A COMPREHENSIVE ANALYSIS OF EDIBLE AND NON-EDIBLE BIODIESEL FEEDSTOCKS

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ABSTRACT

Traditionally, biodiesel has been produced from edible oils due to their low free fatty acids. However, their use has raised some issues such as food versus fuel and many other problems that have negatively affected their economic viability. Therefore, exploration of non-edible oils may significantly reduce the cost of biodiesel especially in poor countries which can hardly afford the high cost of edible oils. This research aims to produce biodiesel from several edible and non-edible oils that are readily available in the South East Asian market. These oils include; *Jatropha curcas, Calophyllum inophyllum, Sterculia foetida*, *Moringa oleifera*, *Pangium edule*, *Croton megalocarpus, Patchouli, Elaeis guineensis* (palm), *Cocos nucifera* (coconut), Manketti (*Schinziophyton rautanenii*), *Brassica napus* (canola) and *Glycine Max* (soybean) oils. This was followed by an investigation of physico-chemical properties of the produced biodiesel such as kinematic viscosity, density, flash point, cloud point, pour point, cold filter plugging point, viscosity index and oxidation stability. This research also discusses biodiesel-biodiesel and biodiesel-diesel blending to improve some of the properties of these feedstocks. Moreover, the effect of biodiesel-diesel blends of 10% and 20% by volume on engine performance and emissions was evaluated in a multi-cylinder Mitsubishi Pajero turbocharged diesel engine.

It has been found that most of the properties of biodiesels are following the standard specified by ASTM D 6751. Moreover, biodiesel-biodiesel blending has resulted in remarkable improvement in some properties such as kinematic viscosity, cloud point, pour point and cold filter plugging point. For instance, blending of SFME and CoME improves the viscosity of SFME from 6.3717 mm^2/s to 5.3349 mm^2/s (3:1), 4.4912 mm^2/s (1:1) and

3.879 mm^2/s (1:3). It was also found that blending has improved the cold flow properties of PME, CIME and JCME respectively. Over the entire range of speed, it was found that B_{10} and B_{20} of CMME, CIME and COME give average reduction in torque, brake power (BP) and increased brake specific fuel consumption (BSFC) compared to B_0. In case of engine emission, the fuel blends give an average reduction in carbon monoxide (CO) and hydrocarbon (HC) emissions. However, CMME and COME blends increased nitrous oxides (NO) emission while CIME emits lower NO compared to B_0. In conclusion, it is concluded that B_{10} and B_{20} can be used as a diesel fuel substitute with no modifications.

ABSTRAK

Pada asalnya, biodiesel dihasilkan dari minyak yang boleh dimakan kerana ianya mempunyai kandungan asid lemak bebas yang rendah. Walaubagaimanapun, penggunaannya telah menimbulkan beberapa isu seperti makanan melawan bahan api dan banyak lagi masalah lain yang boleh mendatangkan kesan negatif kepada kemajuan ekonpremonominya. Oleh itu, penerokaan minyak yang tidak boleh dimakan boleh mengurangkan kos biodiesel terutamanya di negara-negara miskin yang tidak mampu untuk membayar kos yang tinggi bagi minyak yang boleh dimakan. Kajian ini bertujuan untuk menghasilkan biodiesel dari beberapa jenis minyak yang boleh dimakan dan tidak boleh dimakan yang sedia ada di pasaran Asia Tenggara. Minyak-minyak ini termasuklah minyak dari Jatropha curcas, Calophyllum inophyllum, Sterculia foetida, Moringa oleifera, Pangium edule, Croton megalocarpus, Patchouli, Elaeis guineensis (sawit), Cocos nucifera (kelapa), Brassica napus (kanola) dan Glycine Max (kacang soya). Ini diikuti dengan kajian terhadap ciri-ciri fizikal-kimia biodiesel seperti kelikatan kinematik, ketumpatan, takat kilat, titik awan, titik curahan, titik pemasangan penapis sejuk, indeks kelikatan dan kestabilan pengoksidaan. Kajian ini juga membincangkan tentang konsep campuran biodiesel-biodiesel dan biodiesel-diesel untuk memperbaiki beberapa ciri-ciri bahan mentah ini. Selain itu, kesan campuran 10% dan 20% biodiesel-diesel mengikut isipadu terhadap prestasi enjin dan kadar pembebasan telah dikaji ke atas sebuah enjin diesel multi-silinder Pajero Mitsubishi berkuasa turbo.

Ia telah mendapati bahawa kebanyakan sifat-sifat biodiesels mengikuti standard yang ditetapkan oleh ASTM D 6751. Selain itu, biodiesel biodiesel adunan telah menyebabkan

peningkatan yang luar biasa dalam beberapa hartanah seperti kelikatan kinematik, titik awan, tuangkan titik dan penapis sejuk memasang mata. Sebagai contoh, pengadunan SFME dan datang memperbaiki kelikatan SFME dari 6,3717 mm^2/s untuk 5,3349 mm^2/s (3:1) , 4,4912 mm^2/s (1:1) dan 3,879 mm^2/s (1:3). Ia juga mendapati bahawa pengadunan telah meningkatkan sifat aliran sejuk PME, CIME dan JCME masing-masing. Keseluruhan julat kelajuan, didapati bahawa B10 dan B20 daripada CMME, CIME dan DATANG memberikan pengurangan purata dalam tork, kuasa brek (BP) dan peningkatan penggunaan brek tertentu bahan api (BSFC) berbanding B0. Dalam kes pelepasan enjin, campuran bahan api memberikan purata pengurangan karbon monoksida (CO) dan hidrokarbon (HC) pelepasan. Walau bagaimanapun, CMME dan DATANG campuran meningkat oksida nitrus (NO) pelepasan sementara CIME mengeluarkan NO lebih rendah berbanding dengan B0. Kesimpulannya, ia membuat kesimpulan bahawa B10 dan B20 boleh digunakan sebagai pengganti bahan api diesel tanpa pengubahsuaian.

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NOMENCLATURE

ASTM	American society for testing and materials
AV	Acid value
B_0	(100% diesel and 0% biodiesel)
B_{10}	(90% diesel and 10% biodiesel)
B_{20}	(80% diesel and 20% biodiesel)
BP	Brake power
BSFC	Brake specific fuel consumption
CCaO	Crude Canola oil
CCIO	Crude *Calophyllum inophyllum* L. oil
CCO	Crude Coconut oil
CCMO	Crude *Croton megalocarpus* L.oil
CFPP	Cold filter plugging point
CIME	*Calophyllum inophyllum* methyl ester
CJCO	Crude *Jatropha curcas* L. oil
CME	Canola methyl ester
CMME	*Croton megalocarpus* methyl ester

CMO	Crude Manketti oil
CMOO	Crude *Moringa oleifera* L. oil
CN	Cetane number
CoME	Coconut methyl ester
CO	Carbon monoxide
CO_2	Carbon dioxide
CP	Cloud point
CPaO	Crude *Patchouli* oil
CPEO	Crude *Pangium edule* oil
CPO	Crude Palm oil
CSFO	Crude *Sterculia foetida* L. oil
CSO	Crude Soybean oil
CV	Calorific value
FAC	Fatty acid composition
FAME	Fatty acid methyl ester
FP	Flash point
GHG	Greenhouse gas emission

GJ	Gigajoule
HC	Hydrocarbons
IV	Iodine value
JCME	*Jatropha curcas* methyl ester
kJ/kg	Kilojoule/kg
KV	Kinematic viscosity
MOME	*Moringa oleifera* methyl ester
MME	Manketti methyl ester
NO	Nitrogen oxide
OS	Oxidation stability
PEME	*Panium edule* methyl ester
PaME	*Patchouli* methyl ester
PME	Palm oil methyl ester
PP	Pour point
rpm	Revolution per minute
SFME	*Sterculia foetida* methyl ester
SME	Soybean methyl ester

SN	Saponification number
VI	Viscosity index

CHAPTER 1

INTRODUCTION

1.1 Overview

Energy is a crucial factor for humanity to continue the economic growth and maintain high standard of living. It is anticipated that the world will need 50% more energy in 2030 than today, of which 45% will be accounted for by China and India (International Energy Agency (IEA), 2007; Shahid & Jamal, 2011). Historically, fossil fuels have played a vital role in the global energy demand. They have been used for running vehicles, power plants and motor engines in the transportation, agricultural and industrial sectors, respectively. However, they are not sustainable and their prices are not stable (Figure 1.1). From this figure, it can be observed that the price projection for 2020 has already been achieved as of today. Moreover, it is believed that climate change, acid rain and smog are currently the most pressing global environmental problems that are attributed to burning fossil fuels. Fossil fuels are the main contributor of carbon dioxide (CO_2), nitrogen oxide (NO_x), volatile organic compounds (VOC) and hydrocarbons (HC). It is predicted that CO_2 will boost up to 40 thousand billion kg in 2030. If the average global temperature increases by more than 2 °C, up to one million species could become extinct and hundreds of millions of people could lose their lives (Ahmad et al., 2011). In 2005 a French economics, industry and finance ministry report suggested that the peak oil production may occur in 2013. However, few models predicted the peak year has already taken place in 2010, while other models predicted that it was in 2005. There are few other studies that reported the peak extraction will occur in 2020. The World Energy Forum (WEF) has predicted that reserves will be exhausted in less than another 10 decades. Others belief that it will be depleted in fewer than 45 years if consumed at an increasing rate of 3% per annum (British petroleum (BP), 2010; Y. C. Sharma, Singh, B., 2009).

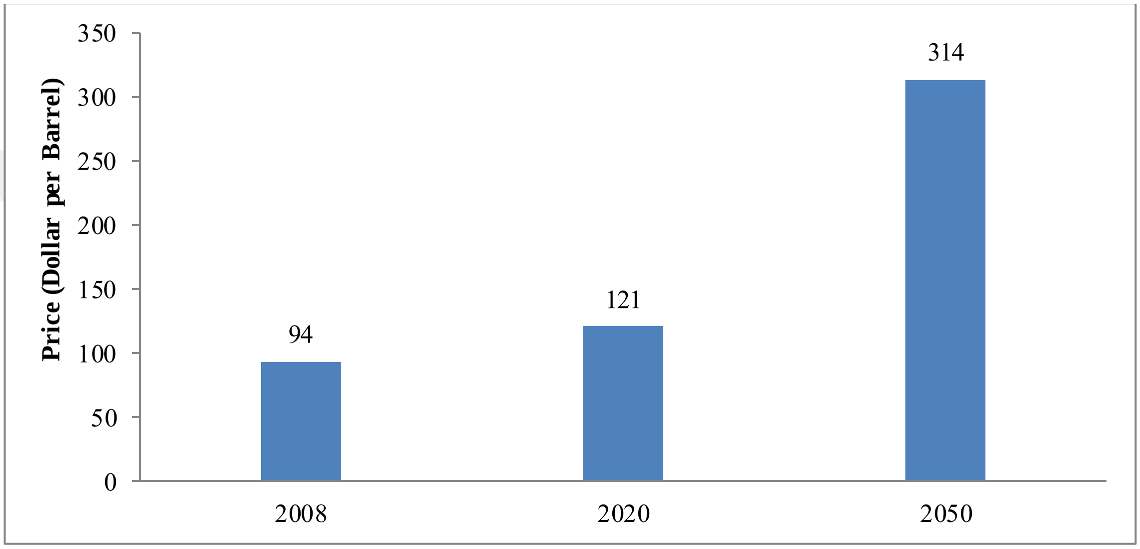


Figure 1.1: Oil price forecast between 2008 to 2050 (Jatrofuels, 2012)

Declining reserves of fossil fuels beside recognition that climate change is stemmed by growing carbon dioxide emissions has generated the interest in promoting biofuels as one of the leading renewable energy sources. The sustainable production of biofuels is a valuable tool in stemming climate change, boosting local economies, particularly in lesser-developed parts of the world, and enhancing energy security for all (Jatrofuels, 2012).

The 2009 United Nations Climate Change Conference, commonly known as the Copenhagen Summit, underscored how renewable and clean fuels sustainably created from bioenergy feedstocks can reduce greenhouse gas emissions (GHGs), improve food security, stimulate economic development and reduce global poverty. The forecast world biodiesel production of 16.4 billion litres is projected to result in a reduction of GHG emissions of 35.9 million tons. The combined biofuels GHG emission reduction is 123.5 million tonnes, an average reduction of about 57% compared to the emissions that would have occurred from the production and use of equivalent quantities of petroleum fuels. This is almost equal to the national GHG emissions of Belgium (131.3 million tons) or Greece (131.8 million tons) (Jatrofuels, 2012).

Biodiesel seems very interesting for several reasons; it is highly biodegradable and has minimal toxicity, can replace diesel fuel in many different applications such as boilers and internal combustion engines without major modifications. Furthermore, a small decrease in performances is reported, and it almost emits zero emissions of sulphates, aromatic compounds and other chemical substances that are destructive to the environment. The carbon dioxide (CO_2) emissions are relatively low when the whole life-cycle is considered (including cultivation, production of oil and conversion to biodiesel) and it appears to cause significant improvement of rural economic potential (Ahmad et al., 2011). Biodiesel has been in use in many countries such as United States of America, Malaysia, Indonesia, Brazil, Germany, France, Italy and other European countries. Therefore, there is a good potential for its production and application. Globally, annual biodiesel production increased from 15 thousand barrels per day in 2000 to 289 thousand barrels per day in 2008 (U.S Energy Information Administration, 2011).

1.2 Research background

Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production (Bart et al., 2010). The wide range of available feedstocks for biodiesel production represents one of the most significant factors of producing biodiesel. To consider any feedstock as a biodiesel source, the oil percentage and the yield per hectare are important parameters. As much as possible the feedstock should fulfil two main requirements: low production costs and large production scale. The availability of feedstock for producing biodiesel depends on the regional climate, geographical locations, local soil conditions and agricultural practices of a country. Feedstock alone represents 75% of the overall biodiesel production cost. Therefore, selecting the cheapest feedstock is vital to ensure low production cost of biodiesel (Atadashi et al., 2010; Bart et al., 2010; Janaun & Ellis, 2010; Shahid & Jamal, 2011).

Edible oil resources are considered as the first generation of biodiesel feedstock. Currently, more than 95% of the world biodiesel is produced from edible oils. However, their use raises many concerns such as food versus fuel crisis and major environmental problems such as serious destruction of vital soil resources, deforestation and usage of much of the available arable land. Moreover, in the last ten years the prices of vegetable oil plants have increased dramatically which will affect the economic viability of biodiesel industry (Balat, 2011; Balat & Balat, 2010; Deng et al., 2011). Furthermore, the use of such edible oils to produce biodiesel is not feasible in the long-term because of the growing gap between demand and supply of such oils in many countries. For instance, dedicating all US soybean to biodiesel production would meet only 6% of diesel demands (Chapagain et al., 2009).

Non-edible oil resources are easily available in many parts of the world especially in wastelands that are not suitable for food crops, they eliminate competition for food, reduce deforestation rate, are more efficient, more environmentally friendly, produce useful by-products and they are very economical comparable to edible oils. The main sources for biodiesel production from non-edible oils are *Jatropha curcas*, *Pongamia pinnata, Calophyllum inophyllum*, *Hevea brasiliensis*, *Croton megalocarpus*, *Cerbera odollam*, *Azadirachta indica* and *Madhuca indica*. Non-edible oils are regarded as the second generation of biodiesel feedstocks. Recently, there have been several publications which highlighted the positive effects of blending different oils on the basic properties of biodiesel (Jena et al., 2010; A. Sarin et al., 2009; Sarin et al., 2007).

It is well known that high viscosity and low volatility are the main barriers that prevent the use of direct vegetable oils in conventional diesel engines which cause some problems in engines such carbon deposition, ring sticking, injector choking and lubricating oil thickening. Therefore, there are many efforts to develop and improve vegetable oil properties in order to approximate the properties of diesel fuels (Singh & Singh, 2010). These problems can be overcome by four methods: pyrolysis, dilution with hydrocarbons blending, micro-emulsion and transesterification.

Blending and transesterification are the most common methods to reduce the viscosity of vegetable oils. Blending is simple, as it does not contain any chemical modification of the vegetable oil. However, blending is undesirable because it requires purification of the vegetable oil before the blending process. Transesterification has been regarded worldwide as the best method among other approaches due to its low cost and simplicity. Transesterification process includes two main processes: catalytic and non-catalytic method. A catalyst is used to commence the reaction. The catalyst is vital as alcohol is barely soluble in oil or fat. The catalyst enhances the solubility of alcohol and thus increases the reaction rate. Under catalytic process, there are two methods namely homogenous and heterogeneous (Balat & Balat, 2010; Jain & Sharma, 2010a; Parawira, 2010; Shahid & Jamal, 2011; Y. C. Sharma, Singh, B., 2009).

1.3 Problem Statement

Biodiesel has been accepted worldwide as an immediate solution to the heavy dependence on diesel fuel. However, the prolonged reliance on edible oils as feedstocks for biodiesel production has threatened the supply of edible oil to food industry and raised some environmental problems such as serious destruction of vital soil resources, deforestation and usage of much of the available arable land. Moreover, in the last ten years the prices of vegetable oil plants have increased dramatically which will affect the economic viability of biodiesel industry. Due to these factors, it is crucial to find other alternative oil feedstock to substitute edible oil in the production of biodiesel. Therefore, the main objective of this research is to synthesize biodiesel from various non-edible feedstocks such as *Jatropha curcas*, *Calophyllum inophyllum*, *Sterculia foetida*, *Croton megalocarpus*, *Pangium edule*, *Patchouli* and *Moringa oleifera* and then compare them with edible oils such as coconut, palm, soybean and canola oils.

1.4 Objectives

Having recognized that fossil fuels are expected to be depleted, and proven the necessity and the importance of utilizing renewable energy resource, this dissertation will show the way to promote biodiesel as one of the leading renewable energy sources. This research aims to achieve the following objectives:

(a) To identify and select several promising potential oil bearing plants (both edible and non-edible) for biodiesel production.

(b) To investigate physical and chemical properties of these feedstocks followed by production of biodiesel using conventional esterification and transesterification technology.

(c) To characterize and determine physical and chemical properties and fatty acid compositions of the produced biodiesel.

(d) To investigate biodiesel-biodiesel and biodiesel-diesel blending opportunities to improve the final properties using the polynomial curve fitting method.

(e) To conduct engine performance and emissions analysis of some selected edible and non-edible biodiesel feedstocks.

The outcome of this investigation is expected to give the operators many useful choices that can be considered when choosing fuel for any specific applications.

1.5 Scope of Study

There are more than 350 oil-bearing crops recognized as prospective sources for biodiesel production (Bart et al., 2010). Based on this fact, the scope of this research aims mainly to identify and select some potential oil bearing plants (edible and non-edible) for biodiesel production. These feedstocks include; *Calophyllum inophyllum, Croton megalocarpus*, *Jatropha curcas, Moringa oleifera*, *Patchouli*, *Sterculia foetida*, *Pangium edule*, Manketti (*Ricinodendron rautonemii*), Canola (*Brassica napus*), Coconut (*Cocos nucifera*), Soybean (*Glycine Max*) and Palm *(Elaeis guineensis*). In this research, production of biodiesel from *Patchouli* and *Pangium edule* has been reported for the first time. Physical and chemical properties of crude oils and the produced biodiesel such as kinematic viscosity, calorific value, density, flash point, cloud point, pour point, cold filter plugging point, copper strip corrosion and oxidation stability have been investigated and compared with ASTM D6751 standard. Moreover, the fatty acid compositions of methyl esters have been also determined and compared with existing literature. The effect of biodiesel blending on the final properties using the polynomial curve fitting method has been also suggested and covered in this study. Finally, engine performance and emissions analysis of some selected feedstocks of only B_{10} and B_{20} fuel blends is presented. Other aspects such as optimization of biodiesel production using response surface methodology (RSM), engine performance using additives and techno-economic and sensitivity analysis have not been covered in this research.

1.6 Organization of dissertation

This dissertation is made up of five chapters. The organization of the chapters is listed as follows:

Chapter 1 gives an overview of the research topic. It starts by giving an introduction to the importance of energy, GHG emissions, climate change, increasing prices and expected depletion of fossil fuels, importance of biofuels, and suggests biodiesel as a solution for the current world energy crisis. This is followed by a background that shows the importance of biodiesel and gives some examples of biodiesel feedstocks around the world and the possible methods to overcome the high viscosity and low volatility of vegetable oils in conventional diesel.

Chapter 2 gives a historical overview of global transportation sector energy consumption and emissions production trends followed by discussing biodiesel as an emerging energy resource, advantages and disadvantages of biodiesel, biodiesel feedstocks, biodiesel extraction methods, biodiesel production technologies, biodiesel standards and characterization, properties and qualities of biodiesel and problems and potential solutions of using straight vegetable oils.

Chapter 3 explains in detail the research methodology and design.

Chapter 4 is dedicated to show all the results that have been obtained from the experimental work and present the findings of the study followed by a detailed discussion and analysis of these findings besides comparing them with the existing results included in the literature.

Chapter 5 provides a summary of the key findings in the light of the research and puts forward some recommendations for the future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews major publications and reports that will provide insight and understanding about the topic and related issues. The review also reveals the challenges encountered in biodiesel research.

This chapter also gives an overview of global transportation sector energy consumption and emissions production trends followed by discussing biodiesel as an emerging energy resource, advantages and disadvantages of biodiesel, biodiesel feedstocks, non-edible vegetable resources, fatty acid composition, biodiesel extraction methods, biodiesel production technologies, biodiesel standards and characterization, properties and qualities of biodiesel and problems, potential solutions of using straight vegetable oils and engine performance and emissions production of some selected edible and non-edible biodiesel.

2.2 Overview of global transportation sector consumption and emissions production

2.2.1 Global transportation sector energy consumption

Nowadays, energy has become a crucial factor for humanity to continue the economic growth and maintain high standard of living especially after the inauguration of the industrial revolution in the late 18th and early 19th century. In the past 30 years, the transportation sector has experienced a steady growth due to the increasing numbers of cars around the world. It has been estimated that the global transportation energy use is expected to increase by an average of 1.8% per year from 2005 to 2035 (U.S Energy Information Administration, 2010). Globally, the transportation sector is the second largest energy consuming sector after the industrial sector and accounts for 30% of the world's total delivered energy, of which 80% is road transport. It is believed that this sector is currently responsible for nearly 60% of world oil demand and will be the strongest growing energy demand sector in the future. Nearly all fossil fuel energy consumption in the transportation sector is from oil (97.6%), with a small amount from natural gas. Between 2006 and 2030, around three quarters of the projected increase in oil demand is expected to come from this sector (An, 2010; Rabe, 2010; U.S Energy Information Administration, 2010). Figure 2.1 shows projected total world, transportation and other sectors oil consumption by end-use sector between 2007 and 2035 (Atabani et al., 2011; U.S Energy Information Administration, 2010).

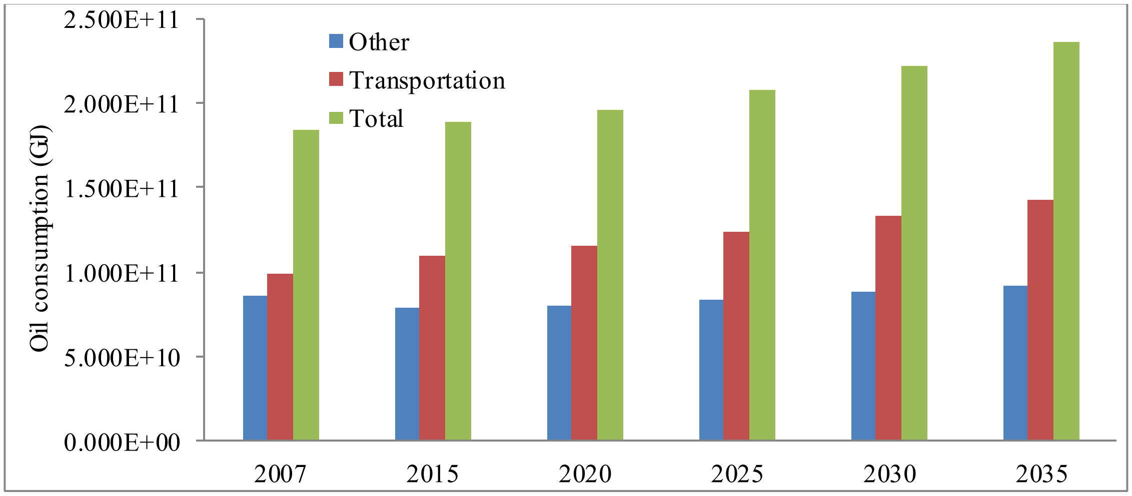


Figure 2.1: Total world oil consumption, transportation oil consumption and other sectors oil consumption (GJ) between 2007 and 2035 (Atabani et al., 2011; U.S Energy Information Administration, 2010)

Figure 2.2 shows the history of oil proved reserves between 1980 and 2009. Figure 2.3 presents the trends of oil production and consumption between 1965 and 2009. Although oil is expected to remain the largest source of energy, the oil share of world marketed energy consumption is expected to decline from 35% in 2007 to 30% in 2035 as can be seen in Figure 2.4 (U.S Energy Information Administration, 2010). In 2005 the French Economics, Industry and Finance Ministry report suggested that the peak oil production may occur in 2013. However, few models predicted the peak year has already taken place in 2010, while other models predicted that it was in 2005. There are few other studies that reported the peak extraction will occur in 2020. The World Energy Forum has predicted that reserves will be exhausted in less than another 10 decades. Other believes that it will be depleted in fewer than 45 years if consumed at an increasing rate of 3% per annum (Ahmad et al., 2011; British petroleum (BP), 2010; Y. C. Sharma, Singh, B., 2009).

