EXPERIMENTAL STUDY OF ENGINE PERFORMANCE AND EMISSION OF PALM, MUSTARD AND *CALOPHYLLUM* BIODIESEL BLENDS IN A DIESEL ENGINE

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DISSERTATION SUBMITTED IN FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF ENGINEERING SCIENCE

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2014

Universiti Malaya

<u>ORIGINAL LITERARY WORK DECLARATION</u>

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Name of Degree: **Masters of Engineering Science**

Title of Thesis: **EXPERIMENTAL STUDY OF ENGINE PERFORMANCE AND EMISSION OF PALM, MUSTARD AND *CALOPHYLLUM* BIODIESEL BLENDS IN A DIESEL ENGINE.**

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ABSTRACT

Present energy situation of the world is unsustainable due to unequal geographical distribution of natural wealth as well as environmental, geopolitical and economical concerns. Ever increasing drift of energy consumption due to growth of population, transportation and luxurious lifestyle has motivated researchers to carry out research on biofuels as a sustainable alternative fuel for diesel engine. Biodiesel seems as one of the best choices among other alternative fuel sources due to its renewability, cost effectiveness and reduction of pollutants in exhaust gas emission which are promoting biofuels as a suitable substitute of diesel fuel in near future. This research endeavor aims to produce and evaluate the comparative performance and emission of palm, mustard and *Calophyllum inophyllum* biofuels in a four cylinder diesel engine. This was followed by the production of palm, mustard and *Calophyllum inophyllum* biodiesel from their respective oils and blending them with diesel fuel. Detailed characterization of physicochemical properties of pure biodiesel and their blends meet standard ASTM specifications. Engine performance and emission were evaluated by measuring brake specific fuel consumption (BSFC), brake thermal efficiency (BTE), engine power, engine torque, carbon monoxide (CO), hydrocarbon (HC), and nitric oxide (NO) emission. The results of engine performance revealed that biodiesel blended fuels produced average reduction in engine BTE, power and torque with increased BSFC. In case of engine emission, biodiesel blends showed an average reduction in CO and HC with a slight increase in NO & CO_2 emission. Overall, *Calophyllum inophyllum* biodiesel blends showed better engine performance and emission compared to palm and mustard biodiesel blends. The peak cylinder pressure and heat release of biodiesel blends were found higher and closer to top dead centre compared to diesel fuel. This is due to the shorter ignition delay and higher cetane number of biodiesel.

In conclusion, palm, mustard and *Calophyllum inophyllum* are potential feedstock for biodiesel production and up to 20% of their blends could be used in the diesel engine without any modification. Besides, as producing biofuel from edible oil source has received criticism worldwide, therefore using non-edible vegetable oils like: calophyllum as biofuel can replace the current dependence on the edible oil source.

ABSTRAK

Taburan sumber alam semulajadi yang tidak seimbang serta unsur alam sekitar, politik dan ekonomi, telah meletakkan isu tenaga global berada dalam keadaan yang tidak mampan. Penggunaan tenaga semakin meningkat selaras dengan perkembangan dari segi populasi sedunia, pengangkutan dan cara hidup mewah. Situasi ini telah mendorong penyelidikan dalam bidang bahan api bio sebagai bahan api alternatif yang mampan untuk enjin diesel. Biodiesel merupakan salah satu pilihan yang terbaik di antara sumber-sumber bahan api alternatif kerana sifatnya yang boleh diperabaharui, berkesan dari segi kos dan mesra alam. Biodiesel juga berpotensi menjadi pengganti bahan api diesel pada masa akan datang. Penyelidikan ini bermatlamat untuk menghasilkan bahan api bio daripada sawit, mustard dan Calophyllum inophyllum untuk enjin diesel empat silinder. Dengan menggunakan bahan api bio tulen yang berlainan ini, prestasi dan pelepasan enjin dibandingkan. Perbandingan turut dijalankan dengan menggunakan bahan api yang dihasilkan daripada campuran diesel dengan biodiesel kelapa sawit, mustard dan *Calophyllum inophyllum* masing-masing. Pencirian terperinci atas ciri fisikokimia biodiesel tulen dan bahan api campuran menunjukkan semua bahan api bio yang dihasilkan memenuhi spesifikasi standard ASTM untuk biodiesel. Prestasi enjin dan pelepasan dinilai dengan mengukur penggunaan bahan api tentu brek (BSFC), kecekapan haba brek (BTE), kuasa enjin, tork enjin , dan pelepasan karbon monoksida (CO), hidrokarbon (HC), dan oksida nitrik (NO). Keputusan prestasi enjin mendedahkan bahawa bahan api biodiesel campuran menunjukkan pengurangan dalam BTE, kuasa dan tork dengan peningkatan dalam BSFC. Bagi pelepasan enjin, biodiesel campuran memaparkan pengurangan dalam penghasilan CO dan HC secara purata dengan sedikit peningkatan dalam pelepasan NO. Secara keseluruhan, biodiesel campuran *Calophyllum inophyllum* menunjukkan prestasi enjin dan pelepasan yang lebih

baik berbanding dengan biodiesel campuran sawit dan biodiesel campuran mustard. Kesimpulannya, kelapa sawit, mustard dan *Calophyllum inophyllum* merupakan bahan mentah yang berpotensi dalam penghasilan biodiesel dan setinggi 20% daripada campuran mereka boleh digunakan secara terus dalam enjin diesel tanpa sebarang pengubahsuaian.

ACKNOWLEDGEMENT

I would like to thank almighty Allah s.w.t, the creator of the world for giving me the fortitude and aptitude to complete this thesis.

I would especially like to thank my supervisors Professor Dr. Masjuki Hj. Hassan and Dr. Md. Abul Kalam for their helpful guidance, encouragement and assistance throughout this work. I would like to express my gratitude to the Ministry of Higher Education (MOHE) for HIR Grant for the financial support through project no. UM.C/HIR/MOHE/ENG/07. I also would like to convey appreciation to all lecturers and staff of the Department of Mechanical Engineering, University of Malaya for preparing and giving opportunity to conduct this research.

Additional thanks to Mr. S.M. Ashrafur Rahman, Mr. M.J. Abedin and all members in “Centre for Energy Sciences” research group for their valuable ideas and discussion and Mr. Nur Azam Ali, Mr. Kamarul Bahrin Bin Musa, Mr. Asri and Mr. Sulaiman Ariffin for their technical help and assistance.

Last but not least, take pleasure in acknowledgement the continued encouragement and moral support of my parents, my beloved wife and other family members. Their love, motivation and support had contributed a lot toward the success of this thesis.

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ASTM	American Society of Testing Materials
ATDC	After Top Dead Centre
BP	Brake Power
BHP	Brake Horse Power
BMEP	Brake Mean Effective Pressure
BSEC	Brake Specific Energy Consumption
BSFC	Brake Specific Fuel Consumptions
BTE	Brake Thermal Efficiency
CI	Compression Ignition
CB	*Calophyllum* Biodiesel
COME	*Calophyllum* Oil Methyl Ester
CP	Cloud Point
CPO	Crude Palm Oil
CO	Carbon Monoxide
CO_2	Carbon Dioxides

CN	Cetane Number
Dg-aMCPO	De-acidified mixed crude palm oil
DF	Diesel Fuel
DI	Direct Injection
EGR	Exhaust Gas Recirculation
EGT	Exhaust Gas Temperature
EPA	Energy Protection Agency
EN	European Union
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GHG	Greenhouse gas
h	Hour
Ha	Hectare
HC	Hydrocarbon
HRR	Heat Release Rate
IC	Internal Combustion
IEA	International Energy Agency
IOP	Injector Opening Pressure
IP	Induction Period
IPCC	International Panel on Climate Change

IV	Iodine Value
JB	Jatropha Biodiesel
kg	Kilogram
kW	Kilowatt
MB	Mustard Biodiesel
MJ	Mega Joule
MSO	Mustard Seed Oil
Mtoe	Million Tons of Oil Equivalents
N-m	Newton Meter
NO	Nitric Oxide
NOx	Oxides of Nitrogen
OD	Ordinary Diesel
OECD	Organization for Economic Co-operation and Development
PB	Palm Biodiesel
PD	Plunger Diameter
POME	Palm Oil Methyl Ester
PM	Particulate Matter
PP	Pour Point
ppm	Part Per Million
rpm	Revolution Per Minute

SAE	Society of Automotive Engineers
SN	Saponification Number
Wt%	Percentage Weight

CHAPTER 1: INTRODUCTION

1.1 Background

Modern civilization is very much dependent on non-renewable fossil resources like coal, petroleum and natural gas. In recent years, ever increasing trend of energy consumption due to industrialization and development has caused serious threat to the energy security and environment. Global fossil fuel consumption grew 0.6 million barrels per day and cost $ 111.26 per barrel in 2011 which means a 40% increase than 2010 level (British Petroleum, 2011). Current reserve of liquid fuel has the capacity to meet only half of the usual energy demand until 2023 (Owen et al., 2010). Besides, this tremendous drift of fossil fuel use, hazardously effecting world's environment, which includes global warming, deforestation, eutrophication, ozone depletion, photochemical smog and acidification (Armas et al., 2006).

1.1.1 Present and future energy scenario

Major portion of the petroleum and natural gas reserve is distributed within a small region of the world. Middle East countries are the dominant petroleum suppliers and possess 63% of global petroleum reserve. On contrary, Renewable energy sources are more evenly distributed than fossil fuel and hence, coming up as a secured energy source in near future (Demirbas, 2009a). Greater energy security, reducing environment pollution, saving foreign exchange and other socio-economic issues stimulating rapid growth of biofuel industries over the next decade (Demirbas, 2009b). Staniford demonstrated a projection back in 2008 on global marketed primary energy production from 1970 to 2050 which strongly supports the increasing trend of renewable energy consumption (Staniford, 2008). The projection is presented in Figure 1.1. U.S Energy

Information Administration (EIA) also showed a similar projection which was projected until 2035. In a reference case, showed by EIA, renewable energy possessed 10% share of the total energy used in 2008 and it will be increased to 14% in 2035. They mentioned it as world's fastest growing form of energy (U.S. Energy Information Administration, 2011). Biodiesel is progressively gaining acceptance as an alternative and renewable energy source and market demand will rise intensely in near future (Basha SA, 2009; K. Foo & B. Hameed, 2009; Janaun & Ellis, 2010). According to International Energy Agency (IEA), around 27% of total transport fuel will be replaced completely by biofuels within 2050 (International Energy Agency(IEA), 2011).

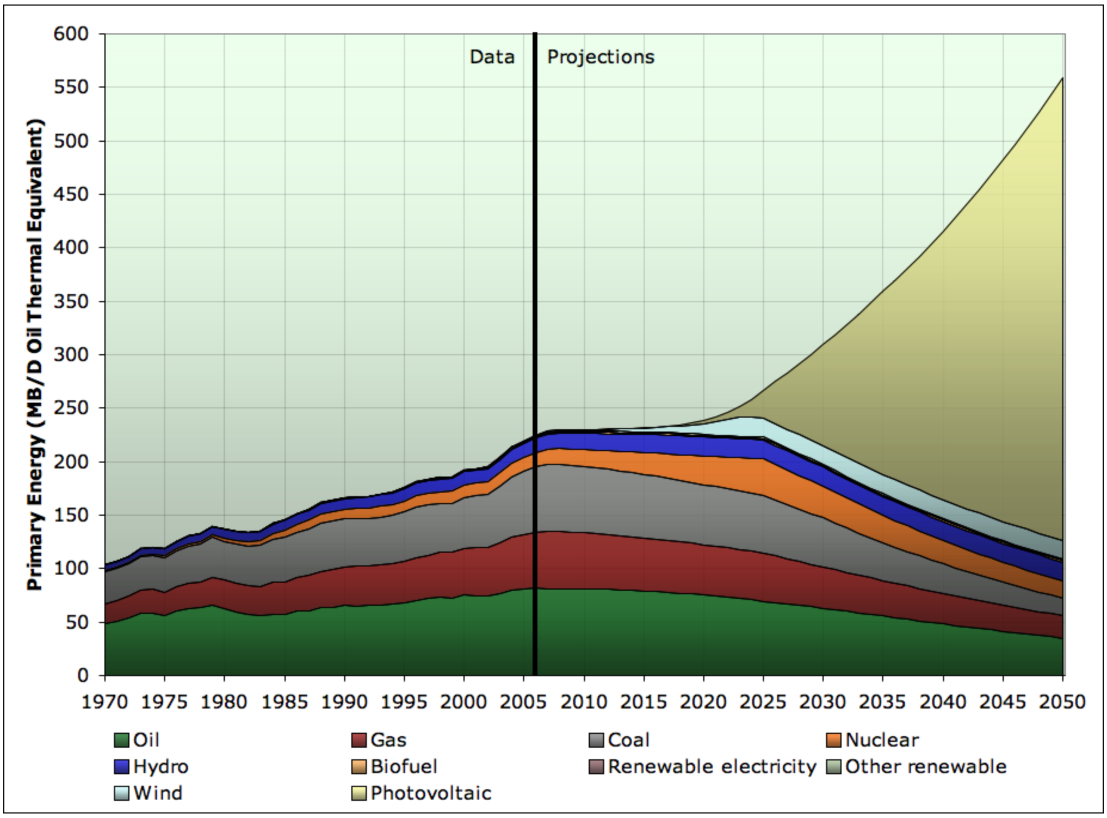


Figure 1.1: Projection of Global marketed primary energy production 1970-2050 (International Energy Agency (IEA), 2011)

1.1.2 Environmental concern

An UN-commissioned group of scientists known as International Panel on Climate Change (IPCC) confirmed that carbon di oxide (CO_2) is the main cause of global warming. There are of course other gasses that can trap more heat than CO_2 does (e.g. methane, nitrous oxide, and chlorofluorocarbons); however these gasses are not comparable with CO_2 in concentration. Consequently, the effect of greenhouse gas (GHG) is understood as the equivalent amount of CO_2. The amount of “carbon dioxide equivalent” release in the world from 1990 is 6 billion metric ton, which represents an increase more than 20%. For the first time in man's history, greenhouse gas carbon di oxide in the atmosphere hits the record of 400 parts per million (ppm) ("The keeling curve. ," 2013).

North America, with emission of 6703.99 million metric ton of the gas in 2012, currently is the second largest producer of CO_2 gas after Asia. Forecasts show that emission of the gases form the source of fossil fuel will increase by 35% in 2035, if no counter measure is taken to deal with the threat (EIAU, 2011) .Carbon dioxide emission due to energy consumption for 2012 and the forecasts for 2035 is listed in Figure 1.2 for different regions. Fighting the increase of carbon emission is one of the principal reasons of the recent trend toward Renewable Energy solution in Malaysia. Considerable aggregation of the gasses in the atmosphere surely results in intense climate change, acid rain and smog. Furthermore, extraction, processing, and transferring the fossil fuel, by itself, needs a great deal of energy and consequently causes more harmful effects on the world ecology. On the other hand, domestic economic development is subject to the extent to which energy demands are supplied.

Emission of CO_2 in Asia-Pacific Economic Cooperation (APEC) regions is expected to grow about 40% from 2010 (19.0 billion ton) to 2035 (25.1billion ton). About one half of this amount is emitted by electricity and heat generation utilizations (APEC, 2013). Among the countries in the regions, Malaysia in the 4th position and after China Taipei, Thailand, and Singapore, emits 191.444 million ton of CO_2 (EIAU, 2012). Projected emission of CO_2 from fuel combustion as reported by APEC is portrayed in Figure 1.2 (Oxley, 2005). In the Copen Hagen Climate Change Summit on December 2009, the PM of Malaysia agreed with conditions to initiate reduction of emission of carbon up to 40% in terms of emissions intensity of GDP by 2020 on the basis of statistics of 2005, along with preservation of the forest of the country (Omer, 2008).

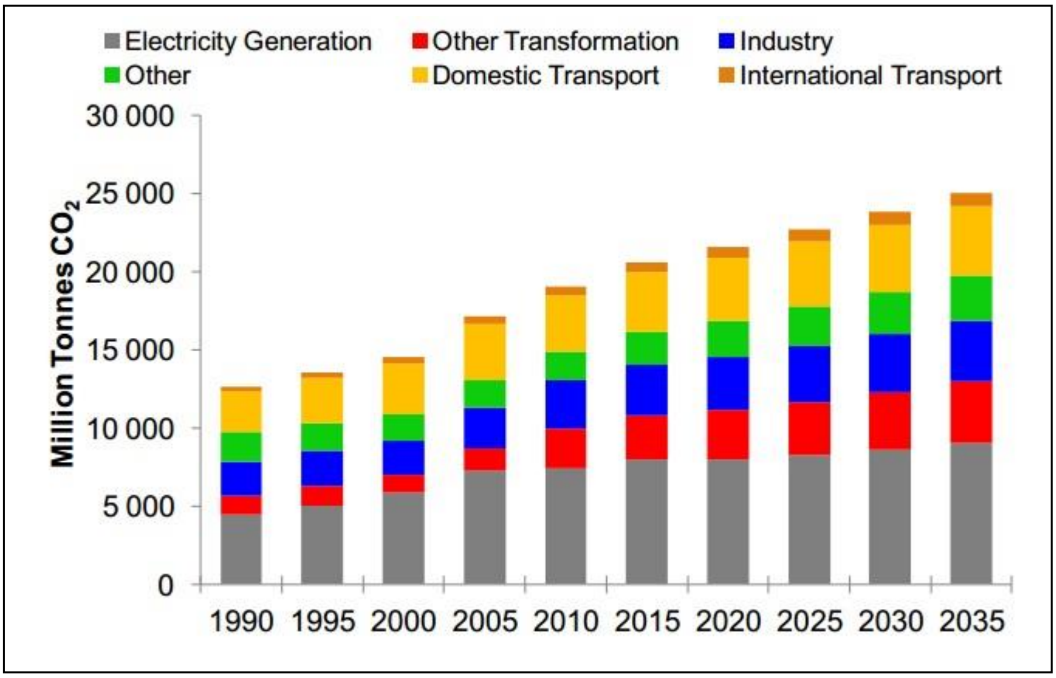


Figure 1.2: Projection of CO_2 production by APEC till 2035

1.1.3 Importance of biodiesel

Vegetable oils are quite favourable alternative fuels for diesel engines (Sahoo et al., 2007). Biodiesel fuels are mono alkyl esters and generally derived from fatty ester of vegetable oil or animal fat (Knothe, 2006). Suitable sources of biodiesel vary from country to country depending upon available vegetation and environmental condition. Crude vegetable oils are not suitable as engine fuel in terms of lower heating value, high viscosity, low volatility, freezing point etc. But many chemical treatments are available to improve physicochemical properties of crude vegetable oils. Trans-esterification is the most popular chemical treatment to reduce viscosity and improve other properties (Balat & Balat, 2008). Trans-esterified vegetable oils are widely being used in diesel engines at present (McCarthy et al., 2011) and meet standard specifications of ASTM and EN test method. Biodiesels and their blends have similar properties as diesel fuel and favoured due to lower exhaust emission.

Moreover, all carbons released by the combustion of biofuel are fixed by the plant through the process of photosynthesis. This is the concept of "carbon neutral fuel", emphasized by Kyoto Protocol, which establishes the contribution of using biofuel in the prevention of global warming (Balat & Balat, 2008). The surge of interest in biodiesels has highlighted a number of environmental effects associated with its use. Biodiesel proponents argue that unlike fossil fuels which release carbon dioxide that has been stored for millions of years beneath the earth‘s surface, biodiesel produced from biomass have the potential to be ‘‘carbon–neutral" over their life cycles as their combustion only returns to the atmosphere the carbon dioxide absorbed from the air by feedstock crops through photosynthesis. It thus has the potential to replace fossil-based fuels and contribute to the mitigation of GHG emissions (Wahlund et al., 2004). According to the EPA's Renewable Fuel Standards Program Regulatory Impact

Analysis, released in February 2010, biodiesel from soy oil results, on average, in a 57% reduction in greenhouse gases compared to fossil diesel, and biodiesel produced from waste grease results in an 86% reduction (EPA., 2010.).

1.1.4 Limitations of biofuel

Massive increase in fuel production from edible feedstock has raised a highly controversial "food vs. fuel" debate which is not new in the international agenda (Kuchler & Linnér, 2012). In present situation more than 95% of biofuel is produced from edible oil source. Rapeseed, palm, sunflower and soybean are the main edible sources of biofuel industry (Wang et al., 2012). Use of edible feedstock for producing biofuel puts threat on food security and cultivable land which has been criticized by many environmentalists worldwide. Besides, biofuel feedstock are expensive than diesel fuel. Cost of biofuel feedstock comprises around 70% of the total expenditure involved in the production process. Thus, minimizing the cost of biofuel feedstock has been the main requirement for most biofuel producers around the globe (Phan & Phan, 2008). To ensure food security, one promising option is to establish a multiple non-edible feedstock pattern for biodiesel production. *Calophyllum inophyllum*, *Jatropha curcas* and *Pongamia pinnata* are now being considered as very prospective non-edible feedstock for biodiesel production (Atabani et al., 2013). Most of them are cultivated in sandy and saline soil, barren land and mountainous area which also put no threat on existing cultivable land. Waste edible oil can also come to aid this situation. Low quality seed pressed oil can also be used as biofuel feedstock. Use of WCO will not affect the food chain and can reduce the feedstock cost around four times than fresh edible oil feedstock. By proper management system, efficient supply chain and promoting non-edible biofuel feedstock can reduce the production cost as well as secure food supply.

1.1.5 Scope of the study

This work is focused on the possibilities and comparative evaluation of using palm, mustard and *Calophyllum* inophyllum biofuels in diesel engine. Palm is the most productive plant among all biofuel feed stocks. At present more than 95% of world's biofuel production is produced from edible oils (M. Gui et al., 2008; Tan et al., 2009). However, producing biofuel from edible oil source has received criticism from several non-governmental organisations worldwide (Tan et al., 2011). Therefore, using non-edible vegetable oils as biofuel which are not suitable for human food can replace the current dependence on the edible oil source. *Calophyllum inophyllum* can be trans-esterified and is a very promising non-edible source of biofuel. It's production is still in nascent state compared to Palm or Jatropha biodiesel industry. Mustard oil is also a potential feedstock of biofuel. In most of the literatures reviewed, it was found that low-quality seeds which are unsuitable for food use, are adopted for fuel production (Niemi et al., 2002). Canola or rapeseed has gained widespread acceptance as biodiesel feedstock which is from the same plant family of mustard. But advantage of mustard oil is it contains high amount of erucic acid which makes it generally non edible (although mustard oil is used as condiment). Hence, mustard oil is suitable for industrial use and unlike canola using mustard as biodiesel feedstock would not interfere with the food supply (Zheljazkov et al., 2012). Another major advantage of mustard oil is that it reduces NO_x emission than any other biofuels. Therefore, mustard is seemed to be a more feasible feedstock for biodiesel production (Niemi et al., 1997).

1.2 Objective

The considered aims of study are as follows:

- Transesterification of Palm, Mustard and *Calophyllum* oil and measuring physicochemical properties.
- Preparing blends for Palm, Mustard, *Calophyllum* biodiesels with diesel fuel at different proportions and comparison of different physicochemical properties for biodiesel blends with diesel fuel.
- Analyzing combustion, engine performance, and emission pollutants at different engine loading conditions for biodiesel blends and diesel fuel.
- Justify the appropriateness of using biodiesel by analyzing all data and experimental results.

CHAPTER 2: LITERATURE REVIEW

2.1 Potentiality of palm oil

Palms are most popular and most extensively cultivated amongst the plant families. Around 202 genera and approximately 2600 species of palms are currently known and available mostly at tropical, subtropical and climates where weather is warm. Among them, oil palm is originated from the species *Elaeis guineensis* belongs to genus *Elaeis* and family *Palmae* (Singh et al., 2010). Basically oil palm tree is originated from West Africa where it was growing wild and human started using palm oil 5000 years ago. Later cultivation started mostly in all tropical areas of the world considering its economic aspects.

Worlds total palm oil production is 45 million tonnes per year and maximum production is in South East Asia. As shown in Figure 2.1 about 87% of world palm oil production is contributed by Malaysia, Indonesia and Thailand. From 1990 to 2013 palm crop plantation area increased from 2.03 to 4.49 million hectares in Malaysia which means an increase of 121.2% (USDA (United States Department of Agriculture). Indonesia: palm oil pro-duction prospects continue to grow. Washington; USDA (United States Department of Agriculture). Palm oil: world supply and distribution. Washington).

