rpm

8.6 Hydrocarbon (HC) Emission

The variation in HC emission with changing speed for PB, PWCB, BLB and JB at B5, B10 and B20 at full load condition is presented in Figures 8.17 (a), (b), (c) and (d), respectively. The HC emission decreases with increase in speed over the entire range of engine speed (1200 rpm-2400 rpm). At low engine speed, the ignition delay is longer which is due to the slow swirling velocity of air and therefore, higher HC emission is produced (Imdadul et al. 2016). In addition, the higher HC emission at low engine speed is because of its high fuel density and viscosity as these factors critically impacted the fuel atomisation and ignition in the combustion chamber (Koçak et al. 2007). Moreover, the higher HC emission could be attributed to the fuel trapping into the crevice volumes of the combustion chamber (Imdadul et al. 2016). Similar to, CO emission, the reduction in HC emission at higher speed can be explained owing to the fuel properties and combustion phenomenon (Sajjad et al. 2015).

Figure 8.17 exhibits the variation in HC emission with increase in the percentage of biodiesel in the blend (B5, B10 and B20) for all fuels tested. Overall, B20 shows a greater reduction in

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HC emission than B5 and B10. This could be attributed to the presence of higher CN which shortens the ignition delay, and ultimately restricted the formation of over-lean regions. Furthermore, the presence of inherently high oxygen content in biodiesel blend induces a lot of beneficial conditions, such as post-flame oxidation and high flame speed, throughout the air-fuel interactions especially in the fuel-rich regions (Sajjad et al. 2015). Due to all these above conditions the proper oxidation of unburned HC is ensured, resulting in a significant reduction in HC emission (Ozsezen et al. 2009). PB20, PWCB20, BLB20 and JB20 produced average HC emissions of 9.47 ppm, 9.55 ppm, 9.63 ppm and 9.51 ppm which are 3.16%, 2.93%, 2.85% and 4.67% lower than PB5, PWCB5, BLB5 and JB5, and 1.65%, 1.47%, 1.48% and 3.25% lower than PB10, PWCB10, BLB10 and JB10 over the entire range of engine speed, respectively. All biodiesel blended fuels show the lower HC emission in comparison to diesel.
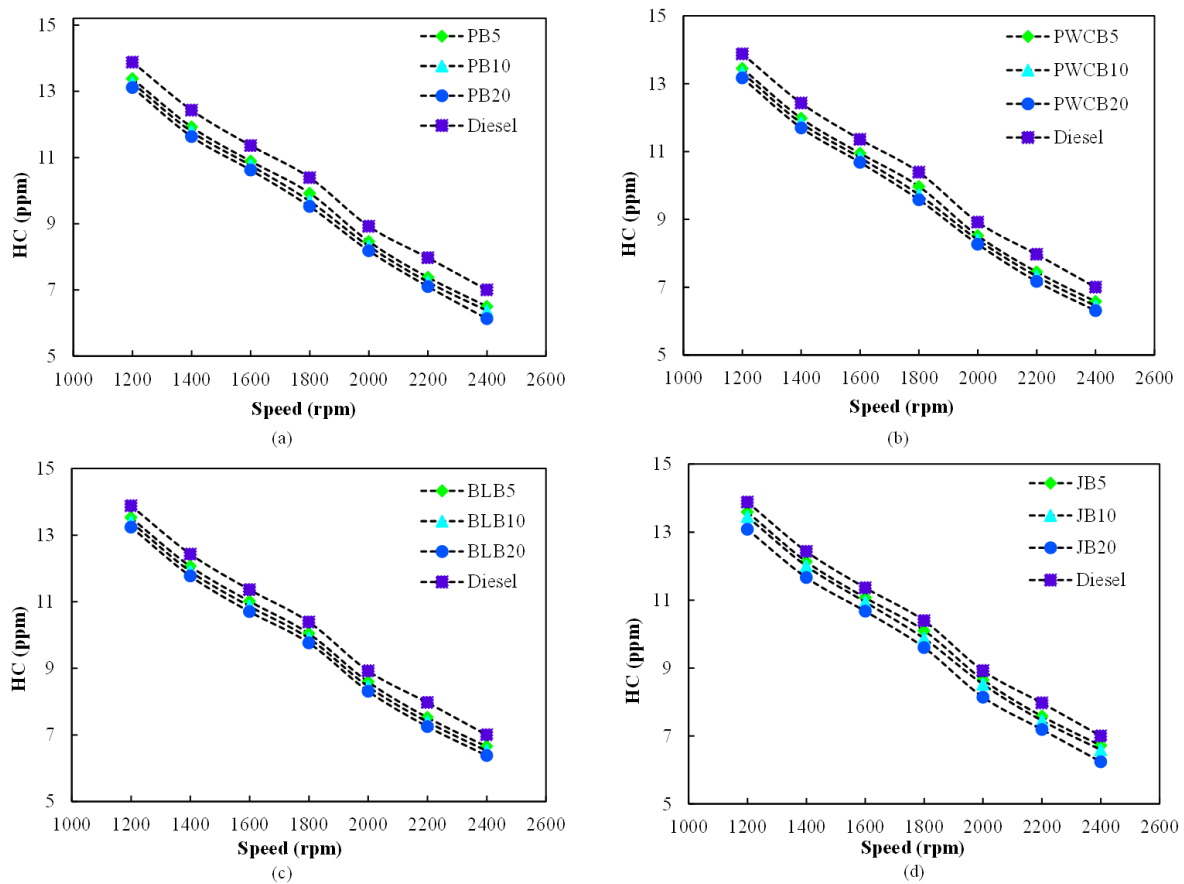
Figure 8.17: Relationship between HC and speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

The lower HC emission in biodiesel-diesel blends is because of the better combustion of the fuels (Godiganur et al. 2010). In addition, this could be attributed to the higher oxygen, less carbon and hydrogen content in biodiesel blend which assisted in completing the combustion

(Lin et al. 2009, Mofijur et al. 2014b, Qi et al. 2010b). In contrast, the formation of HC emission in diesel engines could be attributed to the over-lean fuel mixture (excessive fuel-air ratio) throughout the ignition delay period, improper mixing of fuel adjacent to the spray during combustion and quenching of flames which is caused by the impingement of fuel spray on the bordering areas in the combustion chamber (Yongcheng et al. 2006). The average percentage (%) reduction in HC emission at B5, B10 and B20 for all biodiesel fuels tested at full load condition in comparison to diesel is shown in Table 8.9. The highest and lowest decrease in HC emission is found at B20 for PB (7.85%) and for JB (2.95%) at B5, respectively, in comparison to diesel (Table 8.9).

Table 8.9: Average percentage (%) reduction in HC emission for B5, B10 and B20 for all fuels tested at full load condition compared to diesel

Biodiesel samples	HC (% reduction)		
	Blend level		
	B5	B10	B20
PB	4.85	6.30	7.85
PWCB	4.25	5.65	7.05
BLB	3.55	4.90	6.30
JB	2.95	4.35	7.45

Figures 8.18 (a), (b), (c) and (d) show the variation in unburned HC emission for PB, PWCB, BLB and JB at B5, B10 and 20 with changing load varied from 25%-100%, respectively. HC emission increases with increase in engine load for both diesel and biodiesel blends. Several researchers reported similar results that HC emission increases with increase in load (Agarwal et al. 2006, Gumus & Kasifoglu 2010, Lertsathapornsuk et al. 2008, Vallinayagam et al. 2013). This could be attributed to the mass of fuel entering into the cylinder is more and the fuel to air ratio is increased at high engine loads (Gopal et al. 2014). HC emissions for all biodiesel fuels tested at B5, B10 and B20 and for all loading conditions are lower in comparison to diesel. At each load, the lowest HC emission is observed at B20 for all fuels tested compared to diesel which indicates the better combustion of fuel.
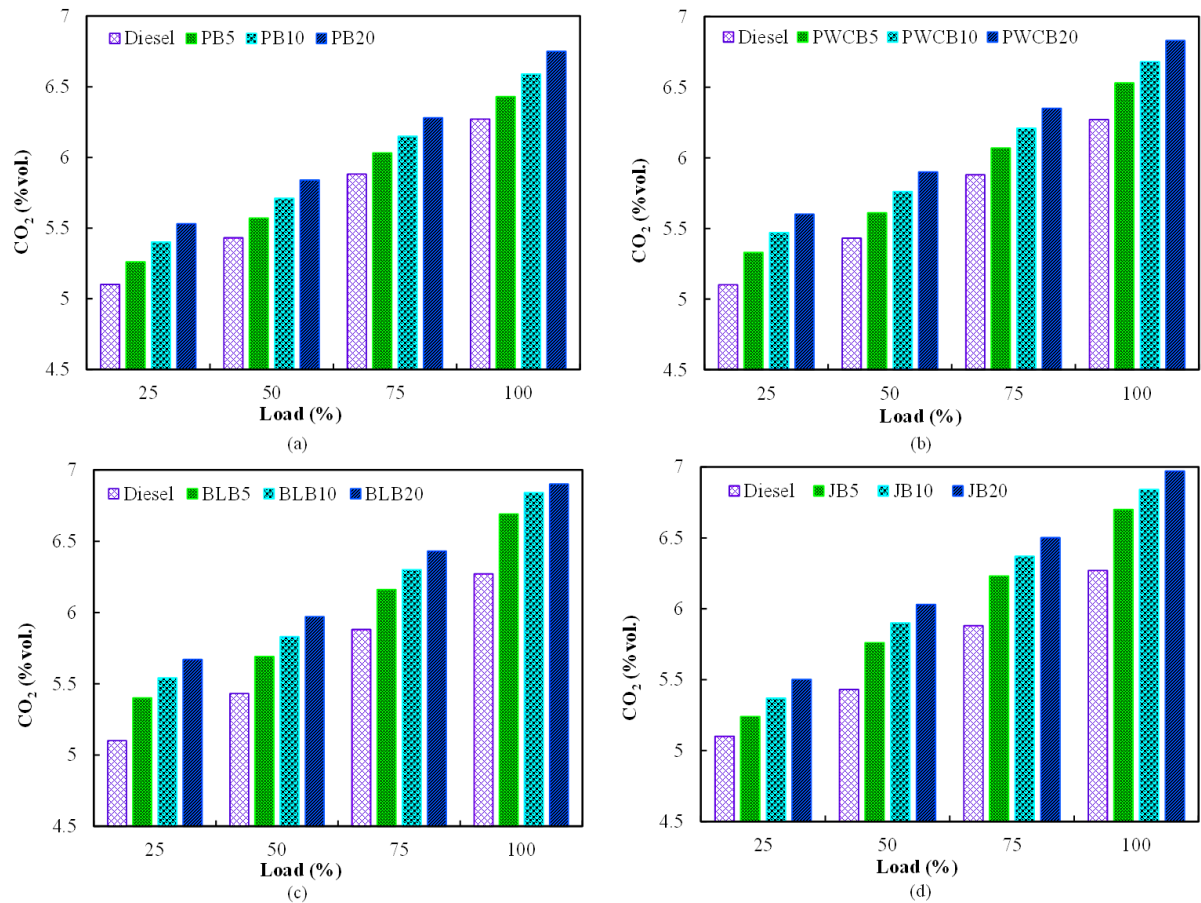
Figure 8.18: Variation in HC with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

The percentage (%) reduction in HC emission for all samples tested at B5 and 1400 rpm for different loading conditions in comparison to diesel is presented in Table 8.10. It can be seen from Table 8.10 that the maximum and minimum reduction in HC emission is observed at 25% load for PB (9.65%) and at 100% load for JB (2.40%), respectively, compared to diesel. The relation between HC and speed for PB5, PWCB5, BLB5 and JB5 with different loading conditions varied from 25%-100% is presented in Figures 8.19 (a), (b), (c) and (d), respectively. Over the entire range of speed (1200 rpm-2400 rpm), HC emission decreases with decrease in load from 100%-25% for all samples tested. For all loading conditions, the highest and lowest HC emission is observed for all fuels tested at 1200 rpm and 2400 rpm, respectively. At B5, the lower HC emission is found for PB, PWCB, BLB and JB for all loading conditions in comparison to diesel.