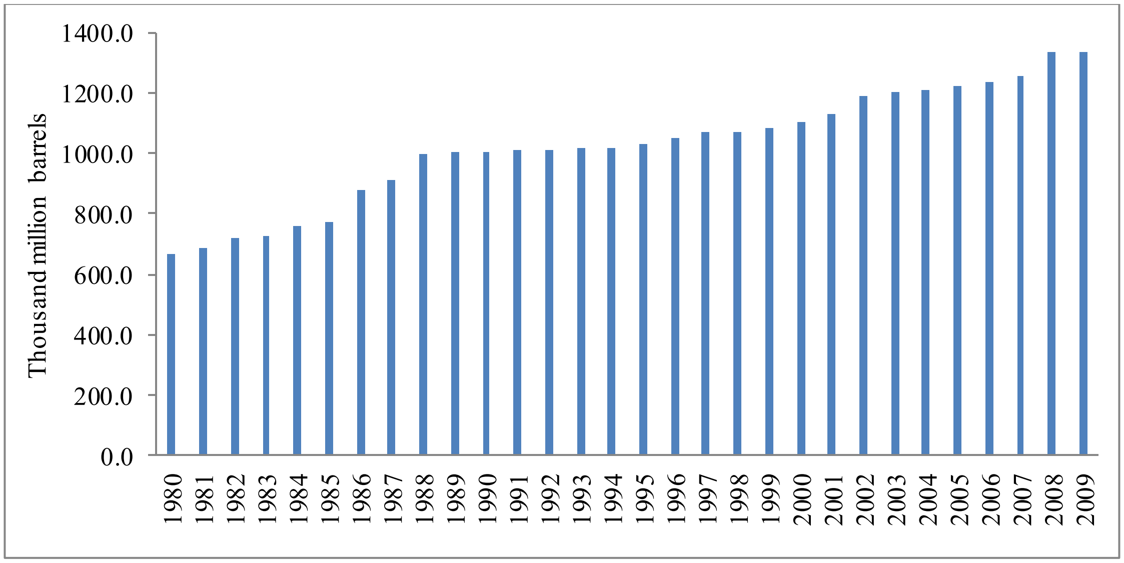


Figure 2.2: Total oil proved reserves between 1980 and 2009 (Thousand million barrels) (British petroleum (BP), 2010)

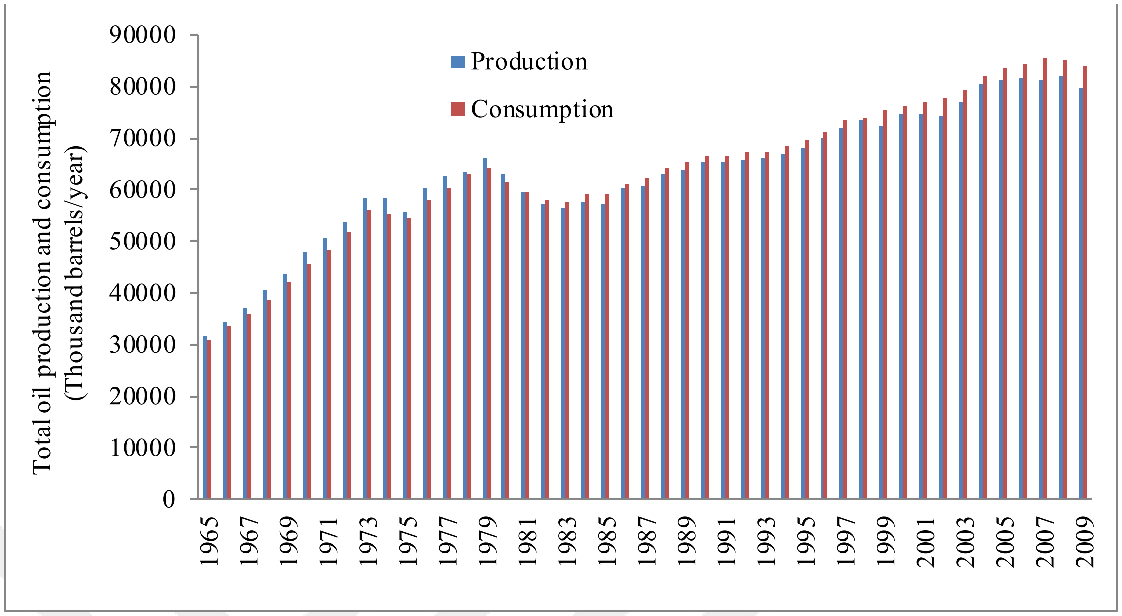
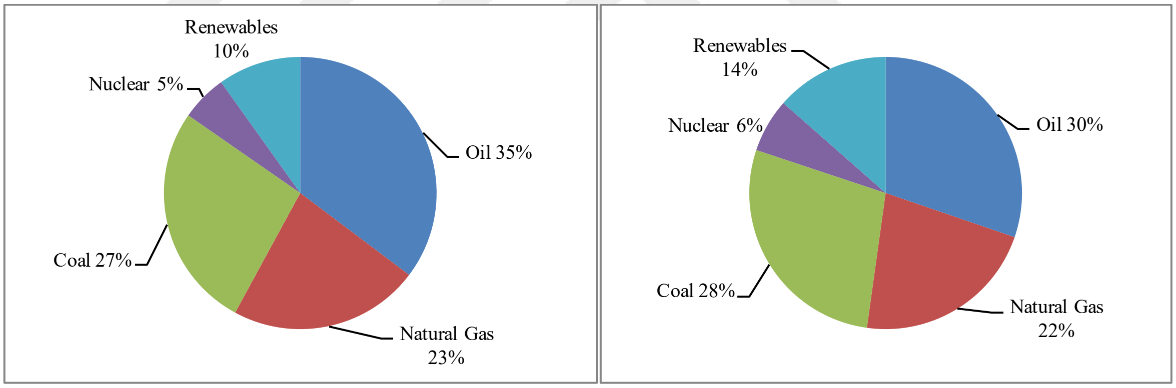


Figure 2.3: Total oil production and consumption between 1965 and 2009 (Thousand Barrels/year) (British petroleum (BP), 2010)



(a) 2007 (b) 2035

Figure 2.4: Breakdown of world energy consumption by fuel in 2007 and 2035 (U.S Energy Information Administration, 2010)

2.2.2 Global transportation sector emissions production

It is believed that climate change is currently the most pressing global environmental problem. If the average global temperature increases by more than 2 °C, up to one million species could become extinct and hundreds of millions of people could lose their lives (Ahmad et al., 2011).

Globally, the transportation sector accounted for about 23% and 22% of total world CO_2 emissions in 2007 and 2008 respectively (International Energy Agency (IEA), 2010). Within this sector, road transport accounted for 10% of global GHG emissions. According to the United Nations' Intergovernmental Panel on Climate Change, the transportation sector was responsible for about 23% of energy-related greenhouse gas emissions in 2004. Passenger vehicles account for about 45% of this total (Atabani et al., 2011). In Europe, transportation sector accounts for more than 20% of greenhouse gas emissions. Between 1990 and 2001, emissions of greenhouse gases (GHGs) from transport (excluding international transport) increased by 20% (European Environment Agency (EEA), 2011a, 2011b). In Australia, the transport sector contributed to 13.7% of Australia's net emissions in 2006. Road transport was responsible for 87% of these emissions or 12% of Australia's total emissions. In 2008, Almost 30% of total U.S. greenhouse gas (GHG) emissions come from the transportation sector, making transportation the second largest source of GHG emissions in the United States after the electric power sector (35%) (Atabani et al., 2011).

The majority of transportation GHG emissions (95%) are composed of carbon dioxide (CO_2). An additional 1% comes from methane (CH_4) and nitrous oxides (N_2O). The leakage of hydro fluorocarbons (HFCs) from vehicle air conditioning systems is responsible for the remaining 3% of GHG emissions. Transportation sources also emit ozone, carbon monoxide (CO), and aerosols. These substances are not counted as greenhouse gases but are believed to have an indirect effect on global warming, although their impact has not been quantified with certainty (Atabani et al., 2011).

2.3 Biodiesel as an emerging energy resource

Globally, the awareness of energy issues and environmental problems associated with burning fossil fuels has encouraged many researchers to investigate the possibility of using alternative sources of energy instead of oil and its derivatives. Among them, biodiesel seems very promising for several reasons: it is highly biodegradable and has minimal toxicity, it can replace diesel fuel in many different applications such as boilers and internal combustion engines without major modifications, only small decrease in performances is reported, results in almost zero emissions of sulphates, aromatic compounds and other chemical substances that are destructive to the environment, has only a small net contribution of carbon dioxide (CO_2) when the whole life-cycle is considered (including cultivation, production of oil and conversion to biodiesel), and it appears to cause significant improvement of rural economic potential (Ahmad et al., 2011). The invention of the vegetable oil fuelled engine by Sir Rudolf Diesel dated back in the 1900s. However, full exploration of biodiesel only came into light in the 1980s as a result of renewed interest in renewable energy sources for reducing greenhouse gas (GHG) emissions, and alleviating the depletion of fossil fuel reserves. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats and alcohol with or without a catalyst (Janaun & Ellis, 2010; Kafuku & Mbarawa, 2010; Satyanarayana & Muraleedharan, 2011; Shahid & Jamal, 2011). Compared to diesel fuel, biodiesel produces less sulphur, carbon dioxide, carbon monoxide, particulate matters, smoke and hydrocarbons emission and more oxygen. More free oxygen leads to the complete combustion and reduced emission (Fazal et al., 2011).

Biodiesel has been in use in many countries such as United States of America, Malaysia, Indonesia, Brazil, Germany, France, Italy and other European countries. However, the potential for its production and application is much more. Table 2.1 shows the list of the top 10 biodiesel producing countries. Form this table, it can be seen that Malaysia is far ahead among the rest (Atadashi et al., 2011; Balat & Balat, 2010; Johnston & Holloway, 2007; Y. C. Sharma, Singh, B., 2009).

Table 2.1: Top 10 countries in terms of biodiesel potential (Atadashi et al., 2011; Balat & Balat, 2010; Johnston & Holloway, 2007; Y. C. Sharma, Singh, B., 2009)

Rank	Country	biodiesel potential (ML)	Production ($/L)
1	Malaysia	14,540	0.53
2	Indonesia	7,595	0.49
3	Argentina	5,255	0.62
4	USA	3,212	0.70
5	Brazil	2,567	0.62
6	Netherlands	2,496	0.75
7	Germany	2,024	0.79
8	Philippines	1,234	0.53
9	Belgium	1,213	0.78
10	Spain	1,073	1.71

Biodiesel has a massive potential to be a part of a sustainable energy mix in the future. Globally, annual biodiesel production increased from 15 thousand barrel per day in 2000 to 289 thousand barrel per day in 2008 as shown in Figure 2.5 (U.S Energy Information Administration, 2011). It is believed that, 85% of biodiesel production comes from the European Union. The demand for biodiesel in European countries is expected to be up to 10.5 billion litres by 2010 (Ahmad et al., 2011).

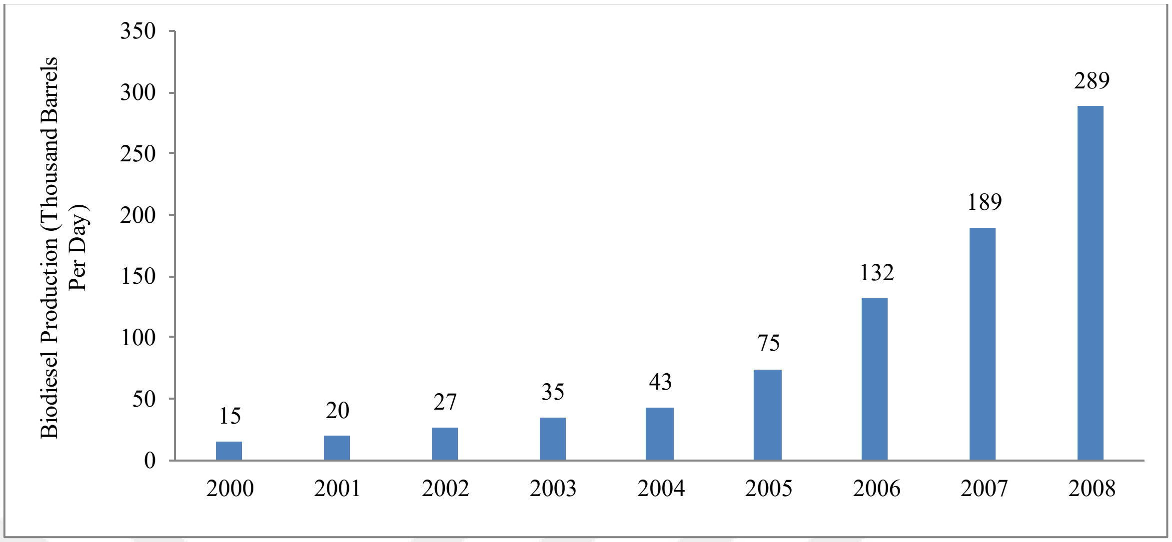


Figure 2.5: Total world biodiesel productions (Thousand Barrels Per Day) between 2000-2008 (U.S Energy Information Administration, 2011)

2.4 Advantages and disadvantages of biodiesel

Table 2.2 gives a summary of the advantages and disadvantages of biodiesel.

Table 2.2: Advantages and disadvantages of biodiesel (Atabani et al., 2012)

Advantages of biodiesel
Biodiesel has 10-11% of oxygen; this makes biodiesel a fuel with good combustion characteristics.
Biodiesel reduces net carbon-dioxide emissions by 78% on a lifecycle basis when compared to conventional diesel fuel and reduces smoke due to free soot.
Biodiesel is renewable, non-toxic, non-flammable, portable, readily available, biodegradable, sustainable, eco-friendly and free from sulphur and aromatic content, this makes it an ideal fuel for heavily polluted cities. Biodiesel also reduces particular matter content in the ambient air and hence reduces air toxicity. It provides a 90% reduction in cancer risks and neonatal defects due to its less polluting combustion.
Biodiesel helps rural development to restore degraded lands over a period. Moreover, it has good potential for rural employment generation
Biodiesel serves as climatic neutral in view of the climatic change that is presently an important element of energy use and development.
Biodiesel has higher cetane number (about 60 to 65 depending on the vegetable oil) than petroleum diesel (53) which reduces the ignition delay.
Production can be raised easily and is less time consuming. No need for drilling, transportation, or refining like petroleum diesel. Therefore, each country has the ability to produce biodiesel as a locally produced fuel. Moreover, there is no need to pay tariffs or similar taxes to the countries from which oil and petroleum diesel is imported.
Biodiesel has superior better lubricity properties. This improves lubrication in fuel pumps and injector units, which decreases engine wear, tear and increases engine efficiency.
Biodiesel is safe for transportation, handling, distribution, utilization and storage due to its higher flash point (above 100-170 °C) than petroleum diesel (60-80 °C)
Biodiesel reduces the environmental effect of a waste product and can be made out of used cooking oils and lards.
Biodiesel may not require engine modification up to B_{20}. However, higher blends may need some minor modification.

Disadvantages of biodiesel
Biodiesel has 12% lower energy content than diesel, this leads to an increase in fuel consumption of about 2-10%. Moreover, biodiesel has higher cloud point and pour point, higher nitrogen oxide emissions than diesel. It has lower volatilities that cause the formation of deposits in engines due to incomplete combustion characteristics.
Biodiesel causes excessive carbon deposition and gum formation (polymerization) in engines and the oil gets contaminated and suffers from flow problem. It has relatively higher viscosity (11-18 times diesel) and lower volatility than diesel and thus needs higher injector pressure.
Oxidation stability of biodiesel is lower than that of diesel. It can be oxidized into fatty acids in the presence of air and causes corrosion of fuel tank, pipe and injector.
Due to the high oxygen content in biodiesel, advance in fuel injection and timing and earlier start of combustion, biodiesel produces relatively higher NO_x levels than diesel in the range of 10-14% during combustion.
Biodiesel can cause corrosion in vehicle material (cooper and brass) such as fuel system blockage, seal failures, filter clogging and deposits at injection pumps.
Use of biodiesel in internal combustion engine may lead to engine durability problems including injector cocking, filter plugging and piston ring sticking etc.
As more than 95% of biodiesel is made from edible oil, there have been many claims that this may give rise to further economic problems. By converting edible oils into biodiesel, food resources are being used as automotive fuels. It is believed that large-scale production of biodiesel from edible oils may bring about a global imbalance in the food supply-and-demand market.
Lower engine speed and power, high price, high engine wear, engine compatibility
Transesterification process is expensive (cost of fuel increases), these oils require expensive fatty acid separation or use of less effective (or expensive acid catalysts).
The transesterification has some environmental effects such as waste disposal and water requirement for washing, soap formation, etc.

2.5 Biodiesel feedstock

Globally, there are more than 350 oil-bearing crops identified as potential sources for biodiesel production (Bart et al., 2010). Table 2.3 shows main feedstocks of biodiesel. The wide range of available feedstocks for biodiesel production represents one of the most significant factors of producing biodiesel (Atadashi et al., 2010; Janaun & Ellis, 2010; Shahid & Jamal, 2011). As much as possible the feedstock should fulfil two main requirements: low production costs and large production scale. The availability of feedstock for producing biodiesel depends on the regional climate, geographical locations, local soil conditions and agricultural practices of any country. From literature, it has been found that feedstock alone represents 75% of the overall biodiesel production cost as shown in Figure 2.6. Therefore, selecting the cheapest feedstock is vital to ensure low production cost of biodiesel. Figure 2.7 shows pictures of some biodiesel feedstocks. In general, biodiesel feedstock can be divided into four main categories as below (Ahmad et al., 2011; Kafuku & Mbarawa, 2010; Karmee & Chadha, 2005):

1- Edible vegetable oil: rapeseed, soybean, peanut, sunflower, palm and coconut oil.
2- Non-edible vegetable oil: *jatropha*, *karanja*, sea mango, algae and halophytes.
3- Waste or recycled oil.
4- Animal fats: tallow, yellow grease, chicken fat and by-products from fish oil.

Table 2.4 shows primary biodiesel feedstock for some selected countries around the world (Ahmad et al., 2011; Karmakar et al., 2010).

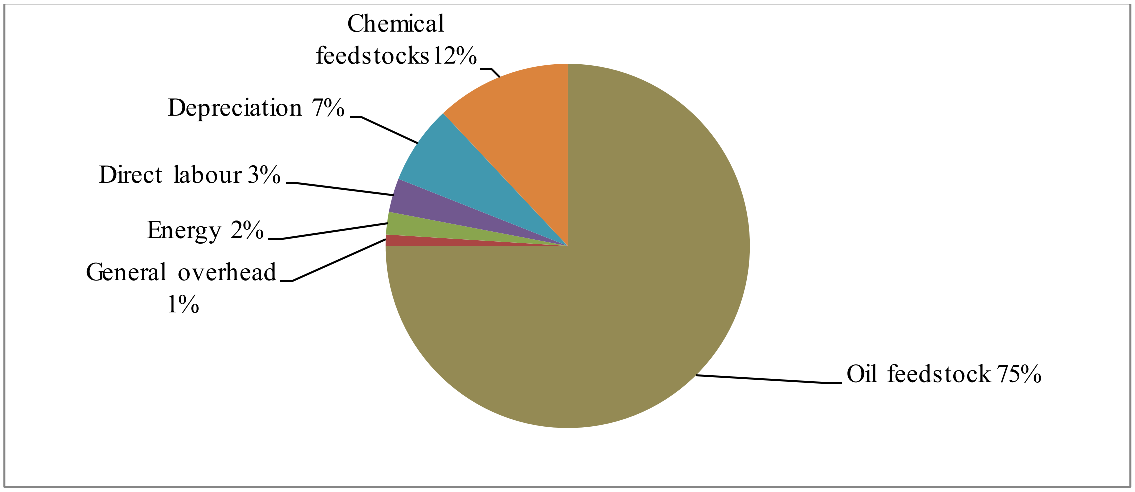
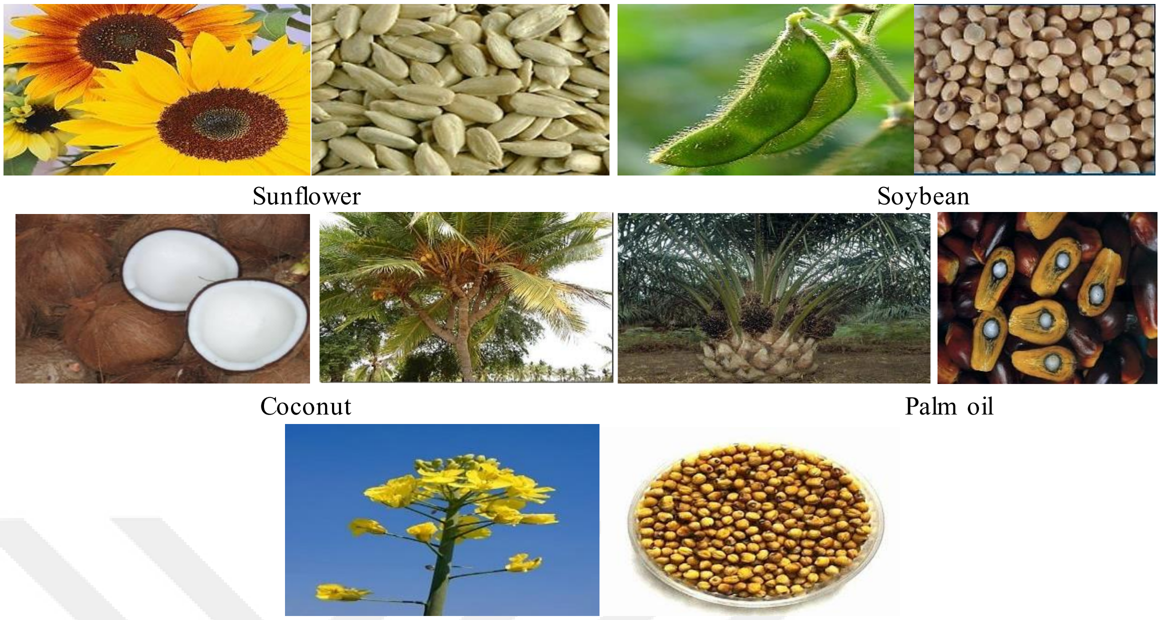


Figure 2.6: General cost breakdown for production of biodiesel (Ahmad et al., 2011)

Table 2.3: Main feedstocks of biodiesel (Atabani et al., 2012)

Edible oils	Non-edible oils	Animal Fats	Other Sources
Soybeans (Glycine max)	Jatropha curcas	Pork lard	Bacteria
Rapeseed (Brassica napus L.)	Mahua (Madhuca indica)	Beef tallow	Algae (Cyanobacteria)
Safflower	Pongamia (Pongamia pinnata)	Poultry Fat	Microalgae (Chlorellavulgaris)
Rice bran oil (Oryza sativum)	Camelina (Camelina Sativa)	Fish oil	Tarpenes
Barley	Cotton seed (Gossypium hirsutum)	Chicken fat	poplar
Sesame (Sesamum indicum L.)	Cumaru		switchgrass
Groundnut	Cynara cardunculus		miscanthus
Sorghum	Abutilon muticum		Latexes
Wheat	Neem (Azadirachta indica)		Fungi
Corn	Jojoba (Simmondsia chinensis)		
Coconut	Passion seed (Passiflora edulis)		
Canola	Moringa (Moringa oleifera)		
Peanut	Tobacco seed		
Palm and palm kernel (Elaeis guineensis)	rubber seed tree (Hevca brasiliensis)		
Sunflower (Helianthus annuus)	Salmon oil		
	Tall (Carnegiea gigantean)		
	Coffee ground (Coffea arabica)		
	nagchampa (Calophyllum inophyllum)		
	Croton megalocarpus		
	Pachira glabra		
	Aleurites moluccana		
	Terminalia belerica		



Sunflower

Soybean

Coconut

Palm oil

Rapeseed

(a) Edible oil feedstocks

Calophyllum inophyllum

Melia *azedarach*

Cerbera odollam

Simmondsia chinensis

Sapindus mukorossi

Argemone mexiana

Azadirachta indica

Ricinus communis

Panama pinnata

Putrajinva roxburghi

Scheleichera triguga

Thevatia peruviana

Madhuca indica


Jatropha Curcas *Simmondsia chinensis (jojoba)* *Scheleichera triguga*

Hevea brasiliensis *Terminalia chebula* *Terminalia arjuna* *Terminalia Belerica*

(b) Non-edible oil feedstocks

Figure 2.7: Main biodiesel feedstocks (a) Edible (b) Non-edible (Atabani et al., 2012)

Table 2.4: Current potential feedstocks for biodiesel worldwide (Atabani et al., 2012)

Country	Feedstock
USA	Soybeans / waste oil / Peanut
Canada	Rapeseed / Animal fat / Soybeans / Yellow grease and Tallow / Mustard / Flax
Mexico	Animal fat/ Waste oil
Germany	Rapeseed
Italy	Rapeseed / Sunflower
France	Rapeseed / Sunflower
Spain	Linseed oil / Sunflower
Greece	Cottonseed
UK	Rapeseed / Waste cooking oil
Sweden	Rapeseed
Ireland	frying oil / animal fats
India	Jatropha / Pongamia pinnata (karanja) / Soybean / Rapeseed / Sunflower / Peanut
Malaysia	Palm oil
Indonesia	Palm oil / Jatropha/ Coconut
Singapore	Palm oil
Philippines	Coconut / Jatropha
Thailand	Palm / Jatropha / Coconut
China	Jatropha / Waste cooking oil / Rapeseed
Brazil	Soybeans / Palm oil / Castor / Cotton oil
Argentina	Soybeans
Japan	Waste cooking oil
New Zealand	Waste cooking oil / Tallow

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

To consider any feedstock as a biodiesel source, the oil percentage and the yield per hectare are important parameters. Table 2.5 shows the estimated oil content and yields of different biodiesel feedstocks.