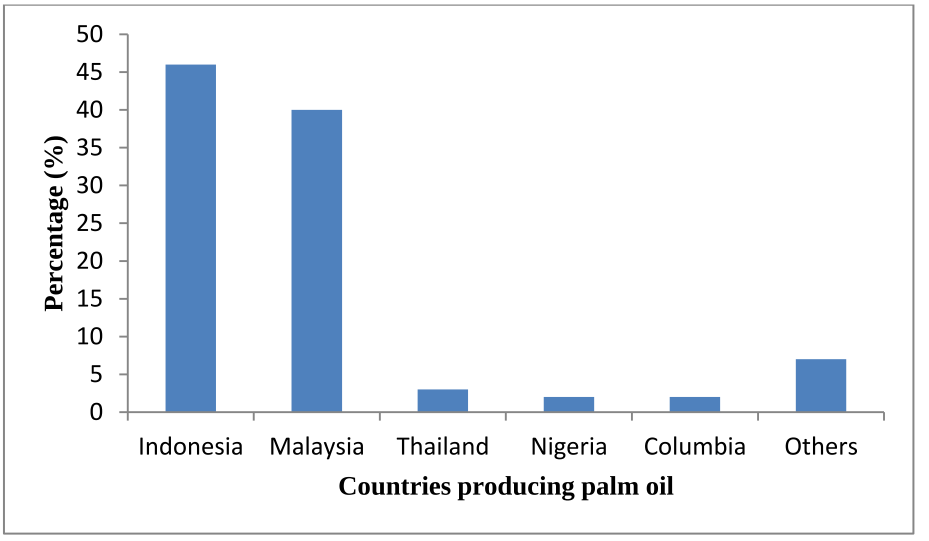


Figure 2.1: World palm oil production 2013 (USDA (United States Department of Agriculture). Palm oil: world supply and distribution. Washington)

Elaeis Guineensis Jacq is most highly productive species and can be cultivated in all tropical areas where weather is humid and hot like Malaysia and Indonesia. This particular variety can annually produce 10-35 tonnes/ha of palm fruits. As shown in Figure 2.2, a single stemmed, matured palm tree can grow up to 20-30 m height (Edem, 2002). Pinnate leaves can be 3 to 5 m long and the flowers are densely clustered. Each small flower consists of three sepals and three petals (Abdullah, 2003).

Figure 2.2: Palm tree and fruits

The oil palms do not spread by off-shoots; they are propagated by sowing seeds. It takes almost 5-6 months to get matured fruits starting from pollination. Fruit comprises two portions: an oily and fleshy outer layer and a seed inside, which is very rich in oil. Seed is called palm kernel and is surrounded by soft pulp. Each kernel contains 20-21% oil (Borugadda & Goud, 2012). Fruits are small plum size and grows in heavy bunches of palm trees, each bunch weighing 10-20 kg. Oil is extracted from both the pulp and the seed. Oil palm trees are commercially cultivated to serve edible oil to the market (K. Y. Foo & B. H. Hameed, 2009). Comparison of Oil production per hectare of Palm with other biodiesel feedstock is shown in Figure 2.3.

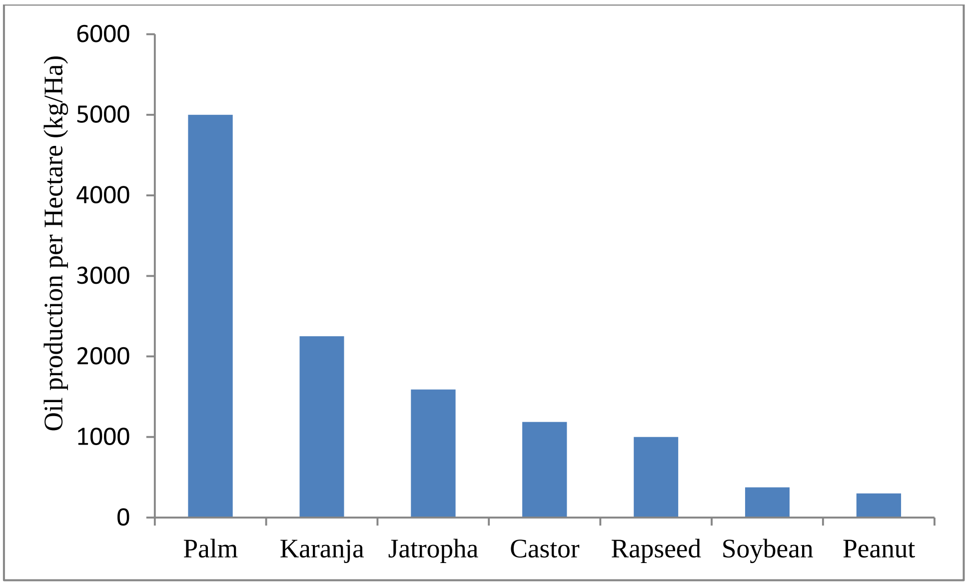


Figure 2.3: Comparison of oil production per hectare of palm with other biodiesel feedstock (M. M. Gui et al., 2008)

2.2 Palm oil performance

A research on performance and emission of an IDI-turbo automobile diesel engine, operated with degummed de-acidified mixed crude palm oil ($D_{g\text{-}a}$MCPO) was carried out by Leevijit & Prateepchaikul (2011). The research explores the performance and emission comparison between ordinary diesel (OD) and D_{g-a}MCPO at three different proportions as 20, 30 and 40 vol.% of blends. This experimental study showed that all blends provide same maximum brake torque corresponding to same maximum brake power at any operating speed ranged from 2000 to 3000 rpm. The more the portion of D_{g-a}MCPO was increased in the biodiesel blend the engine had to supply slightly a higher mass flow rate. The engine work efficiency was satisfactory when operated at high loads of > 25 KW. Highest brake thermal efficiency (BTE) and lowest brake specific fuel consumption (BSFC) were obtained at full load condition. Overall BSFC of the 20,30, 40 vol.% blends were higher than OD fuel at about +4.3%, +5.9%, and +7.6% respectively, while BTEs were lower at about -3.0%,-4.1%, and -5.2% respectively. This trend is also supported by the experiments conducted by Sharon et al. (2012). Yusaf et al. (2011) had similar findings regarding engine torque in a CI engine. At lower speed (Below 2000 rpm) using crude palm oil showed higher torque than OD fuel, but at high speed torque was slightly lesser than OD fuel. Generally, Fuel consumption rate was found relatively low at lower speed than operating at higher speed if biodiesel is considered alone. But BSFC was found higher at low engine speed and better fuel consumption was found at higher engine speed using palm oil blends than OD fuel. This phenomenon is also agreed by Kalam et al.(2003). Ndayishimiye and Tezerout (2011) used preheated palm oil and palm oil blended at 5, 10, 20 and 30% by wt. with diesel to investigate the performance and emission of a DI diesel engine. They found BTE of preheated palm oil blends were around 27% higher than OD. But the BSFC were higher at 2-6% for palm oil diesel blends and 14-17% for preheated pure palm oils than OD. Kalam and Masjuki (2002) conducted research using palm oil blends with 50 ppm corrosion inhibitor in a diesel engine and found excellent results. Experiments showed 12.4 KW and 11.44 KW maximum brake power obtained from 7.5% and 15% palm oil blends respectively, running at 1600 rpm. Corrosion inhibitor increased fuel conversion from heat energy to work resulting higher brake power. Besides use of Crude Palm Oil (CPO) blends had some adverse effects like heavy carbon deposits inside the engine cylinder, wear of piston rings, uneven spray formation, shorter ignition delay etc. Thus Long term use of CPO may deteriorate engine performance parameters. Bari et al. (2002) investigated 500 h cumulative running of diesel engine with CPO which resulted reduced maximum power up to 20% and BSFC was increased up to 26 %. Experimental results of Lin et al. (2006) also agreed with this higher BSFC and lower power output phenomena using palm oil blends in a diesel generator. Moreover, as many researchers found almost same power output and engine performances of palm oil compared to diesel fuel, hence use of palm oil as an alternative fuel is acceptable (Sapuan et al., 1996).

2.3 Palm oil emission

Ndayishimiye and Tezerout (2011) found Exhaust Gas Temperature (EGT) increases 6-8% more than OD fuel using preheated palm oil which indicates higher ignition delay due to the lower cetane number of blends than diesel at lower speed. Due to the higher viscosity of blends atomization is poor and some unburnt fuels burn in the late combustion phase, resulting lower thermal efficiency and higher exhaust temperature (Kumar et al., 2006). At full load condition Leevijit and Prateepchaikul (2011) reported slightly lower EGT than OD fuel. EGT was lower at -2.7%, -3.0% and -3.4% respectively for 20, 30 and 40 vol.% palm oil blends than OD fuel. Yusaf et al. (2011) found that with the increase of CPO percentage in the blend EGT was increasing. For 25% CPO blend the EGT was comparable to diesel at low speed and lower at high speed range. For 50% CPO, EGT was found higher at low speed range and comparable at high speed range and finally for 75% CPO, EGT was higher than diesel over all speed ranges.

During 100-h of engine operation Kalam and Masjuki (2004) found CPO produces lowest level of Carbon monoxide (CO) emissions than OD and emulsified CPO. Preheated CPO contributes to complete combustion which leads to produce less CO than emulsified CPO. Ng and Gan (2010) experimented the effect of Exhaust Gas Recirculation (EGR) on CO emission and reported that CO is minimum when EGR is within the .75-.85 range and CO emission further improves with the proportional increase of palm oil methyl ester (POME). Tremendous CO decreasing phenomena was observed by Kalam and Masjuki (2002) using corrosion inhibitor. Palm oil blended with corrosion inhibitor decreases CO concentration value even less than 0.01% where maximum acceptable limit is 1%. CO results from incomplete combustion which is reduced at increased load condition. High load condition results high combustion temperature and better mixing, hence leads more complete combustion. Leevijit and Prateepchaikul (2011) reported at full load condition CO emission was significantly lower (about -70%) for 20% palm oil blend than OD fuel. But using 30 and 40 vol.% palm oil blend showed similar and slightly higher CO emission trend than OD fuel respectively. Therefore, 20% blend is suitable considering CO emission. Hydro Carbon (HC) emission shows similar trend like CO emission, preheated CPO produces less HC emission than OD fuel (Kalam & Masjuki, 2004). During 350 h operation of a diesel generator by palm oil, de Almeida et al. (2002) found HC emission of PO is higher at partial charge but lower at higher percentage of charge than diesel fuel . Though many studies showed HC formation less than OD at different engine conditions using palm oil higher viscosity and lower cetane number of palm oil results some HC emissions unavoidable (Çelikten et al., 2010).

Soot, heavy HC absorbed on the soot, and sulphates, these three are major components of particulate Matter (PM). Experimental study of Lin et al. (2006) showed PM emission of 10, 20 and 30% palm oil blends are smaller than pure diesel but larger in case of 50,75 and 100%. According to Peterson et al. (1996) analytically optimum blending ratio of palm oil is 35% when PM emission becomes equal to OD fuel. After running a diesel engine, Kalam and Masjuki (2004) measured PM at 30^{th} h and 100^{th} h of operation for OD and preheated CPO. Results were 0.60 g/KW h and 0.51 g/KWh at 30^{th} h, and 0.77 and 0.70 g/KWh at 100^{th} h for OD and CPO respectively.

Many researchers have found different functions influencing NO_x level. NO_x level increases with the increase in combustion temperature. It was seen that NO_x level decreases with increase of palm oil percentage in the blend. Masjuki et al. (2000) reported, increasing amount of palm oil blend lowers heat release at premix combustion phase and results lower peak combustion temperature inside engine cylinder. Thus, NO_x level decreases from 147 to 135 ppm while palm oil blend raised from 7.5 to 15%. According to Graboski and Cornimik (1998), NO_x emission is a function of speed and load. Kalam and Masjuki (2004) used emulsified palm oil which helped to reduce NO_x level. With the increase of only 2% water in CPO, the NO_x level decreased from 179 to 174 ppm at 100th h of engine operation. Experimental results of Leevijit and prateepchaikul (2011) clearly indicated that NO_x increases with increasing loads in CI engine. Enormous fuel supply created larger flame zones stimulating combustion temperature, hence increased NO_x. In comparison to diesel they also found higher NO_x emission using 20 vol.% palm oil blend.

Experiments of De Almeida et al. (2002) revealed almost same O_2 and CO_2 emission percentage compared to the diesel fuel and showed same trend with varying charge. It was found by many researchers that CO_2 emission is reduced by using palm oil (Ong et al., 2011). Experimental results of Yusaf et al. (2011) showed 2.8-19.7 kg CO_2 equivalent per kg of palm oil. For 25 and 50% CPO blends O_2 content was higher than OD fuel at speed above 2000 rpm. Besides exhaust gas contains lower O_2 content compared to OD fuel at all speeds using 75% diesel fuel. Though Presence of oxygen indicates complete combustion there is always some possibilities of oxygen presence in the emission due to imperfect air fuel mixture.

2.4 Potentiality of mustard oil

Wild mustard belongs to the Brassicaceae family and also known as field mustard. The Brassicacea plant family is a very rich source of many important biodiesel feedstock. *Brassica alba* L., *Camelina sativa* L., *B. carinata* L., *B. napus* L., *Paphanus sativus* L. oils are some recently reported potential feedstock of this plant family. Among them Canola or Rapseed (*Brassica napus* L.) has gained widespread acceptance as a common commodity feedstock for biodiesel production (Jham et al., 2009).

Wild mustard (*Brassica juncea* L.) have high yield potential for producing biodiesel, especially when cultivated in humid, dry and hot weathers like Bangladesh, India and Pakistan (M. Bannikov, 2011). Morphologically wild mustard has been identified as *Sinapsis arvensis* L. Intensive research is going on currently to improve its productivity. Besides commercial cultivation, mustard plant also abundantly grows in orchard, plantation crops, waste lands and along roadside. Canada is a major producer of winter mustard and winter canola. Winter mustard is also cultivated in northern latitudes of United States such as Washington, North Dakota, Idaho and Montana. Recently, in Australia, Indian mustard (*B. juncea* L.) has been introduced as a short season oil seed crop in the cropping regions where rainfall is low (Gunasekera et al., 2006).

Mustard seed plant is an annual herbaceous plant and can grow from two to eight feet tall with small yellow flowers as shown in Figure 2.4 (Jham et al., 2009). Each flower has four petals up to 1/3 inch across and green leaves are covered in small hairs. These yellow flowers produce hairy seed pods. Each pod contains around a half dozen seeds. Just before these pods become ripe and bursting, seeds are harvested. Seeds are hard round and usually around 1 to 1.5 millimetres in diameter with a colour ranging from yellow to light brown. Oil is extracted by pressing these seeds and a crop yield of around 1200 kg/hectare (500 kg/acre) is a realistic harvest in Finland. Around 300 litres of mustard oil can be obtained from 1200 kg of seed (Niemi et al., 2002). The energy content of oil is four times the energy consumed to produce oil which means production to fuel energy ratio is 4.0. Zheljazkov et al. (2012) found mustard oil yields would provide 590-875 kg biodiesel oil per ha. As the cost of pressing device in oil production is very low mustard seed oil can be produced at a cost comparable with untaxed diesel fuel and appears to be an economically acceptable feedstock for biodiesel production (Niemi & Illikainen, 1997).

Figure 2.4: Mustard plant and seed

2.5 Mustard oil performance

Biodiesel produced from mustard oil through trans-esterification can be successfully used in diesel engine but optimum performance might be deviated slightly (M. Bannikov, 2011; Hasib et al., 2011; Rattan & Kumar, 2012). In practical case a farmer of south western Finland operated his tractor engine with his own non-esterified cold pressed mustard seed oil for more than eight years which inspired Niemi et al. (2002) to conduct in depth research on emission and performance on a intercooled, turbo charged, direct injection tractor diesel engine. Experiments showed break thermal efficiency (BTE) of mustard seed oil (MSO) is very similar to diesel fuel. At 1800 rpm same 42% BTE was obtained and at highest speed slightly lower BTE was obtained compared to OD fuel. Overall efficiency did not varied more than 2.5% compared to diesel fuel. BMEP of mustard seed oil was 11.9 bar and for diesel oil it was 11.5 bar while running at full load condition (Niemi & Hatonen, 1998; Niemi et al., 1997). Different injection timing also brought no significant change in the performance. Heat release rate and intake pressure were also similar but faster burning occurred. Almost same break torque was obtained by advancing injection timing 17° and 19° and highest BMEP value was 11.4 bar (Niemi & Illikainen, 1997). Anbumani and Singh (2006) experimented with different blending ratios of mustard and neem biodiesel in C.I. engine and found mustard oil at 20% blend performs best among them. Basically mustard oil was used in esterified butyl ester form and its 20% blend with diesel satisfies ASTM standard properties for biodiesel. Specific fuel consumption was slightly decreased (0.135 to 0.045 KJ/KW-hr) due to better fuel combustion. Break thermal efficiency (BTE) showed increasing trend up to 16 kg load level and started to decrease beyond that level. Rattan and Kumar (2012) experimented with 20, 30 and 50% mustard oil blended with diesel and found BSFC is inversely proportional to load. By studying lub oil temperature they suggested SAE-30 lubricant is suitable. Specific fuel consumption increases with the percentage increase of mustard oil blends. Azad et al. (2012) and Hasib et al. (2011) had similar findings regarding BSFC. From graphical representation they clearly showed that crude bio-fuel blends results lower BSFC than trans-esterified one and BSFC is inversely proportional to thermal efficiency. Regarding overall thermal efficiency, 20% mustard oil blend and regarding maximum thermal efficiency, 30% mustard oil blend performed best. Bannikov (2011) conducted his research on a direct injection diesel engine using mustard methyl ester as fuel and calculated 15% increase of BSFC and 3% reduction of brake fuel conversion efficiency compared to diesel fuel while mechanical efficiency was unchanged. Hasib et al. (2011) concluded hat poor atomization and lower heating value than diesel fuel are responsible for high BSFC and low BTE of mustard oil than diesel fuel.

2.6 Mustard oil emission

Banikov (2011) reported EGT of diesel engine remains unchanged using mustard methyl ester. Hasib et al. (2011) found different findings regarding EGT. Among different mustard oil blends they found that except 30% and 40% blends, all others result higher EGT than diesel fuel. But 30% and 40% both blends showed lower EGT than diesel fuel at higher load condition.

Regarding smoke content mustard oil is favourable over diesel fuel (Niemi et al., 1997). Smoke varied from 0.2 to 2.4 Bosch number for mustard oil and varied 1.3-3.7 Bosch number for diesel fuel. High oxygen content is responsible for this reduced smoke generation. According to Anbumani et al. (2006) smoke intensity showed no significant variation, however 20% mustard oil blend resulted less smoke intensity compared to other blends. About 40% decrease of exhaust opacity than diesel fuel was reported by

Bannikov (2011) at all loads using mustard methyl ester and same exhaust opacity for both mustard and OD fuel at rated speed.

According to Niemi et al. (1997) at high load range MSO produced less CO but at low load range produced more CO than diesel fuel. Similar results were achieved in their previous tests (Niemi & Illikainen, 1997; Niemi et al., 2002). When the engine is in idling condition, MSO emitted 550 ppm and diesel oil emitted 300 ppm of CO. Engine complied ISO 8178-4/C1 standard for CO emission limit successfully (Niemi & Hatonen, 1998). Some contradictory result was found by Bannikov that CO was increased by 25% at full load condition than OD fuel (M. Bannikov, 2011; M. G. Bannikov & Vasilev, 2012). Thus, regarding CO emission diesel oil is favourable at low load and vegetable oil is favourable at high load condition (Kampmann, 1993).

Bannikov (2011) found slight variation in overall hydrocarbon emission compared to diesel fuel, using mustard methyl ester. Some researchers found HC emission was low in case of mustard seed oil compared to diesel fuel but no strong conclusion can be made from this finding. Thus Niemi et al. (1997) measured several hydrocarbon components separately by using FT-IR. Acetylene contents were varied from 1 to 4 ppm and benzene contents were varied from 0 to 1.8 ppm during retarded ignition timing. Even at idling condition only 0.9 ppm aromatic HC was recorded at its highest level. Aldehyde contents were higher in case of mustard seed oil than diesel. Some indication suggested ignition timing retardation may reduce alcohol emission but overall alcohol emission of mustard oil was slightly higher than that of diesel fuel. For both diesel and mustard seed oil only a very small amount of methane was found which remained constant against load. FT-IR results higher methane emission than gas chromatography analysis (Lappi & Rihko, 1996). Irregular olefin emission was found in case of mustard oil and no olefins were found in the exhaust while using diesel. Thus, Niemi et al. (1997) summarised that aldehydes, aromatics, acetylene, alcohols and non-methane paraffins were lower and olefins emission was higher with mustard seed oil than diesel fuel. Non-methane paraffins emission also resulted no significant comparative change, 0.74 ppm was the highest amount recorded (Niemi & Hatonen, 1998). Bannikov (2011) found slight overall hydrocarbon variation using mustard methyl ester compared to diesel fuel.

Experiments performed by Niemi et al. (2002) showed reduction of NO_x emission at all loads by using MSO and which is also supported by Bannikov (2011). Retardation of injection timing reduced it further. At high load range MSO and diesel fuel both produces almost same amount of NO_x. At middle load range amount of NO_x was considerably low and at low speed range it was remarkably low in case of MSO than diesel fuel. At idling condition, wet exhaust NO_x content was 360 ppm for diesel fuel whereas it was 160 ppm for MSO. Bannikov (2011) also supported that NOx emission decreased at all loads compared to diesel fuel while running the engine with mustard methyl ester. So if NO_x emission is considered mustard seed oil is superior than diesel fuel (Niemi & Hatonen, 1998).

After 154 hours of operation performed by Niemi et al. (1998) it can be said that combustion and mixture formation of mustard seed oil were satisfactory as NO_x , smoke and CO emission were low. But it is not a good burning fuel at very low idling condition. Results of these studies of using mustard seed oil differs from those reported in Çelikten et al., (2012). Çelikten et al., (2012) conducted research on rapeseed oil, another plant of Brassica family, found more CO, NO_x, CO_2 emission than diesel fuel which may strengthen the appropriateness of using mustard oil as biofuel.

2.7 Potentiality of *Calophyllum inophyllum*

Calophyllum inophyllum L. belongs to the Clusiaceae (formerly Guttiferae) plant family and found in shorelines and warm coastal areas across the Pacific and Indian oceans (Okano D. Friday JB, 2006.). Scientific name *Calophyllum* is a Greek word means "beautiful leaf" and *inophyllum* refers to the straight lines made by the veins in the leaves. *Calophyllum inophyllum* is native to tropical shorelines across Indian and pacific oceans, from Madagascar to Tahiti and Marquesas island. It was first found in Northern Marianas Island at north and the Ryukyu islands in southern Japan at south and westward throughout Polynesia (Okano D. Friday JB, 2006). Different vernacular names of *Calophyllum inophyllum* in various countries of the world are shown in Table 2.1.

Calophyllum inophyllum is a large tree, usually grows 12-20 m, (40-65 ft) in height. Open grown trees can become wider than height, often leaning with broad and spreading crowns. The bark is grey with flat ridges and sap is milky white and sticky. *Calophyllum inophyllum* leaves are glossy and heavy, oval shaped with rounded tips. Leaves are 10-20 cm (4-8 in) long and 6-9 cm (2.4-3.6 inch) wide. Young leaves are light green and old leaves are dark green in colour. *Calophyllum inophyllum* flowers are white with yellow stamens, blooms on long stalks in leaf axils. Around 4-15 flowers are borne in a cluster. Young fruits are like round green balls and around 2-5 cm (0.8-2 inch) in diameter. Matured fruits are yellow in colour and wrinkled when ripe. A single seed kernel is surrounded by a thin inner layer and this layer is surrounded by a hard shell as shown in Figure 2.5.

Kernels of *Calophyllum inophyllum* have a very high oil content (75%) and most of them (71%) are unsaturated oleic and linoleic acid (Said T, 2007;30(3–4):203–10.). Physicochemical properties and fatty acid composition of *Calophyllum inophyllum* is given in Table 1 and Table 3. Fruits are usually borne twice a year, in April-June and again in October-December. Once grown, a *Calophyllum inophyllum* tree produces up to 100 kg fruits and about 18 kg oil. There are about 100-200 fruits/kg in shell with the skin and pulp removed (Dweck AC, 2002; 24:1–8).

Table 2.1: Dialectal names of *Calophyllum inophyllum* in different regions of the world (Okano D. Friday JB, 2006; "Institute for Medical Research. *Calophyllum inophyllum* L.;," 2010; Porcher Michel, 2005)

Country	**Common names**
Bangladesh	Punnang
Cook Island	Tamanu
Cambodia	Kchyong, Khtung.
English	Beach mahogany, Alexandrian laurel, Beauty leaf, Ball nut.
Fiji	Dilo
Guam	Da'ok, Da'og
Hawaii	Kamanu, Kamani
India	Poon, Polanga, Undi, Sultan champa.
Indonesia	Bintangur, Nyamplung
Kiribati	Te itai
Malaysia	Bintangor, Penang laut
Marquesas	Tamanu
Myanmar	Ponnyet
Northern Marianas	Da'ok, Da'og
Nauru	Tomano
Palau	Btaches
Papua New Guinea	Beach calophyllum
Philippines	Bitaog, Butalau, Palo maria
Solomon Islands	Dalo
Society Islands	Tamanu
Tahiti	Tamanu
Thailand	Naowakan, Krathing, Saraphee

Figure 2.5: *Calophyllum inophyllum* plant and seed (Okano D. Friday JB, 2006.)