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Table 8.10: The percentage (%) decrease in HC emission for all fuels at B5 in comparison to diesel for different loading conditions

Biodiesel samples	HC (% decrease)			
	Load (%)			
	25	50	75	100
PB	9.65	6.65	4.90	4.10
PWCB	9.15	6.15	4.25	3.60
BLB	8.65	5.65	3.75	3.00
JB	8.15	5.20	3.15	2.40
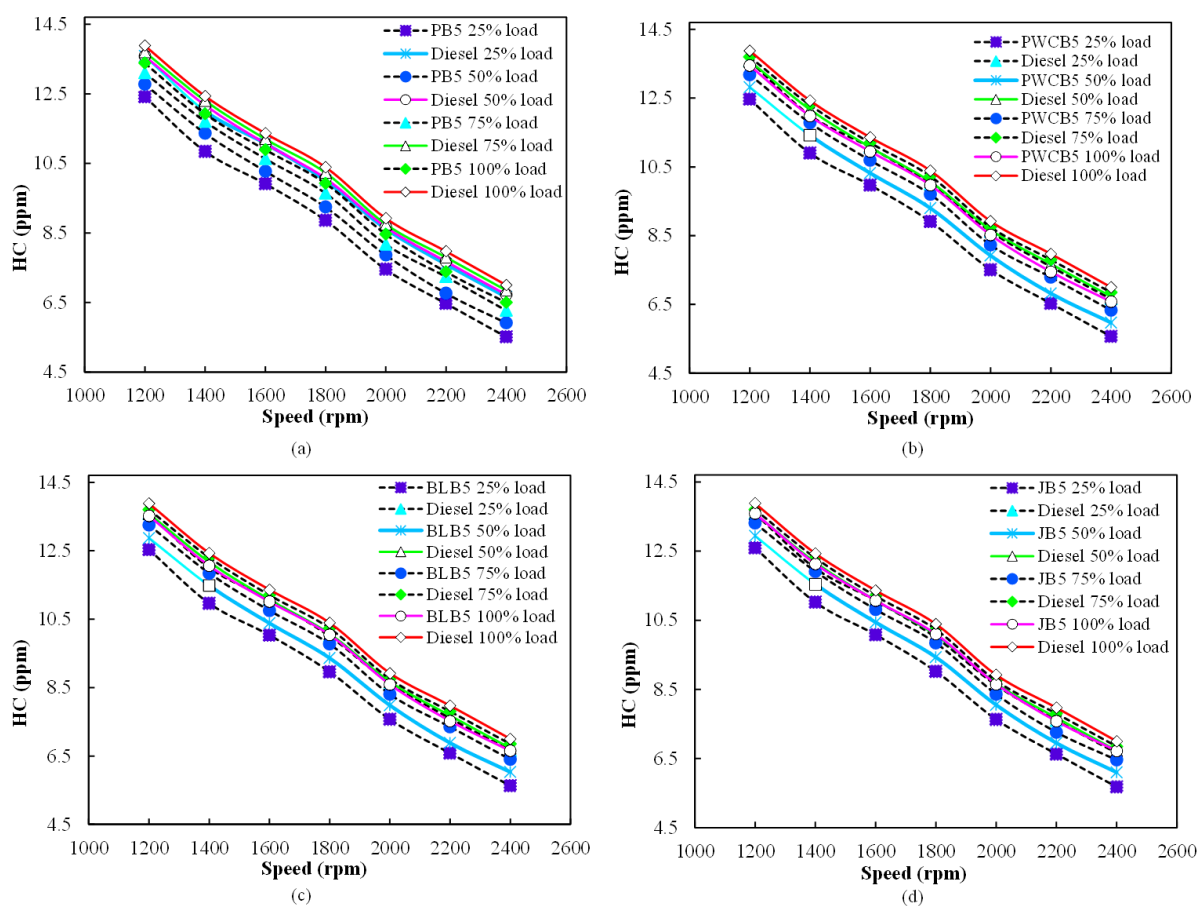
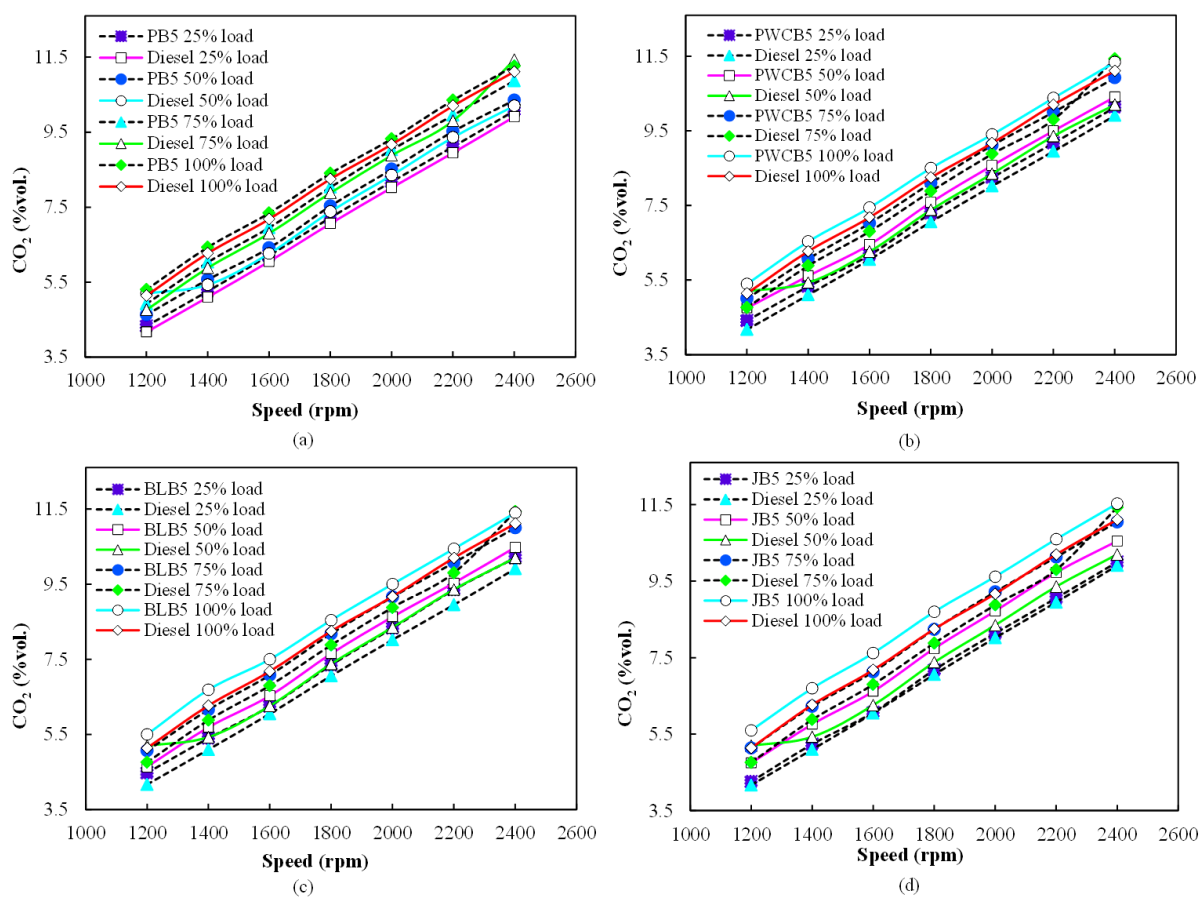
Figure 8.19: Variation in HC with changing speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions

The variation in HC with biodiesel-diesel blend compositions for PB, PWCB, BLB and JB for different speeds and loads is exhibited in Figures 8.20 (a) and (b), respectively. As expected, the lowest HC emission is observed at PB20 amongst all other biodiesel-diesel blends at 1400 rpm and 100% load.
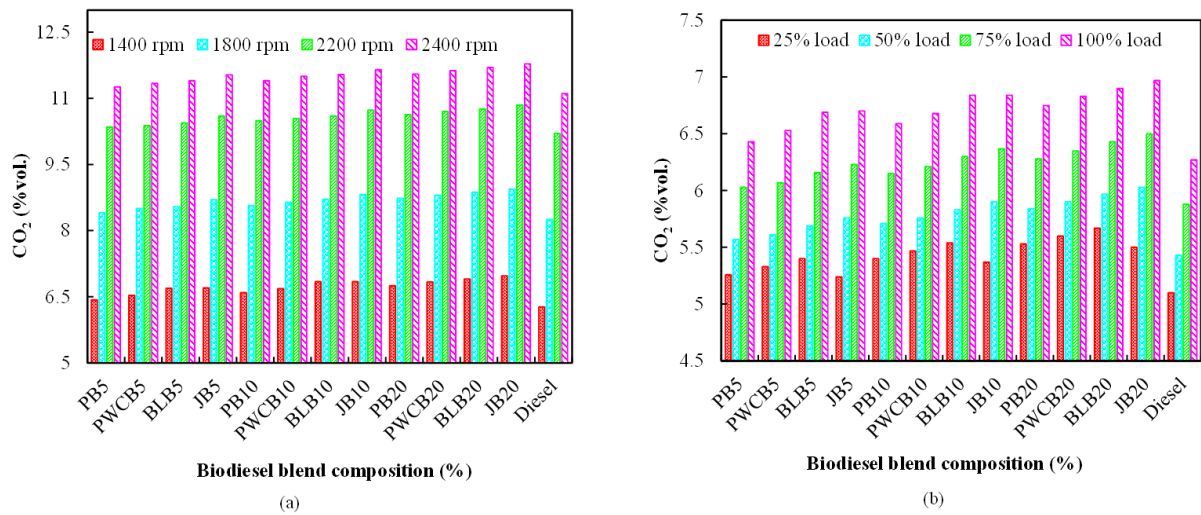