Table 2.5: Estimated oil content and yields of different biodiesel feedstocks (Atabani et al., 2012)

Feedstocks	Oil content (%)	Oil yield (L/ha/year)
Castor	45-50	1413
Jatropha	50-60	1892
Linseed	35-45	-
Neem	20-30	-
Pongamia pinnata (Karanja)	30-40	225-2250[a]
Soybean	15-20	446
Sunflower	25–35	952
Calophyllum inophyllum L.	65	4680
Moringa oleifera	40	-
Euphorbia lathyris L.	48	1500-2500[a]
Sapium sebiferum L.	Kernel 12-29	-
Rapeseed	38-46	1190
Tung	16-18	940
Pachira Glabra	40-50	-
Palm oil	30-60	5950
Peanut oil	45-55	1059
Olive oil	45-70	1212
Corn (Germ)	48	172
Coconut	63-65	2689
Cottonseed	18-25	325
Rice bran	15-23	828
Sesame	-	696
Jojoba	45-50	1818
Rubber seed	40-50	80-120[a]
Sea mango	54	-
Microalgae (low oil content)	30	58,700
Microalgae (medium oil content)	50	97,800
Microalgae (high oil content)	70	136,900

[a] (kg oil/ha)

Edible oil resources such as soybeans, palm oil, sunflower, safflower, rapeseed, coconut and peanut are considered as the first generation of biodiesel feedstock because they were the first crops to be used for biodiesel production. Their plantations have been well established in many countries around the world such as Malaysia, USA and Germany. Currently, more than 95% of the world biodiesel is produced from edible oils such as rapeseed (84%), sunflower oil (13%), palm oil (1%), soybean oil and others (2%). However, their use raises many concerns such as food versus fuel crisis and major environmental problems such as serious destruction of vital soil resources, deforestation and usage of much of the available arable land. Moreover, in the last ten years the prices of vegetable oil plants have increased dramatically which will affect the economic viability of biodiesel industry (Balat, 2011; Balat & Balat, 2010; Deng et al., 2011). Furthermore, the use of such edible oils to produce biodiesel is not feasible in the long-term because of the growing gap between demand and supply of such oils in many countries. For instance, dedicating all US soybean to biodiesel production would meet only 6% of diesel demands (Chapagain et al., 2009).

One of the possible solutions to reduce the utilization of the edible oil for biodiesel production is by exploiting non-edible oils. Non-edible oil resources are gaining worldwide attention because they are easily available in many parts of the world especially wastelands that are not suitable for food crops, eliminate competition for food, reduce deforestation rate, more efficient, more environmentally friendly, produce useful by-products and they are very economical comparable to edible oils. The main sources for biodiesel production from non-edible oils are jatropha (*Jatropha curcas*), karanja or honge (*Pongamia pinnata), Aleurites moluccana, Pachira Glabra*, nagchampa (*Calophyllum inophyllum*), rubber seed tree (*Hevca brasiliensis*), Desert date (*Balanites aegyptiaca*), *Croton megalocarpus*, Rice bran, Sea mango (*Cerbera odollam*), *Terminalia belerica*, neem (*Azadirachta indica*), Koroch seed oil (*Pongamia glabra vent.*), mahua (*Madhuca indica and Madhuca longifolia*), Tobacco seed (*Nicotiana tabacum L.*), Chinese tallow, silk cotton tree (*Ceiba pentandra*), jojoba (*Simmondsia chinensis*), babassu tree and *Euphorbia tirucalli*. Non-edible oils are regarded as the second generation of biodiesel feedstocks. Animal fats such as beef tallow, poultry fat and pork lard, waste oils and grease are also considered second generation feedstocks. The use of these types of feedstock eliminates the need to dispose them. However, it has been reported that second generation feedstocks may not be plentiful enough to satisfy the global energy demand. Moreover, biodiesel derived from vegetable oils and animal fats has a relatively poor performance in cold weather. Furthermore, for many types of animal fats the transesterification process is difficult because they contain high amount of saturated fatty acids. In case of waste cooking oil, collection infrastructure and logistics could be hurdle as the sources are generally scattered (Ahmad et al., 2011; Kafuku & Mbarawa, 2010; L. Lin et al., 2011; Y. C. Sharma, Singh, B., 2009; Singh & Singh, 2010).

More recently, microalgae have emerged to be the third generation of biodiesel feedstock. Microalgae are photosynthetic microorganisms that convert sunlight, water and CO_2 to algal biomass but they do it more efficiently than conventional crop plants. It represents a very promising feedstock because of its high photosynthetic efficiency to produce biomass, higher growth rates and productivity and high oil content compared to edible and non-edible feedstocks (Table 2.6). Microalgae have the potential to produce an oil yield that is up to 25 times higher than the yield of oil palm and 250 times the amount of soybeans as can be seen in Table 2.5. This is because microalgae can be grown in farm or bioreactor. Moreover, they are easier to cultivate than many other plants. It is believed that microalgae can play an important role in solving the problem between the production of food and that of biodiesel in the near future. Moreover, among other generations of biodiesel feedstocks, microalgae appear to be the only source of renewable biodiesel that is capable of meeting the global demand for transport fuels and can be sustainably developed in the future. The main obstacle for the commercialization of microalgae is its high production cost from requiring high-oil-yielding algae strains and effective large-scale bioreactors. Recent studies indicate that algae for biodiesel production can grow on flue gas, giving opportunities in consuming greenhouse gas as feedstock (Ahmad et al., 2011; Y. C. Sharma, Singh, B., 2009; Singh & Singh, 2010). Table 2.6 shows the comparison of biodiesel production from algae and oil plants.

Table 2.6: Comparison of biodiesel production from algae and oil plants (Atabani et al., 2012)

	Biodiesel produced from algae	Biodiesel produced from plants
Technology	Cell bioengineering, automatically produced in pilot plant	Agriculture in farm
Production period	5 – 7 days for a batch cultivation	Several months or years
Oil content	30% (low oil content), 50% (medium oil content), 70% (high oil content)	Less than 20% in seeds or fruits
Land occupied	0.010 – 0.013 hectare for producing $1x10^3$ L oil[a]	2.24 ha for producing $1x10^3$ L oil[b]
Cost performance	$2.4 per litre microalgal oil	$0.6 – 0.8 per litre plant oil
Development potential	Unlimited (work just beginning)	Limited (many works have been done)

[a] Based on soybean cultivation in farmland.
[b] Based on projected area of bioreactor in pilot plant.

(Knothe et al., 2010) reported that the use of the terms first, second and third generation are sometimes misleading and should not be used to imply that biodiesel derived from second or third generation feedstock may have superior fuel properties over first generation. For instance, biodiesel from Jatropha oil possesses poorer cold flow properties than biodiesel derived from soybean, palm or rapeseed oil. Recently, there have been several publications which highlighted the positive effects of blending different oils on the basic properties of biodiesel (Jena et al., 2010; A. Sarin et al., 2009; Sarin et al., 2007).

(Janaun & Ellis, 2010) and (L. Lin et al., 2011) show that genetically engineered plants such as poplar, switchgrass, miscanthus and big bluestem can be considered new feedstocks for biodiesel production. These feedstocks will create new bioenergy crops that are not associated with food crops. Therefore, they are expected to represent a sustainable biodiesel feedstock in the future. However, precaution on biosafety must be considered for these feedstocks.

2.5.1 Non-edible vegetable resources

Non-edible vegetable oils are not suitable for human food due to the presence of some toxic components in the oils (Ahmad et al., 2011). The selection of non-edible vegetable oils as feedstocks for biodiesel production requires reviewing the existing works. Recent comprehensive reviews on biodiesel production from various feedstocks show the advantages of non-edible oils over edible oils. Production of biodiesel from non-edible oils feedstocks can overcome the problems of food verse fuel, environmental and economic issues related to edible vegetable (Gui et al., 2008). Moreover, Non-edible biodiesel crops are expected to use lands that are largely unproductive and those that are located in poverty-stricken areas and in degraded forests. They can also be planted on cultivators' field boundaries, fallow lands, and in public land such as along railways, roads and irrigation canals. Non-edible biodiesel development could become a major poverty alleviation program for the rural poor apart from providing energy security in general and to rural areas in particular and upgrading the rural non-farm sector. All of these issues have a great impact on the sustainability of biodiesel production. Many researchers have concluded that non-edible feedstocks of biodiesel should be considered as sustainable and alternative fuels (Ahmad et al., 2011; Ravi & Sastry, 2009; Syers et al., 2007).

Non-edible oils plants are well adapted to arid, semi-arid conditions and require low fertility and moisture demand to grow. Moreover they are commonly propagated through seed or cuttings. Since these plants do not compete with food, seed cake after oil expelling may be used as fertilizer for soil enrichment (Azam et al., 2005). Several potential tree borne oilseeds (TBOs) and non-edible crop source have been identified as suitable feedstock for biodiesel (Razon, 2009; Syers et al., 2007). Table 2.7 shows a list of some potential tree borne oilseeds (non-edible oils) for biodiesel production. A collection of some potential non-edible sources for biodiesel industry has already been shown in Figure 2.7. In the following section, a brief description of various types of non-edible plant oils will be presented.

Table 2.7: Non-edible sources of vegetable oil (Atabani et al., 2013)

Non-edible vegetable source	Distribution	Plant type	Plant part	Oil content		Yields of various plant oils		Uses
				Seed (wt%)	Kernel (wt%)	kg oil / ha	litres oil / ha	
Azadirachta indica (neem)	Native to India, Burma, Bangladesh, Sri Lanka, Malaysia Pakistan and Cuba, growing in tropical and semitropical regions	tree	seed, kernel	20-30	25-45	2670	-	oil-illuminant, timber, firewood, biodiesel
Aphanamixis piolystachya (wall.) Parker	Growing in India, China	tree	kernel	-	35	-	-	oil-illuminant
Annona muricata	The Caribbean and Central America but now growing in tropical climates throughout the world	tree	seed	-	20-30	-	-	oil
Asclepias syriaca (milkweed)	Distributed to the northeast and north–central United States	herbaceous perennial	seeds	20-25	0.019	-	-	
Barringtonia racemosa Roxb. (L.) Spreng.	Widely spread in East Africa, Southeast Asia and the Pacific islands	tree	seed	-	-	-	-	oil-illuminant used in lamps
Brassica carinata (ethiopian mustard)	Ethiopia	herbaceous annual	seed, kernel	42	2.2-10.8	-	-	
Balanites aegyptiaca (desert date)	Growing in arid regions in Africa and Asia	tree	kernel		36-47	-	-	oil, biodiesel
Bombax malabaricum	India	tree	seed	18 – 26	-	-	-	
Calophyllum inophyllum L.	Tropical regions of India, Malaysia, Indonesia, and the Philippines.	tree	seed, kernel	65	22	4680	-	oil-used for burning, timber
Crambe abyssinica	Mediterranean, Ethiopia, Tanzania, East of Africa, Italia, Argentina	herb	seed	30-38	-	1129	-	oil, lubricant
Cerbera odollam (sea mango)	Native to India and other parts of Southern Asia	tree	seed, kernel	54	6.4	-	-	illuminant (release thick smoke)
Croton tiglium	China, Malabar, Ceylon, Amboina (of the Molucca islands), the Philippines and Java	herbaceous perennial	seed, kernel	30-45	50-60	-	-	biodiesel, resin, oil
Cuphea	The eastern United States, North-central USA to Argentina	herbaceous annual	seed	20-38	-	900	-	biodiesel
Eruca sativa gars	Northwest of China, South Asia	herbaceous perennial	seed	35	-	420-590	-	
Guizotia abyssinica L. (niger)	Cultivated in Ethiopia and India	herbaceous annual	seed	50-60	-	200-300	-	Commercial oil, biodiesel
Hevea brasiliensis (rubber)	Grow in Nigeria, India, Brazil, Southeast Asia, West Africa	tree	seed	40-60	40-50	50	-	surface coatings including paints, printing inks, rubber/plastic processing, pharmaceuticals, lubricants, cosmetics, chemical intermediates and diesel fuel substitute/extender
Idesia polycarpa var. vestita fruit oil	The provinces to the south of Qinling mountain and Huaihe River in China	tree	fruit, seed	26.15-26.26	-	2250-3750	-	oil, biodiesel

Jatropha curcas L.	Indonesia, Thailand, Malaysia, Philippines, India, Pakistan, Nepal	tree	seed, kernel	20-60	40-60	1590	1892	oil-Illuminant (burns without soot), lubricant, biodiesel
Linum usitatissimum (linseed)	Distributed to the region extending from the eastern Mediterranean to India, wider cultivation of this crop in Europe and its adapted to wide range in Canada and Argentina	herbaceous annual	seed	35-45	-	402	478	oil for wall paint and floor oil, biodiesel resin, fibre, surface coating applications stains, linoleum.
Madhuca indica	India	tree	seed, kernel	35-50	50	-	-	biodiesel
Michela chaampaca	Eastern Himalayas, Assam, Burma, China, Western Ghats and throughout India.	tree	seed	45	-	-	-	oil, biodiesel
Mesua ferrea	Forest in North East India, Karnataka, Kerala		seed	35-50	-	-	-	soaps, lubricants, illumination
Nicotiana tabacum (tobacco)	Greece, Turkey, Bulgaria, Macedonia, India, England, Pakistan, Serbia, Brazil, Cuba, Columbia, East Africa, Ecuador, Fiji, Guatemala, Haiti, India, Iran, United States, Tanzania	herb	seed, kernel	36-41	17	2825	-	oil, ethnomedicinal
Pongamia pinnata (karanja)	Native Western Ghats in India, northern Australia, Fiji and in some regions of Eastern Asia.	tree	seed, kernel	25-50	30-50	900-9000	-	oil-illuminant, timber, firewood
Putranjiva roxburghii	Distributed in India	tree	seed	41-42	-	-	-	oil-burning, Kernel yield , seeds yield a fatty, oil used for burning an essential oil
Pongamia glabra (koroch seed)	Naturally distributed in tropical and temperate Asia, from India to Japan to Thailand to Malaysia to north and north-eastern Australia to some Pacific islands	tree	seed	33.6	-	225-2250	-	Oil for diesel generator, firewood
Ricinus communis (castor)	Cuba, Brazil, China, India Italia, French and the countries of the former Soviet Union	tree/shrub	seed	45-50	-	1188	1413	seed oil-fuel, Seeds yield castor oil, a fatty oil used as cathartic and also for lubrication and illumination
Simmondsia chinensis (jojoba)	Grows in the Mojave and Sonoran deserts of Mexico, California, and Arizona	shrub	seed	45-55	-	1528	1818	
Sapium sebifeum L. Roxb (stillingia)	Native in China, Japan, India and grows well in the southern coastal United States.	tree	seed, kernel	13-32	53-64	-	-	fatty oil known as strillengia oil, drying oil
Sapindus mukorossi (soapnut)	Asia (India, Nepal, Bangladesh, Pakistan), America, Europe	tree	seed, kernel	51.8	-	-	-	oil, biodiesel
Tomato seed	Turkey, Greece and growing in tropical and semitropical regions	tree	seed	32-37	-	5500	-	oil, manufacture of soaps, pressed cake is used as fodder for cattle and fertilizer
Tung	Southwest China	tree	seed	35-40	-	790	940	oil, biodiesel
Terminala catappa	Brazil	tree	seed	49	-	200-500	-	timber, oil, biodiesel
Ximenia americana	Widespread throughout the tropics: Africa, India and South East Asia to Australia, New Zealand, Pacific Islands, West Indies, Central and South America.	tree	kernel	-	49-61	-	-	oil, lubricant

2.5.1.1 *Jatropha curcas* L.

Jatropha curcas L. is a small tree or large shrub, up to 5-7 m tall, belonging to the Euphorbiaceae family (Balat, 2011; Kibazohi & Sangwan, 2011; Misra & Murthy, 2011). It is a drought-resistant plant capable of surviving in abandoned and fallowed agricultural lands (Kibazohi & Sangwan, 2011; Kumar & Sharma, 2011; Pinzi et al., 2009). It is a tropical plant that able to thrive in a number of climatic zones with rainfall of 250-1200 mm. The plant is native to Mexico, Central America, Africa, India, Brazil, Bolivia, Peru, Argentina and Paraguay (Azam et al., 2005; Kibazohi & Sangwan, 2011; Kumar & Sharma, 2011). It is well adapted in arid and semi-arid conditions and has low fertility and moisture demand. It can also grow on moderately sodic and saline, degraded and eroded soils. The ideal density of plants per hectare is 2500. It produces seeds after 12 months and reaches its maximum productivity by five years and can live 30 to 50 years. Seed production ranges from 0.1 $tha^{-1}y^{-1}$ to more than 8 $tha^{-1}y^{-1}$depending on the soil conditions (Azam et al., 2005; Kibazohi & Sangwan, 2011). Depending on variety, the decorticated seed of *Jatropha* contain 43-59% of oil (No, 2011).

2.5.1.2 *Pongamia pinnata L.* (Karanja)

Pongamia pinnata (L.) Pierre, (karanja or honge) an arboreal legume is a medium sized evergreen tree belongs to the family (Legumnosae; Pappilonaceae), more specifically the Millettieae tribe, which grows in Indian subcontinent and south-east Asia and has been successfully introduced to humid tropical regions of the world as well as parts of Australia, New Zealand, China and the USA (Karmee & Chadha, 2005; Pinzi et al., 2009; Scott et al., 2008). A single tree is said to yield 9-90 kg seeds, indicating a yield potential of 900-9000 kg seed/ha (assuming 100 trees/ha) (Karmee & Chadha, 2005). It is one of the few nitrogen fixing trees (NFTS) that produce seeds with a significant oil content (Gui et al., 2008). The plant is fast growing, drought resistant, moderately frost hardy and highly tolerant of salinity. It can be regenerated through direct sowing, transplanting and root or shoot cutting. Its maturity comes after 4-7 years. Historically, this plant has been used in Indian and neighbouring regions as a source of traditional medicines, animal fodder, green manure, timber, water-paint binder, pesticide, fish poison and fuel. Recently, *Pongamia pinnata* has been recognized as a viable source of oil for the burgeoning biofuel industry. The tree may be planted with a spacing of 3×3 m (Kumar & Sharma, 2011; Sanford et al., 2009; Tuli, 2011). The seed oil content ranges between 30-40 wt.% (Azam et al., 2005; Balat & Balat, 2010; Karmee & Chadha, 2005). The oil is reddish brown and rich in unsaponifiable matter and oleic acid (Sanford et al., 2009).

2.5.1.3 *Croton megalocarpus*

Croton megalocarpus is a member of the Euphorbiaceae family. It is a dominant upper canopy forest tree with heights ranging from15-40 m. It can grow between the altitudes of 1200 m and 2450 m respectively (Kibazohi & Sangwan, 2011). *Croton megalocarpus* is a tree indigenous to East Africa and the seeds have oil content 40-45% oil (Aliyu et al., 2010). A tree of *Croton megalocarpus* produces up to 50 kg of seeds and a hectare produces 5 to 10 t of seeds per year (Kibazohi & Sangwan, 2011).

2.5.1.4 *Moringa oleifera*

Moringa oleifera is a member of the Moringaceae family, grows throughout most of the tropics, it is drought-tolerant and can survive in harsh, poor and infertile land. *Moringa oleifera* is indigenous to northwest India, Africa, Arabia, Southeast Asia and South

America. However, it had distributed in the Philippines, Cambodia and Central and North America nowadays. *Moringa oleifera* oil is containing high in oleic acid which is around 70% of the total fatty acid profile (Rashid et al., 2008). The plant starts bearing Pods 6-8 months after planting and reaches an average of 3 tons of seed per hectare per year. The seed contains on average 40% oil by weight (Kibazohi & Sangwan, 2011).

2.5.1.5 *Aleurites moluccana*

Aleurites moluccana is another member of the Euphorbiaceae family. It is generically known as the candle nut tree and Hawaiian tree. It thrives in wet or dry subtropical and tropical forest zones. *Aleurites moluccana* grows optimally between the altitudes of 0-1200 m; a temperature of 18-28 °C, a rainfall of 650-4300 mm and a soil pH of 5-8. The tree produces spherical fruits, 5 cm or more in diameter, with a thick, rough, and hard nut shell making up to 64-68% of fruit, and the nut shell is difficult to separate from its oil-rich kernel. In plantations, nut yields are estimated at 5-20 tha^{-1} y^{-1}, each tree producing 30-80 kg of nuts. Oil production varies from 15-20% of nut weight. The oil is rich in polyunsaturated oils: linolenic, oleic and various linoleic acids (Kibazohi & Sangwan, 2011).

2.5.1.6 *Pachira glabra*

Pachira glabra belongs to the Malvaceae family, in the Bombacaceae subfamily. It is also known as French peanut, Guinea peanut or money. The tree is originally a Brazilian native tree, now grown throughout the tropics and subtropics. It produces green fruits which upon reaching maturity split open releasing seeds. Trees begin to fruit at about 4-5 years, producing fruits containing 10-25 rounded seeds of average 2.5 cm diameter, with 40-50% oil content (Kibazohi & Sangwan, 2011).

2.5.1.7 *Ricinus communis* (Castor)

Ricinus communis belongs to the Eurphorbiaceae family and also called castor beans. It is non-edible oilseed crop that is easily grown and resistant to drought (Gui et al., 2008; Lopez & Neto, 2011; Sanford et al., 2009). The tree is grown in many countries such as United States, India, China, Central Africa, Brazil and Australia with different cultivation cultures (Gui et al., 2008; Kumar & Sharma, 2011; Lopez & Neto, 2011; Ogunniyi, 2006; Pinzi et al., 2009). Its oil is viscous, slightly odour, pale yellow, non-volatile and non-drying oil with a bland taste and is sometimes used as a purgative. On the average, the seeds contain about 46-55% oil (Ogunniyi, 2006).

2.5.1.8 *Calophyllum inophyllum* L. (Polanga)

Calophyllum inophyllum L. commonly known as polanga or honne, is a non-edible oilseed belongs to the Clusiaceae family. It is a large and medium sized, evergreen sub-maritime tree which grows best in deep soil or on exposed sea sands. The rainfall requirement is 750-5000 mm/year. This plant has multiple origins including East Africa, India, South East Asia and Australia (Azam et al., 2005; Sahoo et al., 2007; Venkanna & Venkataramana, 2009). The tree supports a dense canopy of glossy, elliptical, shiny and tough leaves, fragrant white flowers, and large round nuts. Its size typically ranges between 8-20 m (25-65 ft) tall at maturity, sometimes reaching up to 35 m (115 ft). The growth rate of the tree is 1 m (3.3 ft) in height per year on good sites. Its leaves are heavy and glossy, 10-20 cm (4-8 in) long and 6-9 cm (2.4-3.6 in) wide, light green when young and dark green when older. Fruits are spherical drupes and arranged in clusters. The fruit is at first pinkish-green later turning bright green and when ripe, it turns dark grey-brown and wrinkled. The tree yields 100-200 fruits/kg. In each fruit, one large brown seed 2-4 cm (0.8-1.6 in) in diameter is found. The single, large seed is surrounded by a shell (endocarp) and a thin, 3-5 mm layer of pulp. Oil yield per unit land area has been reported at 2,000 kg/ha. The oil is tinted green, thick, and woodsy or nutty smelling (Hathurusingha et al., 2011; Sahoo et al., 2007; Venkanna & Venkataramana, 2009). The seed oil has very high oil content (65-75%) (No, 2011; Venkanna & Venkataramana, 2009).

2.5.1.9 *Sterculia foetida L.*

Sterculia foetida L. plant belongs to sterculiaceae family with 2000 type of species and classified as non-drying oils. It is a wild plant and well adapted to tropical and subtropical area (30 °North Latitude - 35 °South Latitude), although more humid environmental conditions are shown to result in a better crop performance. The plant has an average life span of more than 100 years. *Sterculia foetida* L. is a large, straight, deciduous tree growing up to 40 m in height and 3m in girth, with the branches arranged in whorls and spreading horizontally (Vipunngeun & Palanuvej, 2009), the diameter of trees is 100-120 cm (Gaikwad & Swamy, 2008). The ideal planting pitch has been found to be 3×3 m. The fruit is large, woody, red, nearly smooth and about 10 cm long. It contains from 10 to 15 seeds each, which are black and about 2 cm long. *Sterculia foetida* L. gives a yield of about 200-350 kg/tree/year of seed and the kernel seeds oil content of 50-60% (Devan & Mahalakshmi, 2009c).

2.5.1.10 *Madhuca indica*

M*adhuca indica* is mainly found in India (Balat & Balat, 2010; Demirbas, 2009; Jena et al., 2010). It belongs to the Sapotaceae family and grows quickly to approximately 20 m in height, possesses evergreen or semi-evergreen foliage, and is adapted to arid environments (Kumar & Sharma, 2011; Pinzi et al., 2009). M*adhuca indica* is one of the forest based tree-borne non-edible oils with large production potential of about 60 million tons per annum in India. The M*adhuca indica* tree starts producing seeds after 10 years and continues up to 60 years. The kernel constitutes about 70% of the seed and contains 50% oil (Balat, 2011; Balat & Balat, 2010; Kumar & Sharma, 2011). Each tree yields about 20-40 kg of seed per year depending upon the maturity and size of the tree and the total oil yield per ha is 2.7 t per year. Its seed contains about 35-40% of *Madhuca indica* (Jena et al., 2010).

2.5.1.11 *Sapium sebiferum (Linn.) Roxb* (Chinese tallow)

Sapium sebiferum (Linn.) Roxb (Chinese tallow tree) is also commonly referred to as Stillingia tree. It belongs to the Euphorbiaceae family. The tree grows rapidly and can reach maturity within approximately 3-4 years. It can generate economic yields in its productive lifespan of which ranges between 70-100 years. The tree can be grown on marginal land is adapted to alkaline, saline, droughty, and acidic soils. The tree is native to eastern Asia (China, Japan and India) and grows well in the southern coastal of the United States to prevent soil erosion. The tree produces 4-10 tons of seed every year (Liu et al., 2009; No, 2011; R. Wang et al., 2011). The seeds contain 45-60% oil. Historically, the tree has been used in soap and candles making, herbal medicine and to prevent soil erosion. Currently, It has been considered useful in the production of biodiesel because it is the third most productive vegetable oil producing crop in the world, after algae and oil palm (Sanford et al., 2009).