2.8 *Callophyllum inophyllum* oil performance

Sahoo et al. (2009) evaluated performance of neat 100% (CB100), 50% (CB50) and 20% (CB20) *Calophyllum inophyllum* biodiesel blends in a CI tractor engine. All important performance parameters were evaluated and compared with diesel fuel and different blends of Jatropha and Karanja biodiesels. For CB20 and CB50, fuel economy was improved compared to diesel fuel. On an average, measured fuel economy for CB20, CB50 and CB100 was 180.55, 181.15 and 189.97 gms/BHP-hr respectively at rated speed. At low speed range of 1200 to 1400 rpm no significant change in power was observed using biodiesel blends but a slight power reduction was obtained for CB20 and CB100. Power was decreased by 1.93% compared to diesel fuel for CB20 over the entire speed range. In case of CB50 an improvement in power from 0.19% to 0.88% was obtained. But no such trend of power variation was found for CB100. Brake specific energy consumption (BSEC) decreased with the increase of blending percentage and BSEC increased with the speed. BSEC was deteriorated for all biodiesels but among karanja, jatropha and *Calophyllum inophyllum* blends, CB20 was suggested to be the best one as BSEC deterioration was minimum (2.59%). CB20 was recommended as the optimum fuel blend.

Belagur and Reddy (2010) operated a DI diesel engine with neat diesel and a 50% blend of *Calophyllum inophyllum* with 50% diesel fuel. Rate of injection and ignition delay was controlled by changing plunger diameter (PD). Higher BTE was resulted from the dominance of premixed combustion phase assisted by the increase of injection rate as well as PD. BTE were plotted with respect to load for various PD. Considering obtained BTE, 8 mm and 9 mm PD were found to be the best for OD fuel and *Calophyllum* blends respectively.

Venkanna & Reddy (2011) investigated a DI diesel engine fueled with *Calophyllum inophyllum* oil methyl ester (COME) and OD fuel at various injector opening pressure (IOP) ranged from 200 to 260 bar. It was observed from the graph that the BSFC of COME decreased as IOP increased. BTE was increased gradually with the increase of load. BSFC was slightly higher and BTE was slightly lower than OD fuel using COME. At 25% load, decrease in BTE was 7.67% and increase in BSFC was 20.73%, at 50% load, decrease in BTE was 5.56% and increase in BSFC was 17.92%, at 75% load decrease in BTE was 1.94% and increase in BSFC was 13.54%, and at 100% load, decrease in BTE was 4.11% and increase in BSFC was 16.18% using COME compared to OD fuel. Best performances for COME regarding BSFC were found at 75% and 100% loads with IOP 260 bar.

Bora et al. (2012) investigated performance and emission of a CI engine with neat Calophyllum inophyllum (CB), koroch and jatropha biofuel and compared with biodiesel obtained from mixing of these feed stocks (BOMF). BSFC showed a decreasing trend with increasing load and BSFC of CB was found 2.06% higher than BOMF. Thermal efficiency of CB was 2.2% higher than karanja biodiesel and 0.61% lower than BOMF. In another set of experiments, Bora et al. (2008) used a mixture of *Calophyllum inophyllum*, karanja and jatropha oil with OD fuel and measured performance and emissions of a diesel engine. BSFC and thermal efficiency decreased slightly than OD fuel at all loads for biodiesel. Due to lower heating value of biodiesel, higher blending was needed to produce same amount of energy compared to OD fuel.

Mohanty et al. (2011) blended 10% (CD10), 30% (CD30) and 50% (CD50) *Calophyllum inophyllum* oil with diesel fuel on a volumetric basis to run a diesel engine and investigated combustion, performance and emission. At fully loaded condition experiments showed 28.96%, 28.73% and 28.28% BTE for CD10, CD30 and CD50 biodiesel blends respectively while it was 28.6% for OD fuel. As fuel consumption for blends of two different fuels having different heating values are not reliable enough, BSEC was measured instead of measuring BSFC. Variation of BSEC with load showed less BSEC requirement for CD10 and CD30 biodiesel blends compared to OD fuel.

2.9 *Callophyllum inophyllum* oil emission

EGT of *Calophyllum inophyllum* biodiesel blends are found very similar and sometimes slightly higher compared to diesel fuel found by many researchers. Mohanty et al. (2011) found EGT rises from 160°C to 380°C at no load and full load condition respectively for CD50 and EGT rises from 140°C to 300°C at no load and full load condition respectively for CD30. These values of EGT are slightly higher than that of OD fuel. Experiments of Belagur and Reddy (2010) showed EGT using 50% *Calophyllum* biodiesel blend were almost same for all PD and were higher than diesel fuel. As almost same amount of fuel was consumed per hour Bora et al. (2008) found similar EGT for mixed *Calophyllum inophyllum* biodiesel and diesel fuel and EGT increased with increasing load.

Sahoo et al. (2009) found smoke opacity of CB20, CB50 and CB100 at full throttle position were 29.22%, 44.15% and 69.48% less than diesel fuel respectively at rated speed and comparatively these values were even less than karanja and jatropha biodiesel blends. At part throttle position and rated speed smoke emission for CB20 CB50 and CB100 were 1.19, 1.04 and 1.32 Bosch respectively and amount of smoke emission for CB100 was 1/9th of that of OD fuel. Variation of smoke opacity at different loads and different plunger diameter were shown in figure. Venkanna and Reddy (2011) reported 11%-20% reduction of smoke opacity compared to DF by using COME at light load operation. At medium and high load, smoke opacity increased rapidly for COME but in fact remains lower than OD fuel. Smoke emissions of *Calophyllum* biodiesel blend were found less than diesel fuel in all cases and least value was corresponding to 10 mm PD (Belagur & Reddy PhD, 2010).

Experiments of Venkanna and Reddy (2011) revealed lower CO and HC emission than OD fuel while using COME and this scenario was improved more when blended biodiesel was used. Better combustion was obtained at higher injection rate which leads to higher injection pressure and satisfactory spray formation, hence reducing CO and HC emission. Graphical representation of CO and HC versus load showed that CO emission using COME remains almost invariable throughout the entire load range, while it gets towards more danger region in case of OD fuel. A general tendency of increasing HC with increasing load for all fuels was clearly evident from the graph. Injector opening pressure also influenced these emission characteristics and it was quite difficult to sort out reliable mutual dependency and further research is needed. Therefore, CO and HC emission were lower for 10 mm than 8mm PD using 50% *Calophyllum* biodiesel blend. Bora et al. (2008) also reported similar findings regarding CO and HC reduction when *Calophyllum* oil is used with other mixed non-edible oils. CO emission not always reduced using *Calophyllum inophyllum* biodiesels and sometimes, it shows dependency on blending ratios. Experiments performed by Sahoo et al. (2009) showed 1.75, 1.32 and 1.12 gm/kwh of cumulative CO emission for CB20, CB50 and CB100 respectively. In percentage, CO emission was -12.96%, 34.24% and 2.59% more compared to OD fuel CO emission for CB100, CB20 and CB50 respectively compared to OD fuel. Graphical comparison of different biodiesel blends and DF revealed CB100 as the optimum fuel regarding CO emission. Regarding HC emission again *Calophyllum* biodiesel stands as the better solution than OD fuel and other biodiesel blends. Total HC reduction for CB20, CB50 and CB100 were 6.84%, 2.73% and 6.75% respectively compared to OD fuel. Therefore, CB20 was the optimized solution according to experimental results. Sometimes using *Calophyllum inophyllum* biodiesel emits more CO and HC emission than diesel fuel. Experiments of Mohanty et al. (2011) showed CO emission for OD fuel was less than CD10, CD30 and

CD50 which was an indication of incomplete combustion using biodiesel. Regarding HC emission, 3-5 ppm lesser HC emission was found by DF than *Calophyllum* inophyllum blends. Among CD10, CD30 and CD50 blends, CD30 resulted in more complete combustion and less HC emission than OD fuel.

NO_x emission increases with the increase of temperature and pressure inside the cylinder which depends on PD and other operating conditions. Belagur and Reddy (2010) showed NO_x emission increases with the increase of PD and highest amount was obtained at 10 mm PD using 50% blend of *Calophyllum* biodiesel. OD fuel and *Calophyllum* blend were tested under same operating conditions and PD and enormous amount of NO_x was produced by OD fuel in comparison with biodiesel blends. However, experiments of Sahoo et al. (2009) revealed 14.87%, 17.31% and 22.5% increase in NO_x emission for CB20, CB50 and CB100 biodiesels respectively compared to OD fuel. Investigations of Bora et al. (2012) revealed that amount of NO_x increases with increasing the percentage of *Calophyllum* oil in the blend. NO_x emission from 20% blend was nearly same with OD fuel and NO_x emission showed decreasing trend with increasing BMEP. Some exceptional results were found by Mohanty et al. (2011) where NO_x emission was lower than OD fuel using CD10, and CD50 except for CD30. According to them, higher cetane number and lower heating value of CD10 and CD50 contributed to lower NO_x emission.

2.10 Summary and analysis of biofuels emission and performance reviewed

Table 2.2: Research findings of different performance parameters for palm, mustard and *Calophyllum inophyllum* biofuel

Performance parameter	Palm oil	Mustard oil	*Calophyllum inophyllum*
BSFC increase	Blended: Lin et al. (2006), Preheated: de Almeida et al. (2002), Blended: Yusaf et al. (2011), Blended: Ndayishimiye and Tazerout (2011), Degummed deacidified crude: Leevijit and Prateepchaikul (2011), Methyl and ethyl ester of palm oil: Ndayishimiye and Tazerout (2011)	Methyl ester: Bannikov (2012), Rattan and Kumar (2012), Blended: Hasib et al. (2011), Blended: Azad et al. (2012).	Methyl Ester: Venkanna and Reddy (2010), Mixed: Bora et al. (2008).
BSFC decrease		Blended: Anubumani and Singh (2006).	
BTE increase	Preheated: de Almeida et al. (2002), Blended: Ndayishimiye and Tazerout (2011).	Blended: Anubumani and Singh (2006).	Blended: Mohanty et al. (2011).
BTE decrease	Degummed deacidified crude: Leevijit and Prateepchaikul (2011), Methyl and ethyl ester of palm oil: Ndayishimiye and Tazerout (2011).	Crude: Niemi et al. (1997), Crude: Niemi et al. (1998), Crude: Niemi et al. (2002), Blended: Hasib et al. (2011). Crude: Niemi et al. (1997), Blended: Azad et al. (2012).	Blended: Belagur and Reddy (2010), Mixed: Bora et al. (2008).
Brake Power increase	Methyl ester of palm oil: Ozesezen and Canakci (2011), Blended with additive: Kalam and Masjuki (2002).		
Brake Power decrease	Blended: Yusaf et al. (2011).		Blended: Sahoo et al. (2009).

Table 2.3: Research findings of different emission constituents for palm, mustard and *Calophyllum inophyllum* biofuel

Emissions	Palm oil	Mustard Oil	*Calophyllum inophyllum*
EGT increase	Preheated: de Almeida et al. (2002), Preheated: Ndayishimiye and Tazerout (2011), Kumar et al. (2006), Blended: Yusaf et al. (2011), Methyl and ethyl ester of palm oil: Ndayishimiye and Tazerout (2011).	Blended: Hasib et al. (2011)	Blended: Mohanty et al. (2011), Blended: Belagur and Reddy (2010).
EGT decrease	Degummed deacidified crude: Leevijit and Prateepchaikul (2011), Blended: Ndayishimiye and Tazerout (2011).		Mixed: Bora et al. (2008).
Smoke opacity increase			Blended: Belagur and Reddy (2010).
Smoke opacity decrease	Degummed deacidified crude: Leevijit and Prateepchaikul (2011), Methyl ester of palm oil: Ozesezen and Canakci (2011).	Crude: Niemi et al. (1997), Crude: Niemi et al. (2002), Crude: Niemi et al. (1997).	Methyl Ester: Venkanna and Reddy (2011), Blended: Sahoo et al. (2009), Mixed: Bora et al. (2008).
CO increase	Preheated: de Almeida et al (2002), Blended: Yusaf et al. (2011), Methyl and ethyl ester of palm oil: Ndayishimiye and Tazerout (2011) Blended: Ndayishimiye and Tazerout (2011) Preheated: Ndayishimiye and	Crude: Niemi et al. (1997) Crude: Niemi et al. (2002) Methyl ester: Bannikov (2012) Crude: Niemi et al. (1998)	Blended: Mohanty et al. (2011), Blended: Belagur and Reddy (2010), Blended: Sahoo et al. (2009).

	Tazerout(2011)		
CO decrease	Degummed deacidified crude : Leevijit and Prateepchaikul (2011) Blended with additive: Kalam and Masjuki (2002) Methyl ester of palm oil: Ozesezen and Canakci (2011) Preheated Crude: Kalam and Masjuki(2004)		Methyl Ester: Venkanna and Reddy (2011), Mixed: Bora et al. (2008).
HC increase	Preheated: de Almeida et al (2002), Blended: Ndayishimiye and Tazerout (2011).	Methyl ester: Bannikov (2012).	Blended: Mohanty et al. (2011), Blended: Belagur and Reddy (2010), Methyl Ester: Venkanna and Reddy (2011).
HC decrease	Methyl and Ethyl ester: Ndayishimiye and Tazerout (2011), Preheated: Ndayishimiye and Tazerout (2011), Blended with additive: Kalam and Masjuki (2002), Methyl ester of palm oil: Ozesezen and Canakci (2011), Preheated Crude: Kalam and Masjuki (2004).	Crude: Niemi et al (1997), Crude: Niemi et al (2002).	Blended: Sahoo et al. (2009), Mixed: Bora et al. (2008).
NO_x increase	Degummed deacidified crude : Leevijit and Prateepchaikul (2011), Preheated Crude: Kalam and Masjuki (2004), Blended: Ndayishimiye and Tazerout (2011),		Blended: Belagur and Reddy (2010) Blended: Sahoo et al. (2009) Mixed: Bora et al. (2008)

	Methyl ester of palm oil: Ozesezen and Canakci (2011).		
NO_x decrease	Blended: Yusaf et al. (2011), Preheated: de Almeida et al. (2002), Blended with additive: Kalam and Masjuki (2002), Methyl and ethyl ester of palm oil: Ndayishimiye and Tazerout (2011), Emulsified: Kalam and masjuki (2004).	Crude: Niemi et al. (2002), Crude: Niemi et al. (1997). Methyl ester: Bannikov (2012), Crude: Niemi et al.(1998), Crude: Niemi et al. (1997).	Blended: Mohanty et al. (2011), Methyl Ester: Venkanna and Reddy (2011).
CO_2 increase	Preheated: de Almeida et al. (2002).		
CO_2 decrease	Methyl ester of palm oil: Ozesezen and Canakci (2011).		
PM increase	Emulsified: Kalam and masjuki (2004).	Crude: Niemi et al. (2002).	
PM decrease	Preheated Crude: Kalam and Masjuki (2004), Blended: Lin et al. (2006).		
PAH increase			
PAH decrease	Blended: Lin et al. (2006)		

2.11 Analysis of engine performance for biodiesel

2.11.1 Brake specific fuel consumption

BSFC refers to consumption of fuel per unit power and in a unit time. Generally using biofuel results higher BSFC than that of diesel fuel. As biofuels have higher density and lower calorific value than diesel fuel, increase of BSFC is obvious (Leevijit & Prateepchaikul, 2011; Ndayishimiye & Tazerout, 2011; Utlu & Koçak, 2008). Injection pressure and atomization rate also have some effects on BSFC. Most of the papers reviewed here reported increase or closely similar BSFC of biofuels compared to OD fuel. But there were also some exceptions.

Anbumani and Singh (2006) found lower BSFC than OD fuel by running the engine with esterified blends of mustard oil. They explained this improvement was due to better combustion of high oxygen containing biodiesel and high cetane number of mustard oil than that of OD fuel.

2.11.2 Brake thermal efficiency

As biodiesels have lower calorific value than OD fuel and different biofuels have different calorific values and densities, comparing them in the basis of BSFC could be misleading. For this reason BTE can be considered instead of BSFC. Using biofuels resulted both increasing and decreasing phenomena regarding BTE. BTE was improved in cases where crude oils were used without blending and BTE deteriorated for trans-esterified blends. As crude oil provides higher lubricity, frictional loss is reduced and BTE increased. At partial and no load condition BTE was increased in most of the cases but a slight drop was observed at full load condition. Complete combustion due to high oxygen content and enough time available for combustion are responsible for high BTE than diesel fuel at partial and no load condition. But at full load, time taken for complete combustion is decreased, oxygen molecules get small time to change its state to atomic oxygen, hence BTE drops slightly (Anbumani & Singh, 2006; Bagby et al., 1987). Most reports showed very similar BTE of biodiesels compared to diesel fuel. BTE deteriorated in some experiments and in such cases, higher viscosity and lower cetane index are responsible for poor thermal performance (Enweremadu & Rutto, 2010).

2.11.3 Brake effective power

Most of the research papers reviewed here, reported slight brake power reduction compared to OD fuel, with the increase of biofuel percentage in the blends. Many authors mentioned lower heating values of biofuels and their blends are responsible for this phenomenon. However, other physicochemical properties of biodiesel like higher density, viscosity etc. result poor atomization and problems in fuel flow. These are also some justified causes of low power output reported by some researchers. To maintain the same power as obtained by OD fuel BSFC will be higher for the biofuels (Enweremadu & Rutto, 2010; Kalam et al., 2011).

Some literature reviewed surprisingly found increase in brake power especially in case of palm biodiesel which may be explained due to higher cetane number and improved combustion. Improved combustion may be resulted due to high oxygen content of biodiesels than diesel fuel. Higher flow rate and energy input increases brake power at low speed range (Yusaf et al., 2011). Using corrosion inhibitor increases brake power effectively (M. A. Kalam & H. H. Masjuki, 2002).

2.12 Analysis of engine emission for biodiesel

2.12.1 Exhaust gas temperature

Effective use of heat energy contained in the fuel is indicated by EGT. Emission characteristics of biodiesels discussed above show a wide range of reports regarding EGT. Lower value of EGT is an indication of good burning of fuel inside the engine cylinder. To get same output of energy by biofuels as it is obtained by OD fuel, BSFC is to be increased but it does not cause the engine to get thermally overloaded as EGT remains lower for biofuel. Heating value, cetane number, density and kinematic viscosity these four physiochemical properties also have potential impact on EGT. As all discussed biodiesels have higher cetane number and lower heating value than diesel fuel, ignition delay occurred which results lower EGT. Higher density and kinematic viscosity of biodiesel causes poor fuel atomization and leads to EGT reduction (Enweremadu & Rutto, 2010).

In most literatures reviewed EGT increased at full load condition. Causes behind this phenomenon perhaps, high oxygen content and more fuel burning at higher load condition resulted in improved combustion, hence increased EGT. Due to longer physical delay of biofuels some fuel particles do not get enough time to be burnt completely initially after injection and get burnt at later part of expansion. As a result, afterburning occurs which leads to high EGT (De Almeida et al., 2002).

2.12.2 Smoke opacity and particulate matter

Soot, heavy hydrocarbons and sulphates these three are main components of PM. Typically 40-80% mass of PM is soot. Increasing percentage of water in the biodiesel results incomplete combustion. Incomplete combustion results increase in organic compounds in the exhaust finally increases PM emission. On contrary preheated biodiesel ensures better combustion and less PM in the exhaust (Kalam & Masjuki, 2004).

Most of the researchers reported noticeable decrease in smoke opacity and PM emission at high load operation using biofuels. High load operation results diffusion combustion which influences the formation of PM. High oxygen content of biofuel aids to overcome this effect by oxidizing most of the soot particles and reducing smoke opacity and PM emission (Enweremadu & Rutto, 2010).

Amount of air inside the cylinder, fuel composition and oxygen content are the main factors that influence smoke opacity. Lapuerta et al. (2008) explored the effect of alcohol in smoke opacity and found significant difference between the smoke opacity of used cooking oil ethyl and methyl ester.

No clear conclusion can be made about whether smoke opacity and PM emissions depend on the types of biodiesel feedstock or not. WCO and soybean oil were tested on similar engines by Canakci and Gerpen (2003) and no significant variation in PM emission observed. Oxygen content is the main factor which effects PM emission and this property remains almost same for all biodiesels.

2.12.3 Carbon monoxide (CO)

Incomplete combustion occurs when flame temperature cools down and progression to CO_2 remains incomplete. When flame front approaches to relatively cool cylinder liner and in crevice volume, combustion process is slowed down and flame front is extinguished. If the air fuel mixture is too rich amount of oxygen becomes insufficient for complete combustion.

Most of the literatures, reviewed in this paper showed a decrease in CO emission while diesel fuel is replaced by different biofuels. However a few researchers found similar trend and some also reported noticeable increase in CO emission by using biodiesel compared to diesel fuel. Crude biodiesel produces less CO than the blended one. Emulsified fuel also produces higher CO and amount increases with the increase of water percentage. Addition of water results incomplete combustion hence increases CO (Kalam & Masjuki, 2004). Advancing injection timing also increases CO (Carraretto et al., 2004).

Different characteristics of biofuels have important impact on CO emission. Increase in saturation level decreases CO emission (M. Graboski et al., 2003). CO emission increases with increasing the percentage of acid values in the biodiesel. Higher acid value refers to higher hydroperoxide concentration which leads to CHO, HCHO and CO formation (Hamasaki K, 2001.).

Many experimental results showed less CO emission by using biodiesel than diesel fuel which indicates complete combustion of biofuel than OD fuel (D.K. Bora et al., 2008; Leevijit & Prateepchaikul, 2011; A.N. Ozsezen & Canakci, 2010). Explanation of this finding is additional oxygen content of biodiesel which ensures complete combustion of the fuel. Higher cetane number and lower compressibility of biodiesel compared to diesel fuel reduce the probability of advanced injection and forming fuel rich zone. As a result ignition delay becomes shorter, duration of combustion process increases and combustion gets completed properly.

2.12.4 Hydrocarbon (HC)

Hydrocarbons present in the emission are either partially burned or completely unburned. Generally a sharp decrease in the trend of HC emission is observed while running the engine with biofuel. However, HC emission is not influenced by types of feedstock which was reported by Canakci and Van Gerpen (2003). They revealed Ethyl ester of crude oil produced less HC than methyl ester which can be explained by lower heat of vaporization of ethyl esters.

Similar to CO emission, HC emission is also resulted from incomplete combustion due to flame quenching at cylinder lining and crevice region. Engines operating conditions, fuel spray formation, fuel properties etc. are some other important HC emission influencing conditions. The more the blending percentage, cetane number and oxygen content of the biodiesel increases, hence leads to more complete combustion and increases combustion efficiency. Higher combustion efficiency reduces unburned HC emission. At higher engine speed, as injection pressure is higher and atomization ratio is also increased, HC emission shows similar trend regardless of the fuel type. Enhanced air flow inside engine cylinder at high speed range helps to create more homogeneous mixture and reduces HC emission.

2.12.5 Nitrogen oxides (NO_x)

Generally NO_x emission is influenced by in cylinder pressure, temperature and oxygen content of fuel. A slight increase in NO_x emission was found in most of the literature reviewed. Some mentioned increase in NO_x emission under certain test and operating conditions. Mustard oil is an exception in this case, as almost all researchers reported NO_x decreasing characteristics of mustard oil at all load and test conditions compared to diesel fuel.

Various reasons are mentioned for the increase of NO_x emission while using biofuels and their blends. Due to their chemical structure all biofuel contain invariably some level of excessive oxygen compared to OD fuel. In addition to inducted air inside the engine cylinder, oxygenated biofuels add some more oxygen which may influence the formation of NO_x. Higher combustion temperature increases NO_x by stimulating NO_x forming reactions. Improved combustion is resulted due to lower ignition delay and enhanced fuel- air mixing at higher engine speed, which contributes to high in cylinder temperature.

NO_x emission increases with the decrease of mean carbon chain length and increase in unsaturation hence increase in iodine number. Density, compressibility, cetane number and unsaturation these properties are closely related to iodine value. NO_x emission is directly related to degree of molecular saturation (Assessment and Standards Division (Office of Transportation and Air Quality of he US Environmental Protection Agency). Biofuels having more unsaturated bonds produce more NO_x than saturated biodiesels. In fact unsaturated bonds are more reactive and start combustion reactions more readily.

Yusaf et al. (2011) found NO_x was decreased at low engine speed than OD fuel by using palm biodiesel. At low engine speed due to oxygen deficiency and lower heat release rate, biodiesel produces lower level of NO_x. Adding fuel additives with biodiesel limits the formulation of ions which catalyses the oxidation process. This effect contributes to the lower heat release rate at premixed combustion phase and lowers peak temperature of combustion process, hence reduces NO_x. Low sulphur and aromatics content of biofuels specially mustard oil, may influence low NO_x emission. Fuel spray characteristics like: degree of mixing, size and momentum of fuel droplets, penetration and evaporation rate etc. effect in the flame region which influences NO_x formation later on. As density and other physicochemical properties of biodiesels are different from general OD fuel, all these may bring about lower NO_x formation than OD fuel.

CHAPTER 3: METHODOLOGY

3.1 Production process of biodiesel

Crude oils were poured in a rotary evaporator and heated for 1hr at 95°C in order to eliminate moisture under vacuum condition. To produce biodiesel from crude vegetable oil, transesterification was performed by two steps: (1) Acid esterification and (2) base transesterification process. Methanol was used as solvent with sulphuric acid (H_2SO_4) for acid esterification and potassium hydroxide (KOH) for base transesterification respectively. Acid esterification is needed if the acid value of crude oil is higher than 4 mg KOH/gm. Acid value was calculated by doing titration. For *Calophyllum* oil both steps were needed as its acid value was high and for palm oil and mustard oil only base transesterification was needed.