Figure 8.20: Variation in HC with biodiesel blend composition for: (a) different speeds at full load condition and (b) different loading conditions at 1400 rpm

8.7 Particulate Matter (PM) Emission

The variation in PM emission as a function of speed for PB, PWCB, BLB and JB at B5, B10 and B20 and full load condition is demonstrated in Figures 8.21 (a), (b), (c) and (d), respectively. The PM emission decreases dramatically with the increase in speed up to the maximum speed of 2400 rpm. At low engine speed, the PM is significantly higher which is due to the incomplete combustion and burning of heavy lubricating oil (Datta & Mandal 2016, Sayin 2010). This occurs in the fuel-rich zone in the cylinder at high temperatures and pressures. In contrast, the PM decreases intensely at higher engine speed which could be explained in relation to combustion with biodiesel where fuel bounded oxygen enhanced fuel oxidation in these regions and as a result it led to a reduction in PM (Can 2014, Gürü et al. 2010, Rakopoulos et al. 2006, Tree & Svensson 2007, Tsolakis et al. 2007).

Figure 8.21 indicates that with an increase in the concentration of biodiesel in the blend the PM emission reduces for all samples tested. Several researchers also reported similar reasons for the reduction in PM emission (Dwivedi et al. 2006, El-Shobokshy 1984, Flanigan et al. 1989, Haas et al. 2001, Luján et al. 2009, Spreen et al. 1995). In addition, it has been observed that

the absence of aromatic content in biodiesel may lead to a reduction in PM emission. It can be shown from Figure 8.21 that the lowest reduction in PM is observed at B20 compared to B5 and B10 for all samples tested which is because of the higher oxygen content (Spreen et al. 1995), lower carbon content (Di et al. 2009), lower fuel aromatics (Flanigan et al. 1989) and lower sulphur content (Can 2014, Lapuerta et al. 2008a, Tse et al. 2015). A similar reason was also reported by another researcher (Karavalakis et al. 2009). The average PM emissions of 186.27 (mg/m^3), 193.37 (mg/m^3), 199.86 (mg/m^3) and 201.17 (mg/m^3) are found for PB20, PWCB20, BLB20 and JB20 which are 6.50%, 5.08%, 3.61% and 4.87% lower than PB5, PWCB5, BLB5 and JB5, and 3.25%, 1.55%, 1.19% and 2.09% lower than PB10, PWCB10, BLB10 and JB10 over the whole range of engine speed, respectively.

Generally, PM emission is lower in biodiesel-diesel blend in comparison to diesel. It has been reported that the lower volatility and higher oxygen content in biodiesel blend are the responsible parameters to reduce the PM emission considerably (Karavalakis et al. 2009, Tse et al. 2015). In addition, the higher cetane number of blended fuels in comparison to diesel caused shorter ignition delay and longer combustion duration which resulted in low PM emissions (Lin & Li 2009). The average percentage (%) decrease in PM emission at B5, B10 and B20 for all fuels tested at full load condition in comparison to diesel is shown in Table 8.11. This table shows the highest and lowest decrease in PM emission for PB (13.40%) at B20 and for JB (1.65%) at B5, respectively, in comparison to diesel.

Table 8.11: Average percentage (%) reduction in PM emission for B5, B10 and B20 for all samples tested compared to diesel at full load condition

Biodiesel samples	PM (% reduction)		
	Blend level		
	B5	B10	B20
PB	7.35	10.45	13.40
PWCB	5.25	8.65	10.10
BLB	3.60	5.95	7.10
JB	1.65	4.45	6.45
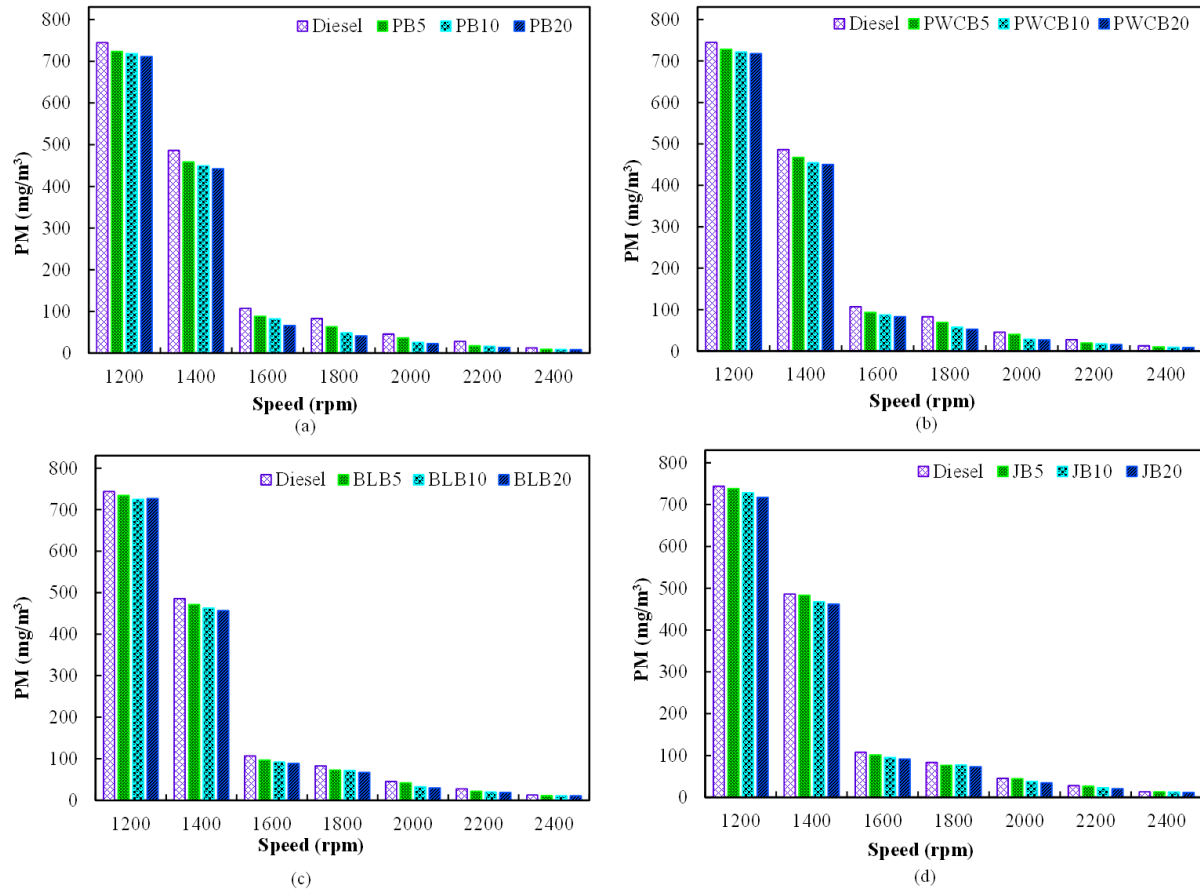
Figure 8.21: Relationship between PM and speed for: (a) PB, (b) PWCB, (c) BLB and (d) JB at full load condition