2.5.1.12 *Aleutites fordii* (Tung)

Aleutites fordii tree is spread widely in western China, Argentina, Paraguay, Africa, India and United States (V. Sharma et al., 2011). It is also commonly referred to as Tung tree. The tree usually bears fruit within 2-4 years and reaches maximum productivity at around 10-12 years of age. The productivity of Tung oil mainly varies from 300-450 kg/ha. The oil content of fruit is between 14-20%, the kernel 53-60% and the seed 30-40%. Tung oil has been used in different industrial applications such as ceramic, paint, paper and cloth production. However, recently it has been regarded as a promising non-edible source of biodiesel production (Shang et al., 2010; V. Sharma et al., 2011).

2.5.1.13 *Azadirachta indica* (Neem)

Azadirachta indica (Neem) tree belongs to the Meliaceae family. It is a multipurpose and an evergreen tree, 12-18 m tall, which can grow in almost all kinds of soil including clay, saline, alkaline, dry, stony, shallow soils and even on solid having high calcareous soil. It is native to India, Pakistan, Sri Lanka, Burma, Malaya, Indonesia, Japan and the tropical regions of Australia. It thrives well in arid and semi-arid climate with maximum shade temperature as high as 49 °C and the rainfall is as low as 250 mm. It can be raised by directly sowing its seed or by transplanting nursery-raised seedlings in monsoon rains. It reaches maximum productivity after 15 years and has a life span of 150-200 years. Planting is usually done at a density of 400 plants per hectare. The productivity of Neem oil mainly varies from 2-4 ton/ha/year and a mature Neem tree produces 30-50 kg fruit. The seed of the fruit contains 20-30 wt% oil and kernels contain 40-50% of an acrid green to brown colored oil (Azam et al., 2005; No, 2011; Ragit et al., 2011).

2.5.1.14 *Hevea brasiliensis* (Rubber seed)

Hevea brasiliensis tree, commonly referred to Rubber tree, belongs to the family Euphorbiaceae. The rubber tree originates from the Amazon rain forest (Brazil). The tree is the primary source of natural rubber and produces 99% of world's natural rubber. Moreover, the tree's sap-like extract (known as latex) can be collected and used in various applications. It is distributed mainly in Indonesia, Malaysia, Liberia, India, Sri Lanka, Sarawak, and Thailand. Growing up to 34 m in height, the tree requires heavy rainfall and produces seeds weighing from 2-4g that do not currently have any major industrial applications (Demirbas, 2009; Gill et al., 2011; Kumar & Sharma, 2011). On an average, a healthy tree can give about 500 g of useful seeds during a normal year and this works out to an estimated availability of 150 kg of seeds per hectare. The seed contains an oily endosperm. Generally 37% by weight of the seed is shell and the rest is kernel. Rubber seed oil is non-edible oil, which contain 50-60wt% oil and kernel contain 40-50wt% of brown colour oil. The oil is high in unsaturated constituents such as linoleic (39.6 wt.%), oleic (24.6 wt.%), and linolenic (16.3 wt.%) acids. Other fatty acids found in rubber seed oil include saturated species such as palmitic (10.2 wt.%) and stearic (8.7 wt.%) acids (Gill et al., 2011; No, 2011; Ramadhas et al., 2005b; Tomes et al., 2011).

2.5.1.15 *Rice bran*

Rice bran is the cuticle between the paddy husk and the rice grain and is obtained as a by-product in the production of refined white rice from brown rice and is common in countries such as China and India. The bran is highly nutritious due to the presence of lipids, protein, minerals and vitamins. It is extracted from white rice bran by which the composition of rice bran varies with the rice type, climatic conditions and rice processing methods (Zheng et al., 2010). The oil content in rice bran varies from 12-25% (Balat, 2011; Sanford et al., 2009). The high FFA content of rice bran oil makes it unsuitable for eating purposes. The estimated potential yield of crude rice bran oil is about 8 million metric tons if all rice bran produced in the world were to be harnessed for oil extraction. Rice bran oil is an underutilized non-edible vegetable oil, which is available in large quantities in rice cultivating countries, and very little research has been done to utilize this oil as a replacement for mineral diesel (Balat, 2011; Balat & Balat, 2010; Saravanan et al., 2008).

2.5.1.16 *Nicotiana tabacum* (Tobacco)

Nicotiana tabacum, commonly referred to tobacco, is a by-product that contains significant amount of oil (35-49% by weight) with an estimated annual yield of 15,000 tons per year. It can be cultivated in more than 100 countries worldwide such as Macedonia, Turkey, South Serbia and widespread in North and South America etc. the tree is commonly grown for the collection of leaves (Moser, 2009; Usta et al., 2011; Veljkovic et al., 2006). The oil extracted from tobacco seed is non-edible with physical, chemical and thermal properties that compare favourably with other vegetable oils and have the potentiality to be considered as a new feedstock for biodiesel production (Usta, 2005a, 2005b; Usta et al., 2011; Veljkovic et al., 2006).

2.5.1.17 *Crambe abyssinica* (Hochst)

Crambe abyssinica (hochst or crambe) is an oil plant belongs to cruciferous family. It is native of the Mediterranean region, from Ethiopia to Tanzania. Being its origin the Mediterranean zone and the high lands of the East of Africa, it adapts very well to the cold weather of the wide extensions of Europe. The tree can reach up to 1-2m height depending on the season and plant density. The flowers are white or yellow. The seeds are held into little capsules and each capsule only contains one greenish brown spherical seed of 0.8-2.6 mm diameter. The capsules generally stay around the seeds after harvest the hull has a volume of 25-30%. The weight of 1000 seeds is approximately 6-10 g. Their seeds contain 35.6-42.8% of oil (Falasca et al., 2010). The oil can be used as a source to produce biodiesel. However, Very little research has been done to produce biodiesel from this oil.

2.5.1.18 *Thevettia peruviana* (yellow oleander)

Thevettia peruviana is an evergreen perennial shrub native in tropical America, especially Mexico, Brazil and West Indies. The tree belongs to Apocynaceae family and is commonly known by various names such as yellow oleander (nerium), gum bush, bush milk, exile tree in India, cabalonga in Puerto Rico, ahanain Guyana, olomi ojo by Yorubas in Nigeria. Its height can reach up to 4.5-6m with deep green linear sword-shaped leaves and funnel shaped (yellow, white or pinkish yellow coloured) flowers. *Thevettia* plants produce annually more than 400-800 fruits depending on the rainfall and plant age. The plant has annual seed yield of 52.5 t/ha and about 1750 L of oil can be obtained from a hectare of waste land. It has high oil content of around 67% in its kernel (Kumar & Sharma, 2011).

2.5.1.19 *Sapindus mukorossi* (Soapnut)

Sapindus mukorossi (Soapnut) is generally found in tropical and subtropical climate areas and various parts of the world including Asia (the outer Himalaya of Uttar, Pradesh, Uttaranchal, Himachal Pradesh, Jammu, and Kashmir), America and Europe. The plant grows very well in deep loamy soils and leached soils. Therefore, cultivation of soapnut in such soil avoids potential soil erosion. The seed is enclosed in a black, smooth and hard globose endocarp. Soapnut seeds contain 23% oil of which 92% is triglycerides. The oil from soapnut has been considered as promising non-edible oil having significant potential for biodiesel production. This is because it is the third most productive vegetable oil producing crop in the world, after algae and oil palm (Chhetri et al., 2008; Misra & Murthy, 2011).

2.5.1.20 *Cerbera odollam* (Sea mango)

Cerbera odollam (Sea mango) also sometimes called Cerbera manghas L, is a tree belonging to the poisonous Apocynaceae family (Gaillard et al., 2004). *Cerbera odollam* grows well in coastal salt swamps and creeks in south India and along riverbanks in southern and central Vietnam, Cambodia, Sri Lanka, Myanmar, Madagascar and Malaysia (Kansedo et al., 2009; Kumar & Sharma, 2011). The *Cerbera odollam* tree grows to a height of 6-15 m and has dark green fleshy lanceolate leaves. The large white flowers have a delicate perfume, reminiscent of jasmine. The fruit, when still green, looks like a small mango, with a green fibrous shell enclosing an ovoid kernel measuring approximately 2 cm ×1.5 cm and consisting of two cross-matching white fleshy halves. On exposure to air, the white kernel turns violet, then dark grey, and ultimately brown or black. The oil content of *Cerbera odollam* seeds is 54%. The fatty acid composition of *cerbera odollam* oil is mainly oleic (48.1%), followed by palmitic (30.3%), linoleic (17.8%) and stearic (3.8%) (Kansedo et al., 2009; Kumar & Sharma, 2011).

2.5.1.21 Other feedstocks

***Euphorbia lathyris* L.** which belongs to the Euphorbiaceae family can thrive in drought, frost and arid soils. This plant is native to southern Europe, north-western Africa, southwest Asia and western China. The yield of EL seed ranges from 1.5-2.5 tons/ha/year, and the oil contents is 48wt.% (R. Wang et al., 2011).

Idesia polycarpa var. vestita, a tall tree of about 15m high, is mainly distributed in the provinces to the south of Qinling Mountain and Huaihe River in China. It's a red ripe fruit consists of yellow pulp and dark greenish yellow seed. The oil contents in pulp and seed are about 26.15% and 26.26% (% dry basis) respectively. The yields of oil are 1.5-2.5 kg/tree and 2.25-3.75 tons/ha, respectively. *Idesia polycarpa* has a great potential as a biodiesel feedstock (Yang et al., 2009).

***Guizotia abyssinica* (GA)** belongs to the Compositae family. It is an annual herbaceous plant cultivated in Ethiopia and India in rotation with cereals and pulses. The plant grows to a height of 0.5-1.5 m and reaches the maturity within 110 to 120 days. The crop is widely adapted to all types of soil and is commonly grown in India on poor and acidic soils or on hilly slopes that are low in fertility. It requires moderate rainfall and grows in temperate and tropical areas. Yield is reported to be 200-300 kg/ha, although they can reach 500-600 kg/ha with good management. The seeds are shinning black in appearance and are very light in weight as one-thousand-seeds weigh on 3-5 g. The seed contains about 30% oil with 25% oleic and 55% linoleic acid in fatty acid composition (R. Sarin et al., 2009).

Argemone mexicana L. (Common name: Mexican prickly poppy) belongs to the Papaveraceae family. It is a species of poppy found in Mexico and now widely naturalized in the United States, India and Ethiopia. The plant prefers light (sandy) soils, requires well-drained soil and can grow in nutritionally poor soil. The seeds contain 22-36% of a pale yellow non-edible oil called argemone oil or katkar oil. The main fatty acids present in *Argemone mexicana L.* seed oil are myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid and arachidic acid. The non-edible oil from this tree has been found suitable for biodiesel purpose (Kumar & Sharma, 2011).

Putranjiva roxburghii (Lucky bean tree) tree belongs to the family Euphorbiacae of order Geranials, which was identified by Roxburgh and accordingly the plant is called as *P. roxburghii*. The tree can reach to a height up to 18 m and a girth of 2m. Putranjiva oil is yellow in colour, highly pungent, volatile and rich in oleic acid. The seeds contain 41-42% of oil (Gangal et al., 2009; Haldar et al., 2009; Kumar & Sharma, 2011).

M. azedarach (syringe) tree belongs to the family Meliaceae. It is a deciduous tree that grows between 7-12 m in height. It is native to India, southern China, and Australia. The oil content of dried syringe berries is around 10 wt.% (Kumar & Sharma, 2011).

Simarouba glauca tree belongs to the family Simaroubaceae and is commonly known as paradise tree. The tree is native to Florida in the United States, southern Florida and South America. It is a multipurpose tree capable of growing on the degraded soils and can be adapted to a wide range of temperatures (10-45 °C) and altitudes up to 1000 m above sea level. Its seeds contain 50-65% oil that can be extracted by conventional methods (Jena et al., 2010).

Simmondsia chinensis (Jojoba) tree belongs to the family Simmondsiaceae. It is a perennial shrub that is native to the Mojave and Sonoran deserts of Mexico, California and Arizona. The lipid content of Jojoba seeds vary between 45-55% (Kumar & Sharma, 2011).

Michelia champaca belongs to Magnoliaceae plant family, which is found in Eastern Himalayas, Assam, Burma, China, Western Ghats and throughout India. It is a tall handsome evergreen tree with straight stem and smooth brown bark. Its seeds yielded 45% of oil (Hosamani et al., 2009).

Garcinia indica belongs to Guttiferae plant family, which is found in the tropical rain forests of Western Ghats, Konkana, North Kanara, South Kanara, Bombay, Goa and Coorg. Garcinia indica seeds yielded 45.5% of oil (Hosamani et al., 2009).

***Eruca sativa* L.** is widespread in South Asia and it is known as taramira. It can be considered as a non-edible biodiesel feedstock. *Eruca sativa* L. has a yield of 1106 kg oil/ha and the oil yield is 30% (Chakrabarti et al., 2011).

Hibiscus sabdariffa L. (Roselle) tree belongs to the family Malvaceae. It is also known worldwide by many different common names such as jamaica sorrel, and, in Thai, as krachiap daeng. It is widely cultivated in tropical regions including the northern, south-eastern, central parts of Thailand and China. The seeds contain 18% oil (Nakpong & Wootthikanokkhan, 2010).

2.5.2 Advantages of non-edible oils

Preliminary evaluation of several non-edible oilseed crops for their growth, feedstock and adaptability show that these feedstocks have the following advantages (No, 2011; Syers et al., 2007):

(1) The adaptability of cultivating non-edible oil feedstocks in marginal land and non-agricultural areas with low fertility and moisture demand.

(2) They can be grown in arid zones (20 cm rainfall) as well as in higher rainfall zones and even on land with their soil cover. Moreover, they can be propagated through seed or cuttings.

(3) They have huge potential to restore degraded lands, create rural employment generation and fixing of up to 10 ton/ha/year CO_2 emissions.

(4) They do not compete with existing agricultural resources.

(5) They eliminate competition for food and feed. Non-edible oils are not suitable for human food due to the presence of some toxic components in the oils.

(6) They are more efficient and more environmentally friendly than the first generation feedstocks. Conversion of non-edible oil into biodiesel is comparable to conversion of edible oils in terms of production and quality.

(7) Less farmland is required and a mixture of crops can be used. Non-edible oil crops can be grown in poor and wastelands that are not suitable for food crops.

(8) Non edible feedstock can produce useful by-products during the conversion process, which can be used in other chemical processes or burned for heat and power generation.

For instance, the seed cakes after oil expelling can be used as fertilizers for soil enrichment.

(9) Most of non-edible oils are highly pest and disease resistant.

(10) The main advantages of non-edible oil are their liquid nature portability, ready availability, renewability, higher heat content, lower sulphur content, lower aromatic content and biodegradability.

2.5.3 Problems in exploitation of non-edible oils

Development of non-edible oilseed as alternative biodiesel feedstock in the transportation sector is critical towards achieving higher self-reliance energy security. This situation offers a challenge as well as an opportunity to look for replacement of fossil fuels for both economic and environmental benefits. Under the existing situation of non-edible oils being of forest origin, the problems encountered are (Syers et al., 2007):

(1) Collection from scattered locations, high dormancy and problems in picking and harvesting in avenue and forest plantations.

(2) Non-availability of quality planting material or seed, limited period of availability, unreliable and improper marketing channels.

(3) Lack of post-harvest technologies and their processing, non-remunerative prices, wide gap between potential and actual production, absence of state incentives promoting bio-diesel as fuel, and economics and cost-benefit ratio.

Table 2.8 shows the Agro-climatic preferences of some promising non-edible oils.

2.6 Fatty acid composition profile of various feedstocks

Fatty acid composition is an important property for any biodiesel feedstock as it determines the efficiency process to produce biodiesel. The percentage and type of fatty acids composition relies mainly on the plant species and their growth conditions. The fatty acid composition and distribution of some feedstocks are generally aliphatic compounds with a carboxyl group at the end of a straight-chain. The most common fatty acids are C_{16} and C_{18} acids. However, some feedstocks contain significant amounts of fatty acids other than the typical C_{16} and C_{18} acids (Knothe et al., 2010). Table 2.9 shows the chemical structures of common fatty acids. Table 2.10 shows the fatty acid composition of various feedstocks that were found suitable for production of biodiesel. Moreover, more fatty acid compositions can also be found in references (Azam et al., 2005; Moser, 2009; Pinzi et al., 2009; Singh & Singh, 2010; Tomes et al., 2011) for further reading.

Table 2.8: Agro-climatic preferences of some promising tree-borne oilseeds (Syers et al., 2007)

Non-edible vegetable source	Rainfall (mm)	Temperature °C	Soil Preference	Tree height (m)	Suitability for agro-forestry
Jatropha curcas L.	480-2400	20-28	Any type	3-5	Fence, Alley, Sole
Pongamia	500-2500	Jan-38	Wide range	8-10	Bunds Border
Neem	750-1000	15-45	Deep clay	20	Border, Sole
Mahua	550-1500	Feb-46	Deep clay	18-20	Border, Wastelands
Calophyllum	750-5000	Jul-48	Sand/Loamy	10-25	Wastelands, Sea coast
Simarouba	1000-4000	25-45	Well drained	15	Bunds, Sole

Table 2.9: The chemical structures of common fatty acids (Atabani et al., 2013)

Fatty acid	Structure	Systematic name	Chemical structure
Lauric	(12:0)	Dodecanoic	$CH_3(CH_2)_{10}COOH$
Myristic	(14:0)	Tetradecanoic	$CH_3(CH_2)_{12}COOH$
Palmitic	(16:0)	Hexadecanoic	$CH_3(CH_2)_{14}COOH$
Stearic	(18:0)	Octadecanoic	$CH_3(CH_2)_{16}COOH$
Oleic	(18:1)	cis-9-Octadecenoic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic	(18:2)	cis-9-cis-12-Octadecadienoic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Linolenic	(18:3)	cis-9-cis-12,	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Arachidic	(20:0)	Eicosanoic	$CH_3(CH_2)_{18}COOH$
Behenic	(22:0)	Docosanoic	$CH_3(CH_2)_{20}COOH$
Erucic	(22:1)	cis-13-Docosenoic	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$
Lignoceric	(24:0)	Tetracosanoic	$CH_3(CH_2)_{22}COOH$

Table 2.10: Fatty acid profiles of various feedstocks (Atabani et al., 2013)

non-edible feedstock	C 8:0	C10:0	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	C20:0	C20:1	C20:2	C22:0	C22:1	C24:0	C24:1
Sunflower	-	-	-	-	6.08	-	3.26	16.93	73.73	-	-	-	-	-	-	-	-
Rapeseed	-	-	-	-	3.49	-	0.85	64.64	22.30	8.23	-	-	-	-	-	-	-
Soybean	-	-	-	-	10.58	-	4.76	22.52	52.34	8.19	-	-	-	-	-	-	-
Palm	-	-	-	1	42.80	-	4.5	40.5	10.1	0.2	-	-	-	-	-	-	-
Peanut	-	-	-	0.3	12.3	-	4.6	53.6	29	0.1	-	-	-	-	-	-	-
Coconut	-	-	46.5	19.2	9.8	-	3	6.9	2.2	-	-	-	-	-	-	-	-
Used frying oil	-	-	-	-	12	-	-	53	33	-	-	-	-	-	-	-	-
Tallow	-	-	-	3-6	24-32		20-25	37-43	2-3	-	-	-	-	-	-	-	-
Lard	-	-	-	1-2	28-30	-	12-18	4-50	7-13	-	-	-	-	-	-	-	-
Aphanamixis polystachya (meliaceae)	-	-	-	-	23.1	-	12.8	21.5	29.0	13.6	-	-	-	-	-	-	-
Argemone mexicana	-	-	-	0.8	14.5	-	3.8	18.5	61.4	-	1.0	-	-	-	-	-	-
Asclepias syriaca (milkweed)	-	-	-	-	5.9	6.8	2.3	34.8	48.7	1.2	-	-	-	-	-	-	-
Azadirachta indica (neem)	-	-	-	0.2-0.26	14.9	0.1	20.6	43.9	17.9	0.4	1.6	-	-	0.3	-	0.3	-
Brassica carinata (Ethiopian mustard)	-	-	-	-	4-6	-	1.3	10-17	17-25	10-17	0.7	-	-	-	-	-	-
Babasu	0.5	3.8	48.8	17.2	9.7	-	4	14.2	1.8	-	-	-	-	-	-	-	-
Calophyllum inophyllum L.	-	-	-	0.09	14.6	2.5	19.96	37.57	26.33	0.27	0.94	0.72	-	-	-	2.6	-
Cuphea viscosissima	-	-	-	4.7	18.2	-	3.5	46.9	22.8	2.3	0.6	-	-	0.4	-	0.6	-
Crambe abyssinica	-	-	-	0	2	-	1	19	-	7	2	-	-	1	59	1	-
Camelina	-	-	-	-	5.0	-	2.2	17.7	18	37.9	1.4	9.8	1.6	0.4	4.5	0.3	0.2
Euphorbia lathyris.L	-	-	-	-	6.8	0.5	1.98	81.46	3.71	2.78	-	0.5	-	-	0.2	-	-
Guizotia abyssinica L. (niger)	-	-	-	-	9.2	-	9	71.7	-	-	-	-	-	-	-	-	-
Hevea brasiliensis (rubber)	-	-	-	2.2	10.2	-	8.7	24.6	39.6	16.3	-	-	-	-	-	-	-
Jatropha curcas.L	-	-	-	1.4	12.7	0.7	5.5	39.1	41.6	0.2	0.2	-	-	-	-	-	-
Lesquerella fendleri	-	-	-	0.1	0.9	0.3	1.7	13	5.8	10.6	0.7	-	-	-	-	-	0.4
Linum usitatissimum (linseed)	-	-	-	-	4.4	0.3	3.8	20.7	15.9	54.6	0.2	-	-	0.3	-	0.1	-
Madhuca indica (mahua)	-	-	-	-	16.0-28.2	-	20.0-25.1	41.0-51.0	8.9-13.7	-	0.0-3.3	-	-	-	-	-	-

Melia azedarach	-	-	-	0.1	10.1	1.5	3.5	21.8	64.1	0.4	0.2	0.3	-	-	-	-	-
Nicotiana tabacum (tobacco)	<0.01	<0.01	<0.01	0.09	10.96	0.2	3.34	14.54	69.49	0.69	0.25	0.13	-	0.12	<0.01	0.04	-
Piqui	-	-	-	-	40	-	2	47	4	-	-	-	-	-	-	-	-
Putranjiva roxburghii	-	-	-	-	8.0	-	15.0	56.0	18.0	-	3.0		-	-	-	-	-
Pongamia pinnata (karanja)	-	-	-	-	3.7-7.9	-	2.4-8.9	44.5-71.3	10.8-18.3	-	4.1	2.4	-	5.3	-	1.1-3.5	-
Ricinus communis (castor)	-	-	-	-	1.1	0	3.1	4.9	1.3	0.6	0.7	-	-	-	-		-
Sapium sebifeum Lin. Roxb (stillingia)	-	-	0.4	0.1	7.5	3.71	2.3	16.7	31.5	41.5	-	0.59	-	-	-	-	-
Sesamum indicum (Sesame)	-	-	-	-	11.0		7.0	43.0	35.0	-	-	-	-	-	-	-	-
Sterculia foetida L	-	-	-	-	22.4	-	7.3	16.4	45.6	-	6.46	-	-	-	-	-	-
Thevetia peruviana Merrill	-	-	-	-	15.6	-	10.5	60.9	5.2	7.4	0.3	-	-	0.1	-	-	-
Tung	-	-	-	-	1.8	-	2.1	5.3	6.8	0.7	0.2	0.1	-		-	10.4	-
Terminalia catappa	-	-	-	-	35.0	-	5.0	32.0	28.0	-	-	-	-	-	-	-	-
Terminalia belerica Robx.	-	-	-	-	35.0	-	-	24.0	31.0	-	-	-	-		-	-	-
Ximenia americana Linn	-	-	-	-	-	-	1.2	60.8	6.7	-	-	-	-	-	-	-	-
Zanthoxylum bungeanum	-	-	-	-	10.6	5.2	1.4	32.1	25.6	24.1	-	-	-	-	-	-	-
Ziziphus mauritiana L.	-	-	-	-	10.4	-	5.5	64.4	12.4	-	1.8	2.6	1.2	-	1.7	-	-

2.7 Oil extraction methods

The second step in the production of biodiesel is oil extraction. In this process, the oil contained in the seeds has to be extracted. The main products are the crude oil and the important by-products such as seeds or kernel cakes. There are three main methods that have been identified for extraction of the oil: (i) Mechanical extraction, (ii) Solvent extraction and (iii) Enzymatic extraction. Mechanical pressing and solvent extraction are the most commonly used methods for commercial oil extraction. Before the oil extraction takes place, seeds have to be dried. Seed can be either dried in the oven (105°C) or sun dried (3 weeks). Mechanical expellers or presses can be fed with either whole seeds or kernels or a mix of both, but common practice is to use whole seeds. However, for chemical extraction only kernels are used as feed (Achten et al., 2008; Mahanta & Shrivastava, 2011).