Using acid catalyst, the first step reduced the free fatty acids (FFA) level of crude vegetable oil up to 1-2%. A favorit jacket reactor of 1 litre capacity was used with IKA Eurostar digital model stirrer and Wiscircu water bath arrangement. One litre of crude vegetable oil with 200 ml methanol and 0.5% v/v sulphuric acid were taken in the flask for acid catalysed esterification. The mixture was constantly stirred at 700 rpm and a temperature range of 50-60°C was maintained at atmospheric pressure by circulating hot water through the jacket. To determine the FFA level, 5 ml sample was taken from the flask at every 10 minutes interval and esterification process was carried out until FFA level was reduced up to 1-2%. After completing the acid esterification process the product is poured into a separating funnel where sulphuric acid and excess alcohol with impurities were moved to the top. Top layer was separated and lower layer was collected for base transesterifiacation.

Same experimental setup was used for alkaline catalysed transesterification process. Meanwhile, 1% w/w of KOH (base catalyst) dissolved in 25% v/v of methanol was poured in the flux. Then the mixture was stirred at same speed and temperature was maintained at 70°C. The mixture was heated and stirred for 3 h and again poured into a separating funnel where it formed two layers. Lower layer contained glycerol and impurities and upper layer was methyl ester of vegetable oil. Lower layer was discarded and yellow upper layer was washed with hot distilled water (100% v/v) and stirred gently to remove remaining impurities and glycerol. Biodiesel was then taken in a IKA RV10 rotary evaporator to reduce the moisture content. Finally, moisture was absorbed by using sodium sulphate and final product was collected after filtration.

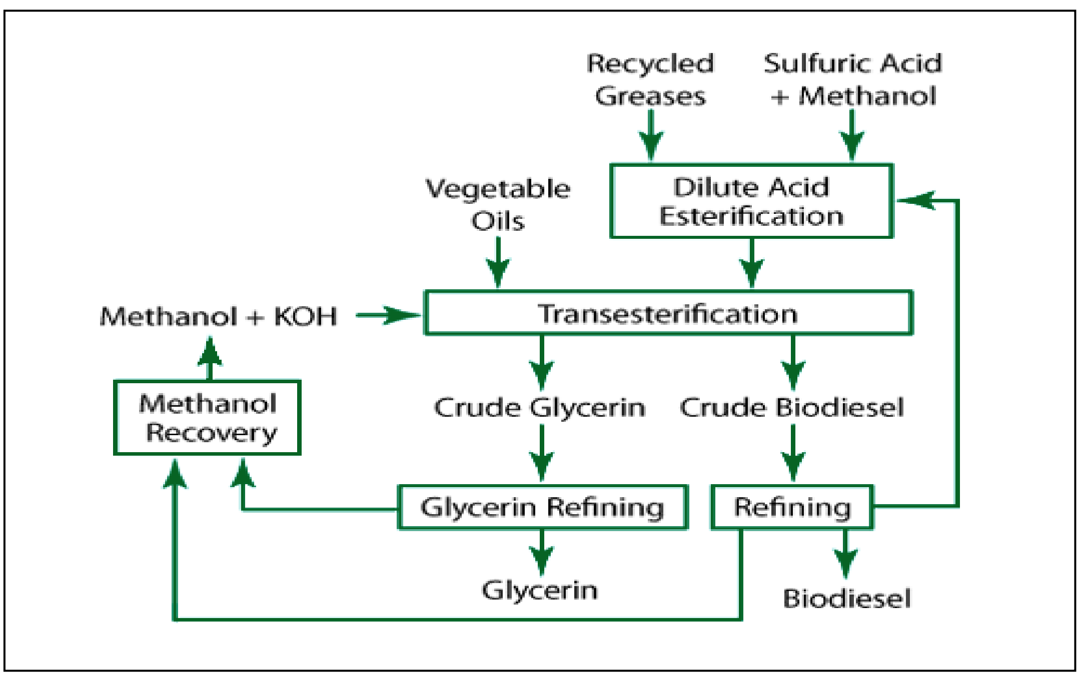


Figure 3.1: Flowchart of biodiesel production process

3.2 Fatty acid composition

Different vegetable oils have different fatty acid compositions (FAC). FAC is unique for a particular species. Gas chromatography (GC) analysis (Agilent 6890 model) was used to get the FAC result. In this test 0.25g of each sample samples was diluted with 5ml n-heptane. The solution was then entered into GC. Table 3.1 shows the GC operating conditions.

Table 3.1: GC operating conditions

Property	Specifications
Carrier gas	Helium
Linear velocity	24.4 cm/sec
Flow rate	1.10 mL/min (column flow)
Detector temperature	260.0 °C
Column head pressure	56.9 kPa
Column dimension	BPX 70, 30.0 m x 0.25 µm x 0.32 mm ID
Injector	240.0 °C
Temperature	140.0 °C (hold for 2 minutes)
Temperature ramp	8°C/min 165.0 °C 8°C/min 192.0 °C 8°C/min 220.0 °C (hold for 5 minutes)

3.3 Experimental equipment and measuring methods

The quality of oil is expressed in terms of the fuel properties such as viscosity, density, calorific value, flash point, pour point, cloud point etc. The important physical and chemical properties of the crude oils and their methyl esters were tested according to ASTM D6751 standard.

3.3.1 Density and viscosity measurement

Density is defined as the ratio of mass to volume and viscosity is the measure of the flow resistance of a fluid. It provides an estimation of the time required for a given volume of fuel to flow through a calibrated glass capillary tube under gravity. In this study, an Anton Paar automatic viscometer (SVM 3000) was used to measure the dynamic viscosity (mPa.s) and density (kg/cm^3) of the fuel according to ASTM D7042. From this result, the viscometer automatically calculates the kinematic viscosity and delivers measurement results which are equivalent to ISO 3104 or ASTM D445. Biodiesel viscosity was measured at +40°C and 100°C. The viscosity index is an important value, especially in the automotive industry. The viscosity index is calculated from the kinematic viscosity at 40 °C and at 100 °C. The SVM 3000 covers the whole measuring range from less than 1 to 20,000 mm^2/s.

However, to calculate the kinematic viscosity from the dynamic viscosity, density result is required. For this reason, a density measuring cell in SVM 3000 has been given. Both cells are filled in one cycle and the measurements are carried simultaneously. However by using mode settings menu, selection of required standard test can be adapted from 10 predefined standards settings. After switching ON, a self-test and the initializing procedure is performed by SVM. After that it becomes ready for measurement and shows the first measuring window. During the measurement, current repeat deviation for density and viscosity can be viewed. If the results of the first repetition are within the limits for the viscosity and density, the state changes to ‘RESULT VALID’ and the display will be frozen. If the result is not within the limits, the repeat deviation for viscosity and density will be displayed and one more refill will be required unless it becomes within the limit automatically.

3.3.2 Flash point measurement

This is the minimum temperature of the fuel at which it gives off enough vapor to produce an inflammable mixture above the fuel surface when heated under standard test conditions. To obtain the flash point value of the fuel according to the ASTM D93 method, a HFP 380 Pensky Martens flash point analyzer as shown in Figure 3.2 was used. The flash point is determined by heating the fuel in a small enclosed chamber until the vapors ignite when a small flame is passed over the surface of the fuel.

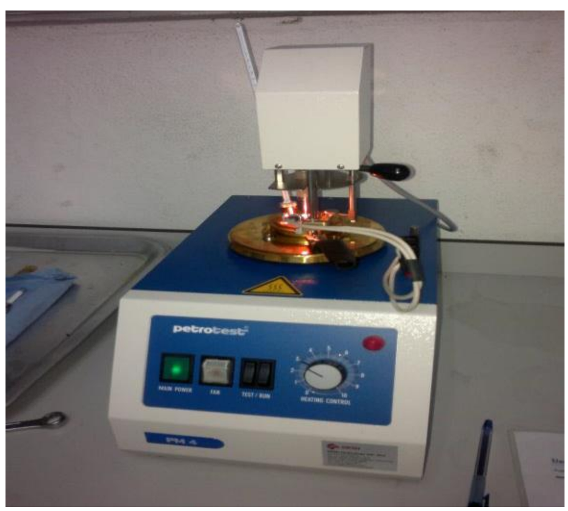


Figure 3.2: Flash Point Tester

The equipment determines the temperature where the vapor formed by the fuel would create a vapor which would then be ignited by a flame source. The test is conducted by first step is fill the fuel sample within level 70 ml in the cup with handle. The main switch is turn ON and the host then connected to the flash point device. Then the cup with fuel sample put inside the mold, also the thermometer positioned properly. Turn on the gas and light up flames at the test cover with ignition. Heating switch is then turns ON and control heating regulator up to boiling point of the sample. Sample was stirred using the hand stirrer and it was checked frequently to ensure when the flash point occurs (the flame exiting the device would burn). Temperature reading then recorded at this stage for flash point of the fuel sample.

3.3.3 Calorific value measurement

The standard measure of the energy content of a fuel is its heating value (HHV) sometimes called the calorific value or heat of combustion. The heating value is obtained by the complete combustion of a unit quantity of solid fuel in oxygen – bomb calorimeter under carefully defined conditions. The higher heating value is one of the most important properties of a fuel (Demirbaş, 2003). Bomb calorimeter is used for determining calorific value of different automobile fuels. A bomb calorimeter is a type of constant-volume calorimeter used in measuring the heat of combustion of a particular reaction. Electrical energy is used to ignite the fuel; as the fuel is burning, it will heat up the surrounding air, which expands and escapes through a tube that leads the air out of the calorimeter. When the air is escaping through the copper tube, it will also heat up the water outside the tube. The temperature of the water allows for calculating calorie content of the fuel. IKA C2000

Bomb calorimeter was used for determining the calorific value of palm biodiesel samples used in this study, 0.5 gm of sample were used for determination of calorific value of each samples as shown in Figure 3.3. At first the 0.5 gm of sample was weighted by a micro balance by pouring it in to the insulating container of the bomb calorimeter. After that digitally the sample was inserted in to the machine and the result was collected from the digital display of the calorimeter.

Figure 3.3: IKA C 2000 Calorimeter

3.3.4 Oxidation stability measurement

Biodiesel which is produced from vegetable oils is considered more vulnerable to oxidation at high temperature and contact of air, because of bearing the double bond molecules in the free fatty acid. The biodiesel and its blends stability was measured by induction period. Oxidation stability of samples was evaluated with commercial appliance Rancimat 743 as shown in Figure 3.4 applying accelerated oxidation test (Rancimat test) specified in EN 14112. The end of the induction period (IP) was determined by the formation of volatile acids measured by a sudden increase of conductivity during a forced oxidation of ester sample at 110 °C with airflow of 10 L/h passing through the sample.

Figure 3.4: Rancimat 743

However during the experiment following procedure was followed:

- The heating block is heated up to the 110° C temperature.
- The measuring vessel is filled with 60 mL deionized water and placed on the Rancimat together with the measuring vessel cover. For long analysis times (> 72 h), it is recommended to increase the volume to compensate evaporation loss. An evaporation rate of 5 … 10 mL water per day has to be taken into account. It has to be ensured that the electrode is immersed into the measuring solution at any time.
- For each determination, a new reaction vessel is used. To remove particles (e.g., from the cardboard box) the reaction vessel is air-cleaned inside and outside by a sharp stream of nitrogen. Then sample is weighed directly into the reaction vessel. For liquid samples and for samples that melt at elevated temperatures a sample size of 3.0 ± 0.1 g is used. For samples with significant water content (> 5%) the sample

size has to be increased to compensate the decrease in volume when the water evaporates. Ensure that the air inlet tube always immerses in the sample. Solid samples which do not melt should only cover the bottom of the reaction vessel. In this case, 0.5 … 1 g of the powdered sample is weighed into the reaction vessel.

- The reaction vessel is closed with a reaction vessel cover assembled with an air inlet tube.
- Before the determination can be started, the temperature of the heating block has to be stable. The two tubing's between Rancimat and reaction vessel and between reaction vessel and measuring vessel are connected. Then the reaction vessel is placed in the heating block and the measurement is started immediately.

3.3.5 Cloud point and pour point measurement

The pour point describes a procedure for testing the fluidity of a fuel at a specified temperature. The cloud point is defined as the temperature of a liquid specimen when the smallest observable cluster of wax crystals first appears upon cooling under prescribed conditions. An automatic NTE 450 (Norma lab, France) Cloud and Pour point tester as shown in Figure 3.5 was used to measure the cloud point and pour point of the samples according to the ASTM D2500 and ASTM D93 respectively.

Figure 3.5: NTE 450 CP and PP Tester (Norma Lab, France)

3.3.6 Determination of acid value, the saponification number (SN), iodine value (IV) and cetane number (CN)

Acid value is the number of milligrams of potassium or sodium hydroxide necessary to neutralize the free acid in 1 g of sample. The acid value can be calculated using the following equation:

$$AV = \frac{MW \times N \times V}{W} \tag{3.1}$$

Where,

MW ≡ Molecular weight of potassium hydroxide (KOH)

N≡ Normality of sodium hydroxide (KOH) solution.

V≡ Volume of sodium hydroxide (KOH) solution used in titration.

W ≡ Weight of oil sample

Saponification number (SN), iodine value (IV) and cetane number (CN) were calculated by using the fatty acid composition results and the following empirical equations (3.2), (3.3) and (3.4) respectively (Devan and Mahalakshmi, 2009; Mohibbe Azam et al., 2005).

$$SN = \sum \frac{(560 \times Ai)}{MWi} \quad (3.2)$$

$$IV = \sum \frac{(254 \times D \times Ai)}{MWi} \quad (3.3)$$

$$CN = 46.3 + \frac{5458}{SN} - \frac{0.225}{IV} \quad (3.4)$$

Where A_i is the weight percentage of each fatty acid component, D is the number of double bond present in each fatty acid; MW_i is the molecular weight of each fatty acid component.

3.4 Biodiesel blending

Each test fuel blend was prepared prior to the properties test and engine test. To conduct the research, 7 fuel blends were prepared. Each test fuel blend was stirred at 2000RPM for 20 minutes in a homogenizer device. The homogenizer was fixed on a clamp on a vertical stand as shown in Figure 3.6, which allows changing of the homogenizer’s height. To mix the fuels by using the homogenizer, the plug is turned ON and the appropriate speed is selected by using the selector which is located on top of the homogenizer.

Figure 3.6: Biodiesel Blending Process

3.5 Engine test setup

The experimental investigation was carried out using 7 fuel samples including diesel fuel and (B10, B20) of each feedstock. These blends was chosen based on the reports by the researchers that up to 20% of biodiesel blend can be used in a diesel engine without any modification. The blend compositions of all fuel samples are given in Table 3.2.

Table 3.2: Blend fuel compositions (% vol)

No.	Fuel Samples	Samples description
01	Diesel	100% diesel fuel
02	PB10	10% Palm biodiesel + 90% diesel fuel
03	PB20	20% Palm biodiesel + 80% diesel fuel
04	CB10	10% *Calophyllym* biodiesel + 90% diesel fuel
05	CB20	20% *Calophyllym* biodiesel +80% diesel fuel
06	MB10	10% Mustard biodiesel + 90% diesel fuel
07	MB20	20% Mustard biodiesel + 80% diesel fuel

A 4-cylinder Pajero engine was used in this experiment; its specifications were summarized in Table 3.3. Schematic diagram of the engine test bed is shown in Figure 3.7. At first the engine was warmed up for 5 minutes so that fluctuation of emissions can be avoided. Tests were carried out at different engine speed ranged from 1000 to 4000 rpm and full load condition. At first engine was started using diesel, and after engine was warmed up it was switched to test fuels. For engine performance and exhaust emission test, every fuel sample has been tested three times and their average results were reported in this study.

The engine was connected with test bed and a computer data acquisition system. Therefore the test bed was connected to the data acquisition board, which collects signal, rectify, filter and convert the signal to the data to be read. The data acquisition board is connected to the laptop, where, user can monitor, control and analysis the data using software through REO-DCA controller. A figure of engine test bed is shown in Figure 3.8.

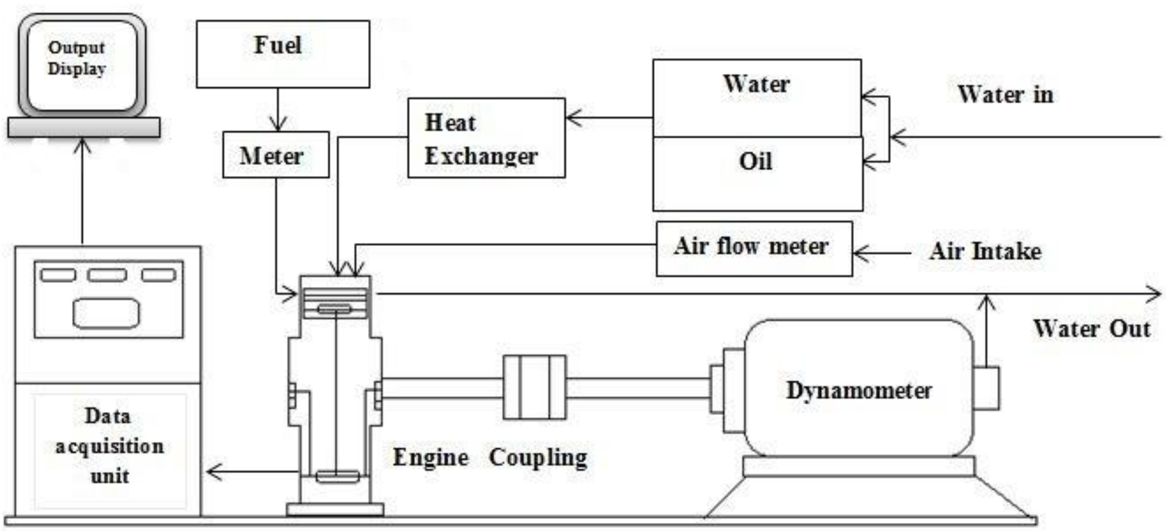


Figure 3.7: Test engine set up

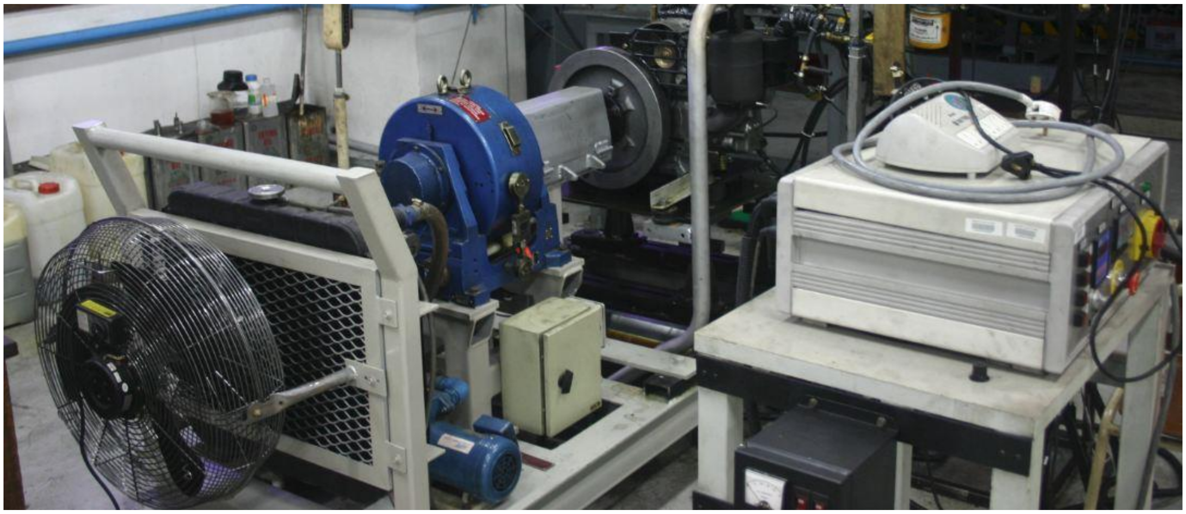


Figure 3.8: Engine Test Bed

Table 3.3: Test engine specification

Engine type	4 cylinder inline
Manufacturer	Mitsubishi Pajero engine
Displacement	2.5 L (2,476 cc)
Bore	91.1 mm
Stroke	95.0 mm
Torque	132 Nm , at 2000 rpm
Maximum engine speed	4200 rpm
Compression ratio	21:1
Cooling system	Water cooled
Combustion chamber	Swirl type
Lubrication system	Pressure feed

All the performance data was measured at step RPM test mode. At every 500 rpm increments, engine stabilizes for 20 seconds and acquires data for next 20 seconds. For performance test, each fuel sample has been tested for three times and their results are averaged. The data logged by the computer are:

- Engine speed
- Dynamometer load

- Throttle position
- Fuel flow rate
- Air flow rate
- Fuel temperature
- Air temperature
- Lube oil temperature
- Coolant temperature
- Inlet and exhaust manifold temperature
- Engine torque
- Brake power
- Brake specific fuel consumption

Before the engine and dynamometer are started, several precautions had to be taken into consideration.

(a) The motor was switched ON to supply cooling water to the dynamometer and the flow out water was controlled to maintain a suitable flow rate by using the water outlet valve.

(b) It was ensured that the water level of the main water tank was always sufficient during the engine test.

(c) The engine lube oil was checked with the dipstick indicator.

(d) The cooling water inlet was adjusted by using the valves to control the flow rate in order to maintain the inlet temperature.

3.6 Apparatus for engine emission studies

A BOSCH exhaust gas analyzer (model BEA-350) was used as shown in Figure 3.9 to measure the exhaust emission gases emission of NO and HC in ppm while CO and CO_2 in volume percent. The details of gas analyzer are shown in Table 3.4 In this research work exhaust emission was measured at various speeds range from 1000 rpm to 4000 rpm at an interval of 500 rpm at full load conditions by inserting probe into the tail pipe. First the engine was run using diesel fuel to get baseline data and other fuel blends were tested accordingly.

To get the average values, all tests were repeated three times. The technology of this analyzer consisted of automatic measurements with microprocessor control and self-test, auto calibration before every analysis, and a high degree of accuracy in analysis of low concentrations of gases found in engine fitted with catalytic converter. After the instrument is switched ON it takes three minutes to warm up. During this time no measurement is possible. After a system adjustment has been conducted with zero gas, the measurement can be taken. Before every measurement the zero point of the analysis system is automatically adjusted with zero gas after the pump is switched on. During the first 15 seconds of the 30 seconds adjustment, zero is indicated in the indicator panels for the gases and the particular upper limit of the effective range is indicated for 15 seconds. During the test, the water condensed in the hose connecting the probe and it is collected in the condensate container and automatically sucked out. However a new condensate filter has to be installed by switching of the measured-gas pump, if the present is badly fouled.

Figure 3.9: Bosch Gas Analyzer (BEA 350)

Table 3.4: Gas analyzer details

Equipment name	Model	Measuring element	Measuring method	Upper limit	Accuracy
BOSCH gas analyser	BEA-350	CO	Non-dispersive infrared	10.00 vol.%	±0.02 vol %
		CO_2	Non-dispersive infrared	18.00 vol.%	±0.03 vol %
		HC	Flame ionization detector	9999 ppm	±1 ppm
		NO	Heated vacuum typechemiluminescence detector	5000 ppm	±1 ppm

3.7. Apparatus for engine combustion studies

Engine combustion characteristics for biodiesel blends were investigated by means of the cylinder gas pressure and heat release. The crank angle was measured using a Crank angle encoder (RIE-360). In cylinder pressure was measured by using a Kistler 6058A type pressure sensor. It was installed in the swirl chamber through the glow plug port. A Kistler 2614B4 type charge amplifier was used to amplify the charge signal outputs from the pressure sensor. A high precision Leine & Linde incremental encoder was used to acquire the top dead center (TDC) position and crank angle signal for every engine rotation. Simultaneous samplings of the cylinder pressure and encoder signals were performed by a computer with a Dewe-30-8-CA data acquisition card. One hundred consecutive combustion cycles of pressure data were collected and averaged to eliminate the cycle-to-cycle variation in each test.