Figures 8.22 (a), (b), (c) and (d) represent the variation in PM as a function of load varied from 25-100% for PB, PWCB, BLB and JB at B5, B10 and B20, respectively. Engine load contributes a significant role to increase PM emissions when the engine is fuelled with biodiesel-diesel blend. It can be seen from Figure 8.22 that the PM increases extensively with increase in load for all fuels tested. This result is consistent with available literature reported by several researchers (Buyukkaya 2010, Lapuerta et al. 2008c, Nabi et al. 2009, Raheman & Ghadge 2007). At low engine load, the lower PM emission could be attributed to the burning of fuel in the premixed mode while more time is essential for soot oxidation (Tse et al. 2015). In contrast, the PM is higher at high load condition which is due to the burning of more fuel in the diffusion mode as more fuel is injected into the combustion chamber for soot oxidation while less time is required (Zhu et al. 2010a).
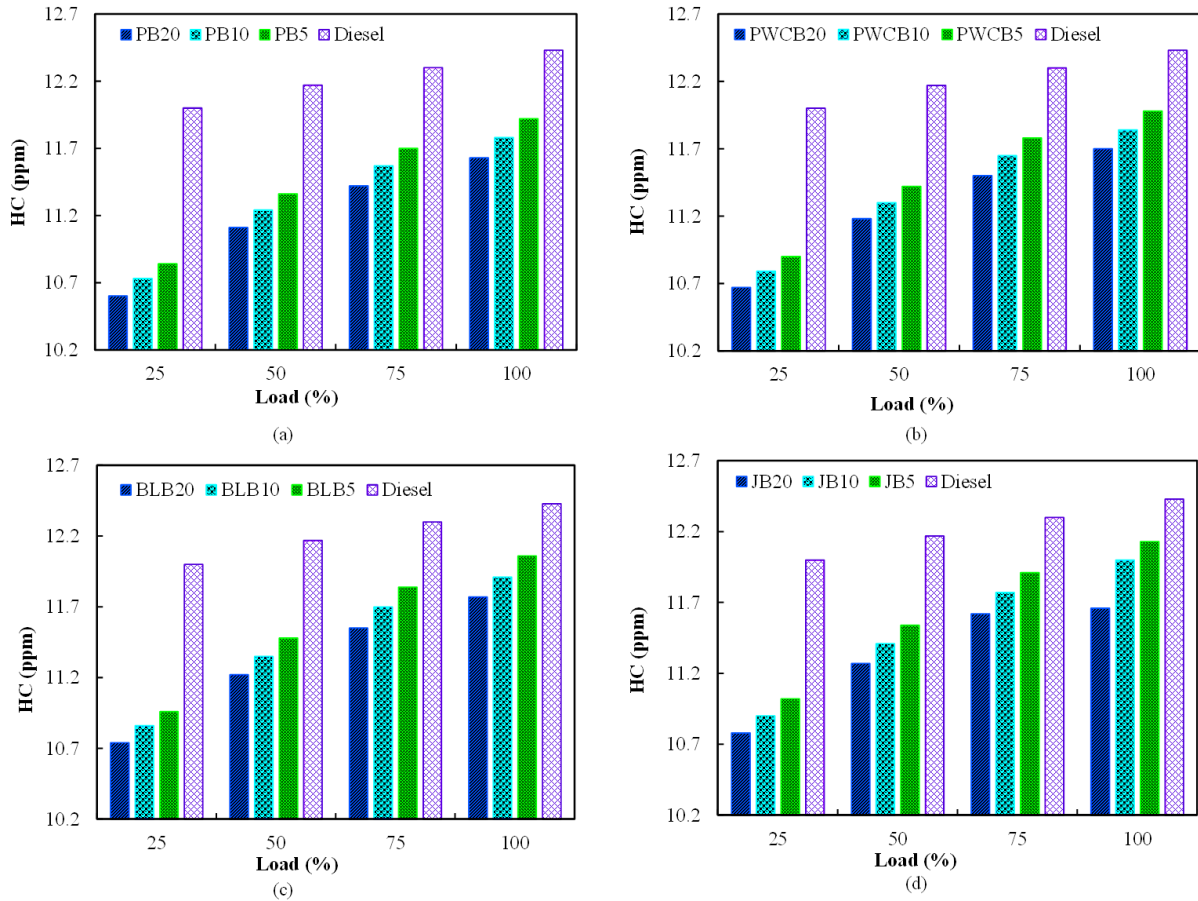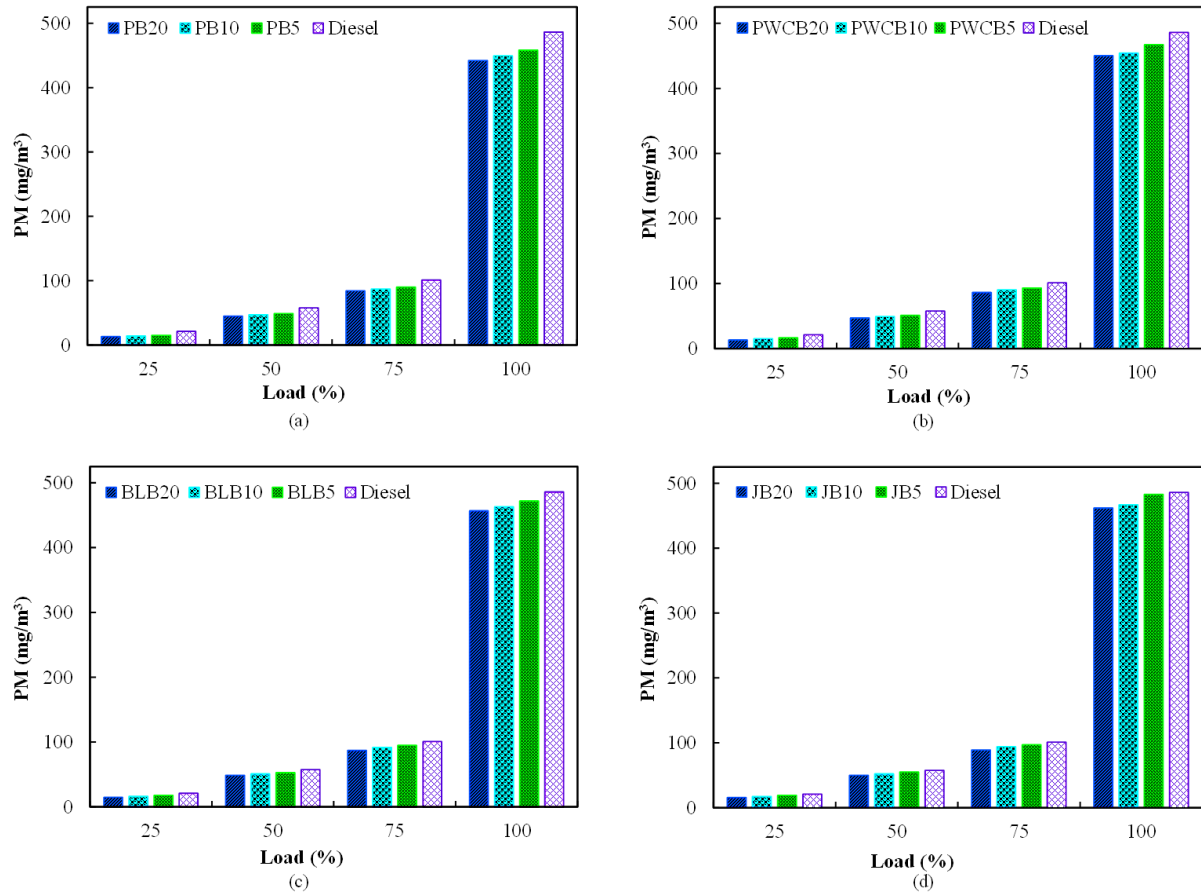
Figure 8.22: Variation in PM with changing load for: (a) PB, (b) PWCB, (c) BLB and (d) JB at 1400 rpm

The percentage (%) reduction in PM emission for all fuels tested at B5 and 1400 rpm in comparison to diesel for different loading conditions is shown in Table 8.12. The maximum and minimum reduction in PM emission is found for PB (29.05%) at 25% load and for JB (0.60%) at 100% load, respectively, compared to diesel.

The variation in PM emission with changing speed at different loads (25, 50, 75 and 100%) for PB5, PWCB5, BLB5 and JB5 is exhibited in Figures 8.23 (a), (b), (c) and (d), respectively. Over the whole range of speed (1200 rpm-2400 rpm), PM emission decreases dramatically with decrease in load from 100%-25% for all fuels tested. The highest and lowest PM emission is observed at 1200 rpm and 2400 rpm for all loading conditions, respectively. The lower PM emission is observed at B5 for all fuels tested in comparison to diesel for all loading conditions.

Table 8.12: The percentage (%) reduction in PM emission for all biodiesels at B5 in comparison to diesel for different loading conditions

| Biodiesel Blend | PM (% decrease) | | | |
| | Load (%) | | | |
	25	50	75	100
PB	29.05	14.80	10.90	5.75
PWCB	22.90	11.30	7.90	3.95
BLB	14.85	7.85	5.95	2.90
JB	8.70	4.35	3.95	0.60
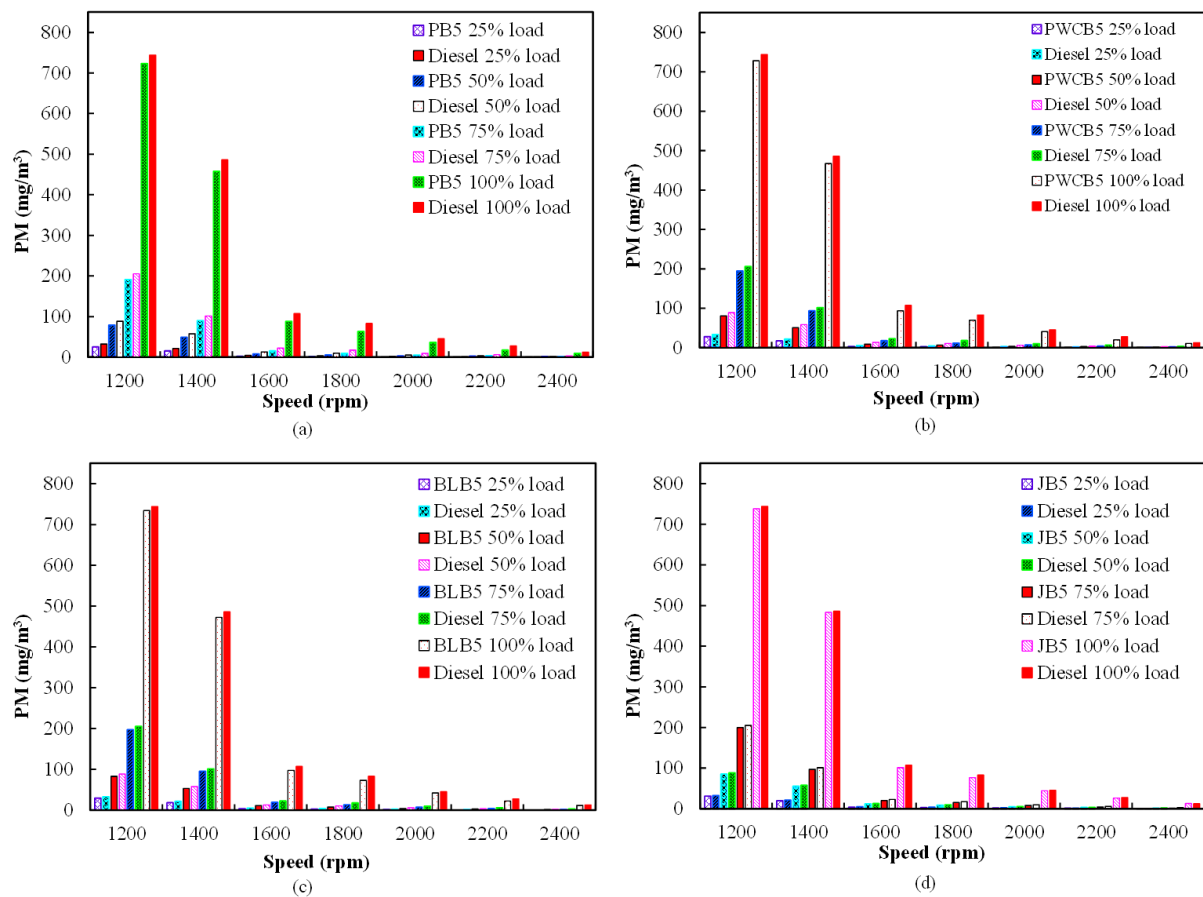
Figure 8.23: Relationship between PM and speed for: (a) PB5, (b) PWCB5, (c) BLB5 and (d) JB5 at different loading conditions