2.7.1 Mechanical extraction

The technique of oil extraction by mechanical presses is the most conventional one among other methods. In this type, either a manual ram press or an engine driven screw press can be used. Engine driven screw press can extract 68-80% of the available oil while the ram presses only achieved 60-65% (Table 2.11). This broader range is due to the fact that seeds can be subjected to a different number of extractions through the expeller (Achten et al., 2008; Mahanta & Shrivastava, 2011). The oil extracted by mechanical presses needs further treatment of filterization and degumming. One more problems associated with conventional mechanical presses are, their design is suited for some particular seeds, and therefore the yield is affected if used for other seeds. It has been found that, pre-treatment of the seeds, such as cooking, can increase the oil yield of screw pressing up to 89% after single pass and 91% after dual pass (Achten et al., 2008; Mahanta & Shrivastava, 2011).

Table 2.11: Calculated oil yields (% of contained oil) of mechanical extraction methods (Atabani et al., 2013)

Press	Oil yield (%)	Necessary treatment
Engine driven screw press	68.0	Filterization and degumming
	80.0	
	79.0	
Ram press	62.5	
	62.5	

2.7.2 Solvent extraction (chemical extraction)

Solvent extraction is the technique of removing one constituent from a solid by means of a liquid solvent. It is also called leaching. There are many factors influencing the rate of extraction such as particle size, the type of liquid chosen, temperature and agitation of the solvent. The small particle size is preferable because it allows for a greater interfacial area between the solid and liquid. The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low to circulate freely. Temperature also affects the extraction rate. The solubility of the material will increase with the increasing temperature. Agitation of the solvent also affects, it increases the eddy diffusion and therefore increases the transfer of material from the surface of the particles. Solvent extraction is only economical at a large-scale production of more than 50t biodiesel per day. There are three methods that are used in this type as follow (Achten et al., 2008; Mahanta & Shrivastava, 2011):

(1) Hot water extraction.

(2) Soxhlet extraction.

(3) Ultrasonication technique.

2.7.3 Enzymatic oil extraction

Enzymatic oil extraction technique has emerged as a promising technique for extraction of oil. In this process suitable enzymes are used to extract oil from crushed seeds. Its main advantages are that it is environment friendly and does not produce volatile organic compounds. However, the long process time is the main disadvantage associated with this technique (Mahanta & Shrivastava, 2011).

Table 2.12 shows the reaction temperature, reaction pH, time consumption and oil yield of different chemical and enzymatic extraction methods. It has been found that the chemical extraction using n-hexane method results in the highest oil yield which makes it the most common type. However, this type consumes much more time compared to other types. Furthermore n-hexane solvent extraction has a negative environmental impacts as a result of the waste water generation, higher specific energy consumption and higher emissions of volatile organic compounds and human health impacts (working with hazardous and inflammable chemicals). Using aqueous enzymatic oil extractions greatly reduces these problems. In aqueous enzymatic oil extraction the use of alkaline protease gave better results. Furthermore, ultrasonication pre-treatment is a more useful step in aqueous oil extraction (Achten et al., 2008; Mahanta & Shrivastava, 2011).

Table 2.12: Reported oil yields percentage for different chemical and enzymatic extraction methods and different reaction parameters (Achten et al., 2008)

Extraction method	Reaction temperature (°C)	Reaction pH	Time consumption (h)	Oil yield (%)
n-hexane oil extraction (Soxhelt) apparatus	-	-	24	95-99
1st acetone	-	-	48	
2nd n-hexane				
Aqueous oil extraction (AOE)	-	-	2	38
	50	9	6	38
AOE with 10 min of ultrasonication as pre-treatment	50	9	6	67
Aqueous enzymatic oil extraction (AEOE)	60	4.5	2	-
(hemicellulase or cellulase)				73
AEOE (alkaline protease)	60	7	2	86
	50	9	6	64
AEOE (alkaline protease) with 5 min of ultrasonic as pretreatment	50	9	6	74
Three-phase partitioning	25	9	2	94

2.8 Problems and potential solutions of using vegetable oils

The direct use of vegetable oils or blends has generally been considered to be impractical for both direct and indirect diesel engines. The high viscosity, low volatility, acid composition, free fatty acid and moisture content, gum formation due to oxidation and polymerization during storage and combustion, poor cold engine start-up, misfire, ignition delay, incomplete combustion, carbon deposition around the nozzle orifice, ring sticking, injector choking in engine and lubricating oil thickening are the major problems of using vegetable oils. In general, the problems associated with using straight vegetable oil in diesel engines are classified into short term and long term. Table 2.13 highlights the problems, probable causes and the potential solutions.

2.9 Biodiesel production technologies

Globally, there are many efforts to develop and improve vegetable oil properties in order to approximate the properties of diesel fuel. It is well known that viscosity is the main barrier that prevents the use of direct vegetable oils in conventional diesel engines. These problems can be overcome by four methods; pyrolysis, dilution with hydrocarbons blending, Micro-emulsion, and transesterification (Demirbas, 2009; Singh & Singh, 2010). (L. Lin et al., 2011) conduct a comparison between different biodiesel production technologies. This comparison is given in Table 2.14.

Table 2.13: Known problems, probable cause and potential solutions for using straight vegetable oil in diesel engines (Mahanta & Shrivastava, 2011; Yusuf et al., 2011)

Problem	Probable cause	Potential solution
Short-term		
1. Cold weather starting	• High viscosity, low cetane number and high flash point of vegetable oils.	• Preheat fuel prior to injection.
2. Plugging and gumming of filters, lines and injectors	• Natural gums (phosphatides) in vegetable oil. Other ash.	• Refine the oil partially to remove gums.
3. Engine knocking	• Low cetane numbers. Improper injection timing.	• Adjust injection timing. • Use higher compression engines. Preheat fuel prior to injection. Chemically alter fuel to an ester.
Long term		
4. Cooking of injector on piston and engine head	• High viscosity of vegetable oil. • Incomplete combustion of fuel. • Poor combustion at part loads with vegetable oils.	• Heat fuel prior to injection. • Switch engine to diesel fuel when operation at part loads. • Chemically alter the vegetable oil to an ester.
5. Carbon deposits on piston and head of engine	• High viscosity of vegetable oil. • Incomplete combustion of fuel. • Poor combustion at part load with vegetable oils.	• Heat fuel prior to injection. Switch engine to diesel fuel when operation at part loads. Chemically alter the vegetable oil to an ester.
6. Excessive engine wear	• High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part loads with vegetable oils. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil.	• Heat fuel prior to injection. • Switch engine to diesel fuel when operation at part loads. • Chemically alter the vegetable oil to an ester. Increase motor oil changes. • Motor oil additives to inhibit oxidation.
7. Failure of engine lubricating oil due to polymerization	• Collection of polyunsaturated vegetable oil blow-by in crankcase to the point where polymerization occurs.	• Heat fuel prior to injection. • Switch engine to diesel fuel when operation at part loads. • Chemically alter the vegetable oil to an ester. • Increase motor oil changes. • Motor oil additives to inhibit oxidation.

Table 2.14: Comparison of main biodiesel production technologies (L. Lin et al., 2011)

Technologies	Advantage	Disadvantage
Dilution (direst blending or micro-emulsion	• Simple process	• High viscosity • Bad volatility • Bad stability
Pyrolysis	• Simple process • No-polluting	• High temperature is required • Equipment is expensive • Low purity
Transesterification	• Fuel properties is closer to diesel • High conversion Efficiency • Low cost • It is suitable for industrialized production	• Low free fatty acid and water content are required (for base catalyst) • Pollutants will be produced because products must be neutralized and washed • Accompanied by side reactions • Difficult reaction products separation
Supercritical methanol	• No catalyst • Short reaction Time • High conversion • Good adaptability	• High temperature and pressure are required • Equipment cost is high • High energy consumption

2.9.1 Pyrolysis (thermal cracking)

Pyrolysis is the thermal decomposition of the organic matters by heat in the absence of oxygen and in presence of a catalyst. The paralyzed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. Many investigators have studied the pyrolysis of triglycerides to obtain suitable fuels for diesel engine. Thermal decomposition of triglycerides produces alkanes, alkenes, alkadienes, carboxylic acids, aromatics and small amounts of gaseous products. The liquid fractions of the thermally decomposed vegetable oils are likely to approach diesel fuels. The pyrolyzate had lower viscosity, flash point, and pour point than diesel fuel and equivalent calorific values. However, cetane number of the pyrolyzate was lower compared to diesel fuel. The pyrolyzed vegetable oils contain acceptable amounts of sulphur, water content, copper corrosion values and sediments but unacceptable ash, carbon residual and pour point. It has been observed that pyrolysis process is effective, simple, wasteless and pollution free (Singh & Singh, 2010).

The pyrolysis process can be divided into three subclasses which are conventional pyrolysis, fast pyrolysis and flash pyrolysis depending on the operating conditions. Table 2.15 presents the range of the main operating parameters for pyrolysis processes.

Table 2.15: The range of the main operating parameters for pyrolysis processes (Atabani et al., 2013)

Parameter	Conventional pyrolysis	Fast pyrolysis	Flash pyrolysis
Pyrolysis temperature (k)	550-950	850-1250	1050-1300
Heating rate (k/s)	0.1-1	10-200	>1000
Particle size (mm)	5-50	< 1	< 0.2
Heating time (sec)	450-550	0.5-10	< 0.5

2.9.2 Dilution

Mainly, vegetable oils are diluted with diesel to reduce the viscosity and improve the performance of the engine. This method does not require any chemical process (Balat & Balat, 2008, 2010; Chauhan et al., 2010; Demirbas, 2009; Koh & Ghazi, 2011; Mahanta & Shrivastava, 2011). It has been reported that substitution of 100% vegetable oil for diesel fuel is not practical. Therefore, blending of 20-25% vegetable oil to diesel has been considered to give good results for diesel engine (Agarwal, 2007; Balat & Balat, 2008; Koh & Ghazi, 2011; Singh & Singh, 2010). The use of blends of diesel fuel with sunflower, coconut, African pear seed, rice bran, PP (Pistachia Palestine), waste cooking, palm oil, soybean, cottonseed, rubber seed, rapeseed, Turpentine, Linseed, Putranjiva roxburghii, Jatropha curcas and Pongamia pinnata oils has been described in literature. For instance, (Ziejewski et al., 1986) investigated the effects of the fuel blend of 25% sunflower oil with 75% diesel fuel (25/75 fuel) in a direct injection diesel engine. The authors found that this blend is not suitable for long-term use in direct injection engines. This is because the viscosity at 313 K was 4.88 cSt (maximum specified ASTM value is 4.0 cSt at 313 K). Further, it was also reported that the viscosity of 25/75 high oleic sunflower oil/diesel fuel blend was 4.92 cSt at 40 ˚C and has passed the 200h EMA (Engine Manufacturers 'Association) test. Generally, direct use of vegetable oils and their blends have been considered to be difficult to use in both direct and indirect diesel engines (Demirbas, 2003; Koh & Ghazi, 2011; Parawira, 2010; Yusuf et al., 2011).

2.9.3 Micro-emulsion

A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructure with dimensions generally into 1 – 150 nm range formed spontaneously from two normally immiscible liquids and one and more ionic or more ionic amphiphiles. Micro emulsion can be made of vegetable oils with an ester and dispersant (co solvent), or of vegetable oils, and alcohol such as ethanol, ethanol, buthanol, hexanol and a surfactant and a cetane improver, with or without diesel fuels. Micro emulsification has been considered as a reliable approach to solve the problem of the high viscosity of vegetable oils. Micro-emulsion with these solvents has met the maximum viscosity requirement for diesel fuel. It has been demonstrated that short-term performances of both ionic and non-ionic micro-emulsions of aqueous ethanol in soybean oil are nearly as well as that of No. 2 diesel fuel (Balat & Balat, 2010; Jain & Sharma, 2010b; Singh & Singh, 2010).

2.9.4 Transesterification (Alcoholysis)

Transesterification is regarded as the best method amongst other approaches due to its low cost and simplicity (Jain & Sharma, 2010a; Parawira, 2010; Y. C. Sharma, Singh, B., 2009). Transesterification or alcoholysis is defined as the chemical reaction of alcohol with vegetable oils. Biodiesel is the main product of this process. This reaction has been widely used to reduce the viscosity of vegetable oil and conversion of the triglycerides into ester. Transesterification consists of a number of consecutive, reversible reactions. In these reactions, the triglycerides are converted step wise to diglycerides, monoglyceride and finally glycerol which sinks to the bottom and biodiesel which floats on top and can be siphoned off as shown in Figure 2.8. Glycerol is an important by-product and can be burned for heat or be used as feedstock in the cosmetic industry. In this reaction, methanol and ethanol are the two main light alcohols used for transesterification process due to their relatively low cost. However, propanol, isopropanol, tert-butanol, branched alcohols and octanol and butanol can also be employed but the cost is much higher (Balat & Balat, 2010; Karmakar et al., 2010; Shahid & Jamal, 2011).

$$\text{Triglycerides} + \text{ROH} \xrightarrow{\text{CATALYST}} \text{Diglycerides} + \text{FAME}$$

$$\text{Diglycerides} + \text{ROH} \xrightarrow{\text{CATALYST}} \text{Monoglycerides} + \text{FAME}$$

$$\text{Monoglycerid} + \text{ROH} \xrightarrow{\text{CATALYST}} \text{Glycerol} + \text{FAME}$$

Figure 2.8: Equation of transestetification reaction (Atabani et al., 2012)

In this reaction, one hundred pounds of fat or oil are reacted with 10 pounds of a short chain alcohol in the presence of a catalyst to produce 10 pounds of glycerine and 100 pounds of biodiesel. As per the transesterification reaction, 3 moles of methanol were required to react with the vegetable oil (Chisti, 2007). Generally, transesterification process includes two main processes; catalytic and non-catalytic method. A catalyst is used to commence the reaction. The catalyst is vital as alcohol is barely soluble in oil or fat. The catalyst enhances the solubility of alcohol and thus increases the reaction rate. The most frequently used process is the catalytic transesterification process. Figure 2.9 shows the detailed classification of transesterification processes.

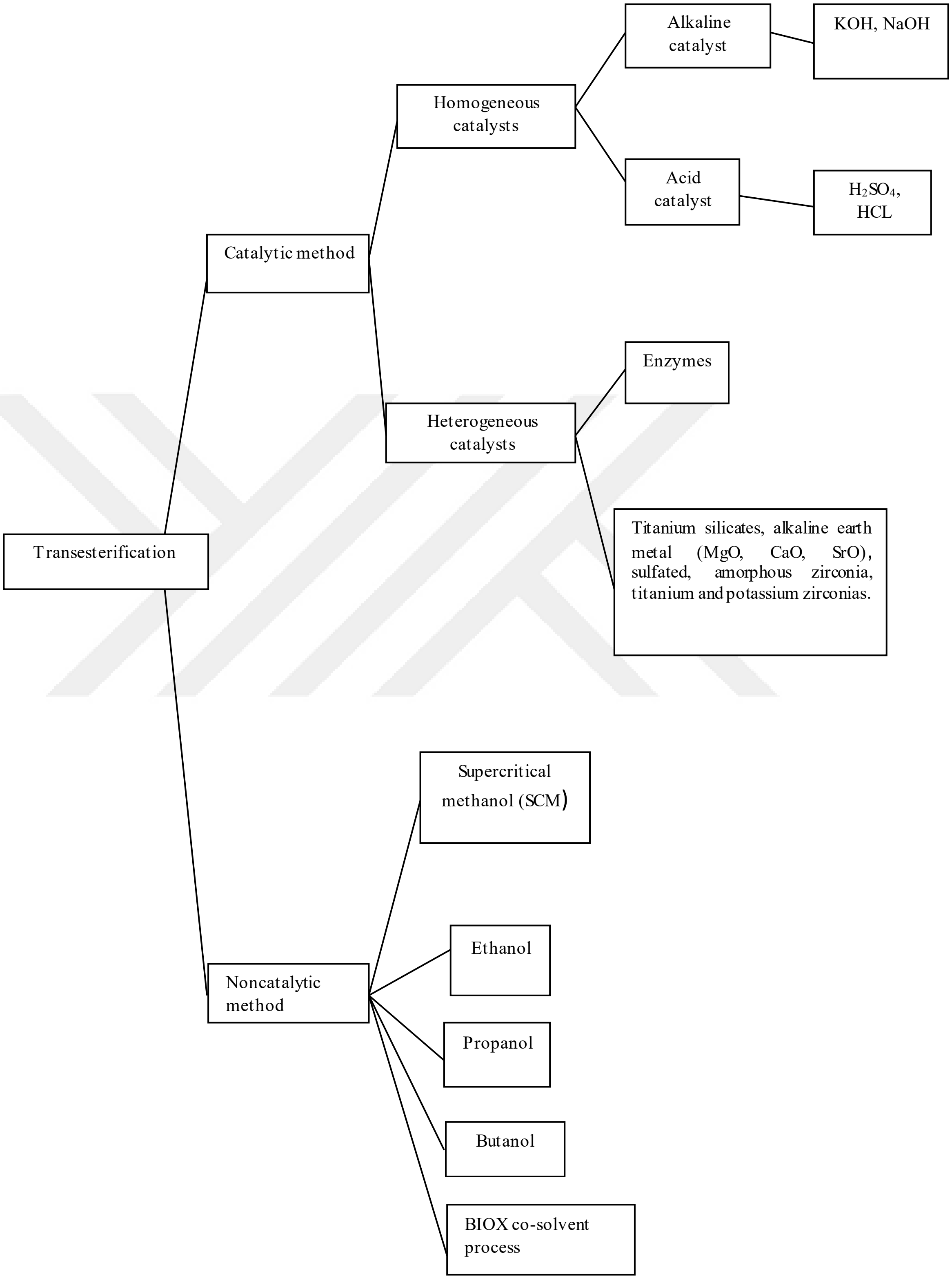


Figure 2.9: Classification of transesterification processes (Atabani et al., 2012)

Alkaline catalytic method is the fastest and most economical method. An alkaline catalyst proceeds at around 4000 times faster than with the same amount of acid catalyst. Moreover, this method can achieve high purity and yield of biodiesel product in a short time (30-60min). Therefore, it dominates the current biodiesel production methods. Alkaline catalysts include catalysts such as NaOH, KOH, $NaOCH_3$, $KOCH_3$, NaMeO and K_2CO_3. Most of biodiesel producers use sodium hydroxide or potassium hydroxide. Even though some authors reported that sodium hydroxide is better than potassium hydroxide and some are of the view that potassium hydroxide is better than sodium hydroxide. However, most of the researchers reported that both sodium and potassium hydroxide perform equally well. Sodium and potassium methoxides return better yield than all catalysts but they are costly, so they are not very frequently used. However, to use alkaline catalysts, free fatty acid (FFA) level should be below a desired limit (ranging from less than 0.5% to less than 3%). Beyond this limit the reaction will not take place and the product formed will be soap and water instead of esters and the yield of esters will be too less. In addition to, this reaction has several drawbacks; it is energy intensive; recovery of glycerol is difficult; the catalyst has to be removed from the product; alkaline wastewater requires treatment and the level of free fatty acids and water greatly interfere with the reaction (Janaun & Ellis, 2010; Shahid & Jamal, 2011; Y. C. Sharma, Singh, B., 2009). The mechanism of the reaction can be found in Ref (Balat & Balat, 2010; Koh & Ghazi, 2011).

Acid catalysts include sulphuric acid, hydrochloric acid, ferric sulphate acid, phosphoric acid, sulfonic acid and Lewis acids ($AlCl_3$ or $ZnCl_2$). Researchers have shown that acid catalysts are more tolerant than alkaline catalysts for vegetable oils having high free fatty acids and water. Therefore, acid catalyst is used to reduce the free fatty acids contents to a level safe enough for alkaline transesterification which is preferred over the acid catalyst after the acid value is reduced to the desired limit. It has been reported that acid-catalysed reaction gives very high yield in esters. However, the reaction is slow (3-48 h). It has been reported that the homogeneous transesterification consumes large amount of water for wet washing to remove the salt produced from the neutralization process, and the residual acid or base catalyst. Nevertheless, there are many companies around the world commercializing this technology because of its relatively lower energy use, high conversion efficiency and cost effective reactants and catalyst (Janaun & Ellis, 2010; Shahid & Jamal, 2011; Y. C. Sharma, Singh, B., 2009). The mechanism of the reaction can be found in Ref (Balat & Balat, 2010; Koh & Ghazi, 2011).

Transesterification using enzyme catalysts is preferred because, using them, soap is not formed; hence there is no problem of purification, washing, and neutralization. Lipase catalysts have shown good tolerance for the free fatty acid level of the feedstock and can convert more than 90% of oil into biodiesel. Moreover, they are known to have a propensity to act on long-chain fatty alcohols better than on short-chain ones. Therefore, the efficiency of the transesterification of triglycerides with ethanol is higher compared to that with methanol in systems with or without a solvent (Table 2.16). In this reaction, there is no need for complex operations for the recovery of glycerol and the elimination of catalyst and soap. However, the reaction yields and the reaction times are still unfavourable compared to the alkaline catalysts. Moreover, lipases are very expensive for large scale industrial production and they are unable to provide the degree of reaction completion required to meet ASTM fuel specifications. Recently, it has been found that the use of solvent-tolerant lipases, multiple enzymes and immobilized lipases-making catalysts can be developed as cost-effective enzymes (Balat & Balat, 2010; Karmakar et al., 2010; Singh & Singh, 2010). The mechanism of the reaction can be found in Ref (Koh & Ghazi, 2011). In general, chemically catalysed processes, including alkali catalysed and acid catalysed ones have been proved to be more practical than the enzyme catalysed process (Corro et al., 2010).

The catalytic transesterification has some problems such as; high time consumption, lag of reaction time caused by the extremely low solubility of alcohol in triglyceride phase and the need for separation of the catalyst and saponified impurities from biodiesel. Furthermore, the wastewater generated during biodiesel purification is not environment friendly.

These problems are not faced in the non-catalytic transesterification methods. For instance, supercritical methanol method uses lower energy and completes in a very short time (2-4 min) compared to catalytic transesterification. Further, since no catalyst is used, the purification of biodiesel and the recovery of glycerol are much easier, trouble free and environment friendly (Demirbas, 2009; Karmakar et al., 2010; Mahanta & Shrivastava, 2011; Shahid & Jamal, 2011). However, the method has a high cost in reactor and operation (due to high pressures and high temperatures) and high methanol consumption (e.g., high methanol/crude-oil molar ratio of 40/1) (Deng et al., 2011; Koh & Ghazi, 2011; Shahid & Jamal, 2011).

A variety of studies have been conducted for transesterification reaction for different catalysts, alcohols and molar ratios and different temperatures. The summary of these studies are given in Table 2.17. Many researchers have been working on biodiesel production from various feedstocks under different conditions using supercritical alcohol transesterification. Table 2.18 summarizes some of these studies. Table 2.19 presents a comparison between chemically catalysed processes and a non-catalytic supercritical methanol method for biodiesel production.

Table 2.16: Enzymatic transesterification reactions using various types of alcohols and lipases (Atabani et al., 2012)

No	Oil	Alcohol	Lipase	Conversion (%)	Solvent
1	Rapeseed	2-Ethyl-1-hexanol	C. rugosa	97	None
2	Palm oil	Methanol	Rhizopus oryzae	55 (w/w)	Water
3	Sunflower	Ethanol	M. meihei (Lypozyme)	83	None
4	Soybean oil	Methanol	C. antarctica lipase	93.80	>1/2 molar equivalent MeOH
5	Fish	Ethanol	C. anturctica	100	None
6	Palm kernel	Methanol	I. cepuciu	15	None
7	Recycled restaurant grease	Ethanol	J. cepacia (Lipase PS-30) + C. anturclica (Lipase SP435)	85.4	None
8	Jatropha oil	Methanol	Rhizopus oryzae	80	water
9	Jatropha oil	Ethanol	Pseudomonas cepacia	98	water

Table 2.17: Summary of transesterification method (Atabani et al., 2012)

No	Sample	Catalyst	Alcohol	Temperature	Ration of alcohol to oil	Yields (%)
1	Microalgae	Sulphuric acid	Methanol	30 °C	56:1	60
2	Soybean oil	No catalyst	Supercritical methanol	280 °C	24 and CO_2/methanol=0.1	98
3	Sunflower oil	No catalyst	Supercritical methanol and ethanol	200-400 °C (pressure 200 bar)	40:1	78-96
4	Rice bran	Sulphuric acid	Methanol	60 °C	10:1	< 96
5	Madhuca indica	H_2SO_4 (1% v/v)	Methanol	60 °C	0.3-0.35 v/v	98
6	Peanut oil	NaOH	Methanol	50 °C	-	90
7	Rubber seed oil	H_2SO_4 (0.5% v/v)	Methanol	45 °C	6:1	-
8	Canola oil	NaOH (1% by wt)	Methanol	45 °C	6:1	98
9	Jatropha oil	NaOH (1% by wt)	Methanol	60 °C	5:1	98
10	Cottonseed oil	$NaOCH_3$ (0.65% by wt)	Methanol	65 °C	-	96.9
11	Palm oil	NaOH (1% by wt)	Methanol	60 °C	-	95

Table 2.18: Supercritical transesterification with optimized reaction variables (Atabani et al., 2013)

Non-edible oil	Reactant	Molar ratio	Temperature	Supercritical condition	Reaction time	Alkyl ester yield
Pongamia pinnata & *Jatropha curcas* L.	methanol and ethanol	50 :1	300 ˚C	200 bar	40 min	80- 85%
Linseed oil	Methanol	41 :1	503-523 K	-	8-12 min	88-98%
Jatropha curcas L.	Methanol	43 :1	320 ˚C	8.4 Mpa	4 min	100%

Table 2.19: Comparisons between chemically catalytic processes and supercritical methanol method for biodiesel production from vegetable oils by transesterification (Al-Zuhair, 2007; Shahid & Jamal, 2011)

	Alkali catalytic method	Acid catalytic method	Supercritical method
Reaction temperature (K)	303-338	338	523-573
Reaction pressure (MPa)	0.1	0.1	10-25
Reaction time (min)	60-360	4140	7-15
Methyl ester yield (wt %)	96	90	98
Removal of	Methanol, catalyst	Methanol, catalyst	Methanol
Purification	Glycerol, soaps	Glycerol	
Free fatty acids	Saponified products	Methyl esters, water	Methyl esters, water
Process	Complicated	Complicated	Simple
Yield	Normal	Normal	High

2.9.4.1 Variables affecting the transesterification reaction

Transesterification reaction is affected by various parameters depending upon the reaction conditions. The reaction is either incomplete or the yield is reduced to a significant extent if the parameters are not optimized. Each parameter is equally important to achieve a high quality biodiesel which meets the regulatory standards. The most important parameters that affect the transesterification process are mentioned below (Balat & Balat, 2010; Y. C. Sharma et al., 2008; Srivastava & Prasad, 2000):

1- Free fatty acids, moisture and water content.
2- Type of alcohol and molar ratio employed.
3- Type and concentration of catalysts.
4- Reaction temperature and time.
5- Rate and mode of stirring.
6- Purification of the final product.
7- Mixing intensity.
8- Effect of using organic co-solvents.
9- Specific gravity.