Heat release rate analysis is the most effective way to identify the start of combustion and difference in combustion rate. The heat release rate was calculated based on the cylinder gas pressure data collected during the test. By applying the first law of thermodynamics as shown in equation 3.5, heat release rate per crank angle was calculated not taking the cylinder wall heat loss into consideration.

$$\frac{dQ}{d\theta} = \left(\frac{\gamma}{\gamma-1} \times P \times \frac{dV}{d\theta}\right) + \left(\frac{1}{\gamma-1} \times V \times \frac{dP}{d\theta}\right) \tag{3.5}$$

Here, θ is the crank angle, $\frac{dQ}{d\theta}$ is the heat release rate per crank angle, P is the pressure, V is the cylinder volume and g is the specific heat ratio. The value of g is taken to be 1.37 and 1.30 during compression and expansion, respectively (Goering, 1998). The V and $\frac{dV}{d\theta}$ terms are shown in the following equation 3.6 and 3.7.

$$V = V_c + A\,.\,r\left[1 - \cos\left(\frac{\pi\theta}{180}\right) + \frac{1}{\lambda}\left\{1 - \sqrt{1 - \lambda^2 \sin^2\left(\frac{\pi\theta}{180}\right)}\right\}\right] \tag{3.6}$$

$$\frac{dV}{d\theta} = \left(\frac{\pi A}{180}\right) \times r\left\{\sin\left(\frac{\pi\theta}{180}\right) + \frac{\lambda^2 \sin^2\left(\frac{\pi\theta}{180}\right)}{2 \times \sqrt{1 - \lambda^2 \sin^2\left(\frac{\pi\theta}{180}\right)}}\right\} \tag{3.7}$$

Here, $\lambda = \frac{l}{r}$ and $A = \frac{\pi D^2}{4}$, where l= connecting rod length, r = crank radius = 0.5 × stroke, D = cylinder bore and V_c = clearance volume.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, the results of all analysis done throughout the research are presented and discussed. At first, crude oil properties and compositions are discussed. Physicochemical properties of biodiesel-diesel blends ratios of 10% to 90% blends were fully covered and presented. Finally, data of engine performance, emission and combustion characteristics using a total of 7 fuel samples were presented and compared with that of diesel fuel.

4.2 Characterization of palm, mustard and *Calophyllum* oil

Biodiesel production process selection and duration depends on the physicochemical properties of feedstock. Acid value, FFA, density and kinematic viscosity influence the production steps and also the extra processing steps like filtration, heating, centrifuging and drying. Table 4.1 shows the measured physicochemical properties of crude palm, mustard and *Calophyllum inophyllum* vegetable oil feedstock used to produce biodiesel.

Table 4.1: Physicochemical properties of crude vegetable oils

Properties	Units	Standards	Palm oil	Mustard oil	*Calophyllum Inophyllum* oil
Acid value	mg KOH/g oil	ASTM D664	3.47	3.64	10.72
Kinematic viscosity at 40 °C	mm^2/s	ASTM D445	38.10	45.52	48.82
Density at 15 °C	kg/m^3	ASTM D4052	898	896	921
Flash point	°C	ASTM D93	174.5	212.5	217.5
Pour point	°C	ASTM D97	5	-14	-3
Cloud point	°C	ASTM D2500	17	-13	-2
Calorific value	MJ/kg	ASTM D240	39.4	40.10	38.4
Oxidation stability	h	EN ISO 14112	3.42	11.30	2.72

To produce biodiesel from crude vegetable oil, transesterification was performed by two steps: (1) Acid esterification and (2) base transesterification process. Acid esterification is needed if the acid value of crude oil is higher than 4 mg KOH/gm. For *Calophyllum* oil both steps were needed as its acid value was found higher than 4 mg KOH/gm and for palm oil and mustard oil only base transesterification was needed.

From Table 4.1 it can be seen that *Calophyllum inophyllum* oil showed highest kinematic viscosity and density value followed by mustard oil and palm oil. Due to these higher values of viscosity and density, crude oil cannot be used in the diesel engine directly or without any modification. High viscosity value negatively affects the volume flow and spray characteristics in the injection manifold as well as leads to blockage and gum formation. Therefore, it is suggested that vegetable oil should be converted to biodiesel to reduce viscosity and density before using in diesel engines.

The flash point results showed that *Calophyllum inophyllum* oil possesses highest flash point followed by mustard and palm oil. All of these crude vegetable oils have very high flash points (>160ºC) which conclude that these feedstock are safe for storage, transportation and handling.

Mustard oil showed the lowest cloud point and pour point among all tested feedstock. Analyzing the cloud point and pour point result it can be concluded that mustard oil possesses better cold flow properties than palm and *Calophyllum inophyllum.*

Calorific value is an important fuel selection parameter. Again mustard oil was found superior than other two biodiesel feedstock considering its highest calorific value followed by palm and *Calophyllum inophyllum* oil.

Oxidation stability results showed that mustard oil has the highest oxidation stability followed by palm and *Calophyllum inophyllum* feedstock. Thus, it would not get easily oxidized during storage and transportation.

4.3 Characterization of biodiesel

The quality of biodiesel can be assessed by measuring its physical and chemical properties. Physicochemical properties of biodiesel show variation depending upon the feedstock quality, chemical composition, production process, storage and handling process.

4.3.1 Analysis of fatty acid composition

Single bonded fatty acids are known as saturated fatty acids. Besides fatty acid containing double or more bonds are known as unsaturated fatty acids. Table 4.2 shows the FAC of all produced biodiesels. From FAC analysis, it was found that MB contains only 5% saturated fatty acids, left are unsaturated. Moreover MB contains 16 different types of fatty acids in which more than 53% is erucic acid. Presence of this huge amount of erucic acid is a unique characteristic for this feedstock. This high amount of erucic acid makes it less edible. PB and CB contained 43% and 30% saturated fatty acid respectively, left are unsaturated. PB is constituted by 4 different types of fatty acids in which more than 40% is palmitic acid and more than 43% is oleic acid. On contrast CB is constituted by 9 different types of fatty acids in which more than 41% is oleic acid. PB and CB both contain highest percentage of oleic acid in their fatty acid distribution profile.

Table 4.2: Fatty acid composition of biodiesels

No	Fatty acid name (common)	Fatty acid name (systematic)	Structure	Formula	Molecular mass	MB (Wt%)	PB (Wt%)	CB (Wt%)
01	Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$	200	-		
02	Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$	228	-		
03	Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$	256	1.9	40.1	14.4
04	Palmitoleic	Hexadec-9-enoic	16:1	$C_{16}H_{30}O_2$	254	0.2		0.3
05	Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$	284	1.2	4.3	15.2
06	Oleic	Cis-9-Octadecanoic	18:1	$C_{18}H_{34}O_2$	282	12.7	**43.1**	**41.9**
07	Linoleic	Cis-9-cis-12 Octadecanoic	18:2	$C_{18}H_{32}O_2$	280	12.3	12.5	26.6
08	Linolenic	Cis-9-cis-12	18:3	$C_{18}H_{30}O_2$	278	7.2		0.2
09	Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$	312	1.0		0.8
10	Eicosenoic	Cis-11-eicosenoic acid	20:1	$C_{20}H_{38}O_2$	310	6.4		0.2
11	Eicosadienoic	all-cis-11,14-eicosadienoic acid	20:2	$C_{20}H_{36}O_2$	309	0.4		
12	Eicosatrienoic	11,14,17-Eicosatrienoic Acid	20:3	$C_{20}H_{34}O_2$	306	0.1		
13	Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$	341	0.9		
14	Erucic	13-Docosenoic Acid	22:1	$C_{22}H_{42}O_2$	338	**53.7**		0.5
15	Docosadienoic	13,16-Docosadienoic Acid	22:2	$C_{22}H_{40}O_2$	336	0.8		
16	Nervonic	15-Tetracosaenoic Acid	24:1	$C_{24}H_{46}O_2$	366	1.3		
Saturated						5.0	43.5	30.4
Monounsaturated						74.3	38.6	42.8
Polyunsaturated						20.7	17.9	26.8
Total						100.0	100.0	100.0

4.3.2 Analysis and effect of physicochemical properties

Measured physicochemical properties of produced biodiesels are shown in Table 4.3. Density of the fuel has direct effects on the engine performance characteristics. It influences the fuel atomization and consumption as well. Generally diesel fuel injection systems meter the fuel by volume; therefore, the change of the fuel density will influence the engine output power due to a different mass injected fuel (G. R. Kannan & Anand, 2012). The density is proportional to the bulk modulus. The bulk modulus is a measure of how a unit volume of fluid can be easily discharged when increasing the pressure on it. A higher bulk modulus indicates that the fluid is incompressible. If a fuel is less compressible, the pressure will build more quickly and the fuel will need less time and will be injected in the combustion chamber in the compression cycle, whereas if the fuel is more compressible more time will be required to reach the nozzle opening pressure, and the fuel will be injected into the combustion chamber later. Therefore, higher density and bulk modulus of fuel leads earlier injection timing. The early injection timing can lead to a longer premixed burning phase and produces higher cylinder temperature or more NO_x emission. All tested biodiesels showed higher density values compared to diesel fuel. Density values of PB, MB and CB were found 5%, 5.5% and 4% higher than diesel fuel respectively. CB showed lowest density values than PB and MB. Thus, CB showed superior quality as biodiesel than PB and MB considering density. Thus using CB would be more economical as it might cause lower fuel consumption than PB and MB. However, density values for produced biodiesel were remained within ASTM specification for biodiesel standard.

Viscosity is the most important properties of biodiesel fuels which limit their use in CI engines. Viscosity affects the size of the fuel droplets, the atomization quality and the jet penetration. Therefore, viscosity influences the quality of combustion (Canakci et al., 2009). Low viscous fuel can flow easily and mix with the air. Most of the unburnt hydrocarbon deposits found in the combustion chamber walls and exhaust pipe are mainly due to partially rich mixture and large fuel droplet sizes which is partially caused by higher viscosity. All tested biodiesels showed higher kinematic viscosity and density values compared to diesel fuel. In percentage, kinematic viscosity of PB, MB and CB were found 87%, 53% and 30% higher than diesel fuel respectively. It has been reported that viscosity of the biofuels correlates more strongly with the degree of unsaturation and FAME chain lengths. In another study, it has been reported that when chain length increases in FAMEs, the viscosity increases. As biofuel contains fatty acids with longer chain lengths, viscosity increases. From Table 4.2 it can be seen that MB mostly contains longer chain length (22:1) than PB or CB (18:1), which results in higher viscosity of MB.

Table 4.3: Physicochemical properties of biodiesels

Properties	Units	Standards	ASTM D6751	Mustard Biodiesel	Palm Biodiesel	*Calophyllum* Biodiesel	Diesel
Kinematic Viscosity at 40°C	mm^2/s	ASTM D445	1.9-6	5.767	4.723	4.017	3.0699
Density at 15°C	kg/m^3	ASTM D1298	860-900	864.8	862.2	859.2	821
Flash point	°C	ASTM D93	>130	149.5	182.5	172.5	72.5
Cloud point	°C	ASTM D2500	-	5	6	16	-8
Pour point	°C	ASTM D97	-	-18	3	15	-6
Calorific value	MJ/kg	ASTM D240	-	40.41	39.79	39.91	45.27
Oxidation stability	h	EN ISO 14112	3	15.92	3.92	3.18	-
Cetane number	-	ASTM D613	47 min	76	51	59	48
Iodine value	gI/100g	-	-	102.3066	99	61	-
Saponification value	-	-	-	179.322	202	206	-
Acid value	mg KOH/g	-	-	0.17	0.05	0.24	-
Carbon Conradson	%	ASTM D4530	0	0	0	0	-

Flash point is the lowest temperature at which application of an ignition source causes the vapor above the sample to ignite under specified conditions of the test. The more a fuel is volatile the more lower flash point it possess. PB showed highest flash point among all tested fuels. Thus it provides advantage during storage, transport and handling compared to MB, CB or diesel fuel. PB has lowest volatility than PB, CB or diesel fuel. As biodiesel contains higher molecular weight compounds in their chemical structures compared to diesel fuel, as a result volatility decreases. Lower volatility of biodiesel than diesel fuel is the main reason behind the higher flash point value. In percentage, flash point values of PB, MB and CB were found 152%, 96% and 137%

higher than diesel fuel respectively. Flash point values for all biodiesels were found within ASTM specification for biodiesel standard.

MB showed promising cold flow properties than other tested biodiesels. Cloud point and pour point of MB was found much lower than PB and CB. Thus MB can be used in cold climate where PB or CB might suffer from freezing. A high cetane number ensures good cold starting ability (D. Kannan et al., 2009). As MB has highest cetane number than other fuels, the cold flow properties showed promising characteristics. However, diesel fuel was found still better than all biodiesels considering its use in cold climate.

In percentage, calorific values of PB, MB and CB were found 11.5%, 10% and 11.3% lower than diesel fuel. The chemical structures of biodiesels contain approximately 76–77% carbon, 11–12% hydrogen and 10–12% oxygen by weight (Atabani et al., 2012). Therefore, the energy content or net calorific value of biodiesel is about 10–12% less than that of conventional diesel fuels on the mass basis (Ahmet Necati Ozsezen & Canakci, 2011). As biodiesels are oxygenated fuels and contain less carbon than diesel, decrease in calorific value is obvious. Calorific value of MB was found 40.41 MJ/kg. It might be considered as a unique finding for MB as this value is higher than most of the conventional biodiesel found in the market. Fatty acid profile of MB revealed that MB contains more than 53% erucic acid while the main weight percentage of fatty acids for PB and CB are oleic acid (around 42%). Erucic acid has longer molecular chain length and weight than oleic acid. As a result MB contains more carbon than PB or CB. Thus MB would provide advantage over PB and CB considering calorific value.

As biodiesels are oxygenated fuel, oxidation stability is very important during long time storage. Oxidation stability again depends on the respective fatty acid composition of biodiesels. Oxidation stability results in Table 4.3 show that MB possesses the highest oxidation stability followed by PB and CB respectively. As MB contains longer chain length of carbon compounds ultimately amount of oxygen is lower than PB or CB. Thus, MB is more stable than PB or CB regarding oxidation. Thus MB provides advantage over PB and CB considering storage capability.

In CI engine, cetane number has an important influence on engine start ability, peak cylinder pressure, emissions and combustion noise. A high cetane number ensures good cold starting ability, low noise emission and long engine lifetime (D. Kannan et al., 2009). The cetane number is a measure of a fuel’s auto-ignition quality characteristics. Biodiesel has a higher cetane number than diesel fuel because it is composed of large chain hydrocarbon groups (with virtually no branching or aromatic structures) (Hoekman et al., 2012).Thus the ignition quality represented by the cetane number is found to be one of the most important characteristics of fuel and therefore it is important to quantitatively evaluate the ignition quality and ignition delay time of the biodiesel. The shorter the ignition delay time the higher is the cetane number of fuel and vice versa. Cetane number of PB, MB and CB were found 6%, 58%, and 22% higher than diesel fuel respectively. Therefore, MB should show highest ignition delay during engine combustion compared to PB or MB. Besides, MB showed highest iodine value and CB showed highest saponification number among three tested biodiesels. As cetane number, iodine value and saponification number were calculated from the fatty acid composition of respective biodiesels, these values are completely depends on their chemical composition. On the contrast, PB showed lowest acid value followed by MB and CB respectively. Thus, PB might cause less corrosion to the engine over MB or CB.

4.4 Characterization of biodiesel-diesel blends

Fuel properties are very influencing factors which determine the fuel droplet size, spray characteristics, in-cylinder temperature. These parameters dictate engine performance and emission. Different biodiesels are derived from different sources having different fatty acid and chemical compositions. Chemical properties of fuel affects upon properties such as density, cetane number, calorific value, flash point, oxidation stability etc. All three tested biodiesels were blended with diesel fuel to produce 10% to 90% biodiesel-diesel blends. Kinematic viscosity, density, calorific value, oxidation stability and flash point; these five main physicochemical properties were measured for all these blends and presented graphically in this section to compare their potentiality as biodiesel.

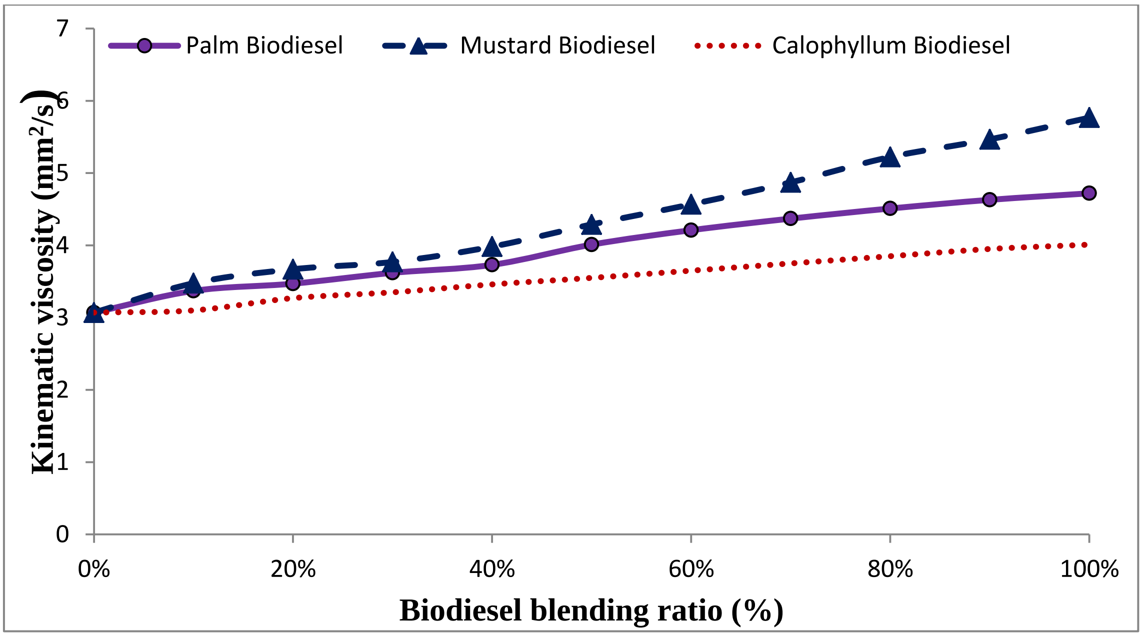


Figure 4.1: Kinematic viscosity versus percentage of biodiesel in blends

Kinematic viscosity is the resistance of liquid to flow and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size. Figure 4.1 shows the variation of kinematic viscosity of different biodiesel blends with increase in biodiesel diesel blending ratio. Kinematic viscosity linearly increases with the increase in biodiesel percentage in the blends. Presence of long chain hydrocarbon in the biodiesel structure is responsible for higher viscosity of biodiesel fuels. MB blends showed highest kinematic viscosity than other two biodiesels. This could be attributed to the presence of higher percentage of unsaturated fatty acids in mustard biodiesel than PB or CB. Kinematic viscosity of MB blends started from 3.47 mm^2/s which gradually increased to 4.28 mm^2/s for 50% MB blends. After 50% blend composition, it showed a sharp increase up to 5.46 mm^2/s for 90% MB blend. CB blends showed lowest kinematic viscosity started from 3.10 mm^2/s for 10% biodiesel, which followed almost a uniform increasing trend up to 3.95 mm^2/s for 90% CB blend. Kinematic viscosity of palm biodiesel blends started from 3.37 mm^2/s which gradually increased to 3.73 mm^2/s for 40% PB blends. After 40% blend composition it showed a sharp increase up to 4.63 mm^2/s for 90% PB blends. However, all biodiesel blends meet the ASTM D6751 standard for biodiesels kinematic viscosity range. This trend could be defined by the fatty acid structure of biodiesel. The more the percentage of biodiesel fuel is increasing in the blend more long chain fatty acids are dominating in the composition. As a result, after a certain level of biodiesel percentage it is showing sharp increase in viscosity values of the blends. Higher viscosity means it receives higher resistance during the flow in fuel line. In addition the higher viscosity also leads to poor fuel atomization and thereby, ultimately, the formation of engine deposits. The higher is the viscosity, the greater the tendency of the fuel to cause such problems. This is again another reason why pure biodiesel is not used for engine operation, blended biodiesels are used instead.

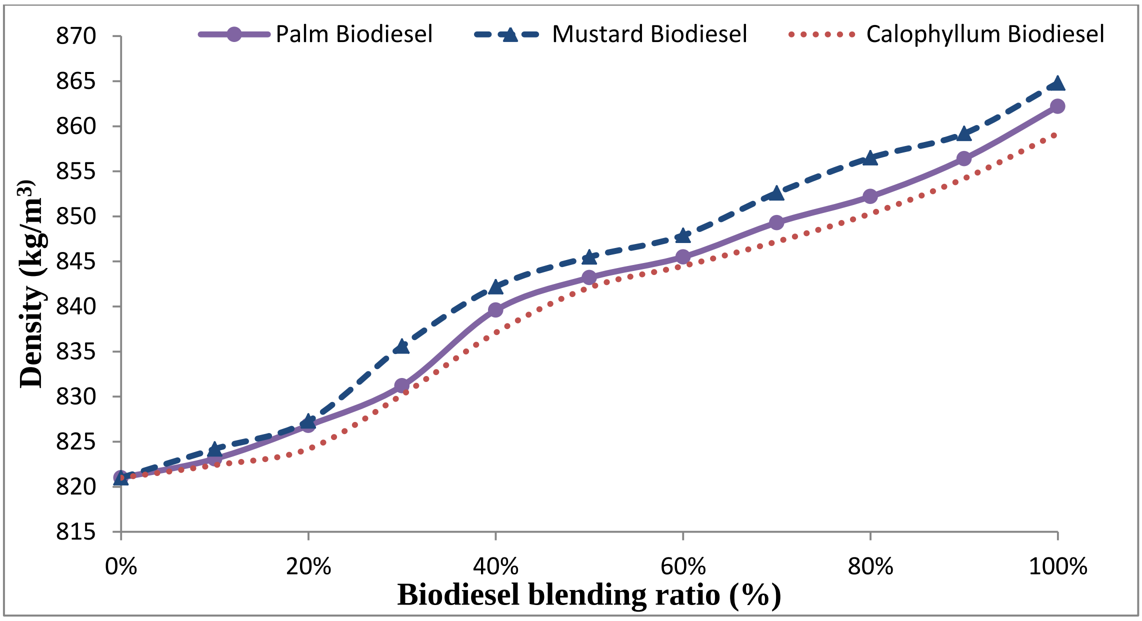


Figure 4.2: Density versus percentage of biodiesel in blends

Figure 4.2 shows the density variation of different biodiesel blends with increase in biodiesel-diesel blending ratio. MB blends showed highest density than other two biodiesels. From the fatty acid profile of MB, it can be seen that MB contains more than 53% erucic acid while the main weight percentage of fatty acids for PB and CB are oleic acid (around 42%). Erucic acid has longer molecular chain length and weight than oleic acid. Presence of this longer chain fatty acid contributes to more dense characteristics of MB than PB or CB. Densities of MB blends were 824.2 kg/m^3 to 859.2 kg/m^3 for 10% to 90% MB blends. CB blends showed lowest density ranged from 822.4 kg/m^3 to 854.2 kg/m^3 for 10% to 90% biodiesel-diesel blends. Densities of PB blends were found 823.1 kg/m^3 to 856.4 kg/m^3 for 10% to 90% biodiesel-diesel blends. As PB and CB contain almost same amount of oleic acid as bulk fatty acid compound, almost similar density trends and values were found for PB and CB blends. However, all biodiesel blends meet the ASTM D1298 standard for biodiesels density range.

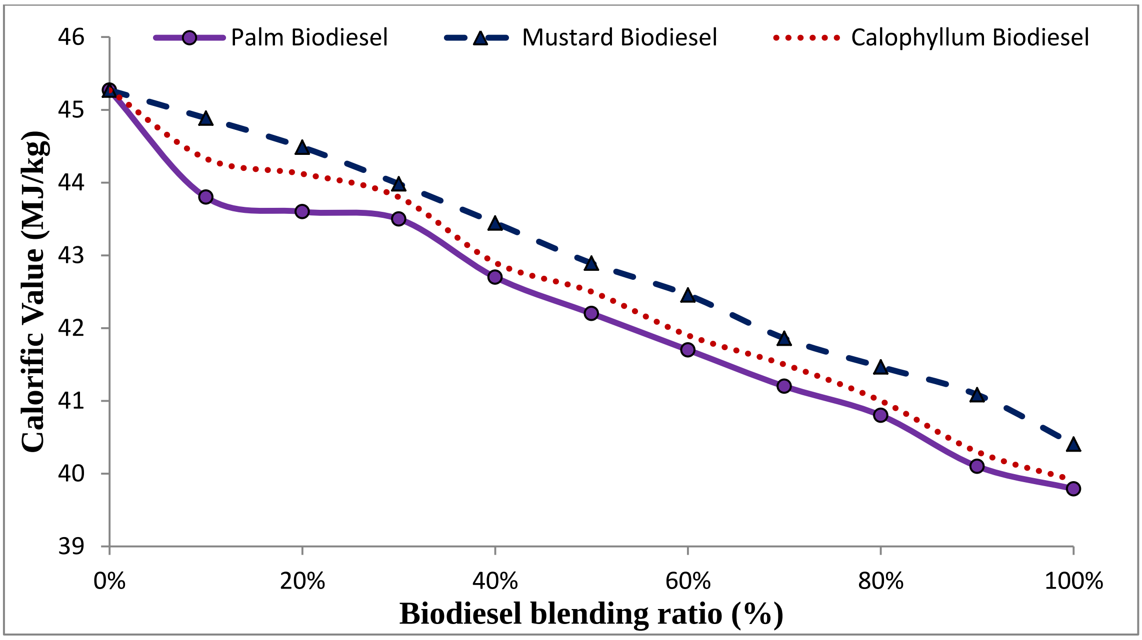


Figure 4.3: Calorific value versus percentage of biodiesel in blends

Among all fuel properties, heating value has been also considered to be one of the most important factors because it influences the combustion in the CI engine and thus both performance and exhaust emissions. Figure 4.3 shows the variation in calorific value for different biodiesel blends with increase in biodiesel diesel blending ratio. The chemical structures of biodiesels contain approximately 76–77% carbon, 11–12% hydrogen and 10–12% oxygen by weight (Atabani et al., 2012). Therefore, the energy content or net calorific value of biodiesel is about 10–12% less than that of conventional diesel fuels on the mass basis (Ahmet Necati Ozsezen & Canakci, 2011). Therefore it is generally accepted that biodiesel fuel has lower mass energy values than diesel fuel, due to its high oxygen content and lower carbon and hydrogen contents compared to diesel fuel. MB blends showed highest calorific value than other two biodiesels. This is due to the presence of higher carbon percentage in MB than PB or CB. Calorific value of MB blends were 44.88 MJ/kg to 41.08 MJ/kg for 10% to 90% mustard biodiesel-diesel blends. Palm biodiesel blends showed lowest calorific value ranged from 43.80 MJ/kg to 40.10 MJ/kg for 10% to 90% palm biodiesel-diesel blends. Calorific values of CB blends were found 44.33 MJ/kg to 40.30 MJ/kg for 10% to 90% biodiesel-diesel blends. Calorific value potentially increases with the increase in diesel fuel in the blends due to the proportionate increase in carbon percentage.