The relation between PM and biodiesel-diesel blend compositions of poppy, PWC, BL and jojoba with different speeds (1400 rpm, 1800 rpm, 2200 rpm and 2400) and loads (25%-100%) are represented in Figures 8.24 (a) and (b), respectively. As expected, the lowest PM is found at PB20 amongst all other blends of PB, PWCB, BLB and JB at 1400 rpm and 100% load, respectively.
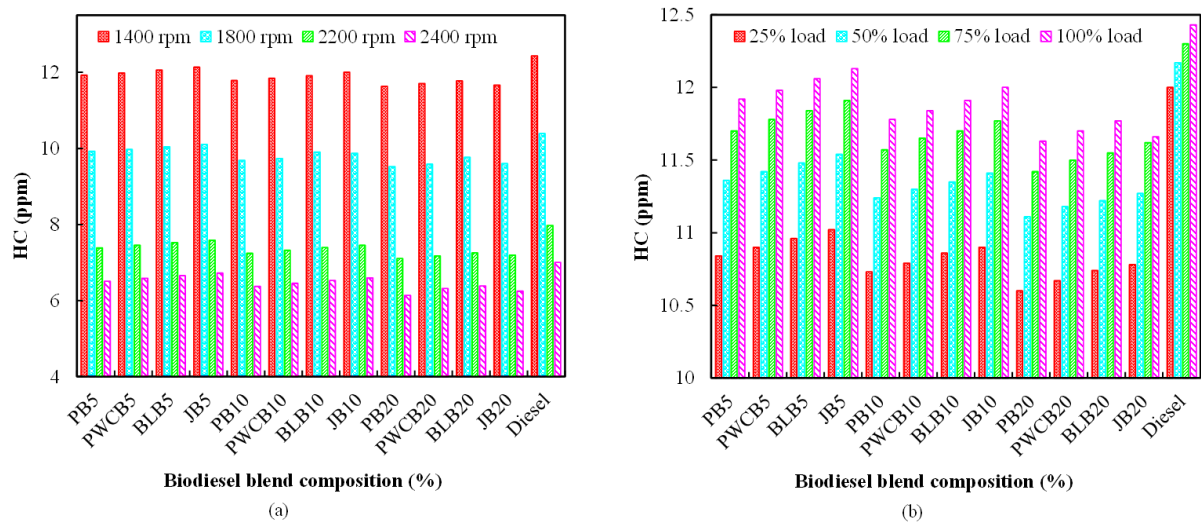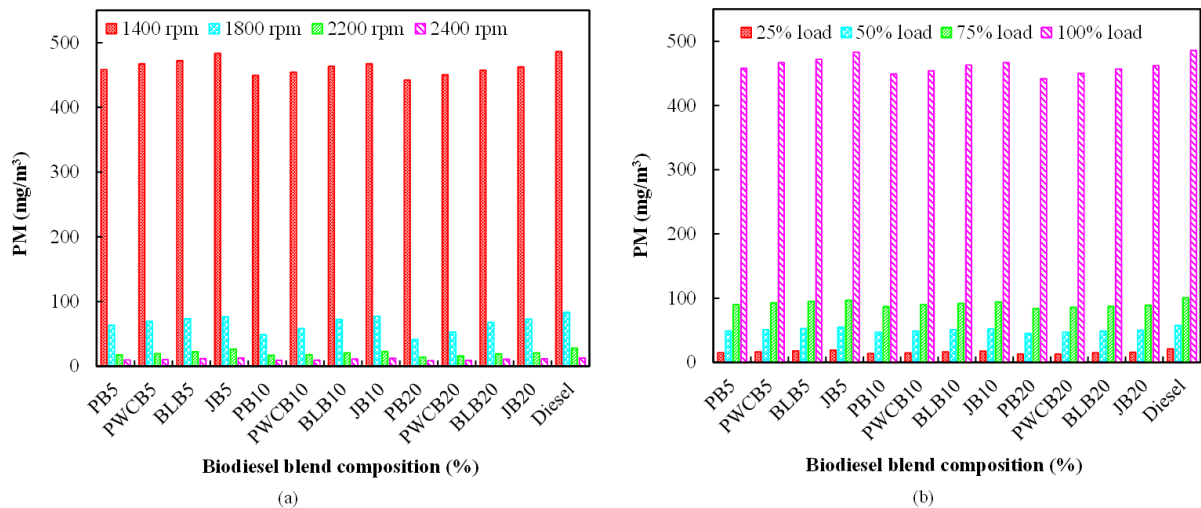

Figure 8.24: Variation in PM with biodiesel blend composition for: (a) different speeds at full load condition and different loading conditions at 1400 rpm

8.8 Conclusion

Biodiesel is one of the promising alternative fuels with the potential to reduce environmental pollution and global warming from fossil-based diesel fuel use. The emission characteristics, such as EGT, NO_x, CO_2, CO, HC and PM results indicate that engines run on diesel-biodiesel blends of B5, B10 and B20 are better comparable with that of petro-diesel.

- In terms of biodiesel-diesel blend fuel properties and exhaust emission characteristics, PB, PWCB, BLB and JB could be regarded as an alternative to diesel fuel.

- Over the entire range of engine speeds (1200 rpm-2400 rpm), the EGT is observed higher than the diesel in all biodiesel-diesel blends (B5, B10 and B20) for all biodiesels tested. In addition, the EGT increases as a function of the percentage of biodiesel in the blend, that is the higher the concentration in biodiesel in the blend the higher the EGT. Furthermore, with increase in load from 25% -100%, the EGT increases gradually.

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- The NO_x emission increases with increase in speed when using biodiesel in comparison to diesel for all biodiesel-diesel blends (B5, B10 and B20) of PB, PWCB, BLB and JB. Moreover, the results also indicate that an increase in the proportion of biodiesel in the blends increases NO_x emission. This increase is mainly due to the higher temperatures and presence of higher oxygen content in biodiesel. Furthermore, NO_x emission increases with increase in load from 25%-100% for all biodiesel-diesel blends of all methyl esters.

- Over the entire range of engine speeds, CO emission reduces when using biodiesel-diesel blends compared to diesel which could be attributed to the higher oxygen content, higher cetane number and lower carbon to hydrogen ratio in blends. Moreover, it is observed that CO emission reduces with an increase in the concentration of biodiesel in the blends (B5-B20) for all biodiesel feedstocks and decreases in load from 100%-25%, respectively.

- The CO_2 emission increases with increase in speed for using biodiesel-diesel blends than the diesel for all biodiesel-diesel blends (B5, B10 and B20) of PB, PWCB, BLB and JB as a result of low carbon to hydrocarbon ratio. In addition, increase in CO_2 is observed for all methyl esters with increase in the percentage of biodiesel in blends (B5-B20) and increase in load (100%-25%), respectively.

- The HC emission reduces when the engine is fuelled with biodiesel-diesel blends instead of diesel over the entire range of engine speeds. This reduction is mainly due to the higher oxygen content and cetane number in blended fuel. Furthermore, reduction in HC emission is found with increase in biodiesel blend level from B5 to B20 and decrease in load from 100%-25%, respectively.

- The reduction in CO and HC is linear with increase in the concentration of biodiesel blends (B5-B20). These reductions in CO and HC indicate the better combustion of fuel.

- The PM emissions are significantly reduced compared to diesel with increase in speed when biodiesel-diesel blend is used instead of diesel. In addition, PM emission decreases with increase in biodiesel blend level (B5-B20) and decreases in load ranging from 100%-25%, respectively.

- It can also be concluded that the blends of biodiesel with small volume could replace diesel to help control air pollution and ease the pressure on scarce resources to a great extent without significantly sacrificing engine power and economy.

Overall, it can be drawn from the experimental results that PB, PWC, BL and JB blend up to B20 could be replaced against diesel in diesel engines to reduce exhaust emissions to a great extent.

CHAPTER 9

CONCLUSIONS AND RECOMMENDA-
TIONS FOR FUTURE STUDY

In recent years, 2nd generation biodiesel has been receiving increasing attention due to its socio-economic benefits and less polluting nature against the conventional petroleum diesel (fossil fuel). This is because the fossil fuel reserves are declining and the environmental pollution is escalating. Biodiesel, an environmentally friendly fuel, can be used in a diesel engine with minimum modifications. The 2nd generation biodiesel, that is biodiesel produced from non-edible oil and waste oil resources, can play a vital role in meeting the energy demand of the growing population and industrialisation. This is particularly important for the BL biodiesel as this feedstock can be generated from marginal and waste lands which require less maintenance, marginal soils, and less water. In addition, the biodiesel produced from BL feedstock represents a reliable source of energy and would, therefore, play an increasingly significant role in providing the energy requirements for transportation.

Findings of the Study

This study aimed to demonstrate the potential of 2nd generation biodiesel feedstock especially Australian 2nd generation BL feedstock. The study commences with oil extraction and optimisation, and refining of crude oil from BL. Biodiesel production and optimisation were also performed. Diesel (CI) engine testing was conducted using neat diesel and biodiesel-diesel blends (B5, B10 and B20) for BL, poppy, PWC, and jojoba biodiesel with the view to evaluating engine performance, combustion and emission characteristics.

Comprehensive literature reviews on 2nd generation biodiesel, oil extraction and optimisation, crude oil refining, biodiesel production and optimisation, physico-chemical properties of 2nd generation biodiesels, engine performance, combustion and emission characteristics were done. The available literature indicated that BL has the potential to grow naturally in degraded and marginal lands that are characterized by low fertility, drought and other stress conditions. Furthermore, establishment of this species is relatively easy and it can grow in a variety of environments. The BL produces large quantities of fruits and the seeds contain up to 60% oil by dry weight. In addition, as a prospective species of high oil content and heating value it can

significantly contribute a major demand of transport fuel which can be classed as 2nd generation biodiesel with a sustainable production. This feedstock could be considered as a prospective future generation fuel due to its low feedstock cost although its oil extraction and biodiesel production technology are similar to that of the other 2nd generation feedstocks.

An experimental investigation was carried out to extract oil from BL kernel using both mechanical and chemical methods. Mechanical extraction was done using a screw press expeller; whereas, chemical extraction was conducted using n-hexane as oil solvent. The optimisation was done in terms of fruit cracking, seed (kernel) preparation, kernel drying, moisture content and the kernel size. Both WKs and GKs were used in screw press technique, whereas, only GK was used in n-hexane method. The highest oil yields in both methods were obtained for the optimum moisture content of the kernel which is 14.4%. The experimental results indicated that the highest oil recovery of 54% was found in n-hexane method for the GK. In contrast, the maximum oil yields of 45% and 35% were obtained with screw press technique for the GK and WK, respectively. In terms of residual oil, cake and sediment recovery, the results were 12% and 60% for the WK in screw press method, respectively. A comparison of fossil energy ratio (FER) was established between these two techniques and the results showed that the net FER in n-hexane technique (4.1) is higher than the screw press technique (3.70), that is, the n-hexane technique is comparatively more efficient than the screw press method.

The crude BL oil extracted by screw press and n-hexane method was used to refine, that is, to use it as a suitable feedstock for biodiesel production by different processes, such as degumming, neutralising and dewaxing. These processes were conducted to remove the gums (phospholipid compounds), FFAs, waxes and other undesirable compounds from the crude oil prior to conversion into biodiesel. In terms of mass and energy, the oil recovery efficiencies were determined which were 80.8% and 81.8%, and 73% and 74.4% in n-hexane and screw press techniques, respectively. The results also revealed that the higher mass and energy recoveries were obtained in the oil extracted via n-hexane technique.