2.10 Biodiesel standards and characterization

Biodiesel has different physical and chemical properties compared to diesel fuel. The quality of biodiesel fuel can be influenced by various factors include: the quality of feedstock, fatty acid composition of the feedstock, type of production and refining process employed and post production parameters. The advancements of biodiesel quality are being developed globally to maintain the quality of the end product and to ensure better criteria of biodiesel storage and feedstock for consumers' confidence and successful commercialization of biodiesel. Since biodiesel is produced from quite differently scaled plants of varying origins and qualities, it is necessary to install a standardization of fuel quality to guarantee an engine performance without any difficulties.

The establishment of standardization for biodiesel has to be wholly owned by many countries. It’s utilized to protect both biodiesel consumers and producers as well as to support the development of biodiesel industries. Austria was the first country in the world to define and approve the standards for rapeseed oil methyl esters (Balat & Balat, 2010; L. Lin et al., 2011). Currently, the properties and qualities of biodiesel must adhere with the international biodiesel standard specifications. These specifications include the American Standards for Testing Materials (ASTM 6751-3) or the European Union (EN 14214) Standards (Atadashi et al., 2010). However, there are some other standards available globally such as in Germany (DIN 51606), Austria (ON) and Czech republic (CSN) (L. Lin et al., 2011).

All alternative biodiesel fuels should meet the international standard specification of biodiesel such as ASTM 6571, EN 14214 and etc. These standards describe the physical and chemical characteristics of variety biodiesel produced from non-edible and edible oil resources. Some of these properties include; caloric value (MJ/kg), cetane number, density (kg/m^3), viscosity (mm$^{2/}$s), cloud and pour points ($^{\circ}$C), flash point ($^{\circ}$C), acid value (mg KOH per g-oil), ash content (%), copper corrosion, carbon residue, water content and sediment, sulphur content, glycerine (% m/m), phosphorus (mg/kg) and oxidation stability (Atadashi et al., 2010; Sanford et al., 2009; Uriarte, 2010). Table 2.20 gives ASTM 6751 and EN 14214 specifications of biodiesel beside ASTM D975 for diesel fuel. Table 2.21 gives a summary of standard specifications of biodiesel in several countries around the world. Moreover, a summary of some important characteristics of biodiesel are listed in Table 2.22.

Table 2.20: ASTM D975, ASTM 6751 and EN 14214 specifications of diesel and biodiesel fuels (Atabani et al., 2012)

		Diesel		Biodiesel			
Property specification	unit	ASTM D975		ASTM D6751		EN 14214	
		Test method	Limits	Limits	Test Method	Limits	Test Method
Flash point	°C	ASTM D975	60 to 80	130 minimum	ASTM D93	101 minimum	EN ISO 3679
Cloud point	°C	ASTM D975	-15 to 5	-3 to -12	ASTM 2500	-	-
Pour point	°C	ASTM D975	-35 to -15	-15 to -16	ASTM 97	-	-
Cold filter plugging point (CFFF)	°C	EN 590	-8	Max +5	ASTM D6371	-	EN 14214
Cetane number		ASTM D4737, EN 590	46	47 minimum	ASTM D613	51 minimum	EN ISO 5165
Density at 15°C	kg/m^3	ASTM D1298	820-860	880	D1298	860-900	EN ISO 3675/12185
Kinematic viscosity at 40°C	mm^2/s	ASTM D445	2.0 to 4.5	1.9-6.0	ASTM D445	3.5-5.0	EN ISO 3104
Iodine number	g I_2/100 g	-	-	-	-	120	EN 14111
Acid number	mg KOH/g	-	-	0.5 maximum	ASTM D664	0.5 maximum	EN 14104
Oxidation stability		ASTM D2274	25 mg/L maximum	-	-	3 hours minimum	EN 14112
Carbon residue	% m/m	ASTM D4530	0.2 maximum	0.050 maximum	ASTM D4530	0.3 maximum	EN ISO 10370
Copper corrosion		ASTM D130	Class 1 max	No.3 maximum	ASTM D130	class 1	EN ISO 2160

Distillation temperature	˚C	ASTM D86	370 maximum	360	ASTM D1160	-	-
Lubricity (HFRR)	□	IP 450	0.460 mm (max) (all diesel containing less than 500ppm sulphur)	520 maximum	ASTM D6079	-	-
Sulphated ash content	%mass	-	-	0.002 maximum	ASTM D874	0.02 maximum	EN ISO 3987
Ash content	%mass	ASTM D482	100 maximum	-	-		
Water and sediment		ASTM D2709	0.05 maximum	0.005 %v maximum	ASTM D2709	500 mg/kg maximum	EN ISO 12937
Moisture	wt %	-	-	-	-	0.05 maximum	EN 1412
Monoglycerides	%mass	-	-	-	-	0.8 maximum	EN 14105
Diglycerides	%mass	-	-	-	-	0.2 maximum	EN 14105
Triglycerides	%mass	-	-	-	-	0.2 maximum	EN 14106
Free glycerine	%mass	-	-	0.02 maximum	ASTM D6584	0.02 maximum	EN 1405/14016
Total glycerine	%mass	-	-	0.24	ASTM D6548	0.25	EN 14105
Phosphorous	%mass	-	-	0.001 maximum	ASTM D4951	0.001 maximum	EN 14107
Calcium	%mass	-	-	-	-	-	-
Magnesium	%mass	-	-	-	-	-	-
Sulphur (S 10grade)		ASTM D5453	10 maximum	-	-	-	-
Sulphur (S 15 grade)	ppm	-	-	150 maximum	ASTM D5453	-	-
Sulphur (S 50 grade)	ppm	ASTM D5453	50 maximum	-	-	-	-

Sulphur (S 500 grade)	ppm	ASTM D5453	500 maximum	500 maximum	ASTM D5453	-	-
Carbon	wt%	ASTM D975	87	77	ASTM PS 121	-	-
Hydrogen	wt%	ASTM D975	13	12	ASTM PS 121	-	-
Oxygen	wt%	ASTM D975	0	11	ASTM PS 121	-	-
Sodium and potassium	mg/kg	-	-	-	-	5 maximum	EN 14108, EN 14109
Methanol content	%mass	-	-	-	-	0.2 maximum	EN 14110
Ester content	%mass	-	-	-	-	96.5 minimum	EN 14103
Linolenic acid methyl ester	%mass	-	-	-	-	12 maximum	EN 14103
Polyunsaturated (³ 4 double bonds) methyl esters	%mass	-	-	-	-	1 maximum	EN 14104
Alkaline metals (Na+ K)	mg/kg	-	-	-	-	5 maximum	EN 14108, EN 14109, EN 14538
Alkaline metals (Ca+ Mg)	mg/kg	-	-	-	-	5 maximum	EN 14538
BOCLE scuff	g	ASTM D975	2000 to 5000	>7000	ASTM PS 121		
Conductivity @ ambient temp	pS/m	ASTM D2624	50 m minimum @ambient temp (all diesel held by a terminal or refinery for sale or distribution)	-	-	-	-
Polyaromatic hydrocarbons (PAHs)	% m/m	IP391	11 maximum	-	-	-	-
Total contamination	mg/kg	-	-	24	ASTM D 5452	24	EN 12662

Table 2.21: Standard and quality of biodiesel in selected countries (Eria., 2011)

Fuel property	Unit	Indonesia (SNI Biodiesel No. 04-7182-2006)			Malaysia (MS 2008:2008)			Thailand (DOEB: 2009)			Vietnam (TCVN 7717: 2007)			China (GB/T 20828-2007)			Republic of Korea (KS M)			Japan (JIS K2390:2008)		
		Min	Max	Test method	Min	Max	Test method	Min	Max	Test method	Mini	Max	Test method	Min	Max	Test method	Min	Max	Test method	Min	Max	Test method
Density	kg/m^3	850 (40°C)	890 (40°C)	ASTM D1298, ISO 3675	860 (15°C)	-	ISO 3675,ISO 12185,ASTM D 4052	860 (15°C)	900 (15°C)	ASTM D 1298	860 (15°C)	900 (15°C)	TCVN (ASTM D 1298)	820	900	GB/T 2540	860	900	ISO 3675 (KS M 2002), ISO 12185	860 (15°C)	900 (15°C)	JIS K 2249
Kinematic viscosity (40 °C)	mm^2/s (cSt)	2.3	6.0	ASTM D 445, ISO 3104	3.50	5.00	ISO 3104 MS 1831	3.50	5.00	ASTM D 445	1.9	6	TCVN (ASTM D 445)	1.9	6.0	GB/T 265	1.9	9-5.0	ISO 3104 (KS M 2014)	3.50	5.00	JIS K 2283
Cetane number		51	-	ASTM D 613, ISO 5165	51	-	ISO 5165, MS 1895	51	-	ASTM D 613	47	-	TCVN (ASTM D 613)	49	-	GB/T 386	-	-	-	51	-	JIS K 2280
Flash point	°C	100	-	ASTM D 93, ISO 2710	120	-	ISO 3679^e, MS 686	120	-	ASTM D 93	130	-	TCVN (ASTM D 93)	130	-	GB/T 261	120	-	ISO 3679 (KS M 2010)	120	-	JIS K 2265
Cloud point	°C	-	-	ASTM D2500	-	-	-	-	-	-	-	Report	TCVN (ASTM D 2500)	-	-	-	-	-	-	-	-	-
Pour point	°C	-	18	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	Agreement between producer and distributor		
CFPP	°C	-	-	-	-	15	EN 116	-	-	-	-	-	-	-	Report	SH/T 0246	-	0	KS M 2411			
Copper strip corrosion	Rating (3 hours at 50 °C)	No 3		ASTM D 130, ISO 2160	Class 1		ISO 2160, MS 787	No.1		ASTM D 130	No.1		TCVN (ASTM D 130)	-	1	GB/T 5096	No. 1		ISO 2160 (KS M 2018)	Class-1		JIS K 2513
Carbon residue		-	-	-	-	-	-	-	-	-	-	0.05	TCVN (ASTM D	-	-	-	-	-	-	-	0.3	JIS K 2270

													4530)									
in undistilled sample, or	% (m/m)	-	0.05	ASTM D 4530, ISO 10370	-	0.30	ISO 10370, ASTM D 4530	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
in 10 % distillation residue	% (m/m)	-	0.3		-	0.05		-	0.3	ASTM D 4530	-	-	-	-	-	-	-	0.1	KS M ISO 10370	-	-	-
Water content	mg/kg	-	-	-	-	500	ISO 12937, ASTM E 203, ASTM D 1160		500	EN ISO 12937	-	-	-	-	0.05	SH/T 0246	-	-	-	-	500	JIS K 2275
Water and sediment	vol%	-	0.05	ASTM D2709	-	-	-	-	-	-	-	0.05	TCVN (ASTM D 2709)	-	None	GB/T 511	-	0.05	KS M 2115	-	-	-
90% (v/v) recovered at distillation temperature	°C	-	360	ASTM D1160	-	-	-	-	-	-	-	360	TCVN (ASTM D 1160)	-	360	GB/T 6536	-	-	-	-	-	-
95% (v/v) recovered at distillation temperature	°C	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ash content (sulfated ash)	% (m/m)	-	0.02	ASTM D 874, ISO 3987	-	0.02	-	-	0.02	ASTM D 874	-	0.02	TCVN (ASTM D 874)		0.02	GB/T 2433	-	0.01	KS M ISO 6245	-	0.02	JIS K 2272
Sulphur content	pm-m (mg/kg) m	-	100	ASTM D5453, ISO 20884	-	10.0	-	-	0.0010	ASTM D 2622	-	0.05	TCVN (ASTM D 5453)	0.005	0.05	SH/T 0689	-	10	ISO 20846,ISO 20884 (KS M 2027)	-	10	JIS K 2541-1,-2,-6 or -7
Phosphorous content	pm-m (mg/kg) m (% m/m)	-	10	AOCS Ca 12-55, FBI -A05-03		10.0	EN 14107, ASTM D 4951	-	0.0010	ASTM D 4951	-	0.001	TCVN (ASTM D 4951)	-	-	-	-	10	EN 14107	-	10	EN 14107

Acid number	mg-KOH/g	-	0.8	AOCS Cd 3-63, FBI-A01-03	-	0.5	EN 14104, MS 2011	-	0.50	ASTM D 664	-	0.05	TCVN (ASTM D 664)	-	0.8	GB/T 264		0.5	KS M ISO 6618	-	0.5	JIS K 2501or JIS K 0070
Free glycerol	%(m/m)	-	0.02	AOCS Ca 14-56, FBI-A02-03	-	0.02	EN 14105, EN 14106, ASTM D 6584	-	0.02	EN 14105	-	0.02	TCVN (ASTM D 6584)	-	0.02	ASTM D 6584		-	-	-	0.02	EN 14105 or EN 14106
Total glycerol	%(m/m)	-	0.24	AOCS Ca 14-57, FBI-A03-03	-	0.25	EN 14105, ASTM D 6584	-	0.25	EN 14105	-	0.24	TCVN (ASTM D 6584)	-	0.24	ASTM D 6584		0.25	EN 14105 (KS M 2412)	-	0.25	EN 14105
Methyl ester content	% wt	-	-	-	-	-	-	96.5	-	EN 14103	-	-	-	-	-	-	-	-	-	-	-	-
Ester content	%(m/m)	-	96.5	Calculated, FBI-A03-03	96.5	-	EN 14103	-	-	-	96,5	-	TCVN (EN 14103)	-	-	-	96.5	-	-	96.5	-	EN 14103
Iodine number	%(m/m) (g-I2/100g)	-	115	AOCS Cd 1-25, FBI-A04-03	-	110	-	-	120	EN 14111	-	120	TCVN (EN 14111)	-	-	-	-	-	-	-	120	JIS K 0070
Total contamination	mg/kg	-	-	-	-	24	EN 12662, ASTM D 5452	-	24	EN 12662	-	-	-	-	-	-	-	-	-	24	-	EN 12662
Oxidation stability (110 °C)	hours	-	-	-	6.0	-	EN 14112	10		EN 14112	6	-	TCVN (EN 14112)	6	-	EN14112	6	-	EN 14112	Agreement between producer and distributor		
Linolenic acid methyl ester	% (m/m)	-	-	-	-	12.0	EN 14111	-	12.0	EN 14103	-	-	-	-	-	-	-	-	-	-	12	EN 14103
Polyunsaturated (>=4 double bonds) methyl esters)	%mass	-	-	-	1.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	N.D	-	-

Methanol content	%mass	-	-	-	-	0.2	EN 14110	-	0.20	EN 14110	-	-	-	-	-	-	0.2		EN 14110	-	0.2	EN14110
Monoglyceride content	%mass	-	-	-	-	0.8	EN 14105, ASTM D 6584	-	0.8	EN 14105	-	-	-	-	-	-	-	-	-	-	0.8	EN 14105
Diglyceride content	%mass	-	-	-	-	0.2	EN 14105, ASTM D 6584	-	0.2	EN 14105	-	-	-	-	-	-	-	-	-	-	0.2	EN 14105
Triglyceride content	%mass	-	-	-	-	0.2	EN 14105, ASTM D 6584	-	0.2	EN 14105	-	-	-	-	-	-	-	-	-	-	0.2	EN 14105
Group I metal (Na+K)	mg/kg	-	-	-	-	5.0	EN 14108,EN 14109	-	5.0	EN 14108, EN 14109, prEN 14538	-	5.0	TCVN (EN 14108 and EN 14109)	-	-	-	-	5	EN 14108, EN 14109	-	5.0	EN 14108 and EN 14109
Group II metals (Ca+Mg)	mg/kg	-	-	-	-	5.0	EN 14538		5.0		-	5.0		-	-	-	-	5	EN 14538	-	5.0	EN 14538
Halphen test		-	Negative	AOCS Cd 1-26, FBI-A06-03	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	

SNI = standard nasional Indonesia

MS = Malaysia standard

DOEB =Thailand standards

GB = *Guobiao* National standards China

JIS = Japan industrial standards

KSM = Korea standard method (Republic of Korea)

Table 2.22: Summary of some important characteristics of biodiesel (Srivastava & Prasad, 2000)

Fuel characteristic	Effects
Cetane number	(i) A ignition quality of diesel fuels (ii) High cetane number implies short ignition delay (iii) Higher molecular weight normal alkanes have high cetane numbers (iv) It influences both gaseous and particulate emissions (v) The cetane index which is very close to cetane number is calculated based on 10, 50, 90% distillation temperatures and specific gravity (vi) The fuels with high auto ignition temperatures are more likely to cause diesel knock
Distillation rang	(i) It affects fuel performance and safety (ii) It is important to an engine's start and warm up (iii) Presence of high-boiling components affect the degree of formation of solid combustion deposits (iv) It is needed in the estimation of cetane index
Specific gravity	(i) It is required for the conversion of measured volumes to volumes at standard temperature of 15 °C (ii) It is used in the calculation of cetane index
Heat of combustion	(i) A measure of energy available in a fuel (ii) A critical property of fuel intended for use in weight-limited vehicles
Flash point	(i) It indicates the presence of highly volatile and flammable materials (ii) To measures the tendency of oil to form a flammable mixture with air (iii) It is used to assess the overall flammability hazard of a material
Viscosity	(i) Proper viscosity of fuel required for proper operation of an engine (ii) Important for flow of oil through pipelines, injector nozzles and orifices (iii) Effective atomization of fuel in the cylinder requires limited range of viscosity of the fuel to avoid excessive pumping pressures
Contamination (water/sediment)	(i) It causes corrosion of equipment (ii) It causes problems in processing (i) It is required to accurately measure net volumes of actual fuel in sales, taxation, exchanges and custody transfer
Copper-strip corrosion	(i) To measure to assess relative degree of corrosively (ii) It is indicates the presence of sulphur compounds
Cloud point, pour point cold-filter plugging point	(i) To measure the performance of fuels under cold temperature conditions (ii) It is used as quality control specification or low temperature handling indicators for large storage tanks and pipelines at refineries and terminals
Carbon residue	(i) It correlates with the amount of carbonaceous deposits in the combustion chamber (ii) Greater carbon deposits expected for higher values of carbon residue
Particulate matter	(i) It indicates the potential of emission of particulate matter (ii) It contains primarily carbon particles (iii) The Soot (carbonaceous particulates formed from gas-phase

	processes) particles absorb and carry carcinogenic materials into environment as emission and can cause an ill effect on human health. Excessive soot particles might clog the exhaust valves
Sulphur	(i) It is controlled to minimize corrosion, wear and tear (ii) It causes environmental pollution from their combustion products (iii) It is corrosive in nature and causes physical problems to engine parts
Ash	(i) Results from oil, water-soluble metallic compounds or extraneous solids, such as dirt and rust (ii) It can be used to decide product's suitability for a given application

2.11 Properties and qualities of biodiesel

The properties of biodiesel are characterized by physicochemical properties. Some of these properties include; cetane number, density (kg/m^3), viscosity (mm$^{2/}$s), cloud and pour points (°C), flash point (°C), acid value (mg KOH per g-oil), ash content (%), copper corrosion, carbon residue, water content and sediment, sulphur content, glycerine (% m/m), phosphorus (mg/kg) and oxidation stability. The physical and chemical fuel properties of biodiesel basically depend on the type of feedstock and their fatty acids composition (Atadashi et al., 2010; L. Lin et al., 2011; Murugesan et al., 2009). A summary of physicochemical properties of diesel and biodiesel produced from different feedstock, ASTM 6751-3 and EN 14214 specifications are shown in Table 2.23. The following section gives explanations of some general properties of biodiesel.

2.11.1 Kinematic viscosity (KV)

Viscosity is defined as the resistance of liquid to flow. It refers to the thickness of the oil, 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 (Raj & Sahayaraj, 2010). It therefore affects the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel (Demirbas, 2009; Fernando et al., 2007). In some cases at low temperatures biodiesel can becomes very viscous or even solidified. Some literatures thought that higher viscosity of biodiesel can affect the volume flow and injection spray characteristics in the engine. At low temperature it may even compromise the mechanical integrity of the injection pump drive systems. The maximum allowable limit according to ASTM D445 ranges are (1.9-6.0 mm^2s^{-1}) and (3.5-5.0 mm^2s^{-1}) in EN ISO 3104 (Balat, 2011; Balat & Balat, 2010; Murugesan et al., 2009).

Table 2.23: Properties and qualities of biodiesel produced from different feedstock in comparison with diesel (Atabani et al., 2012)

Fuel Properties	Diesel fuel	Biodiesel		Test Method	
	ASTM D975	ASTM D6751	DIN 14214	ASTM	DIN
Density 15 °C (kg/m^3)	850	880	860-900	D1298	EN ISO 3675/12185
Viscosity at 40 °C (cSt)	2.6	1.9-6.0	3.5-5.0	D-445	EN ISO 3104
Cetane number	40-55	Min. 47	Min. 51	D-613	EN ISO 5165
Iodine number	38.3	-	Max. 120	-	EN 14111
Calorific value (MJ/kg)	42-46	-	35	-	EN 14214
Acid (Neutralization) value (mg KOH/g)	0.062	Max.0.50	Max.0.5	D-664	EN 14104
Pour point (°C)	-35	-15-16	-	D 97	-
Flash point (°C)	60-80	Min. 100-170	>120	D-93	ISO DIS 3679
Cloud point (°C)	-20	-3-12	-	D-2500	-
Cold filter plugging point (°C)	-25	19	Max. +5	D-6371	EN 14214
Copper strip corrosion (3h at 50 °C)	1	Max. 3	Min.1	D-130	EN ISO 2160
Carbon (% wt)	84-87	77	-	-	-
Hydrogen (% wt)	12-16	12	-	-	-
Oxygen (% wt)	0-0.31	11	-	-	-
Methanol content % (m/m)	-	-	Max. 0.20	-	EN 14110
Water and sediment content (%vol)	0.05	Max. 0.05	Max. 500^{b}	D2709	EN ISO 12937
Ash content % (w/w,)	0.01	0.02	0.02		EN 14214
Sulphur % (m/m)	0.05	Max. 0.05	10^{b}	D 5453	EN ISO 20846
Sulphated ash % (m/m)	-	Max. 0.02	Max. 0.02	D-874	EN ISO 3987
Phosphorus content	-	Max. 0.001	10^{b}	D-4951	EN 14107
Free glycerine % (m/m)	-	Max. 0.02	Max.0.02	D-6584	EN 14105/14106
Total glycerine % (m/m)	-	Max. 0.24	0.25	D-6584	EN 14105
Monoglyceride % (m/m)	-	0.52	0.8	-	EN 14105
Diglyceride % (m/m)	-	-	0.2	-	EN 14105
Triglyceride % (m/m)	-	-	0.2	-	EN 14105
CCR 100% (% mass)	0.17 (0.1)^{d}	Max. 0.05	Max. 0.03	D-4530	EN ISO10370
Distillation temperature (%)	-	Max. 360 °C	-	D-1160	-
Oxidation stability (hrs, 110 °C)	-	3 min	6 min	D-675	EN 14112
Lubricity (HFRR; µm)	685	314	-	-	-

Fuel Properties	Jatropha FAME	Calophyllum inophyllum FAME	Madhuca FAME	Mesua FAME	Camelina sativa FAME	Canola sativa FAME
Density 15 °C (kg/m^3)	879.5	888.6	874	898	-	-
Viscosity at 40 °C (cSt)	4.8[g]	7.724	3.98	6.2	4.15	4.42
Cetane number	51.6	51.9	65	54	52.8	-
Iodine number	104	85	-	-	-	-
Calorific value (MJ/kg)	39.23	-	36.8	42.23	-	-
Acid (Neutralization) value (mg KOH/g)	0.4	0.76	0.41	0.01	0.31	0.01
Pour point (°C)	2	-	6	3	-4	-9
Flash point (°C)	135	151	208	112	>160	>160
Cloud point (°C)	2.7	38	-	-	3	-3.3
Cold filter plugging point (°C)	0	-	-	-	-3	-7
Copper strip corrosion (3h at 50 °C)	1a	1b	-	-	1a	1a
Carbon (% wt)	-	-	-	-	-	-
Hydrogen (% wt)	-	-	-	-	-	-
Oxygen (% wt)	-	-	-	-	-	-
Methanol content % (m/m)	-	-	-	-	-	-
Water and sediment content (%vol)	<0.005	-	-	0.035[b]	< 0.005	< 0.005
Ash content % (m/m,)	0.012	0.026	0.01	0.01	-	-
Sulphur % (m/m)	1.2[a]	16[a]	164.8[a]	70[a]	3[a]	2[a]
Sulphated ash % (m/m)	0.009	-	-	-	<0.005	<0.005
Phosphorus content	<0.1	0.223[a]	-	-	<0.1[a]	<0.1
Free glycerin % (m/m)	0.006	-	-	-	0.002	0.006
Total glycerin % (m/m)	0.1	0.232	-	-	0.08	0.114
Monoglyceride % (m/m)	0.291	-	-	-	0.222	0.363
Diglyceride % (m/m)	0.104	-	-	-	0.125	0.127
Triglyceride % (m/m)	0.022	-	-	-	0.022	0
CCR 100% (% mass)	0.025	0.434	0.02	0.25	0.075	0.03
Oxidation stability (hrs, 110 °C)	2.3	-	-	-	2.5	6.4
Lubricity (HFRR; μm)	-	-	-	-	-	-