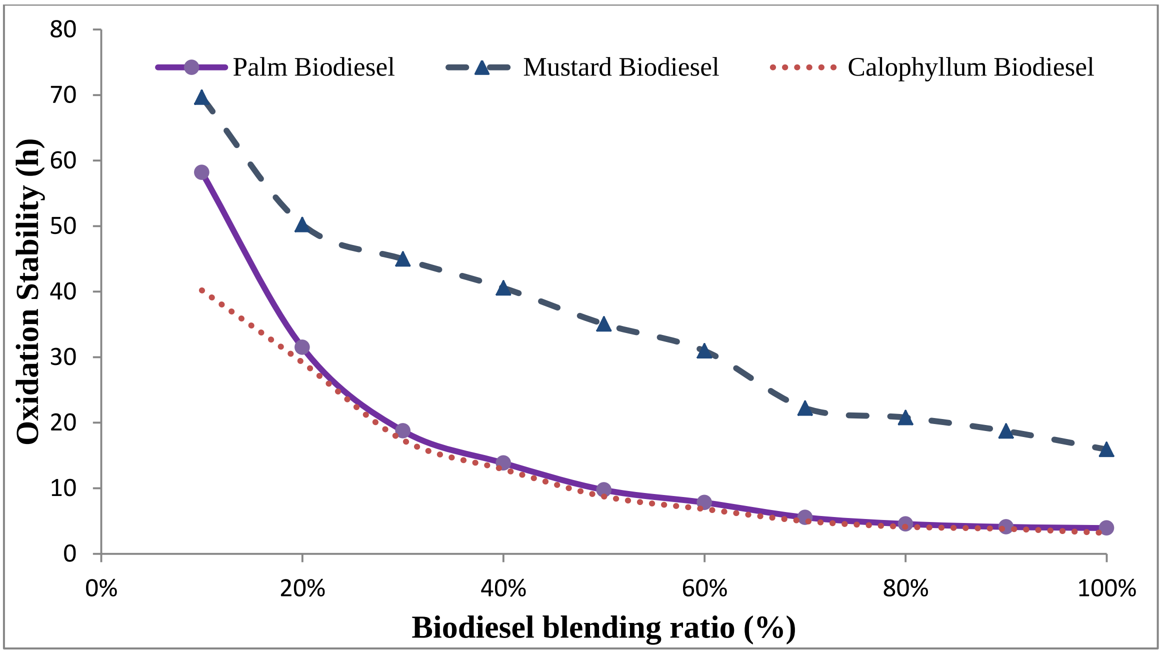


Figure 4.4: Oxidation stability versus percentage of biodiesel in blends

Biodiesel is susceptible to oxidation upon exposure to air, a process known as autoxidation. Biodiesel having higher unsaturation is more susceptible to oxidative degradation. Thus, the oxidation process ultimately affects fuel quality. Figure 4.4 shows the variation in induction period for different biodiesel blends with increase of biodiesel percentage in blends. MB blends showed highest oxidation stability than other two biodiesels. As MB contains longer chain length of carbon compounds ultimately amount of oxygen is lower than PB or CB. Thus, MB is more stable than PB or CB regarding oxidation. Oxidation stability of MB blends started from 69.66 h for 10% MB blend which sharply decreased to 22.23 h for 70% MB blends. After 70% blend composition it followed a gradual decrease. Oxidation stability decreased in an exponential pattern with the increase in biodiesel percentage in the blends. CB blends showed lowest oxidation stability ranged from 40.2 h to 3.18 h for 10% to 90% CB biodiesel-diesel blends. Oxidation stability values of PB blends were found 58.2 h to 4.1 h for 10% to 90% PB blends. However, all biodiesel blends meet the EN ISO 14112 standard for biodiesels oxidation stability range.

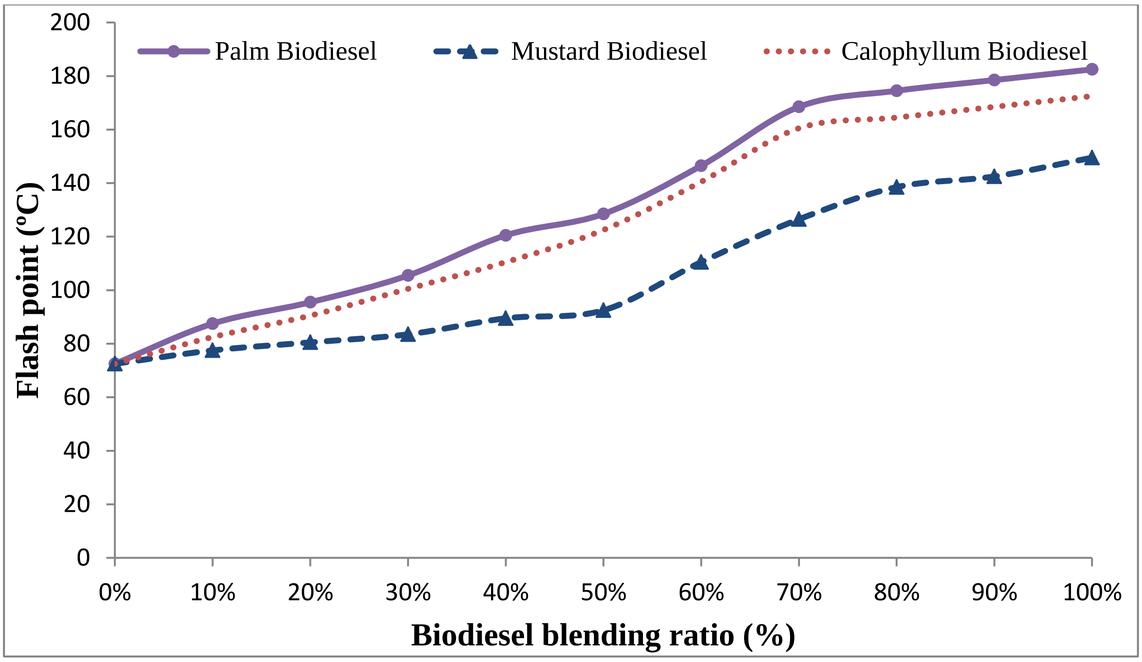


Figure 4.5: Flash point versus percentage of biodiesel in blends

Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark under specified test conditions. Figure 4.5 shows the variation in flash point for different biodiesel blends with increase in biodiesel diesel blending ratio. Flash point gradually increased for all tested biodiesels up to 50% blends. After that the trend followed a sharp increment which indicates the increased volatility of biodiesel blends at higher percentage. PB blends showed highest flash point than other two biodiesels. Flash point of a fuel varies inversely with the fuel volatility (Hoekman et al., 2012). Flash point of PB blends were 87.5 ºC to 182.5 ºC for 10% to 90% biodiesel-diesel blends. MB blends showed lowest flash point ranged from 77.5 ºC to 149.5 ºC for 10% to 90% biodiesel-diesel blends. Flash point values of *Calophyllum* biodiesel blends were found 82.5 ºC to 172.5 ºC for 10% to 90% CB blends. Flash point does not affect the combustion directly, however, with higher value of flash point makes biodiesel safer in terms of storage, fuel handling and transport.

4.5 Engine performance analysis

This section describes the effect of different fuel properties on different engine performance parameters. Performance parameters include brake specific fuel consumption (BSFC), Brake Thermal Efficiency (BTE), Engine Power and Torque. To carry out initial comparison, engine performance and emission test was carried out at constant 100% load and varying speed condition.

4.5.1 Brake specific fuel consumption

BSFC refers to the consumption of fuel per unit power and in a unit time. The BSFC of diesel engine depends on the relationship among volumetric fuel injection system, fuel density, viscosity and lower heating value (Qi et al., 2014). Figure 4.6 shows the variation of BSFC for palm, mustard and *Calophyllum inophyllum* biodiesel blends with respect to engine speed. It can be seen from all of the figures that BSFC of biodiesel is generally higher compared to diesel fuel, which is supported by the literature (Atabani & César, 2014; Can, 2014). Due to higher density, viscosity and lower calorific value of biodiesel, BSFC generally increases compared to diesel fuel. It can be seen that BSFC decreases at first from 1000 to 2000 rpm then increases steadily up to 4000 rpm. However, all tested fuels showed lowest BSFC at 1500-2000 rpm speed range due to increase in atomization ratio in lower speed (Canakci et al., 2009). At higher speed range the frictional loss increases and volumetric efficiency decreases compared to lower speed range, therefore BSFC increases.

Average BSFC for PB10 and PB20 were 7% and 11% higher than diesel fuel. Similar results were also found by other researchers (Leevijit & Prateepchaikul, 2011; Lin et al., 2006). As fuel is fed into the engine on a volumetric basis, to produce certain amount of power, more biodiesel is needed than diesel fuel due to its higher density and lower calorific value. Lowest BSFC values for PB10 and PB20 were 356 g/kWh and 365 g/kWh at 1500 rpm speed.

On average BSFC for MB10 and MB20 were 9% and 12% higher than diesel fuel. Bannikov et al. (2011) also found similar higher BSFC for mustard biodiesel over diesel fuel. Lowest BSFC values for MB10 and MB20 were 359 g/kWh and 365 g/kWh at 1500 rpm speed. On average, the BSFC of MB10 and MB20 were found 2% and 0.5% higher than PB10 and PB20 respectively. This increase of BSFC for mustard biodiesel is due to its higher density and viscosity than palm biodiesel.

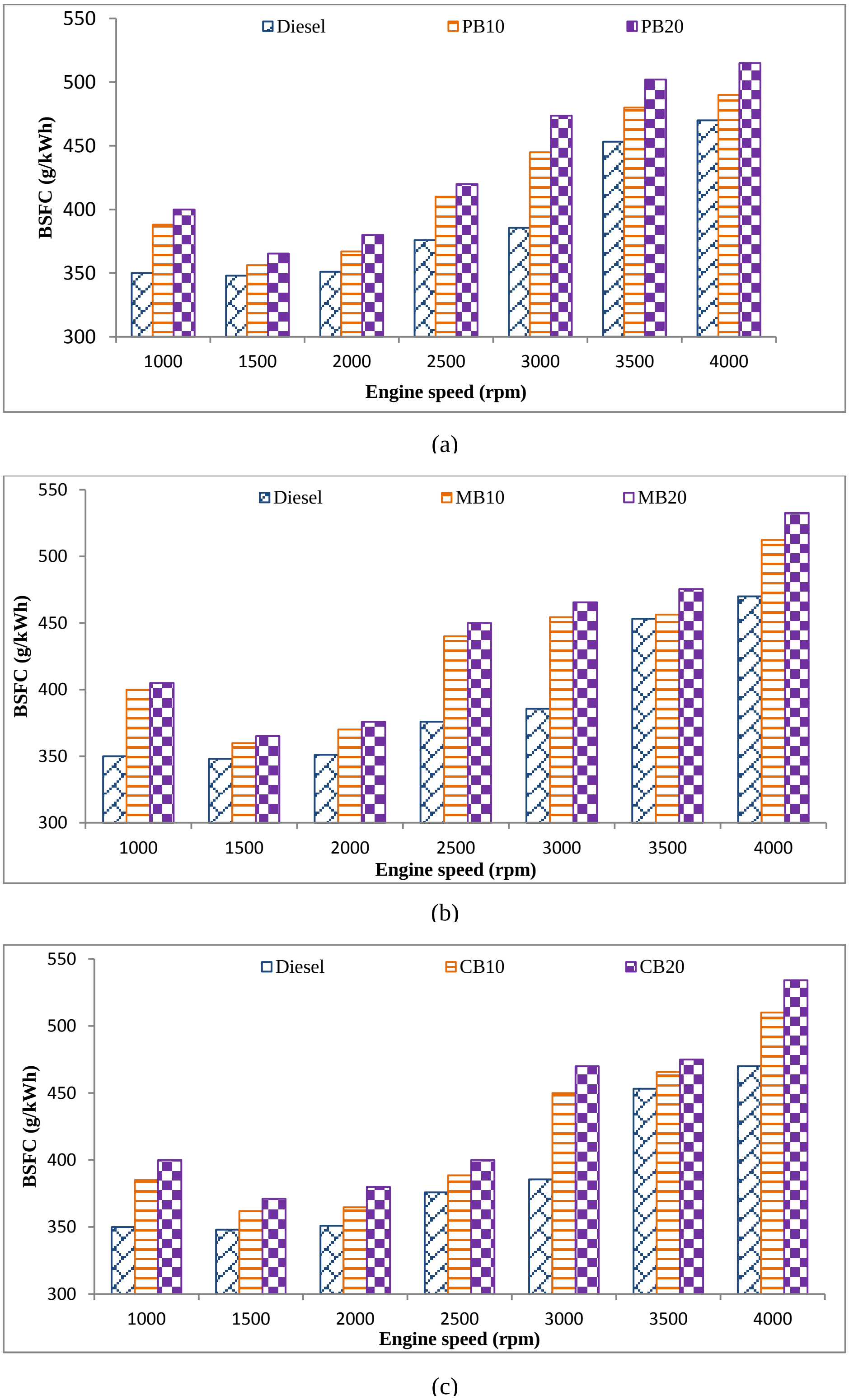


Figure 4.6: BSFC versus engine speed for (a) palm (b) mustard and (c) *Calophyllum inophyllum* biodiesel blended fuel at full load condition

Average BSFC for CB10 and CB20 were 6% and 10% higher than diesel fuel. Similar results were also found by other researchers (Belagur & Reddy PhD, 2010; D.K. Bora et al., 2008). Lowest BSFC values for CB10 and CB20 were 361g/kWh and 371 g/kWh at 1500 rpm speed. Average BSFC of CB10 and CB20 were 0.5% and 1% lower than PB10 and PB20 respectively. This decrease in BSFC for *Calophyllum* biodiesel is due to its lower viscosity and density than palm biodiesel.

4.5.2 Brake thermal efficiency

Brake thermal efficiency (BTE) is another important parameter to measure engine performance using biodiesel. The results of BTE for all biodiesels and diesel fuel are presented in Figure 4.7. BTE is calculated by using equation 4.1.

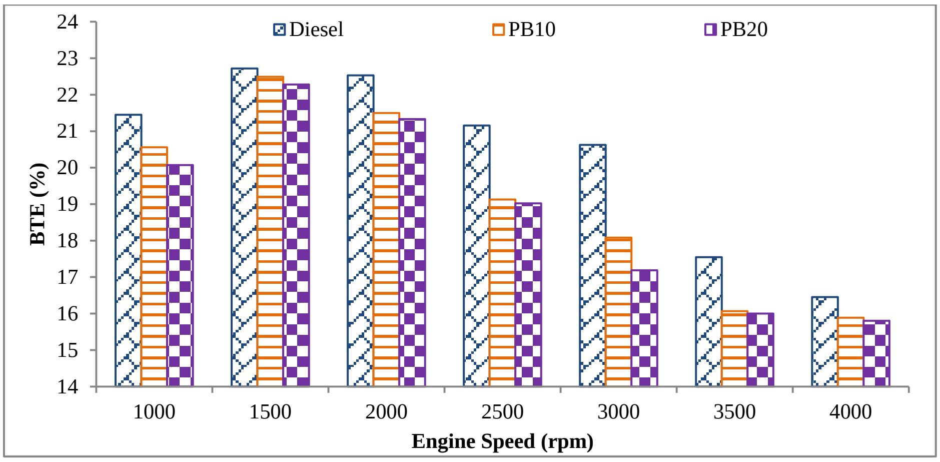
$$\eta \mathrm{bt} = \left[\frac{3.6 \times 10^{6}}{fc \times Hv}\right] \times 100\% \qquad (4.1)$$

Where ηbt is the BTE (%), fc is the BSFC (g/kWh) and Hv is the lower heating value of the fuel (KJ/kg). Highest BTE values were found at 1500-2000 rpm speed range as BSFC values were lowest in that speed range. Initially BTE increases due to lower fuel consumption and higher volumetric efficiency, but at higher speed time taken for complete combustion of fuel decreases with increased mechanical and frictional loss, hence BTE drops.

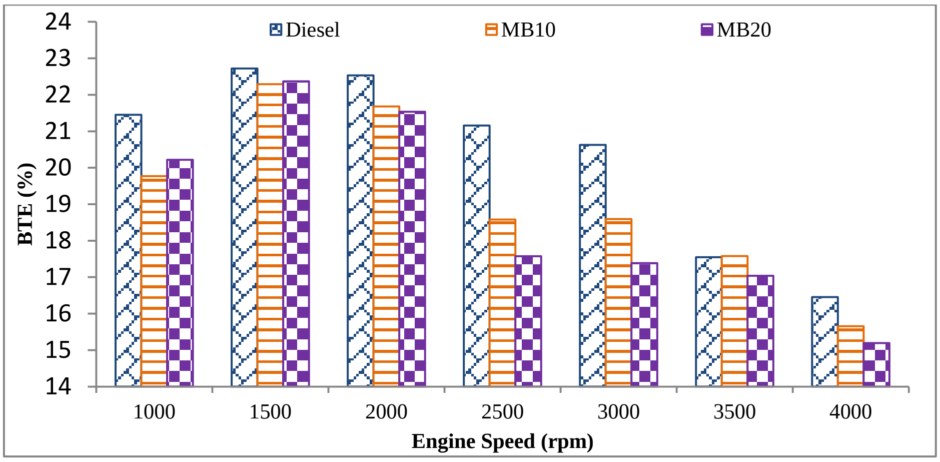
BTE for PB10 and PB20 were found 19.10% and 18.82% in average which were 6% and 7.5% lower than diesel fuel respectively. Highest BTE values for PB10 and PB20 were 22.5% and 22.3% at 1500 rpm speed. BTE for palm biodiesel was also found lower than diesel fuel by other researchers (Leevijit & Prateepchaikul, 2011).

Highest BTE values for MB10 and MB20 were 22.4% and 22.3% at 1500 rpm speed. Average BTE for MB10 and MB20 were found 19.2% and 18.8% which were 5.6% and 7.6% lower than diesel fuel respectively. On the contrary, BTE of MB10 and MB20 were found 6% and 1% lower than PB10 and PB20 respectively. This BTE result of mustard biodiesel can be explained by its higher BSFC than all tested fuels. Though the calorific value of mustard biodiesel was found higher than palm and *calophyllum* biodiesels, the variation of average calorific values of the biodiesel blends were much less than the variation of BSFC. Hence, calorific values put less significant effect in BTE computation by using equation (4). Niemi et al. (1997) found similar findings by using mustard biodiesel in a multi cylinder diesel engine.

Average BTE of CB10 and CB20 were 4% and 6.7% lower than diesel fuel respectively. Similar results were also obtained by Bora et al. (2012). Highest BTE values for CB10 and CB20 were 22.25% and 21.98% at 1500 rpm and 2000 rpm speed respectively. However, variation of BTE for CB10 and CB20 were varied slightly (less than 1%) in comparison with PB10 and PB20.



(a)



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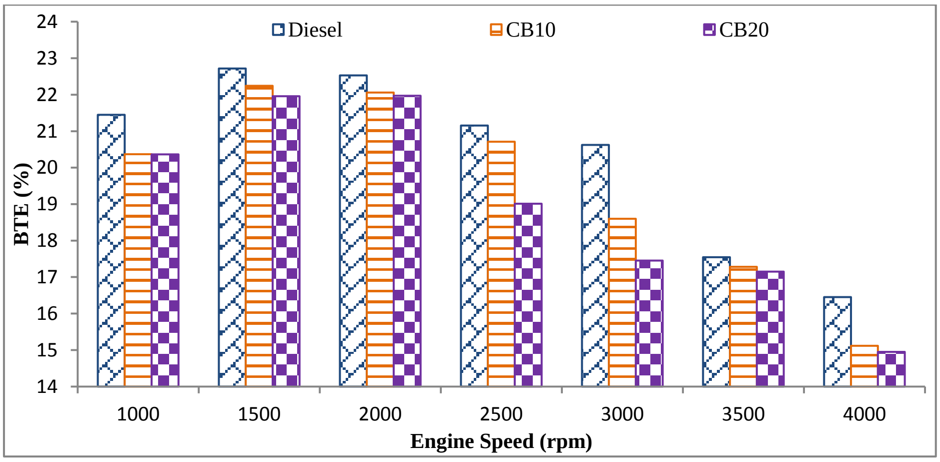


(c)

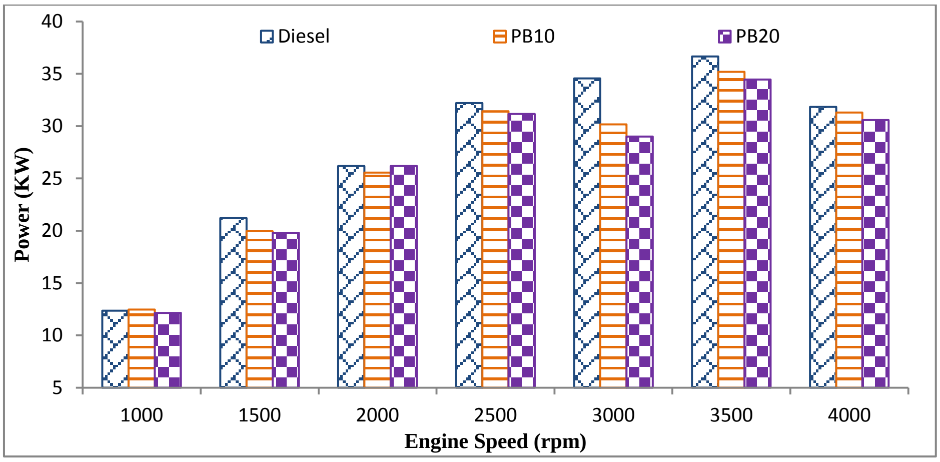
Figure 4.7: BTE versus engine speed for (a) palm (b) mustard and (c) *Calophyllum inophyllum* biodiesel blended fuel at full load condition

4.5.3 Variation of power

The effect of Palm, Mustard and *Calophyllum* biodiesel blends with diesel fuel on the engine brake power with respect to engine speed are shown in Figures 4.8. Considering brake power results, it can be seen that the trend of this parameter for all tested fuels were almost similar with diesel fuel. Brake power increases steadily with engine speed until 3500 rpm and then starts to decrease due to frictional force. It was also evident that brake power decreases slightly with the increasing percentage of biodiesel in the blends.

Maximum power output for PB10 and PB20 were 34.5 kW and 33.8 kW respectively at 3500 rpm engine speed. Maximum power output of PB10 and PB20 were 5.8% and 7.7% less than diesel fuel respectively. Reduction of power for biodiesel may be explained due to higher density and viscosity value which resulted poor atomization and low combustion efficiency (Kalam et al., 2011). This decrease in brake power was also found by other researchers (Yusaf et al., 2011).

Over the whole range of speed, maximum power output for MB10 and MB20 were 35.2 kW and 34.5 kW respectively at 3500 rpm engine revolution. Maximum power output of MB10 and MB20 were 4.1% and 5.8% less than diesel fuel respectively, which was also reported by other researchers (Niemi et al., 1997). Maximum and average power output of mustard biodiesels were found slightly higher compared to the same percentages of palm biodiesels. This can be attributed to the higher viscosity, density, calorific value and cetane number of mustard biodiesel. In pump line nozzle system volumetric injection occurs and higher amount of mass is injected for fuel with higher density. Besides, combustion occurs readily for fuel with higher cetane number, thus more power is developed.