Biodiesel production was performed by single stage (transesterification) and 2 stage processes (esterification and transesterification) from BL crude and refined oil, whereas, biodiesel production and optimisation for poppy and jojoba oil was conducted by 2 stage processes only. Optimisation was done in terms of different influencing parameters on yield of biodiesel, such

as methanol to oil molar ratio, catalyst concentration, reaction temperature and time. The biodiesel yield and optimisation results of BL were compared with those of poppy and jojoba biodiesels. At optimum condition, the optimal variables were observed as follows: methanol to oil ratio of (7.0:1, 6.0:1, 6.5:1, 6.0:1 and 7.5:1), catalyst concentration of (1.0 (wt. %), 0.75 (wt. %), 1.0 (wt. %), 1.0 (wt. %) and 1.25 (wt. %)), reaction temperature of (60 ^{o}C, 60 ^{o}C, 60 ^{o}C, 60 ^{o}C and 60 ^{o}C), and reaction time of (120, 60, 90, 90 and 90 mins) for CEBLO, REBLO, RWEBLO, REPO and CEJO, respectively. The highest biodiesel yields of 91.10%, 92.30%, 82.80%, 93.40% and 83.30% were obtained for CEBLO, REBLO, RWEBLO, REPO and CEJO at optimum condition. Among all the tested fuels, the highest biodiesel yield of 93.40% was found for REPO. The GC analysis was conducted to obtain the FAMEs of BL, poppy, PWC and jojoba biodiesel. The physico-chemical properties of BLME, PME, PWCME and JMEs were characterised according to the ASTM and EN biodiesel standards. The results indicated that almost all the properties fulfilled the ASTM and EN biodiesel standards with a few exceptions.

In this study, the performance of the engine output was evaluated in terms of brake power (BP), torque, brake specific fuel consumption (BSFC), brake thermal efficiency (BTE) and brake mean effective pressure (BMEP). With increasing the engine speed, biodiesel blended fuel lowers the BP and BSFC whereas, increases the torque, BTE and BMEP with a few exceptions. On the other hand, BP, torque, BTE and BMEP increased with the variation in engine load from 25%-100%. But, the BSFC was decreased with increasing the loads due to the higher percentage of increase in brake power with load. The results also revealed that the BP, torque, BTE and BMEP decreased with an increase of biodiesel (regardless of the source) concentration in the blend except BSFC at full load condition. Among all the blended fuels, B5 showed the better performance due to the improved fuel properties compared to B10 and B20. All the results of performance characteristics for biodiesel-diesel blends are observed to be lower in comparison to diesel. The results indicated that the average reductions in BP, torque, BSFC, BTE and BMEP are (0.90%, 2.75%, 4.15% and 5.35%), (0.75%, 1.65%, 2.60% and 3.70%), (1.15%, 3.85%, 6.10% and 8.15%), (0.40%, 2.30%, 3.95% and 5.85%) and (0.75%, 1.65%, 2.60% and 3.70%) for poppy, PWC, BL and jojoba biodiesel at B5 when the results were compared with petrodiesel over the entire range of engine speed, respectively. It can be concluded that the performance of poppy biodiesel blend (PB) is better than that for other biodiesels tested as reductions in performance parameters are less for PB. The lowest

reductions in BP, torque, BTE and BMEP are observed for PB which are 2.65%, 0.90%, 0.45% and 0.90%, respectively, whereas, the highest increase in BSFC is found for JB (8.60%) in comparison to diesel at 1400 rpm for 100% load.

The engine combustion characteristic results are evaluated in terms of CP and HRR for different engine speeds (1400 rpm, 1800 rpm, 2000 rpm and 2400 rpm) at full load condition. The results indicated that the highest CP was observed for the biodiesel-diesel blend in comparison to petrodiesel which could be attributed to the higher CN, higher BSFC, boiling point, oxygen content and progression in starting of the injection timings. On the other hand, the maximum HRR was found for diesel compared to biodiesel-diesel blend. The lower HRR in biodiesel blend is because of the decrease in the premixed air-fuel mixture which is due to the poor atomisation and the slow mixing ratio of air-fuel. In addition, the higher density and viscosity of blended fuel are the affecting parameters which lead to increase physical ignition delay and delayed start of combustion in contrast to diesel. The CP increases, whereas, HRR decreases with an increase in biodiesel blend level, that is, the highest CP was observed at B20, and the highest HRR was observed at B5. The increase in maximum in-CP at the higher blend (B20) could be attributed to the shorter ignition delay and fast burning of the accumulated fuel as a result of the higher oxygen content in the fuel. At B5, the highest HRR could be explained due to the good mixing velocity of fuel-air which is the main affecting parameter of HRR. At 1400 rpm, the maximum CPs at B20 for PB, PWCB, BLB and JB are 3.65%, 2.10%, 3.40% and 1.80% higher than the diesel, respectively; whereas, those are 2.10%, 1.80%, 1.5% and 1.45% higher than the diesel at 2400 rpm at full load condition, respectively. It can be concluded from the above results that the highest increase in CP is observed at PB compared to the diesel.

On the other hand, it is observed that both the CP and HRR increased with increase in engine load (25%-100% for CP and 50%-100% for HRR) for all the fuels tested. The CP increases with increase in engine load which is because of variation in properties of blended fuels. On the other hand, at lower load conditions, the HRR decreases as the amount of fuel prepared for burning during the delay period decreases and the contribution of the gaseous fuel to the heat release is not significant during this stage.

In terms of load, the increases in CP for PB, PWCB, BLB and JB and at 1400 rpm and B20 from 25%-75% load conditions are 3.30%-2.15%, 2.65%-1.25%, 2.25%-2.95% and 3.05%-

2.65%, respectively, compared to petrodiesel. At 2400 rpm and B20, the increase in CP from 25%-75% load conditions for PB, PWCB, BLB and JB are 0.65%-0.45%, 1.00%-0.95%, 0.40%-1.65% and 0.75%-1.25%, respectively, in comparison to diesel. In addition, the highest increase in CP is observed for PB (3.30%) at 25% load and at 1400 rpm, whereas, the lowest increase in CP is also found for PB (0.35%) at 50% load compared to diesel.

At 1400 and 2400 rpm, the reductions in HRR for PB, PWCB, BLB and JB at B5 compared to diesel are (2.40%, 3.10%, 3.80% and 4.05%) and (3.70%, 4.45%, 4.95% and 5.35%) at full load condition, respectively. It can be noted that the PB shows the lower reduction in HRR both at 1400 rpm and 240 rpm in comparison to diesel. On the basis of load, the decreases in HRR at 1400 rpm and B5 in comparison to diesel for PB, PWCB, BLB and JB at 50% load are 5.10%, 3.55%, 3.35% and 3.70%, respectively. At 2400 rpm and B5, the reductions in HRR at 50% load for PB, PWCB, BLB and JB are 1.05%, 4.35%, 3.15% and 1.90%, respectively, compared to diesel. The maximum decrease in HRR is found for JB (5.55%) at 50% load, whereas, the minimum value is found for PB (1.05%) at 50% load in comparison to diesel at 2400 rpm.

The engine emission characteristics were performed on the basis of EGT, NO_x, CO, CO_2, HC and PM for all the biodiesels tested. At full load condition, the results show that the EGT, NO_x and CO_2 increased, whereas, CO, HC and PM decreased with increase in engine speed over the whole range of speed (1200 rpm-2400 rpm). The increase in EGT with increase in speed is due to the increase in fuel quantity in the combustion chamber in a unit time which resulted in increase the amount of heat energy produced in the combustion chamber. Higher oxygen contents, in-cylinder temperature and the residence time are the affecting parameters to increase the NO_x with increase in speed. The decrease in CO with the increases in engine speed is due to the better air-fuel mixing process and/or the increases of the fuel-air equivalence ratio. Longer ignition delay, high fuel density and viscosity are the factors to increase the HC emission with increase in speed. The decrease in PM with increase in speed could be explained in relation to combustion with biodiesel where fuel bounded oxygen enhanced fuel oxidation in these regions. On the other hand, all the results of emission characteristics (EGT, NO_x, CO, CO_2, HC and PM) increase with an increase in the load. The increase in EGT, NO_x, CO, CO_2, HC and PM with increase in load could be attributed to the more quantity of fuel is required in the engine to generate extra power which is essential to take up the additional loading, higher combustion temperature and stoichiometry of the mixture, the decrease in air-fuel ratio, mass

of fuel entering into the cylinder is more and the higher fuel to air ratio, and burning of more fuel in the diffusion mode as more fuel is injected into the combustion chamber for soot oxidation, respectively.

The results indicated that the EGT, NO_x and CO_2 increased, whereas, CO, HC and PM decreased with increase in the percentage of biodiesel (5%-20%) in the blend. The EGT, NO_x and CO_2 increased, whereas, CO, HC and PM decreased with increase in the percentage of biodiesel could be attributed to the higher oxygen content, higher cetane number, fuel properties and combustion phenomenon. The results also revealed that the use of biodiesel-diesel blend led to the substantial reductions in CO, HC and PM emissions with increased in EGT, NO_x and CO_2 in comparison to conventional diesel. The B5 showed the better results in terms of EGT, NO_x and CO_2 emission; whereas, B20 showed the better results for CO, HC and PM emission. The results indicated that the average increases in EGT, NO_x and CO_2 are (0.90%, 2.00%, 2.65% and 3.35%), (2.30%, 3.30%, 4.70% and 6.40%) and (1.90%, 2.90%, 3.95% and 5.30%) at B5 while the average decreases in CO, HC and PM are (8.10%, 6.50%, 4.90% and 3.55%), (4.85%, 4.25%, 3.55% and 2.95%) and (7.35%, 5.25%, 3.60% and 1.65%) at B20 for poppy, PWC, BL and jojoba biodiesel in comparison to diesel over the entire range of engine speed, respectively. It can also be noted that the highest increase in EGT, NOx and CO_2 of 3.35%, 6.40% and 5.30% was observed for JB at B5 in comparison to diesel. On the other hand, the highest decrease in CO (8.10%), HC (4.85%) and PM (7.35%) was observed for PB at B20 compared to diesel.

At 1400 rpm and full load, the lowest increases are observed for EGT, NO_x and CO_2 for PB which is 0.85%, 1.40% and 2.50%, whereas, the highest reductions are observed for CO, HC and PM for also PB which is 8.20%, 4.10% and 5.75%, respectively, in comparison to diesel.

Overall, in terms of performance, emission and combustion characteristics it can be concluded that biodiesel blend up to B20 could be replaced against diesel in diesel engines to reduce exhaust emissions to a great extent with minimum power loss.