Fuel Properties	Rapeseed FAME	Sunflower FAME	Tobacco FAME	Safflower FAME	Cynara cardunculus L FAME	Microalgal 1 FAME	Vernicia forii FAME
Density 15 °C (kg/m^3)	882	880.0	888.5	888.5	0.889[h]	-	864
Viscosity at 40 °C (cSt)	4.439[g]	4.439	4.23[g]	5.8[g]	5.101[g]	4.519	2.5
Cetane number	54.4	49	51.6	56	59	-	53
Iodine number	-	-	136	-	117	-	-
Calorific value (MJ/kg)	37		-	38.122	-	-	-
Acid (Neutralization) value (mg KOH/g)	-	0.027	0.3	-	-	0.022	0.19
Pour point (°C)	-12	-	-	-	-	-	-
Flash point (°C)	170	>160	165.4	148	182	>160	185
Cloud point (°C)	-3.3	3.4	-	-5	-4	-5.2	-
Cold filter plugging point (°C)	-13	-3	-5	-	-10	-7	-
Copper strip corrosion (3h at 50 °C)	-	1a	1a	-	-	1a	-
Carbon (% wt)	81	-	-	59.5	-	-	-
Hydrogen (% wt)	12	-	-	-	-	-	-
Oxygen (% wt)	7	-	-	-	-	-	-
Methanol content % (m/m)	-	-	<0.01	-	-	-	-
Water and sediment content (%vol)	-	<0.005	354.09[b]	-	-	< 0.005	-
Ash content % (w/w,)	-	-	-	-	-	-	-
Sulphur % (m/m)	-	0.2[a]	-	-	<0.02	5.1[a]	-
Sulphated ash % (m/m)	-	<0.005	0.0004	-	-	<0.005	-
Phosphorus content	-	<0.1[a]	4[b]	-	<5	<0.1[a]	-
Free glycerin % (m/m)	-	0.007	0.002	-	-	0.009	0.01
Total glycerin % (m/m)	-	0.121	0.23	-	-	0.091	0.04
Monoglyceride % (m/m)	-	0.387	0.54	-	-	0.265	-
Diglyceride % (m/m)	-	0.092	0.13	-	-	0.078	-
Triglyceride % (m/m)	-	0.0	0.17	-	-	0.02	-
CCR 100% (% mass)	-	0.035	0.29	-	0.36	0.007	0.02
Oxidation stability (hrs, 110 °C)	7.6	0.9	0.8	-	-	8.5	-
Lubricity (HFRR; µm)	-	-	-	-	-	-	-

Fuel Properties	Pongamia (Karanja) FAME	Palm FAME	Soybean FAME	Neem FAME	Hibiscus sabdariffa LFAME (Rossele)	Microalgal 2 FAME	Beef tallow FAME	Evening Primrose FAME
Density 15 ˚C (kg/m^3)	931	864.42[c]	913.8	868	880.1	-	-	-
Viscosity at 40 ˚C (cSt)	6.13	4.5	4.039	5.213[g]	4.588[g]	4.624[g]	4.824[g]	4.112[g]
Cetane number	55	54.6	37.9	-	-	-	-	-
Iodine number	-	54	128-143	-	62	-	-	-
Calorific value (MJ/kg)	43.42	-	39.76	39.81	-	-	-	-
Acid (Neutralization) value (mg KOH/g)	0.42	0.24	0.266	0.649	0.43	0.003	0.147	0.37
Pour point (˚C)	3	15	-	2	-1	-	-	-
Flash point (˚C)	95	135	254	76	>130	>160	>160	>160
Cloud point (˚C)	7	16	0.9	9	-	3.9	16	-7.5
Cold filter plugging point (˚C)	-	12	-4	11	-	2	14	-10
Copper strip corrosion (3h at 50 ˚C)	-	1a	1a	1b	1a	1a	1a	1a
Carbon (% wt)	-	-	-	-	-	-	-	-
Hydrogen (% wt)	-	-	-	-	-	-	-	-
Oxygen (% wt)	-	-	-	-	-	-	-	-
Methanol content % (m/m)	-	-	-	-	-	-	-	-
Water and sediment content (%vol)	-	-	<0.005	< 0.005	450[b]	< 0.005	< 0.005	< 0.005
Ash content % (w/w,)	0.001	-	-	-	-	-	-	-
Sulphur % (m/m)	50[a]	0.003	0.8	473.8[a]	0.00021	0.6[a]	7.0[a]	1.1[a]
Sulphated ash % (m/m)	-	0.002	<0.005	<0.005	<0.005	<0.005	<0.005	0.038
Phosphorus content	-	<0.001	<0.1[a]	<0.1[a]	-	<0.1[a]	<0.1[a]	<0.1[a]
Free glycerin % (m/m)	0.015	0.01	0.012	0	0	0.014	0.008	0.005
Total glycerin % (m/m)	0.0797	0.01	0.149	0.158	0.11	0.102	0.076	0.128
Monoglyceride % (m/m)	-	-	0.473	0.338	0.5733	0.292	0.223	0.386
Diglyceride % (m/m)	-	-	0.088	0.474	0.0163	0.07	0.063	0.134
Triglyceride % (m/m)	-	-	0.019	0	0	0.019	0	0.035
CCR 100% (% mass)	0.781	<0.01	0.038	0.105	0.84	0.042	0.028	0.051
Oxidation stability (hrs, 110 ˚C)	-	10.3	2.1	7.1	2.58	11	1.6	0.2
Lubricity (HFRR; µm)	-	172	-	-	-	-	-	-

[a] ppm

[b] mg/kg

[c] determined at 25 °C

[d] wt.%

[e] kJ/kg

[f] determined at 20 °C

[g] mm^2/s

[h] g/cm^3

[i] determined at 313 K

[j] K

[k] $\mu g g^{-1}$

2.11.2 Density

Density is the relationship between the mass and volume of a liquid or a solid and can be expressed in units of grams per litre (g/L). Density is important because it gives an indication of the delay between the injection and combustion of the fuel in a diesel engine (ignition quality) and the energy per unit mass (specific energy). This can influence the efficiency of the fuel atomization for airless combustion systems (dos Santos et al., 2008; Kaya et al., 2009; Uriarte, 2010). ASTM Standard D1298 and EN ISO 3675/12185 test method are used to measure the density of the biodiesel. According to these standards, density should be tested at the temperature reference of 15 °C (Schumacher et al., 1995; Torres-Jimenez et al., 2011).

2.11.3 Flash point (FP)

Flash point is another important property for biodiesel fuel. Flash point is the temperature at which fuel will ignite when exposed to a flame or a spark. Flash point varies inversely with the fuel's volatility. The flash point of biodiesel is higher than the prescribed limit of diesel fossil fuel, which is safe for transport, handling and storage purpose

(Atadashi et al., 2010; Filemon, 2010; Murugesan et al., 2009). Usually biodiesel has a flash point more than 150 ℃, while conventional diesel fuel has a flash point of 55-66 ℃ (Sanford et al., 2009). (Demirbas, 2009) stated that the flash point values of fatty acid methyl esters are significantly lower than those of vegetable oils. The limit of flash point ranges in ASTM D93 is 93 °C and in EN ISO 3679 is 120 °C (Fernando et al., 2007).

2.11.4 Cloud point, (CP) pour point (PP) and cold filter plugging point (CFPP)

The behaviour of biodiesel at low temperature is an important quality criterion. This is because partial or full solidification of the fuel may cause blockage of the fuel lines and filters, leading to fuel starvation, problems of starting, driving and engine damage due to inadequate lubrication. The cloud point (CP) and pour point (PP) are important for low-temperatures applications for fuel. The cloud point is the temperature at which wax crystals first becomes visible when the fuel is cooled under controlled conditions during a standard test. Pour point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. In general, biodiesel has higher CP and PP than diesel fuel (Demirbas, 2009; Fernando et al., 2007). Cloud and pour points are measured using ASTM D2500 EN ISO 23015 and D97 procedures (Demirbas, 2005; Fernando et al., 2007; Sanford et al., 2009).

Cold filter plugging point (CFFP) is used as indicator of low temperature operability of fuels. It refers to the temperature at which the test filter starts to plug due to fuel components that have started to gel or crystallize. It is a commonly used as indicator of low temperature operability of fuels and reflects their cold weather performance. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. CFPP defines the fuels limit of filterability, having a better correlation than cloud point for biodiesel as well as petro diesel. CFPP is measured using ASTM D6371 (Moser & Vaughn, 2010; Murugesan et al., 2009; Sanford et al., 2009).

2.11.5 Cetane number (CN)

The cetane number (CN) is one of the most important parameters which are considered during the selection of biodiesel. It is the indication of ignition characteristics or ability of fuel to auto-ignite quickly after being injected. Cetane number provides information about the ignition delay (ID) time of a diesel fuel upon injection into the combustion chamber. Better ignition quality of the fuel is always associated with higher CN value. (Balat, 2011; Raj & Sahayaraj, 2010; Saloua et al., 2010). Cetane number increases with increasing chain length of fatty acids and increasing saturation. A higher CN indicates shorter time between the ignition and the initiation of fuel injection into the combustion chamber. Fuels with low CN tend to cause diesel knocking and show increased gaseous and particulate exhaust emissions (PM) due to incomplete combustion. Moreover, excessive engine deposits are reported. CN is based on two compounds which are hexadecane with a CN of 100 and heptamethylnonane with a CN of 15 (Demirbas, 2009; Karmakar et al., 2010; Lapuerta et al., 2008). Generally, biodiesel has higher CN than conventional diesel fuel, which results in higher combustion efficiency (Lapuerta et al., 2008). The CN of diesel, specified by ASTM D613 is 47 min and EN ISO 5165 is 51.0 min (Lapuerta et al., 2008).

2.11.6 Oxidation stability (OS)

The oxidation of biodiesel fuel is one of the major factors that helps assess the quality of biodiesel. Oxidation stability is an indication of the degree of oxidation, potential reactivity with air, and can determine the need for antioxidants. Oxidation occurs due to the presence of unsaturated fatty acid chains and the double bond in the parent molecule, which immediately react with the oxygen as soon as it is being exposed to air (Atadashi et al., 2010; Sanford et al., 2009). The chemical composition of biodiesel fuels make it more susceptible to oxidative degradation than fossil diesel fuel. The Rancimat method (EN ISO 14112) is listed as the oxidative stability specification in ASTM D6751 and EN 14214. A minimum IP (110 °C) of 3 h is required for ASTM D6751, whereas a more stringent limit of 6 hours or greater is specified in EN 14214 (Moser & Vaughn, 2010).

2.11.7 Acid value (AV)

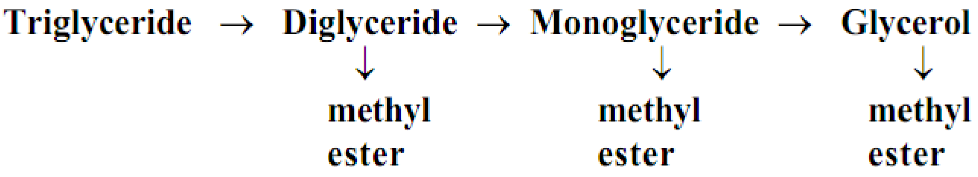
The acid number or neutralization number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds (Raj & Sahayaraj, 2010). Free fatty acids (FFAs) are the saturated or unsaturated monocarboxylic acids that occur naturally in fats, oils or greases but are not attached to glycerol backbones. Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The structures of common fatty acids are given in Table 2.9. Higher amount of free fatty acids leads to higher acid value. Acid value is expressed as mg KOH required for neutralizing 1 gm of FAME. Higher acid content can cause severe corrosion in fuel supply system of an engine. The acid value is determined using the ASTM D664 and EN 14104. Both standards approved a maximum acid value for biodiesel of 0.50 mg KOH/g (Agarwal, 2007; Y. C. Sharma, Singh, B., 2009).

2.11.8 Free glycerine

Free glycerol refers to the amount of glycerol that is left in the finished biodiesel. The content of free glycerol in biodiesel is dependent on the production process. The high yield of glycerol in biodiesel may be resulted from insufficient separation during washing of the ester product. Glycerol is essentially insoluble in biodiesel so almost all of the glycerol is easily removed by settling or centrifugation. Free glycerol may remain either as suspended droplets or as the very small amount that is dissolved in the biodiesel. High free glycerol can cause injector coking and damage to the fuel injection. The ASTM specification requires that the total glycerol be less than 0.24% of the final biodiesel product as measured using a gas chromatographic method described in ASTM D6584 and EN 14105/14106 has limit Max. 0.02% (Fernando et al., 2007; Li et al., 2010).

2.11.9 Total glycerol

Total glycerine is a measurement of how much triglyceride remains unconverted into methyl esters. Total glycerine is calculated from the amount of free glycerine, monoglycerides, diglycerides, and triglycerides (Maceiras et al., 2010). The reactions shown in below:



If the reaction is incomplete, then there will be triglycerides, diglycerides, and monoglycerides left in the reaction mixture. Each of these compounds still contains a glycerol molecule that has not been released. The glycerol portion of these compounds is referred to as bound glycerol. When the bound glycerol is added to the free glycerol, the sum is known as the total glycerol. The ASTM specification requires that the total glycerol be less than 0.24% of the final biodiesel product as measured using a gas chromatographic method described in ASTM D 6584 and 0.25% in EN 14105. Fuels that do not meet these specifications are prone to coking; thus, may cause the formation of deposits on the injector nozzles, pistons and valves (Fernando et al., 2007).

2.11.10 Water content and sediment

Water and sediment contamination are basically housekeeping issues for biodiesel. The presence of water and sediment has two forms, which are either dissolved water or suspended water droplets. While biodiesel is generally considered to be insoluble in water, it actually takes up considerably more water than diesel fuel. Biodiesel can contain as much as 1500 ppm of dissolved water while diesel fuel usually only takes up about 50 ppm. Sediment may consist of suspended rust and dirt particles or it may originate from the fuel as insoluble compounds formed during fuel oxidation (Fernando et al., 2007; Li et al., 2010). Water and sediment testing is done using 100 mL of biodiesel and centrifuging it at 1870 rpm for 11 minutes. If the water and sediment level is below 0.005 % volume (vol), the result is reported as <0.005 % vol (Sanford et al., 2009). Water in the fuel generally causes two problems. First, it can cause corrosion of vital fuel system components such as fuel pumps, injector pumps, fuel tubes, etc. The most direct form of corrosion is rust, but water can become acidic with time and the resulting acid corrosion can attack fuel storage tanks. Water contamination can contribute to microbial growth. The species of yeast, fungi, and bacteria can grow at the interface between the fuel and water at the bottom of a storage tank. The organisms produce sludges and slimes that can cause filter plugging. Moreover, high water contents can also contribute to hydrolysis reaction that is responsible for converting biodiesel to free fatty acids which is also linked to fuel filter blockage. The standard of water content and sediment for biodiesel in ASTM D2709 and EN ISO 12937 specifications is 0.05 (%v) max (Fernando et al., 2007; Sanford et al., 2009).

2.11.11 Sulphur content

Combustion of fuel containing sulphur causes emissions of sulphur oxides. Most of vegetable oils and animal fat-based biodiesel have very low levels of sulphur content. However, specifying this parameter is important for engine operability (Atadashi et al., 2010; Balat & Balat, 2010; Singh & Singh, 2010).

2.11.12 Carbon residue

Carbon residue test is used to indicate the extent of deposits resulting from the combustion of a fuel. Carbon residue which is formed by decomposition and subsequent pyrolysis of the fuel components can clog the fuel injectors. Canradsons carbon residue for biodiesel is more important than that in diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities. Although this residue is not solely composed of carbon, the term carbon residue is found in all standards because it has long been commonly used. The range of limit standard ASTM D4530 is Max 0.050% (m/m) and EN ISO10370 is Max. 0.30% (m/m) (Fernando et al., 2007; Murugesan et al., 2009; Sanford et al., 2009).

2.11.13 Copper strip corrosion

The copper corrosion test measures the corrosion tendency of fuel when used with copper, brass, or bronze parts. A copper strip is heated to 50 °C in a fuel bath for three hours followed by comparison with a standard strips to determine the degree of corrosion. Corrosion resulting from biodiesel might be induced by some sulphur compounds by acids; hence this parameter is correlated with acid number. The ASTM D130 standard mentions that the samples can have class 3 and EN ISO 2160 has class 1 (Fernando et al., 2007; Sanford et al., 2009).

2.11.14 Phosphorous, calcium and magnesium content

Phosphorous, calcium, and magnesium are minor components which are typically associated with phospholipids and gums that may act as emulsifiers or cause sediment, lowering yields during the transesterification process (Vera et al., 2011). The specifications from ASTM D6751 state that phosphorous content in biodiesel must be less than 10 ppm, and calcium and magnesium combined must be less than 5 ppm. Phosphorous is determined using ASTM D 4951 and EN14107, Calcium and Magnesium are determined using EN Standard 14538 (Sanford et al., 2009).

2.11.15 Iodine number

The iodine number is an index of the number of double bonds in biodiesel which determines the unsaturation degree of the biodiesel. This property can greatly influence the oxidation stability and polymerization of glycerides. This can lead to the formation of deposits in diesel engines injectors. Iodine value is directly correlated to biodiesel viscosity, cetane number and cold flow characteristics (cold filter plugging point). The iodine number is set to a maximum value of 120 mgI_2/g according to EN 14111 (Raj & Sahayaraj, 2010).

2.12 Engine performance and emissions production of various feedstocks of some selected edible and non-edible biodiesel

2.12.1 Palm oil

(Ng et al., 2012) studied the engine performance using neat palm oil methyl ester, B_{50} and neat diesel (B_0) at different speeds and load conditions. The result showed that SFC for palm oil methyl ester is higher than diesel fuel due to lower energy contents. They also found that neat palm oil methyl ester (B_{100}) reduces tailpipe NO, UHC and smoke opacity by 5.0%, 26.2% and 66.7%, respectively due to improved combustion, higher cetane number and oxidation of soot. However, it was found that PME content in the fuel blend did not significantly affect tailpipe CO emission, with only a maximum 0.89% reduction achieved with the B_{50} blend. The authors concluded that despite the shortcoming of PME in its higher specific fuel consumption, its overall reduction of regulated tailpipe emissions makes PME green technically viable alternative to fossil diesel in both neat and blended forms for use in light-duty diesel engines.

2.12.2 Canola (Rapeseed)

(Hazar, 2009) studied the effect of canola oil biodiesel and its blend on a low heat loss diesel engine emission and performance with and without coating condition. The author found out that the increase in power for biodiesel is between 1.6% and 3.5% compared to 8.4% for diesel. While the decrease in SFC for biodiesel is between 4.7% and 8% compared to 4.9% for diesel. There is a significant reduction in exhaust gas emission CO (22-24%)

compared to 25% for diesel, and smoke (4.7-8.2%) compared to 9% for diesel. However, NO_x emission increase (4.8-7.3%) compared to 4.9% for diesel. This is attributed to the higher oxygen contents and increase in after combustion temperature due to the ceramic coating. Exhaust gas temperature increases by between 5.4% and 2.6% for biodiesel while it increases by 11.4% for diesel.

2.12.3 Soybean

(Fontaras et al., 2009) studied the effect of soybean oil biodiesel and its 50% by volume blend on a Euro 2 diesel passenger car. The result showed that biodiesel fuel increased specific fuel consumption (SFC). For instance B_{50} increased SFC by 9% and 4.5% over the NEDC and Artemis driving cycles due to the lower energy contents in biodiesel fuel. Moreover, use of B_{50} and B_{100} led to CO increases over NEDC in the order of 54% and 95% respectively. B_{50} and B_{100} increase HC emissions by 31% and 58% respectively over the NEDC cycle. B_{50} leads to equal or slightly lower NO_x emissions than petroleum diesel. However, B_{100} leads to higher NO_x emissions in the range of 6-9%. Use of biodiesel reduced solid particle population but significantly increased the total particle number. The results indicated that maximum engine power output decreased as the biodiesel concentration increased. The authors concluded that biodiesel at high blending ratios may strongly impact emissions, in a rather non-uniform manner, with the actual effect being dependant on driving conditions and blending ratio. However this study does not reach definitive conclusions but rather presents a case that may appear in the European passenger car fleet, which requires further attention and research.

2.12.4 *Jatropha curcas*

(Chauhan et al., 2012) evaluated the performance and exhaust emissions using 5%, 10%, 20% and 30% Jatropha biodiesel blends with diesel fuel on an unmodified diesel engine. The experimental results show that engine performance with biodiesel of Jatropha and its blends were comparable to the performance of diesel fuel. In case of all fuel blends, brake thermal efficiency, HC, CO, CO_2 and smoke density were lower while BSFC and NO_x were higher than that of diesel. The authors concluded that biodiesel derived from Jatropha and its blends could be used in a conventional diesel engine without any modification. However there are various parameters which can be evaluated in the future such as the prediction of best blend with respect to the various engine parameters by varying spray time of fuel using common-rail fuel injection.

2.12.5 Polanga (*Calophyllum inophyllum*)

(Sahoo et al., 2007) evaluated the performance and emission of polanga oil methyl ester (POME) blends (0-100%) in a single cylinder diesel engine at different loads (0-100%). The main findings of the study showed that the performance of biodiesel-fuelled engine was marginally better than the diesel-fuelled engine in terms of thermal efficiency, brake specific energy consumption, smoke opacity, and exhaust emissions including NO_x emission for the entire range of operations. The 100% biodiesel was found to be the best, which improved the thermal efficiency of the engine by 0.1%. Similar trend was shown by the brake specific energy consumption and the exhaust emissions which were reduced. Smoke emissions also reduced by 35% for B_{60} as compared to neat petro-diesel. Decrease in the exhaust temperature of biodiesel-fuelled engine led to approximately 4% decrease in NO_x emissions for B_{100} biodiesel at full load. It was conclusively proved that excess oxygen content of biodiesel played a key role in engine performance. However long term endurance test and other tribological studies need to be carried out before suggesting long term application of polanga oil based biodiesel.

2.13 Summary

This chapter reviewed several important aspects of biodiesel research area. Some of these aspects include; biodiesel feedstocks, fatty acid composition, biodiesel extraction methods, biodiesel production technologies, biodiesel standards and characterization, properties and qualities of biodiesel and engine performance and emissions production of various feedstocks of some selected edible and non-edible biodiesel.

From this literature review, it was understood that searching and identification of new feedstocks for biodiesel production is vital. Moreover, the concept of biodiesel blending has not been well covered in literature. Therefore, this research will focus on identifying some promising biodiesel feedstocks and compare them with other existing feedstocks. Moreover, biodiesel-biodiesel and biodiesel-diesel blending will be also considered in this study.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Research methodology is a crucial factor to bring in an effective research with accredited results. It can be defined in many ways such as procedures, ways, methods and techniques that are applied to incorporate and gather all relevant information for the research.

This chapter explains how the whole research was conducted and shows the methods by which seeds collection, crude oils extraction, crude oils characteristics, biodiesel production, fatty acid composition of biodiesel, physical and chemical properties of biodiesel, biodiesel blending and engine performance and emissions were conducted. The opportunities of biodiesel-biodiesel and biodiesel-diesel blending to improve some of the properties of these feedstocks were also studied in this research. The properties of biodiesel blends were estimated using the polynomial curve fitting method. The equipment list and the apparatus used are also shown in this chapter.

3.2 Structure of research methodology

This research aims to produce biodiesel from various edible and non-edible oils. Therefore, Figure 3.1 gives a brief summary of the implemented flow chart of this research.