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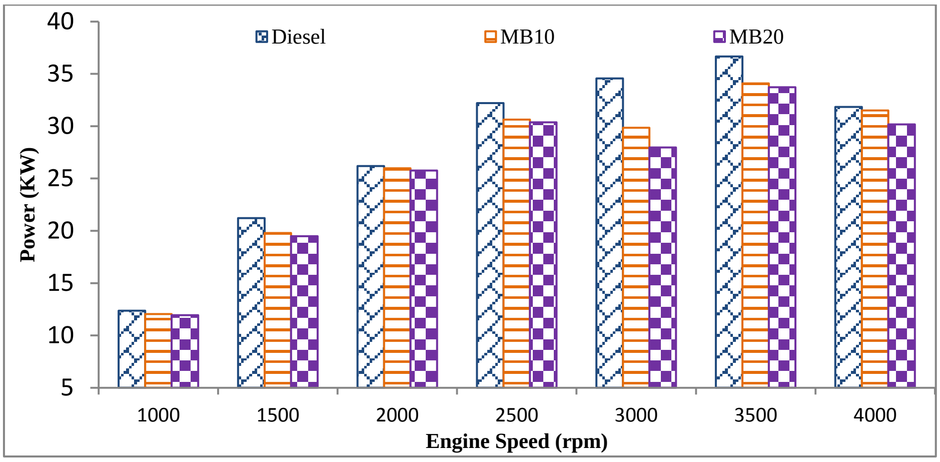

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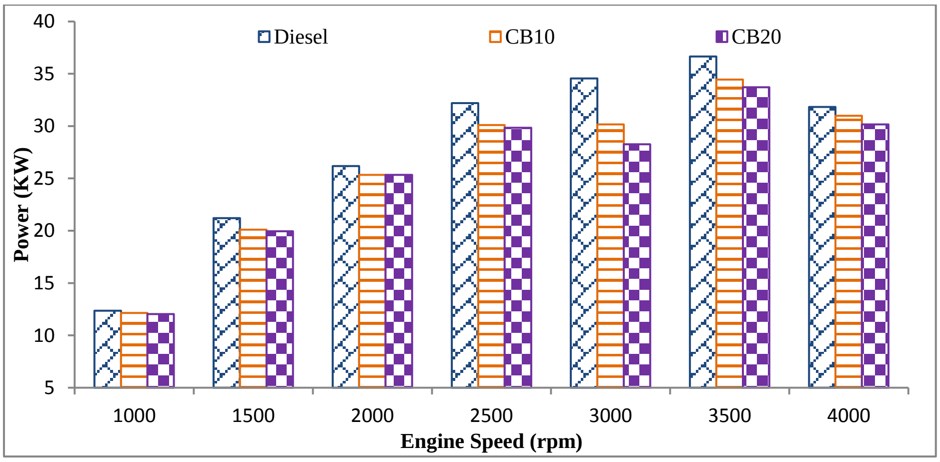

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Figure 4.8: Engine power versus engine speed for (a) palm (b) mustard and (c) *Calophyllum inophyllum* biodiesel blended fuel at full load condition

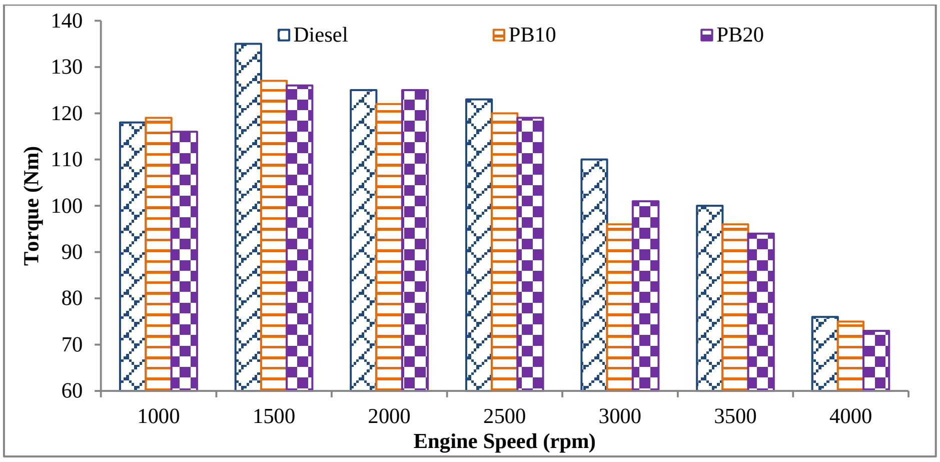
On contrast, for *Calophyllum* biodiesel blends, maximum power output for CB10 and CB20 were 34.1 kW and 33.7 kW respectively at 3500 rpm engine revolution. Maximum power output of CB10 and CB20 were 6.9% and 8% less than diesel fuel respectively Maximum and average power output of *Calophyllum inophyllum* biodiesels were found almost same compared to the same percentages of palm biodiesels.

4.5.4 Variation of torque

Engine torque variations for palm, mustard and *Calophyllum* biodiesel with respect to engine speed are presented in Figure 4.15-4.17. Torque increases steadily to a maximum value at 1500-200 rpm speed range and then decreases with increase in engine speed due to mechanical friction loss and lower volumetric efficiency at higher engine speed. Considering torque output for all the fuel blends tested, it can be seen that the trend of this parameter as a function of speed was almost similar with diesel fuel. Maximum torque was recorded between 124 to 135 Nm range at 1500 rpm engine speed for all tested biodiesels and diesel fuel due to increase in atomization ratio in lower speed. It is also clear that torque decreases slightly with the increasing percentage of biodiesel in the blend.

Maximum torque of PB10 and PB20 were 127 N-m and 126 N-m which were 5.9% and 6.7% lower than diesel fuel respectively. Maximum torque of MB 10 and MB20 were 128 N-m and 127 N-m which were 5.2% and 5.8% lower than diesel fuel respectively. Maximum torque of mustard biodiesel blends were found slightly higher than same percentages of palm biodiesel blends. Higher viscosity, density, cetane number and calorific value of mustard biodiesel than palm biodiesel might cause this slight torque increment.

On the contrary, maximum torque of CB10 and CB20 were 126 N-m and 124 N-m which were 6% and 8% lower than diesel fuel respectively. Maximum torque of *Calophyllum* biodiesel blends were found almost same (varied within 1 N-m range) compared to same percentages of palm biodiesel blends. It can be observed that torque values were lower when biodiesel blended fuels were used which is also supported by many researchers (Kousoulidou et al., 2010; Magín Lapuerta et al., 2008). The reason of reduction in torque can be attributed to the higher viscosity, density and lower calorific value of biodiesel compared to diesel fuel (Kalam et al., 2003).



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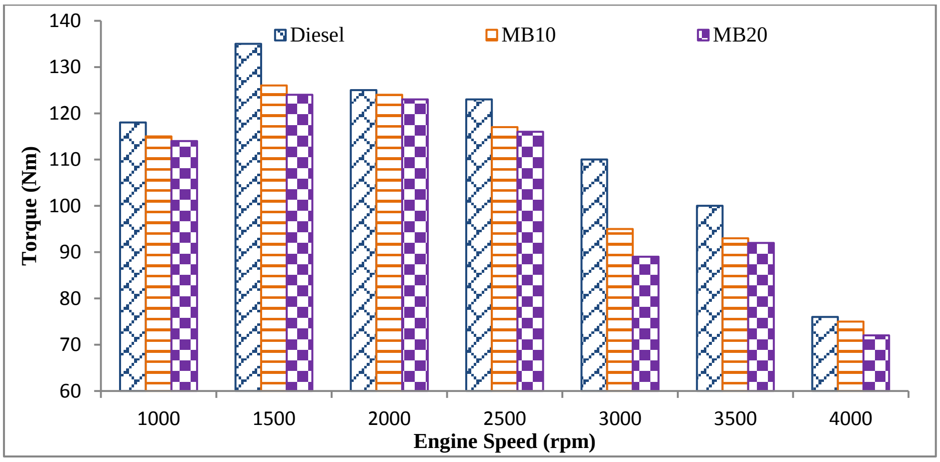

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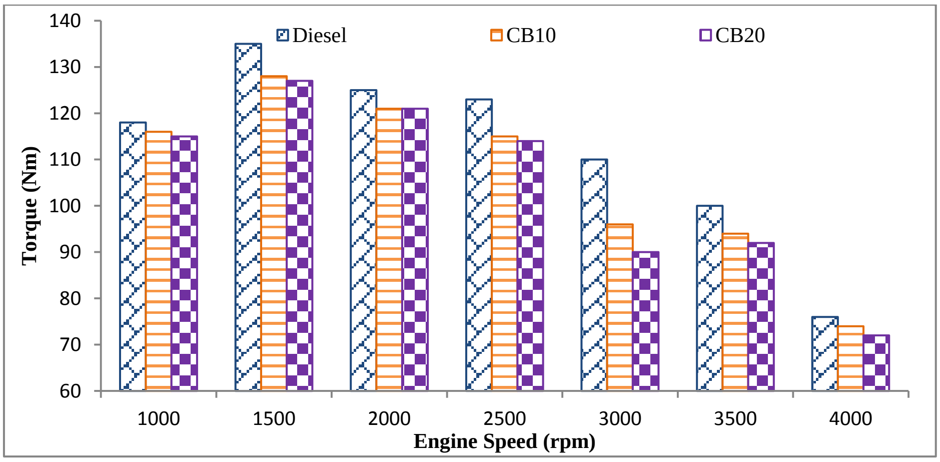

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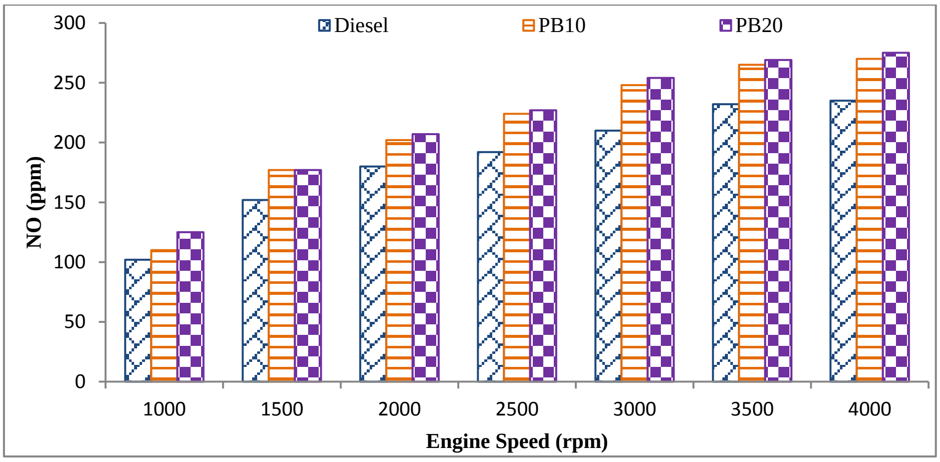
Figure 4.9: Engine torque versus engine speed for (a) palm (b) mustard and (c) *Calophyllum inophyllum* biodiesel blended fuel at full load condition

4.6 Emission analysis

In order to examine emission characteristics of all fuel samples, a portable BOSCH exhaust gas analyzer (model BEA-350) was used to measure the concentration of exhaust gases of the test engine. This section describes the effect of different fuel properties on different engine emission parameters. Emission parameters include Nitric Oxide (NO), Hydrocarbon (HC), Carbon Monoxide (CO) and Carbon dioxide (CO_2) emission. Emission analysis was carried out at all engine speed ranged from 1000-4000 rpm at every 500 rpm interval at 100% load. The exhaust gases emission of NO and HC was measured in ppm while CO and CO_2 in volume percent. In this research work, exhaust emission was measured at various speeds ranged from 1000 rpm to 4000 rpm at an interval of 500 rpm at full load conditions by inserting probe into the tail pipe.

4.6.1 NO emission

Nitrogen and oxygen produces NOx at elevated temperatures during the combustion process. The oxides of nitrogen in the exhaust emissions contain nitric oxide (NO) and nitrogen dioxide (NO_2). The formation of NOx is highly dependent on in-cylinder temperatures, the oxygen concentration, and residence time for the reaction to take place (Palash et al., 2014). The results of NO emission for all biodiesels and diesel fuel are presented in Figure 4.10. It can be observed that PB10 and PB20 produced 14% and 17% higher NO than diesel fuel respectively. Similar results were reported by other researchers (Ndayishimiye & Tazerout, 2011; A.N. Ozsezen & Canakci, 2010). On an average, it can be seen that MB10 and MB20 resulted 9% and 12% higher NO than diesel fuel respectively. On an average, CB10 and CB20 produced 13% and 16% higher NO than diesel fuel respectively.



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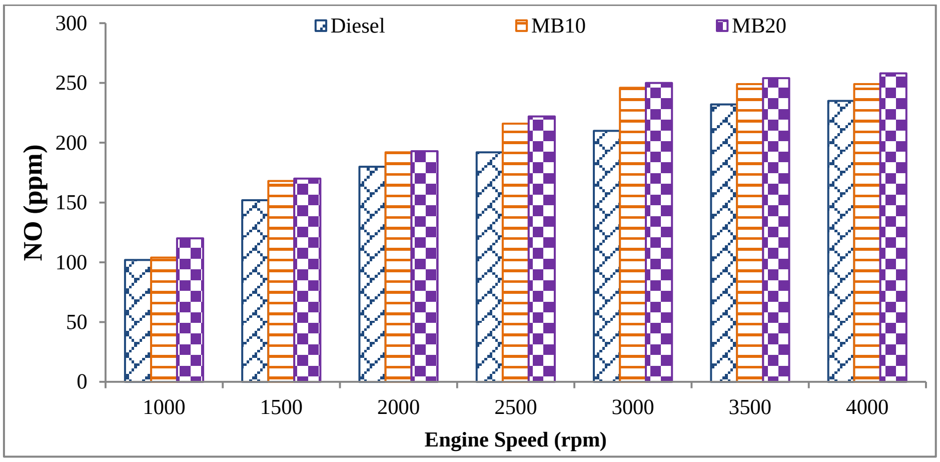

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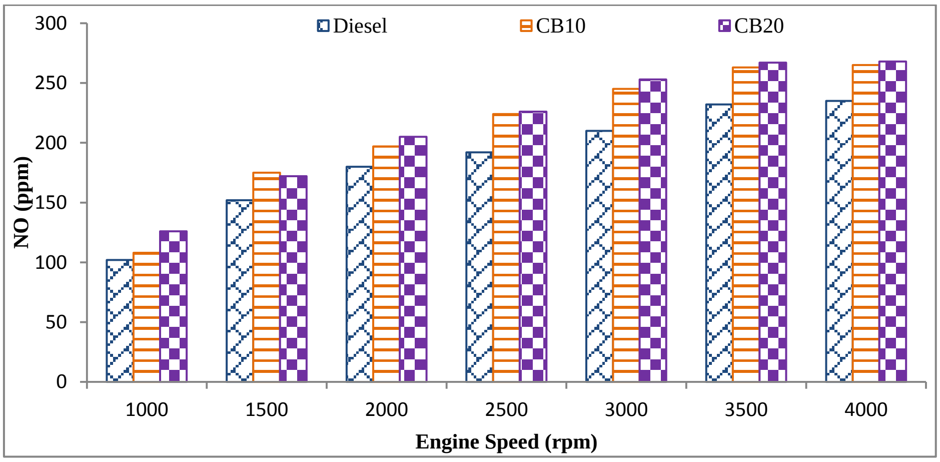

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Figure 4.10: NO emission versus engine speed for (a) palm (b) mustard and (c) *Calophyllum inophyllum* biodiesel blended fuel at full load condition

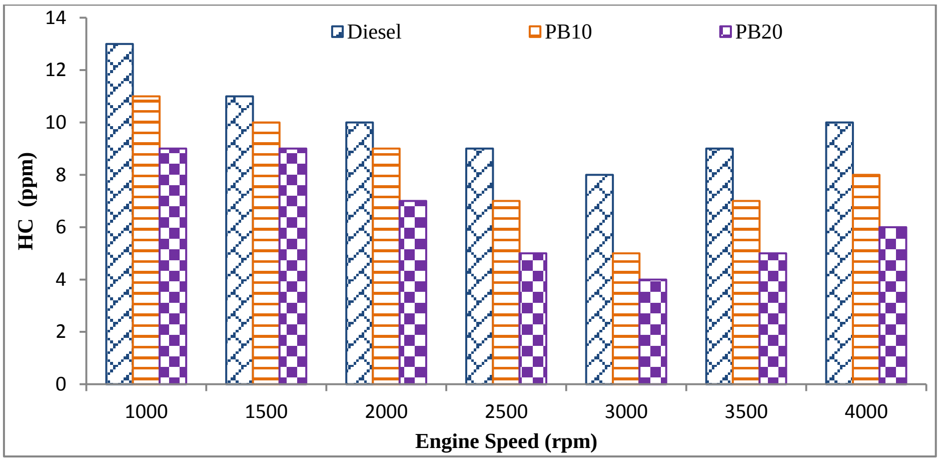
It can be seen that the NO emission values are higher when biodiesel blended fuel is being used. Same observation was observed in literature (El-Kasaby & Nemit-allah, 2013). This can be attributed to the bulk modulus of biodiesel, longer fuel penetration into the engine cylinder, decrease in radiated heat transfer due to reduced soot formation, shorter ignition delay and higher heat release rate. Thus NO emission is increased for biodiesel blend than that of diesel fuel. Moreover, the reason of increasing NO/NOx can be explained in terms of adiabatic flame temperature. Biodiesel fuel contains higher percentages of unsaturated fatty acids that have higher adiabatic flame temperature which causes higher NO/NOx emission (El-Kasaby & Nemit-allah, 2013). Higher cetane number and shorter ignition delay of biodiesel increases NO emission (Rahman et al., 2013). Many researchers found that the higher oxygen content of biodiesel is responsible for increase in NO emission (Palash et al., 2013). Generally, higher oxygen content results in higher combustion temperature which leads to higher NO emission.

4.6.2 HC emission

Hydrocarbons present in the emission are either partially burned or completely unburned. HC emission is resulted from incomplete combustion of fuel due to flame quenching at cylinder lining and crevice region (Kalam et al., 2011). Higher oxygen content of biodiesel ensures more complete combustion which helps to reduce HC emission.

HC emission for palm biodiesel blends at different engine speed is shown in Figure 4.11 (a). It was observed that PB10 and PB20 produced 23% and 38% lower HC than diesel fuel respectively. Variation in average HC emission for mustard biodiesel blends at different engine speed is shown in Figure 4.11 (b). On an average, it was observed that MB10 and MB20 produced 24% and 42% lower HC than diesel fuel respectively. Variation in average HC emission *Calophyllum* biodiesel blends at different engine speed is shown in Figure 4.11 (c). On an average, it was observed that CB10 and CB20 produced 31% and 43% lower HC than diesel fuel respectively.

It can be seen that the HC emission values are lower when biodiesel blended fuel is being used, which is supported by the literature (Niemi & Hatonen, 1998; A.N. Ozsezen & Canakci, 2010; Ulusoy et al., 2004). This can be attributed to the higher oxygen contents and higher cetane number of biodiesel fuel. Biodiesel contains higher oxygen and lower carbon and hydrogen than diesel fuel which trigger an improved and complete combustion process. Thus HC emission is reduced in case of using biodiesel blend in a diesel engine. HC emission decreased steadily to a minimum value up to 3000 rpm speed and then increased with increase in engine speed. At higher speed the time taken for combustion became shorter and comparatively less complete combustion occurred compared to lower engine speed range. Hence, HC emission increased at 3500-4000 rpm speed range.



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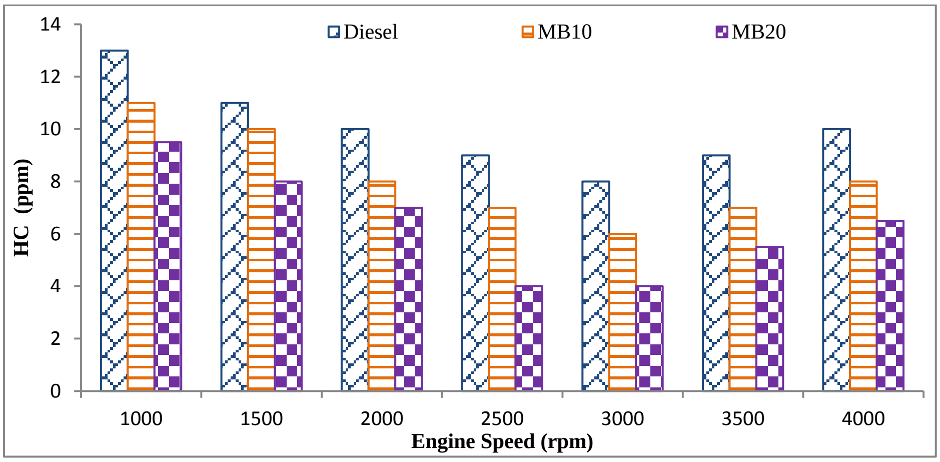

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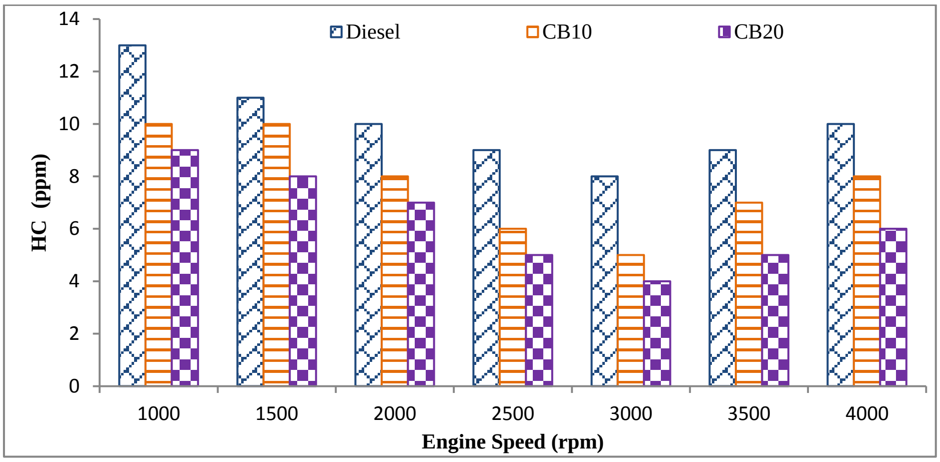

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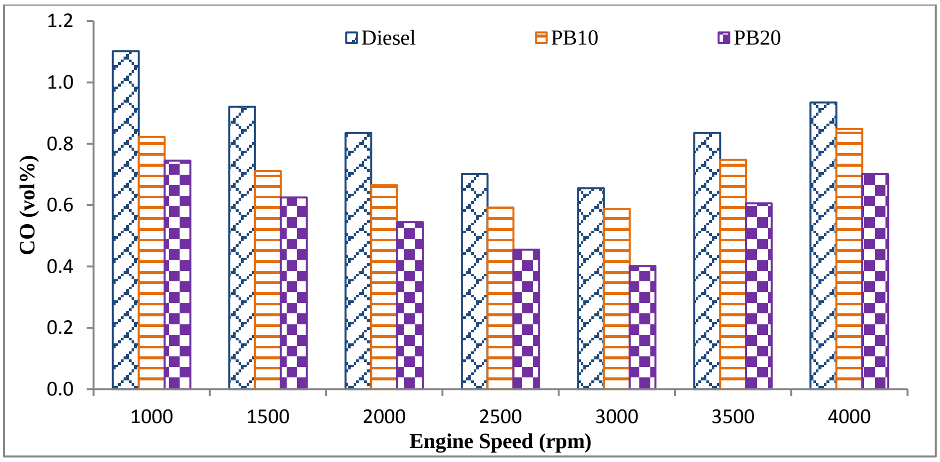
Figure 4.11: HC emission versus engine speed for (a) palm (b) mustard and (c) *Calophyllum inophyllum* biodiesel blended fuel at full load condition

4.6.3 CO emission

Incomplete combustion CO_2 results in CO formation in the exhaust gas. If the combustion is incomplete due to shortage of air or due to low gas temperature, CO will be formed. Mostly, some factors such as air-fuel ratio, engine speed, injection timing, injection pressure and type of fuels have an impact on CO emission (Metin Gumus et al., 2012). Additional oxygen content of biodiesel aids more complete combustion than diesel fuel, hence results in lower CO emission (M. Gumus, 2010). CO emission of mustard, palm and *Calophyllum* biodiesels showed similar variations and slight deviation in amount.

Variation in average CO emission for palm biodiesel blends at different engine speed is shown in Figure 4.12 (a). It was observed that PB10 and PB20 produced 16% and 31% lower CO than diesel fuel respectively. Similar results were also found by other researchers (Ong et al., 2011; A.N. Ozsezen & Canakci, 2010). Variation in average CO emission for MB blends at different engine speed is shown in Figure 4.12 (b). On an average, it was observed that MB10 and MB20 produced 19% and 32% lower CO than diesel fuel respectively.

CO emission for *Calophyllum* biodiesel blends at different engine speed is shown in Figure 4.12 (c). On an average, it was observed that CB10 and CB20 produced 23% and 33% lower CO than diesel fuel respectively. CO emission was also found lower for *Calophyllum* biodiesel compared to diesel fuel by other researchers (Atabani & César, 2014; Dilip Kumar Bora et al., 2012).