Recommendations for Further Study

The following recommendations can be made for further study:

- In solvent extraction technique, n-hexane recovery system should be adapted to minimise the extraction and optimisation cost, and to get the full benefits from BL feedstock. In addition, accelerated solvent extraction (ASE) technique can be used to compare the results of screw press and n-hexane techniques.

- Prior to transesterification to obtain high quality of biodiesel the oil refining processes must be done as there are lots of undesirable chemical components present in the crude oil which are free fatty acids, phosphatides, gums, waxes, colour bodies, trace metals, pesticide residues, oxidation products, water and volatiles containing objectionable odours. Thus, bleaching and deodorisation can be done as a future work as degumming, neutralisation and dewaxing already done in this study.

- Transesterification is the appropriate technique to produce biodiesel, however; methanol recovery system could also be facilitated to minimise the cost of biodiesel production via cost optimisation.

- Optimisation of biodiesel production can be done by response surface methodology where all the reaction parameters are changing simultaneously.

- Refined oil rather than crude oil can be used for production of high quality biodiesel which meet the international specifications of biodiesel standards, such as the ASTM and EN standards.

- The biodiesel produced from single stage and 2 stage methods should be compared with the biodiesel generated from solid catalysts, microwave digestion, and enzyme methods with the view to determine the highest biodiesel yield and cost effectiveness.

- The potential challenge for biodiesel production is the cost. Thus, economic analysis is necessary to assess the commercial viability.

- It can also be noted that supporting policies are important to promote biodiesel research and make their prices competitive with other conventional sources of energy.

APPENDICES

Appendix A

Table A.1: Uncertainty calculation of crude BL oil properties

Density (kg/m^3)

Three tests value (kg/m^3)			Max-min value		Equipment accuracy ($\pm$0.1)		Average value (kg/m^3)	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.1	-0.1		+	-
936.88	937.12	936.9	937.12	936.88	937.22	936.78	937	0.012807	-0.01281

Kinematic viscosity (mm^2/s)

Three tests value (mm^2/s)			Max-min value		Equipment accuracy ($\pm$0.01)		Average value (mm^2/s)	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.01	-0.01		+	-
52.73	52.61	52.66	52.73	52.61	52.74	52.6	52.67	0.113917	-0.11392

Acid value (mg KOH/g)

Three tests value (mg KOH/g)			Max-min value		Equipment accuracy ($\pm$0.001)		Average value (mm^2/s)	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.001	-0.001		+	-
38.8	38.84	38.92	38.92	38.8	38.921	38.799	38.85	0.1544	-0.1544

Calorific value (MJ/kg)

Three tests value (MJ/kg)			Max-min value		Equipment accuracy ($\pm$0.001)		Average value (MJ/kg)	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.001	-0.001		+	-
37.85	37.88	37.78	37.88	37.78	37.881	37.779	37.83	0.13217	-0.13217

Flash point (°C)

Three tests value (°C)			Max-min value		Equipment accuracy (±0.1)		Average value (˚C)	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.1	-0.1		+	-
218	225	228	228	218	228.1	217.9	223	2.242152	-2.24215

Cetane number

Three tests value			Max-min value		Equipment accuracy (±0.1)		Average value	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.1	-0.1		+	-
52.27	52.22	52.13	52.27	52.13	52.37	52.03	52.2	0.1341	-0.1341

Iodine value (g I_2/100 g)

Three tests value (g I_2/100 g)			Max-min value		Equipment accuracy (±0.1)		Average value	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.1	-0.1		+	-
82	86	88	88	82	88.1	81.9	85	3.529412	-3.52941

Oxidation stability (hour)

Three tests value (hour)			Max-min value		Equipment accuracy (±0.01)		Average value	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.01	-0.01		+	-
0.29	0.28	0.27	0.29	0.27	0.3	0.26	0.28	3.571429	-3.57143

Table A.2: Measurement accuracy and uncertainty of the measured quantities

Measurements	Measurement accuracy	Uncertainty (%)
Density at 15 °C	±0.1 kg/m^3	±0.01
Kinematic viscosity at 40 °C	±0.01 mm^2/s	±0.11
Acid value	±0.001 mg KOH/g	±0.15
Calorific value	±0.001 MJ/kg	±0.13
Flash point	±0.1°C	±2.42
Pour point	±0.1°C	±2.23
Cloud point	±0.1°C	±2.24
Cold filter plugging point	±0.1°C	±2.33
Cetane number	±0.1	±0.13
Iodine value	±0.1 g I$_2$/100 g	±3.53
pH at 26 °C	±0.11	±1.09
Oxidation stability	±0.01 hour	±3.57

Table A.3: Uncertainty calculation for CO emission

Three tests value (%vol.)			Max-min value		Equipment accuracy (±0.02)		Average value (%vol.)	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.02	-0.02		+	-
0.73	0.716	0.723	0.73	0.716	0.75	0.696	0.723	0.968188	0.96819
0.668	0.651	0.64	0.668	0.64	0.688	0.62	0.654	2.140673	2.14067
0.61	0.616	0.606	0.616	0.606	0.636	0.586	0.611	0.818331	0.81833
0.565	0.572	0.558	0.572	0.558	0.592	0.538	0.565	1.238938	1.23894
0.525	0.521	0.533	0.533	0.521	0.553	0.501	0.527	1.13852	1.13852
0.484	0.49	0.479	0.49	0.479	0.51	0.459	0.4845	1.135191	1.13519
0.453	0.448	0.457	0.457	0.448	0.477	0.428	0.4525	0.994475	0.99448
Uncertainty level								1.204902	-1.2049

The uncertainty level of CO emission for JB is ±1.20

Table A.4: Uncertainty calculation for BP

Three tests value (kW))			Max-min value		Equipment accuracy (±0.03)		Average value (kW)	% Uncertainty	
Test 1	Test 2	Test 3	Max	Min	0.03	-0.03		+	-
26.21	26.27	26.16	26.27	26.16	26.3	26.13	26.215	0.209804	-0.2098
30.17	30.22	30.12	30.22	30.12	30.25	30.09	30.17	0.165728	0.16573
32.74	32.67	32.71	32.74	32.67	32.77	32.64	32.705	0.107017	0.10702
36.15	36.23	36.19	36.23	36.15	36.26	36.12	36.19	0.110528	0.11053
39.73	39.69	39.64	39.73	39.64	39.76	39.61	39.685	0.113393	0.11339
43.05	43.1	43.13	43.13	43.05	43.16	43.02	43.09	0.092829	0.09283
45.03	45.07	45.1	45.1	45.03	45.13	45	45.065	0.077666	0.07767
Uncertainty level								0.125281	0.12528

The uncertainty level of BP for JB is ±0.13

Appendix B
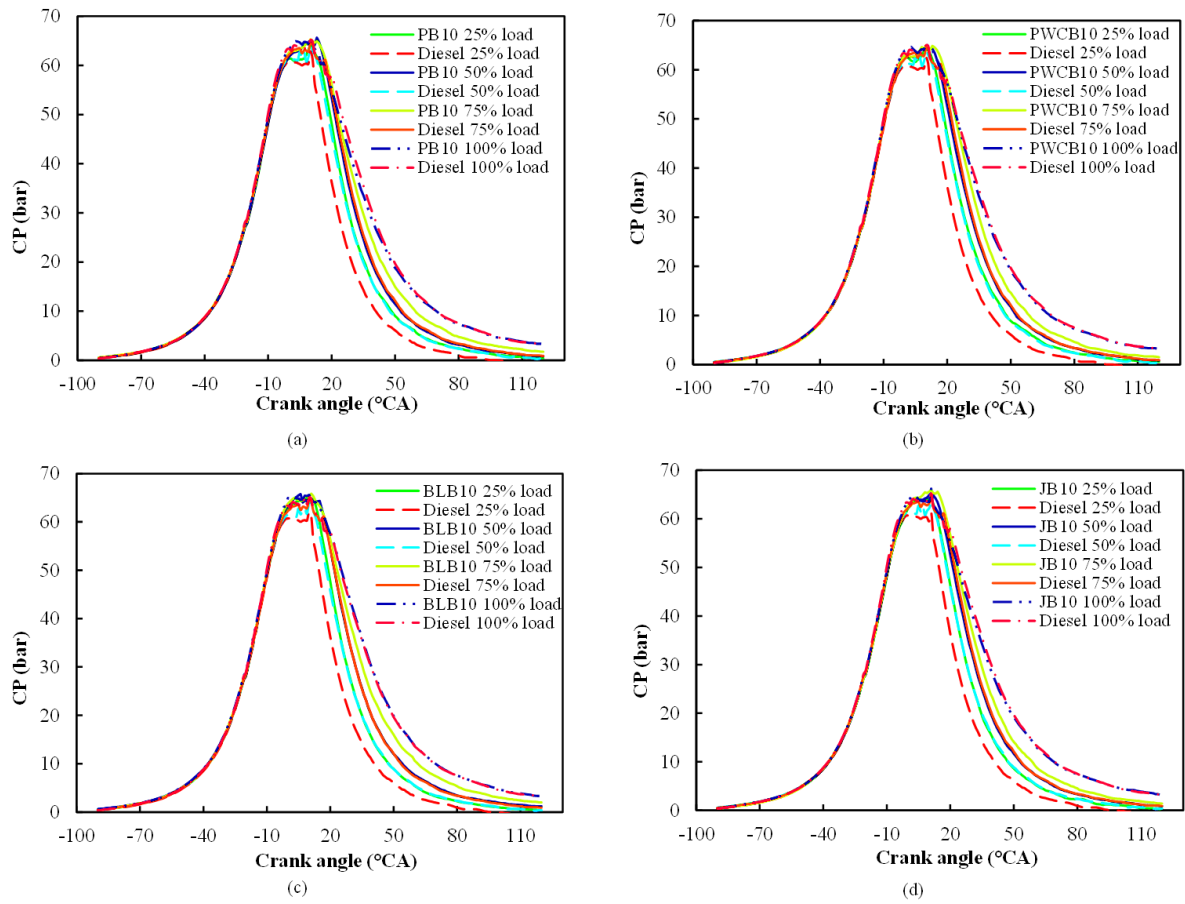
Figure B.1: Variation in CP with CA for PB10, PWCB10, BLB10 and JB10 at different loading conditions and 1400 rpm
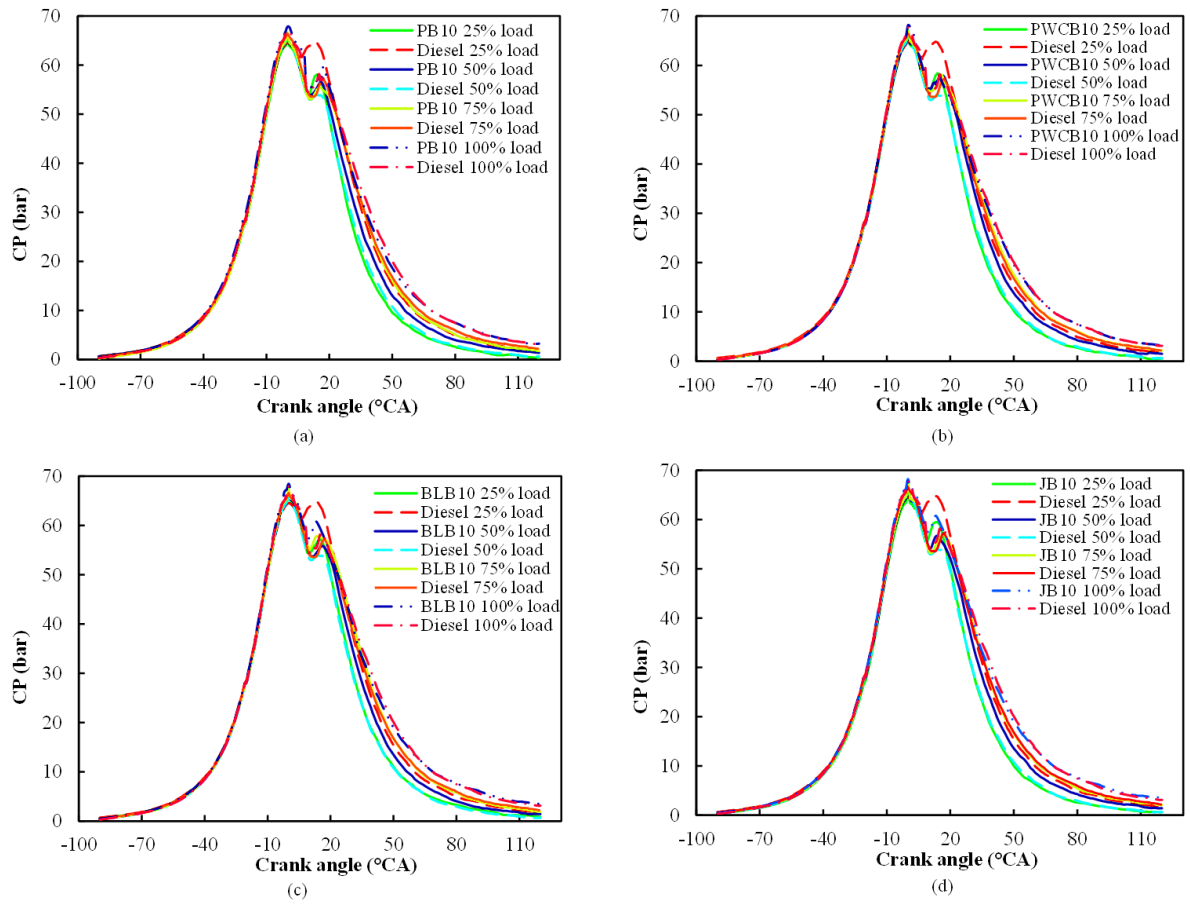
Figure B.2: Variation in CP with CA for PB10, PWCB10, BLB10 and JB10 at different loading conditions and 2400 rpm
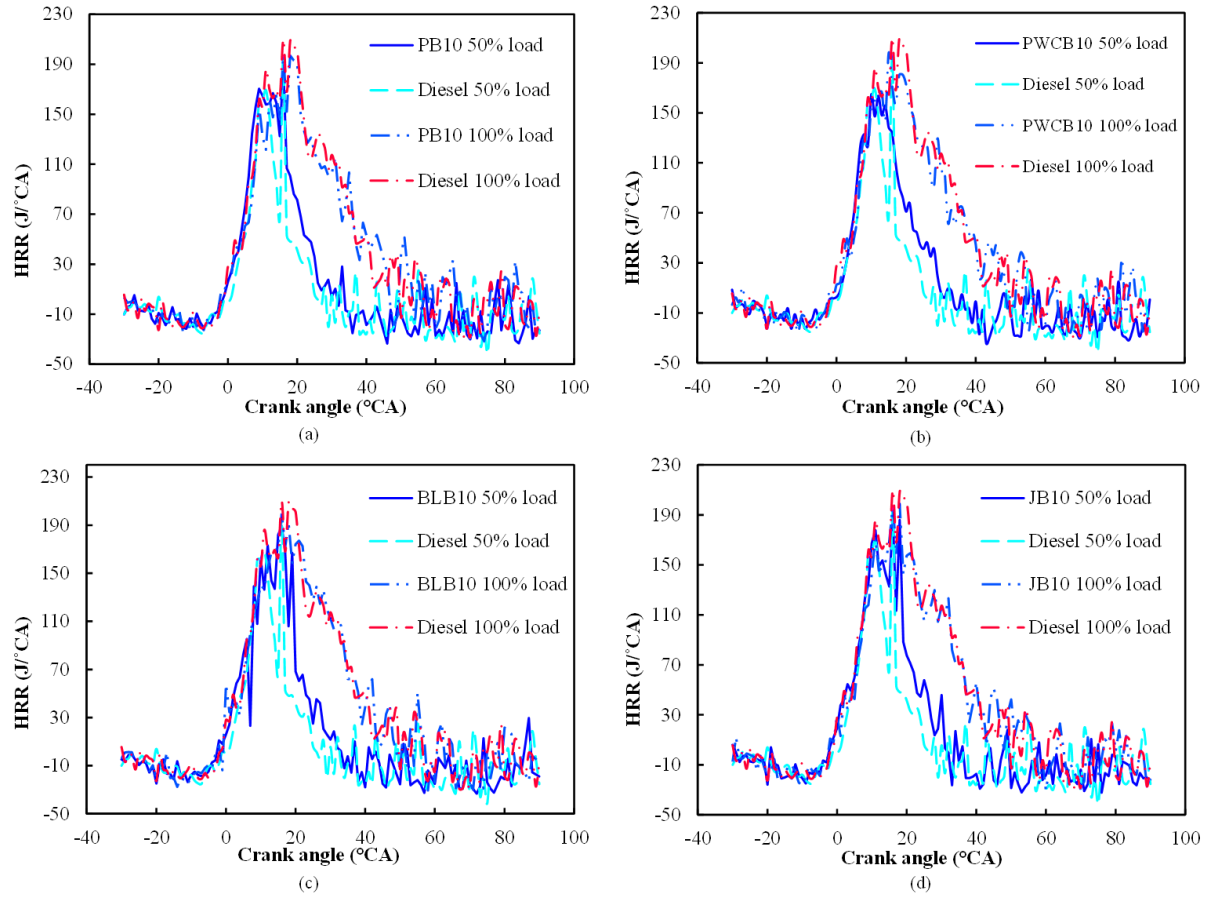
Figure B.3: Relation between HRR and CA for PB10, PWCB10, BLB10 and JB10 at different loading conditions and 1400 rpm

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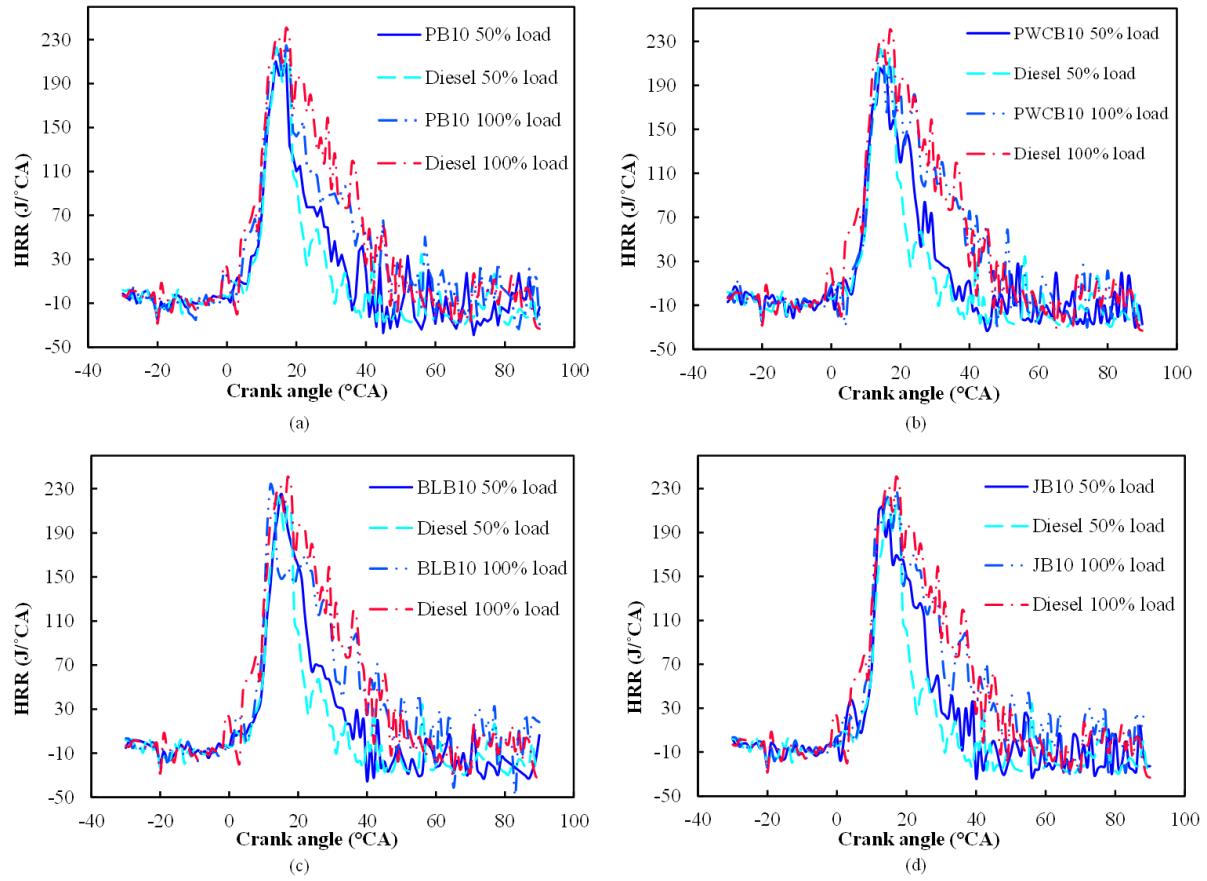
Figure B.4: Relation between HRR and CA for PB10, PWCB10, BLB10 and JB10 at different loading conditions and 2400 rpm

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