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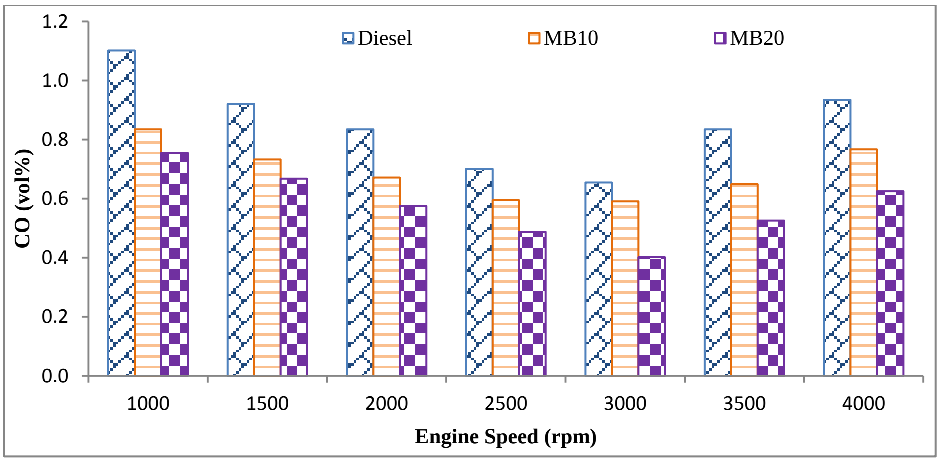

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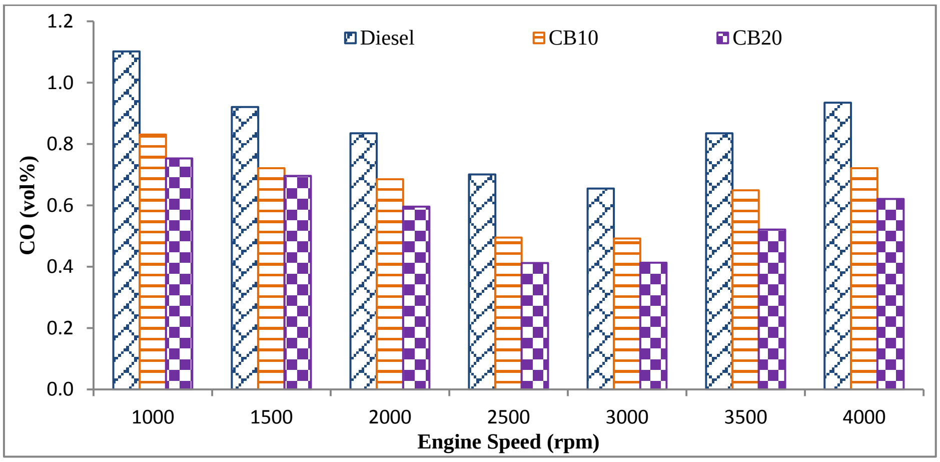

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Figure 4.12: CO emission versus engine speed for (a) palm (b) mustard and (c) *Calophyllum inophyllum* biodiesel blended fuel at full load condition

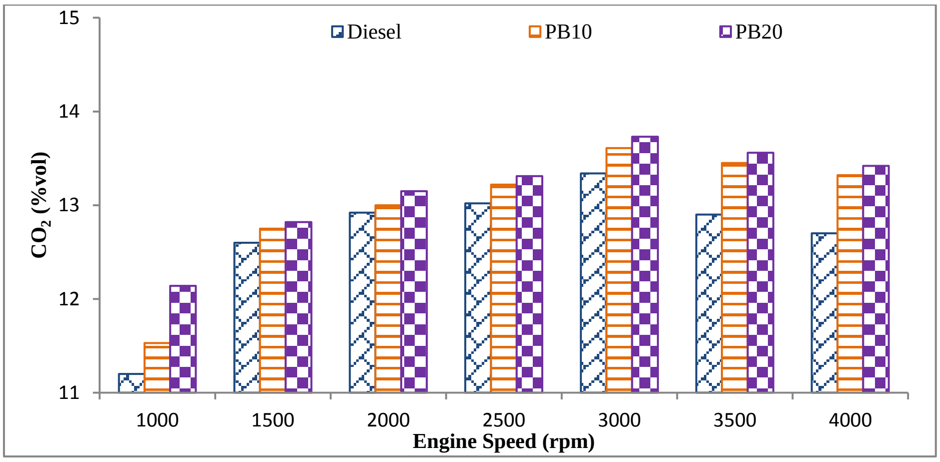
It can be seen that the CO emission values are lower when biodiesel blended fuel is being used, which is supported by the literature (Habibullah et al., 2014; Hirkude & Padalkar, 2014; Qi et al., 2014). This can be attributed to the higher oxygen contents and higher cetane number of biodiesel fuel. It is reported that biodiesel fuel contains 12% higher oxygen. As the percentage of biodiesel increased in the blend, the higher oxygen contents of biodiesel allow more carbon molecules to burn and combustion becomes completed. Thus CO emission is reduced in case of using biodiesel blend in a diesel engine. CO emission decreased steadily to a minimum value up to 3000 rpm speed and then increased with increase in engine speed. At higher speed the time taken for combustion became shorter and comparatively less complete combustion occurred compared to lower engine speed range. Hence, CO emission increased at higher speed range.

4.6.4 CO_2 emission

Complete combustion of fuel produces more CO_2 in the exhaust. The concentration of CO_2 has opposite trend to that of concentration of CO owing to improvement of combustion process (M. Gumus, 2010). Variation in average CO_2 emission for palm biodiesel blends at different engine speed is shown in Figure 4.13 (a). The average CO_2 emission for the entire speed range for PB10 and PB20 were found 1.1% and 2.5% higher than that of diesel fuel. Similar result was also reported by other researchers (Rizwanul Fattah et al., 2014). As biodiesels are oxygenated fuels, more complete combustion occurs and amount of CO_2 increases. CO_2 emission for mustard and *Calophyllum* biodiesel blends at different engine speed are shown in Figure 4.13 (b) and Figure 4.13 (c). On an average, it was observed that MB10 and MB20 produced 1.6% and 3.3% lower CO_2 than diesel fuel respectively. On contrast, CB10 and CB20 produced 1.9% and 5.7% lower CO_2 than diesel fuel respectively. Venkanna & Reddy, (2011) found similar results by using *Calophyllum* biodiesel.

It can be seen that the CO_2 emission values are higher when biodiesel blended fuel is being used. It is also seen that CO_2 emission also increases as the percentages of biodiesel increases in the blend. This is happened due to the higher oxygen contents in the biodiesel fuel which improves the quality of combustion (Metin Gumus et al., 2012). CO_2 emission increases steadily to a maximum value up to 3000 rpm speed and then decreases with increase in engine speed.

At higher speed the time taken for combustion become shorter and comparatively less complete combustion occurred compared to lower engine speed range. Hence, CO_2 emission decreases at higher speed range. The production of CO_2 from the combustion of fossil fuels causes many environmental problems such as the accumulation of CO_2 in the atmosphere. Although biofuel combustion produces CO_2, absorption by crops helps to maintain CO_2 levels (Ramadhas et al., 2005). Therefore, biodiesel combustion can be regarded as definitely causing lower net CO_2 emission than diesel fuel.



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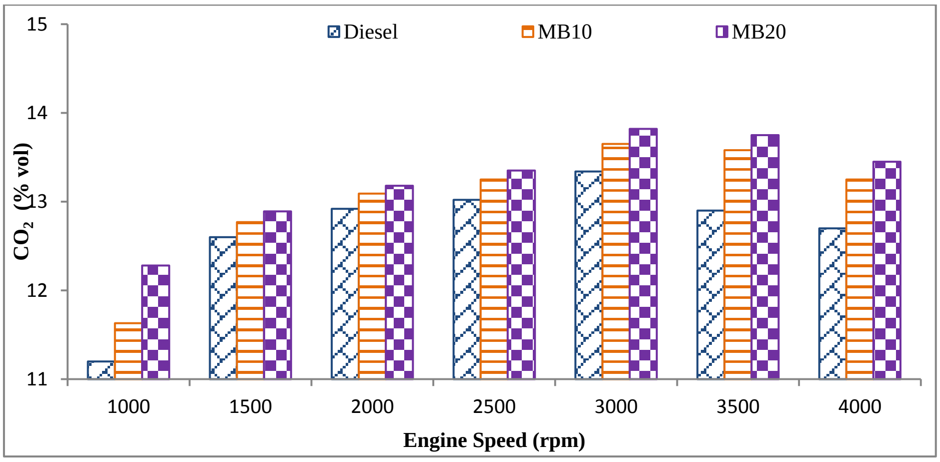

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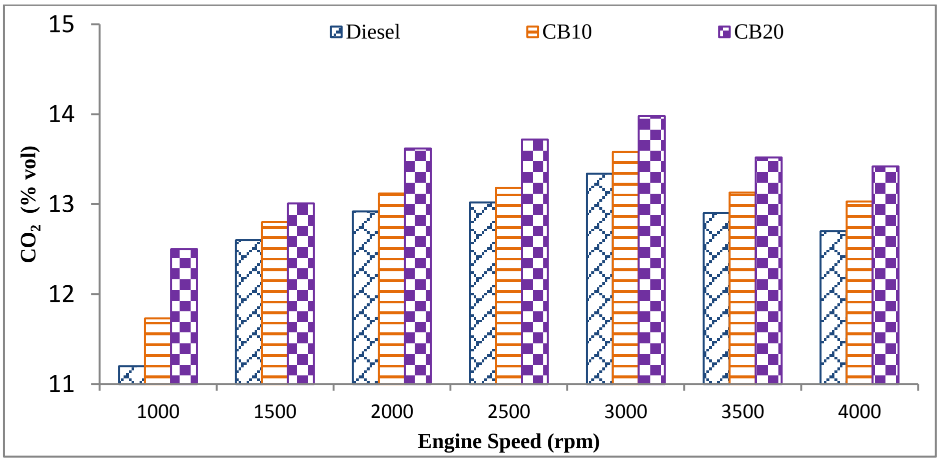

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Figure 4.13: CO_2 emission versus engine speed for (a) palm (b) mustard and (c) *Calophyllum inophyllum* biodiesel blended fuel at full load condition

4.7 Combustion analysis

The cylinder gas pressure depends on the combustion rate in the premixed combustion phase. This phase is controlled by the ignition delay period and the spray behavior of the fuel which are primarily controlled by its viscosity and volatility. Engine combustion characteristics for biodiesel blends were investigated by means of cylinder gas pressure and heat release. The heat release was calculated from the cylinder gas pressure data, collected during the experiment. Engine cylinder pressures for biodiesel blends and diesel were compared under full load at a medium engine speed of 3000 rpm. Biodiesel and its blends followed the similar cylinder pressure pattern to that of diesel. Figure 4.14 shows the changes in cylinder gas pressure with respect to crank angle at 3000 rpm engine speed. No significant trace of knock was found as cylinder pressure smoothly varied over the engine speed range. Table 4.4 shows some main comparable pressure results extracted from Figure 4.14.

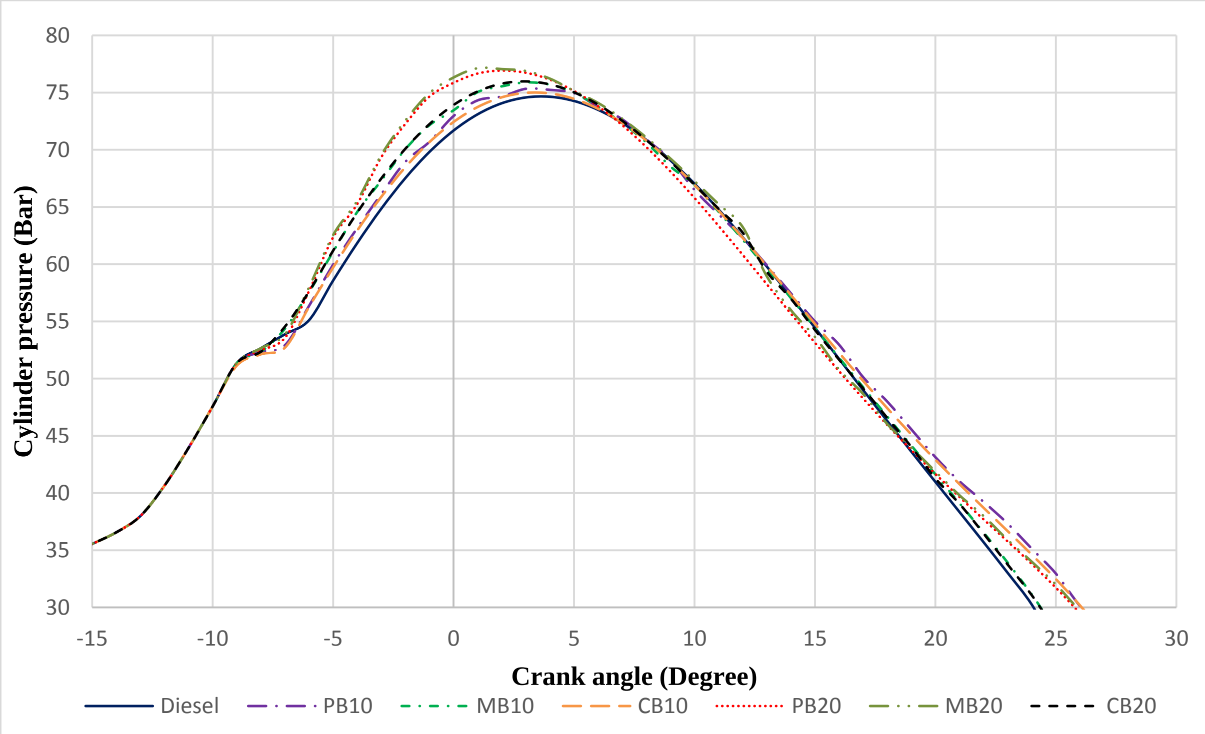

Figure 4.14: Cylinder pressure versus crank angle at 3000 rpm speed and full load condition for all tested fuels.

Table 4.4: Results of in cylinder pressure for all tested fuels

Fuel sample	Peak cylinder pressure (bar)	Crank angle ATDC (Degree)	Percentage increase in peak pressure compared to diesel
Diesel	74.63 bar	4.9º	-
PB10	75.33 bar	4.2º	1.0%
MB10	75.90 bar	4º	1.3%
CB10	74.97 bar	4.4º	0.5%
PB20	76.67 bar	3.7º	2.7%
MB20	77.13 bar	2.9º	3.4%
CB20	75.97 bar	3.9º	1.8%

Maximum cylinder gas pressure occurred within the range of 2º- 5º CA ATDC for all tested fuels. Peak cylinder pressure depends on the burned fuel fraction during the premixed burning phase, i.e. the initial stage of combustion (Mohibbe Azam et al., 2005). Combustion started earlier for biodiesel and its blends than for diesel fuel because of the shorter ignition delay period and higher cetane number of biodiesel. Biodiesel fuel has higher density than diesel fuel. The density is proportional to the bulk modulus. The bulk modulus is a measure of how a unit volume of fluid can be easily discharged when increasing the pressure on it. A higher bulk modulus indicates that the fluid is incompressible. If a fuel is less compressible, the pressure will build more quickly and the fuel will need less time and will be injected in the combustion chamber in the compression cycle, whereas if the fuel is more compressible more time will be required to reach the nozzle opening pressure, and the fuel will be injected into the combustion chamber later. Therefore, higher density and bulk modulus of fuel lead earlier injection timing. The early injection timing can lead to a longer premixed burning phase and produces higher cylinder temperature or more NOx emission. Though ignition delay period was not measured in this study, the start of combustion may reflect the variation in ignition delay among all tested fuels. At high temperature, the chemical reactions during the injection of biodiesel resulted in the break-down of the high molecular weight esters. These complex reactions led to the formation of low molecular weight gases. Rapid gasification of this lighter weight compounds in the fringe of the spray spreads out the jet, ignited earlier and reduced ignition delay period (Agarwal & Khurana, 2013). Therefore, biodiesel blends resulted in higher peak cylinder pressures compared to diesel fuel. Similar results were also found by other researchers (Sahoo & Das, 2009).

The heat release rate indicates the ignition delay and combustion duration. Figure 4.15 shows the calculated heat release rates of all tested fuels as functions of crank position at 3000 rpm and full load condition. All tested fuels indicated rapid premixed burning followed by a diffusion combustion period. Table 4.5 shows the main comparable results of heat release rate for all tested fuels. It can be seen that the start of combustion happens earlier for biodiesel blends as heat release curves are shifted to the left compared to diesel fuel. This behavior can be explained by the low volatility of biodiesel blends (Canakci et al., 2009). Ignition delay is the time from the start of fuel injection to the start of combustion. The cetane number is a measure of a fuel's auto-ignition quality characteristics. Biodiesel has a higher cetane number than diesel fuel because it is composed of large chain hydrocarbon groups (with virtually no branching or aromatic structures) (Hoekman et al., 2012).Thus the ignition quality represented by the cetane number is found to be one of the most important characteristics of fuel and therefore it is important to quantitatively evaluate the ignition quality and ignition delay time of the biodiesel. The shorter the ignition delay time the higher is the cetane number of fuel and vice versa. Cetane number of PB, MB and CB were found 6%, 58%, and 22% higher than diesel fuel respectively. Therefore, MB should show shortest ignition delay during engine combustion compared to PB or MB. Due to their early start of combustion and shorter ignition delay, biodiesel and its blends completed the premixed combustion phase earlier than diesel fuel. The total combustion duration seems to be shorter with the increase in biodiesel blend ratio. However, the heat release rates during the late combustion phase for biodiesel blends were found lower than that of diesel fuel. This is because of the higher oxygen content of biodiesel ensures complete combustion of the fuel that was left over during the main combustion phase and continue to burn in the late combustion phase. The higher heat release rate for biodiesel showed logical impressions in engine emission results. Due to higher heat release rate, hence higher engine in cylinder temperature, NO emission for biodiesel increased around 10-15%. On the contrary HC and CO decreased significantly.

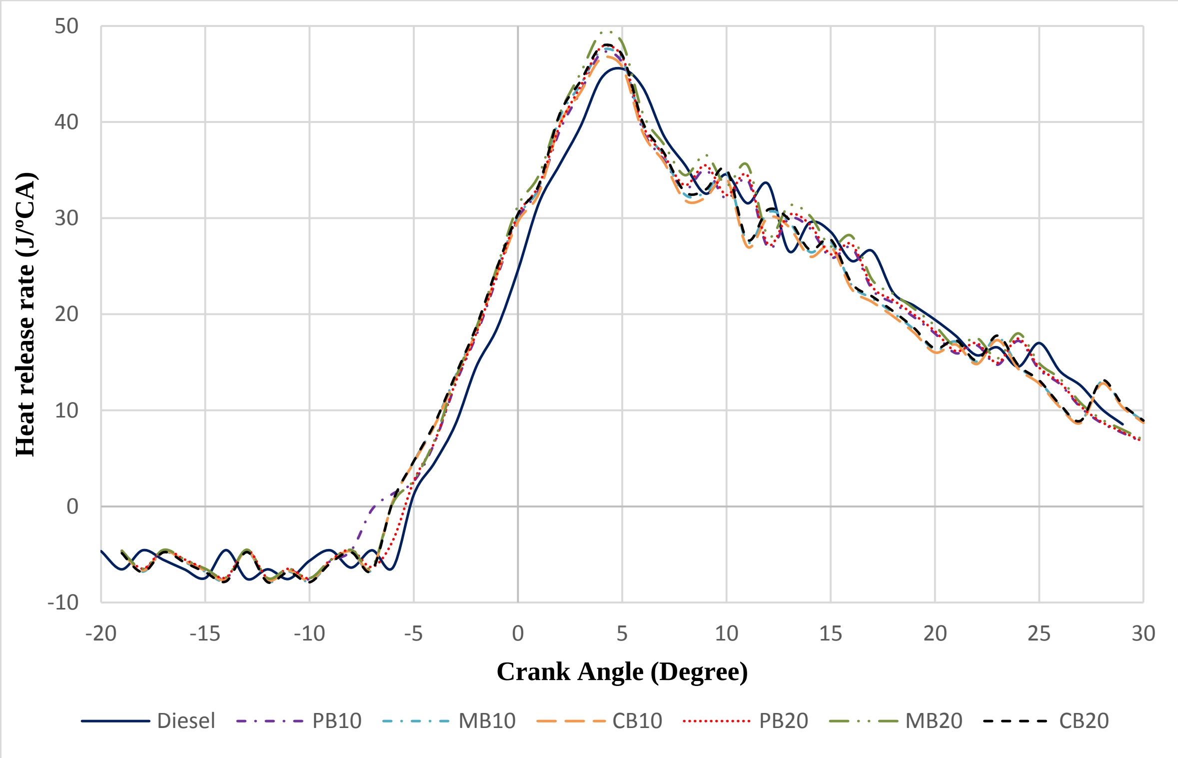

Figure 4.15 Heat release rate versus crank angle at 3000 rpm speed and full load condition for all tested fuels

Table 4.5: Results of heat release rate for all tested fuels

Fuel sample	Peak heat release rate (J)	Crank angle ATDC (Degree)	Percentage increase in peak heat release rate compared to diesel
Diesel	45.54	5.10º	-
PB10	47.17	4.95º	3.56%
MB10	47.46	4.92º	4.21%
CB10	46.63	5.00º	2.39%
PB20	48.11	4.65º	5.64%
MB20	49.29	4.85º	8.23%
CB20	47.78	4.47º	5.00%

CHAPTER 5: CONCLUSIONS AND RECOMMENDATION

The main objective of this research endeavor is to study the potential of palm, mustard and *Calophyllum* oil as a promising biodiesel feedstock that are easily accessible in many parts of the world. Series of experiment were sequentially conducted in this research to characterize the physical and chemical properties of palm, mustard and *Calophyllum* biodiesel and their 10% to 90% by volume blends such as kinematic viscosity, density, flash point, calorific value and oxidation stability. Finally, 10% and 20% biodiesel blends of each feedstock were used to evaluate their performance in an unmodified multi-cylinder diesel engine and compared with that of diesel fuel. Based on this research work, the following conclusion could be drawn:

1. The properties of palm, mustard and *Calophyllum* and their blends such as kinematic viscosity, density, cloud point, pour point, flash point, calorific value and oxidation stability meet the ASTM D6751 standard.

2. Due to the blending of biodiesel with diesel fuel, the key fuel properties such as kinematic viscosity, density, calorific value and oxidation stability are remarkably improved.

3. Mustard biodiesel is much superior than most of the conventional biodiesels regarding oxidation stability and calorific value. Oxidation stability of MB10 and MB20 meets the EN590 specification of European standard (20 h). Most of the conventional biodiesel do not meet this specification in a wide range of blends. Calorific value of mustard biodiesel was found 40.40 MJ/kg. From

published literatures, it was found that all other biodiesels have calorific value less than mustard biodiesel, which is a new finding.

4. Mustard biodiesel has cloud point and pour point (5°C and -18 °C) lower than available biodiesels made from tropical oils like palm oil or biodiesel produced from animal fats. Hence, mustard biodiesel will perform well in cold climate than other biodiesels.

5. The BSFC values for biodiesel blended fuels were higher compared to that of diesel fuel due to their lower calorific value and higher density. Among all biodiesel blended fuels, mustard biodiesel blended fuel showed the highest average BSFC followed by *Calophyllum* and palm biodiesel blended fuels.

6. Engine performance results show that engine torque and brake power for biodiesel blended fuels decreased compared to diesel fuel due to their higher density, viscosity and lower calorific value. The highest torque and brake power compared to diesel fuel was found for mustard biodiesel followed by palm and *Calophyllum* biodiesel blended fuels respectively.

7. In case of engine emission test, a reduction in CO and HC emissions was found for biodiesel blended fuels compared to that of diesel fuel. The highest average reduction in CO and HC was found for mustard biodiesel blended fuel followed by *Calophyllum* and palm biodiesel blended fuels due to the availability of saturated fatty acids composition in the fuels.

8. An increase in NO emissions was found for biodiesel blended fuels compared to that of diesel fuel due to their higher oxygen contents, saturated fatty acids, in cylinder temperature and pressure etc. CO_2 emission also increased due to the complete combustion of biofuel.

9. The maximum in cylinder pressure and HRR occurred within the range of 3º-5º CA ATDC for all tested fuels.

10. The peak cylinder pressure and heat release of biodiesel blends were found closer to TDC compared to diesel fuel. This is due to the shorter ignition delay and higher cetane number of biodiesel.

In conclusion, palm, mustard and *Calophyllum* are potential feedstock for biodiesel production, and up to 20% of their blends can replace diesel fuel without modifying engines to reduce dependency on petro-diesel and produce cleaner exhaust emissions. Like palm, mustard and *Calophyllum* can also be successfully cultivated in hot climates like Malaysia to produce biodiesel.

5.1 Recommendations for future work

This research work has been carried out to produce biodiesel from available feedstocks and to evaluate the performance of biodiesel-diesel blends in a diesel engine. In this regard, the following recommendations for the future work can be suggested:

1. This research work only focused on engine performance and emission, so it is recommended to focus on controlled combustion characteristics of biodiesel

blended fuels in a diesel engine along with corrosion, wear and material compatibility studies.

2. In this research work up to 20% by volume blend of biodiesel was used, it is recommended to use higher percentages blends and then compare the findings with lower blends.

3. Antioxidant can be blended with biodiesel fuel to improve fuel properties and engine performance, combustion and emission can be measured.

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Appendix A
Publication

Sanjid, A., Masjuki, H. H., Kalam, M. A., Rahman, S. M. A., Abedin, M. J., & Palash, S. M. (2014). Production of palm and jatropha based biodiesel and investigation of palm-jatropha combined blend properties, performance, exhaust emission and noise in an unmodified diesel engine. Journal of Cleaner Production, 65(0), 295-303. [ISI indexed, Q1]

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