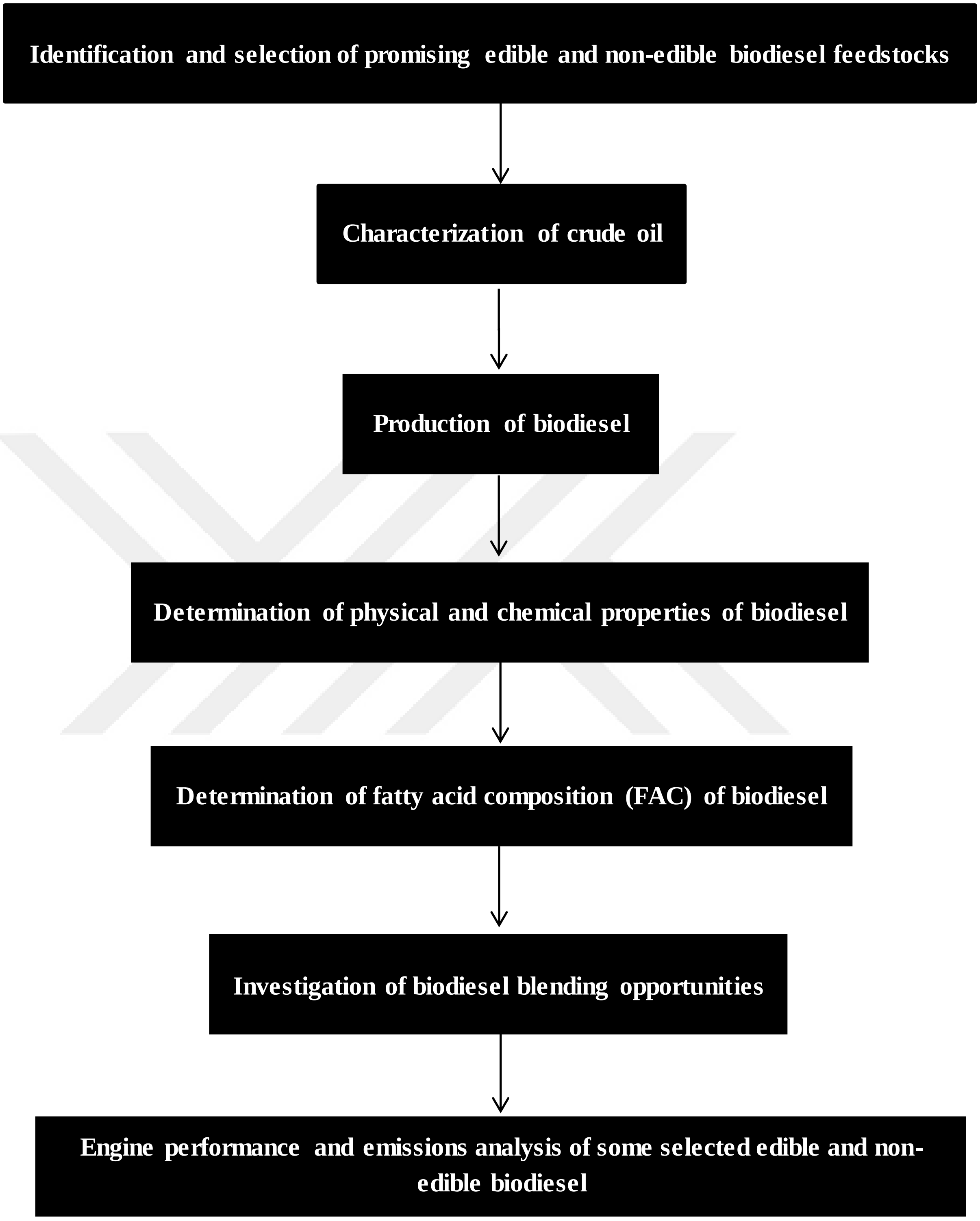


Figure 3.1: Flow chart of the research methodology

3.3 Materials and chemicals

The crude oils of palm, coconut, canola and soybean were obtained from local market. *Moringa oleifera, Croton megalocarpus* and Manketti (*Schinziophyton rautanenii*) oils were supplied from University Science Malaysia (USM). The crude oils of *Jatropha curcas* and *Sterculia foetida* and *Calophyllum inophyllum* and *Pangium edule* seeds were purchased from Ministry of Forestry of the Republic of Indonesia (Bogor, Indonesia). *Patchouli* oil was purchased from Banda Aceh (Indonesia). Reagent grade of methanol (CH_3OH), potassium hydroxide (KOH), sulphuric acid (H_2SO_4 95-97%), 2-Propanol (iso-propyl alcohol), potassium hydroxide solution (0.1 N), sodium sulphate anhydrous (Na_2SO_4) and double rings qualitative filter paper of 125 mm size were used. Figure 3.2 shows some pictures of canola, coconut, soybean, palm, manketti, *Patchouli*, *Croton megalocarpus*, *Moringa oleifera*, *Jatropha curcas* and *Sterculia foetida* feedstocks.


(a) Canola (b) Coconut


(c) Soybean (d) Palm

Figure 3.2: Pictures of Canola, coconut, soybean, palm, manketti, *Patchouli*, *Croton megalocarpus*, *Moringa oleifera*, *Jatropha curcas* and *Sterculia foetida* feedstocks

(e) *Patchouli Pogostemon Cablin* (Blanco) Benth (f) *Croton megalocarpus*

(g) Moringa oleifera (h) Manketti

Figure 3.2: Pictures of Canola, coconut, soybean, palm, manketti, *Patchouli*, *Croton megalocarpus*, *Moringa oleifera*, *Jatropha curcas* and *Sterculia foetida* feedstocks (continued)

(i) *Jatropha curcas*

(j) *Sterculia foetida*

Figure 3.2: Pictures of Canola, coconut, soybean, palm, manketti, *Patchouli*, *Croton megalocarpus*, *Moringa oleifera*, *Jatropha curcas* and *Sterculia foetida* feedstocks (continued)

3.4 Oil extraction

3.4.1 Extraction of crude *Calophyllum inophyllum* oil

The seeds of *Calophyllum inophyllum* were obtained from Bogor, Indonesia. The seeds were dried under sunlight for 2-3 days. It has been found that, the yield of the seeds after drying is 100-150 seeds/kg and the water content inside the seeds is 9-10% when the seeds are heated at 105 °C for 24 h and the ash content is 40.31% when heated at 700 °C for minimum 4 h. The kernel was then separated from the shell and found to have high oil content (70%). The ideal conditions to preserve the kernel are 26-27 °C and 60-70% humidity. The place in which the kernel is stored must be well ventilated and the storing period should not be too long.

Before extraction, the kernels were mixed with rice husk. This is very important to increase the oil yield during the extraction process. There are two types of pressing machine that are used to extract the oil from the kernel: hydraulic manual pressing machine and screw extruder machine. The oil extracted using pressing machine is very low and about 20-30%. Therefore, hydraulic machine was used to increase oil yield from *Calophyllum inophyllum*. The remained cake after extraction was of high commercial and marketing value. Therefore, it can be used either for agricultural or industrial applications. The screw extruder machine and hydraulic manual pressing machine are shown in Figure 3.3. Figure 3.4 shows *Calophyllum inophyllum* tree, seeds and extracted crude oils.

Figure 3.3: Screw extruder machine and hydraulic manual pressing machine

Calophyllum inophyllum

Figure 3.4: Pictures of *Calophyllum inophyllum* tree, seeds and extracted crude oils

3.4.2 Extraction of crude *Pangium edule* oil

The kernels of the *Pangium edule* fruits were obtained manually and cleaned before being dried overnight in an oven at 353 K. Moderate temperature for the drying of the *Pangium edule* kernels was used to prevent possible decomposition or oxidation of the kernels at higher temperature (>373 K) at which the properties of the extracted oil could be affected. The dried *Pangium edule* kernels were ground to fine particles using food processor and then dried for the second time in the oven to remove excess moisture. The oil extraction process was carried out using Soxhlet apparatus and the duration of each extraction process was set at approximately 4 h under temperature of 343K (reflux temperature of the solvent). *Pangium edule* oil was obtained after separating the mixture of solvent and oil using rotary evaporator. The resultant *Pangium edule* oil was decanted mechanically to remove impurities and other components (glycosides) that may be present in the oil.

3.5 Properties analysis and equipment

The quality of any fuel is expressed in terms of the fuel properties such as kinematic viscosity, calorific value, CCR, flash point and cold filter plugging point. In this research, the important physical and chemical properties of the crude oils and their respective methyl esters were tested according to ASTM D 6751 standard. These properties include: viscosity, viscosity index, density, flash point, CP (cloud point), PP (pour point), CFPP (cold filter plugging point), CCR, calorific value, oxidation stability, copper strip corrosion and total sulphur beside some other non-ASTM properties such as transmission, absorbance and refractive index. Table 3.1 shows the equipment used to analyse these properties, their manufacturers and the standards used to measure these properties. All these equipment were located at Energy lab (University of Malay). Most of equipment such as flash point tester, kinematic viscosity tester and cold filter plugging point tester are highly calibrated and fully automatic. For example the equipment for kinematic viscosity (SVM 3000) normally asks to inject the sample 2-3 times until it gets a satisfactory result.

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

The saponification numbers (SN), iodine value (IV) and cetane number (CN) of the methyl esters of were calculated empirically from its fatty acid methyl ester compositions with the help of Eqs. (3.2), (3.3) and (3.4), respectively (Azam et al., 2005; Devan & Mahalakshmi, 2009c, 2009d):

$$SN = SUM\left(\frac{560 \times A_i}{MW_i}\right) \tag{3.1}$$

$$IV = SUM\left(\frac{254 \times D \times A_i}{MW_i}\right) \tag{3.2}$$

$$CN = \left(46.3 + \left(\frac{5458}{SN}\right) - (0.225 \times IV)\right) \tag{3.3}$$

A_i is the percentage of each component, D is the number of double bonds and MW_i molecular mass of each component.

Table 3.1: Equipment list

	Property	Equipment	Manufacturer	ASTM D6751
1	Kinematic viscosity	SVM 3000	(Anton Paar, UK)	ASTM D7042/D445
2	Flash Point	Pensky-martens flash point - automatic NPM 440	(Normalab, France)	D 93
3	Oxidation stability	873 Rancimat	(Metrohm, Switzerland)	D 675
4	Cloud and Pour point	Cloud and Pour point tester - automatic NTE 450	(Normalab, France)	D 2500 and D 97
5	CCR	Micro-Carbone Conradson Residue Tester - automatic NMC 440	(Normalab, France)	D 4530
6	Total Sulphur	Multi EA 5000	(Analytical Jena, Germany)	D 5453
7	CFPP	Cold filter plugging point – automatic NTL 450	(Normalab, France)	D 6371
8	Density	SVM 3000	(Anton Paar, UK)	D 1298
9	Copper strip corrosion	Seta copper corrosion bath 11300-0	(Stanhope-Seta, UK)	D 130
10	Dynamic viscosity	SVM 3000	(Anton Paar, UK)	N/S
11	Viscosity Index (VI)	SVM 3000	(Anton Paar, UK)	N/S
12	Caloric value	C2000 basic calorimeter	(IKA, UK)	N/S
13	Refractive Index	RM 40 Refractometer	(Mettler Toledo, Switzerland)	N/S
14	Transmission	Spekol 1500	(Analytical Jena, Germany)	N/S
15	Absorbance	Spekol 1500	(Analytical Jena, Germany)	N/S

N/S ≡ not specified in ASTM D6751 test method.

3.5.2 Determination of acid value

Acid value is defined as the number of milligrams of potassium or sodium hydroxide necessary to neutralize the free acid in 1g of sample. The following sections explain in details the procedure conducted in this research to measure the acid values of non-edible crude oils.

3.5.2.1 Procedure to prepare phenolphthalein indicator (phph)

Phenolphthalein is a chemical compound with the formula $C_{20}H_{14}O_4$. In titration, it turns colourless in acidic solutions and pink in basic solutions. To prepare titration solution, 0.5 g of phenolphthalein was dissolved in 50% ethanol (ethyl alcohol) solution consisting of 50ml ethanol and 50 ml water. The solution was stored in a stoppered bottle.

3.5.2.2 Titration procedure

Firstly, a measured amount of the crude oil was poured into a beaker or Erlenmeyer flask. This was followed by adding 50 ml of 2-Propanol to the measured amount of crude oil. The mixture was then heated to around 50-55 °C to make sure that the oil was well diluted in 2-Propanol. Before the titration is started, 1-3 drops of phph indicator were then added to the mixture. The titration begins with adding the base titrant (KOH solution) with a known normality (0.1 N) from the burette drop by drop to the mixture until the indicator changes, reflecting arrival at the endpoint of the titration. Depending on the endpoint desired, single drops or less than a single drop of the titrant can make the difference between a permanent and temporary change in the indicator. When the endpoint of the reaction is reached, the volume of reactant consumed is measured and used to calculate the acid value of the crude oil. Therefore, acid value can be calculated using the following equation:

$$AV = \frac{MW \times N \times V}{W} \tag{3.4}$$

where

MW ≡ Molecular weight of potassium hydroxide.

N≡ Normality of potassium hydroxide solution (0.1 N).

V≡ Volume of potassium hydroxide solution used in titration.

W ≡ Weight of oil sample.

Figure 3.5 is a sketch of the setup employed for the titration.

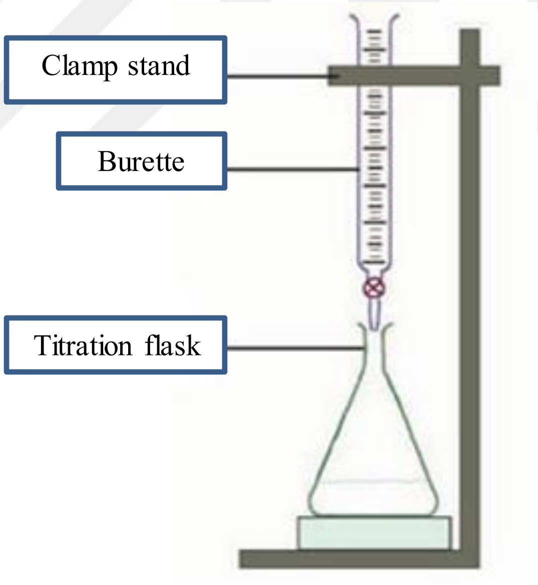


Figure 3.5: Titration apparatus

3.6 Apparatus for biodiesel production

The production of biodiesel was carried using a small scale laboratory reactor consisting of 1L jacketed glass batch reactor (Brand: Favorit), reflux condenser to recover methanol, a sampling device, overhead mechanical stirrer (IKA EUROSTAR digital), refrigerator, circulating water bath (WiseCircu® Fuzzy Control System) to control the reaction temperature. The experimental set up is depicted in Figure 3.6.

Figure 3.6: Experimental set up used to perform biodiesel production (1) reflux condenser; (2) overhead mechanical stirrer; (3) circulating water bath; (4) Jacketed glass batch tank reactor (1 l); (5) hoses; (6) Refrigerator

3.7 Biodiesel production

Alkaline-catalysed transesterification is the most widely used process for biodiesel production because it is very fast and yields large amount of biodiesel. However, to use alkaline catalysts, the free fatty acid (FFA) level should be below a desired limit (ranging from less than 0.5% to less than 3%). Most of non-edible oils have high FFA values. Therefore, transesterification with alkali based catalyst yield a considerable amount of soap which are emulsifiers that make the separation of glycerol and ester phases very difficult.

Acid-catalysed esterification was found to be a good solution to this problem. However the reaction rate was considerably less, requiring lengthy reaction periods. Therefore, the best approach to produce biodiesel from non-edible oils with high FFA values is the *acid-catalysed esterification* process followed by *Alkaline-catalysed transesterification* process.

3.7.1 Biodiesel production from coconut, soybean, manketti, palm and canola oils

The acid values of crude coconut, soybean, palm and canola oils were measured to be less than 4 mgKOH/goil. Therefore, production of biodiesel from these crude oils has been conducted as follow:

(a) Pre-treatment process.

(b) Tranesterification process.

(c) Post-treatment process

3.7.1.1 Pre-treatment process

In this process, crude coconut, soybean, palm and canola oils were entered in a rotary evaporator and heated to remove moisture for 1 h at 95 °C under vacuum.

3.7.1.2 Transesterification process

In this process, crude palm, coconut, manketti, canola and soybean oils were reacted with 25% (v/v) of methanol and 1% (m/m) of potassium hydroxide (KOH) and maintained at 60 $^{\circ}$C for 2 h and 400 rpm stirring speed. After completion of the reaction, the produced biodiesel was deposited in a separation funnel for 12 h to separate glycerol from biodiesel. The lower layer which contained impurities and glycerol was drawn off.

3.7.1.3 Post-treatment process

Methyl ester formed in the upper layer from the previous process was washed to remove the entrained impurities and glycerol. In this process, 50% (v/voil) of distilled water at 60 °C was sprayed over the surface of the ester and stirred gently. This process was repeated several times until the PH of the distilled water became neutral. The lower layer was discarded and upper layer was entered into a flask and dried using Na_2SO_4 and then further dried using rotary evaporator to make sure that biodiesel is free from methanol and water.

3.7.2 Biodiesel production from *Jatropha, Calophyllum, Sterculia, Moringa, Croton, Pangium edule* and *Patchouli* oils

The acid values of crude Jatropha, Calophyllum, Sterculia, Moringa, Croton, Pangium and Patchouli oils were measured to be 17.63, 41.74, 9.49, 8.62, 12.07, 19.62 and 25.2 mgKOH/goil respectively. Therefore, production of biodiesel from these crude oils has been conducted as follow:

(a) Pre-treatment process.
(b) Esterification process.
(c) Tranesterification process.
(d) Post-treatment process

3.7.2.1 Pre-treatment process

This process is same as section 3.8.1.1.

3.7.2.2 Esterification process

In this process, the molar ratio of methanol to refined *Jatropha curcas, Calophyllum inophyllum, Sterculia foetida, Moringa oleifera*, *Croton megalocarpus* and *Patchouli* oils were maintained at 12:1 (50% v/v). 1% (v/v) of sulphuric acid (H_2SO_4) was added to the pre-heated oils at 60 ˚C for 3 h and 400 rpm stirring speed in a glass reactor. On completion of this reaction, the products were poured into a separating funnel to separate the excess alcohol, sulphuric acid and impurities presented in the upper layer. The lower layer was separated and entered into a rotary evaporator and heated at 95 °C under vacuum conditions for 1 h to remove methanol and water from the esterified oil.

Due to the high acid value of *Calophyllum inophyllum*, this process has been conducted twice to reduce the acid value of the oil to less than 4 mgKOH/goil. The first reaction reduced the acid value of *Calophyllum inophyllum* to around 11 mgKOH/goil. While the second reaction reduced the acid value to less than 4 mgKOH/goil

3.7.2.3 Transesterification process

This process is same as section 3.8.1.2.

3.7.2.4 Post-treatment process

This process is same as section 3.8.1.3.

3.8 Determination of fatty acid composition

To determine the fatty acid compositions of biodiesel samples, (1 µL) was injected into gas chromatography (Shidmadzu, GC-2010A series) equipped with a flame ionization detector and a BPX70 capillary column of 30 m x 0.25 µm x 0.32 mm. An initial temperature of 140 °C was held for 2 minutes, which was then increased at 8 °C per minute to 165 °C, 3 °C per minute to 192 °C and finally 8 °C per minute to 220 °C. The column was held at the final temperature for another 5 minutes. The oven, injector and the detector ports were set at 140, 240 and 260 °C, respectively. The carrier gas was helium with column flow rate at 1.10 mL min^{-1} at a 50:1 split ratio. Table 3.2 shows the operating condition used to perform this analysis. The GC was located at Faculty of Science (University of Malay).

Table 3.2: 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 Column Oven	240.0 °C
Temperature ramp	140.0 °C (hold for 2 minutes) 8 °C/min 165.0 °C 3 °C/min 192.0 °C 8 °C/min 220.0 °C (hold for 5 minutes)

3.9 Biodiesel blending

The test fuels were blended using a magnetic stirrer (IKA® C-MAG HS 7) at 2000 rpm for half an hour and shaker (IKA® KS 130 basic) at 400 rpm for half an hour to make sure the blends were well blended.

In this research the effect of biodiesel-biodiesel and biodiesel-diesel blending at different percentages on some physical and chemical properties has been studied. These include flash point, viscosity, cloud point, pour point and cold filter plugging point. Moreover, polynomial curve fitting method was used to estimate the properties of other blends. This method is an attempt to describe the relationship between variable X as a function of available data and a response Y, which seeks to find a smooth curve that best fits the data. Mathematically, a polynomial of order k in X is expressed in the following form:

$$Y = C_o + C_1X + C_2X^2 + \ldots\ldots + C_kX^k \tag{3.5}$$

The percentage error can be calculated using the following formula:

$$A = \frac{|Approximate\ value - Exact\ value|}{|Exact\ value|} \times 100 \tag{3.6}$$

3.10 Engine and emissions tests

The engine used in this research is a Mitsubishi Pajero (model 4D56T) multi-cylinder diesel engine. Table 3.3 shows the technical specifications of the engine. The test rig of the engine is shown in Figure 3.7. Figure 3.8 shows the schematic diagram of the engine setup.

Engine test conditions were monitored by REO-DCA controller connected through a desktop to the engine test bed (Figure 3.7). To measure the exhaust emission gases of NO, HC and CO emission, a BOSCH exhaust gas analyser (model BEA-350) was used. The details of the exhaust gas analyser are shown in Table 3.4. To get the average values, all tests were repeated three times.

The experimental investigation was carried out using diesel (B_0), B_{10} (90% diesel and 10% biodiesel) and B_{20} (20% biodiesel and 80% diesel) blends for fuel blends CMME, CIME and COME respectively. Firstly, the engine was run with diesel for 15 minutes to warm up the engine before running with B_{10} and B_{20} blends. Again, the engine was run by diesel before the engine was shut down. Same procedure was maintained for all fuel blends (CMME, CIME and COME). This is very important to make sure that the engine was free from biodiesel blends before proceeding to the next test. The engine was run at various speeds range from 1000 rpm to 4000 rpm at full load condition.

Table 3.3: Technical specifications of the engine

Engine type		4 cylinder inline
Displacement	L	2.5
Cylinder bore x stroke	mm	91.1 x 95
Valve mechanism		Single overhead camshaft
Rocker arm		Roller flow type
Compression ratio		21:1
Maximum engine speed	rpm	4200
Maximum power	kW	55
Fuel system		Distributor type injection pump
Lubrication System		Pressure feed , full flow filtration
Oil pump		Trochoid type
Combustion chamber		Swirl type
Cooling system		Radiator cooling
Water pump type		Centrifugal impeller type
A/F ratio		26

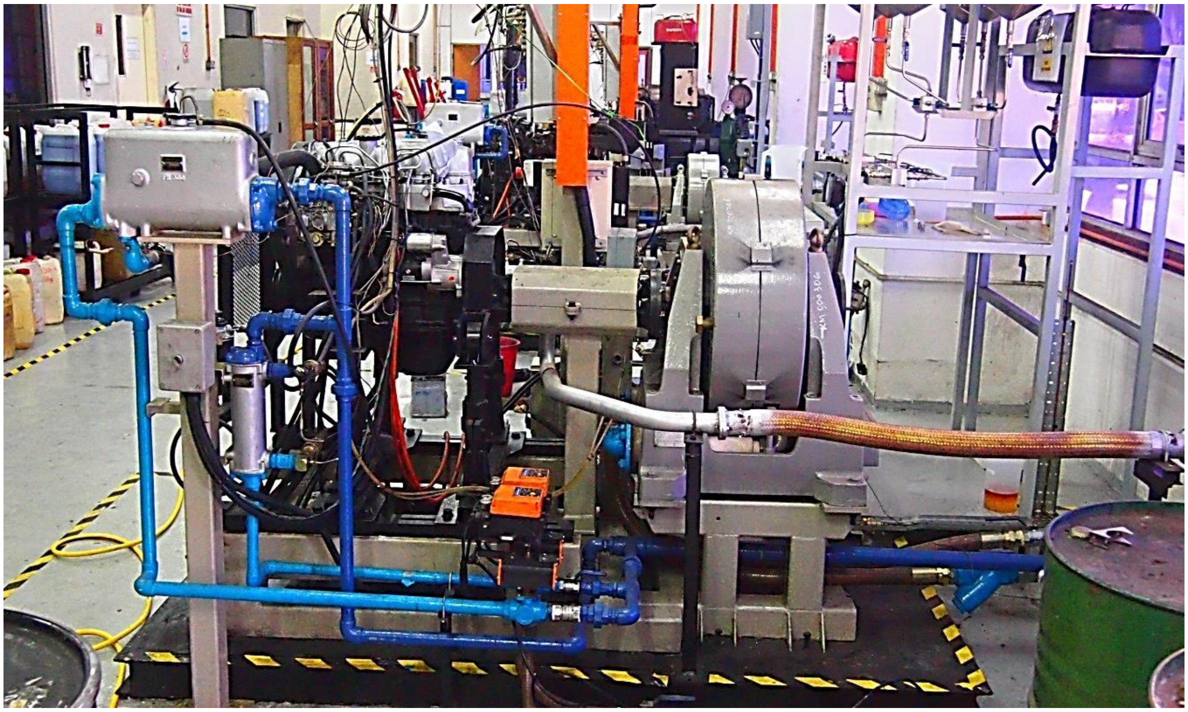
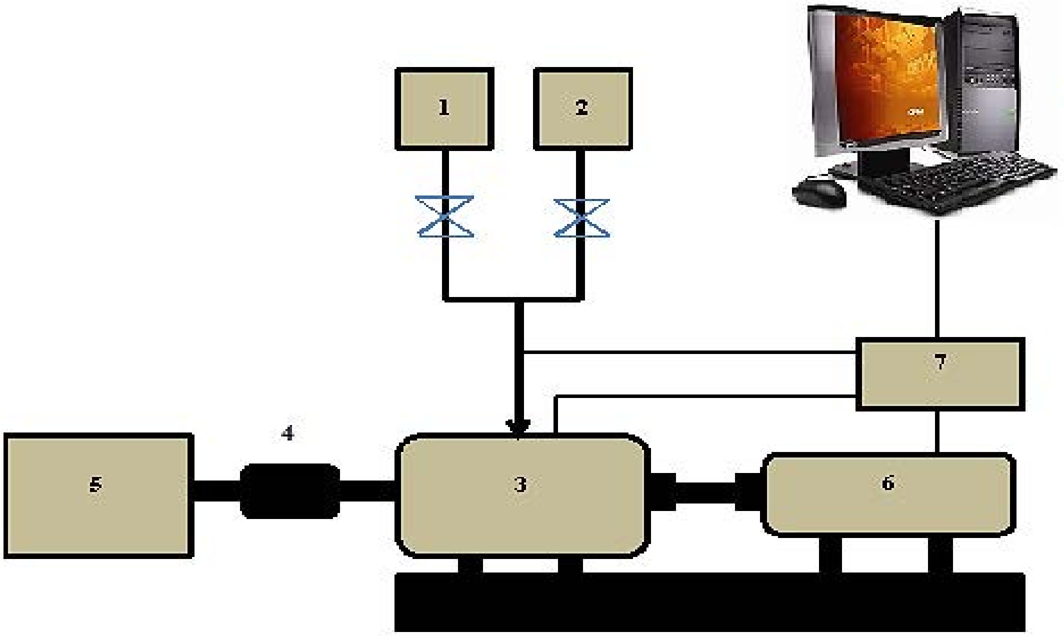


Figure 3.7: Engine test bed set-up



1. Fuel tank for neat diesel
2. Fuel tank for the blends of diesel and biodiesel
3. Mitsubishi Pajero (model 4D56T) multi-cylinder diesel engine
4. Exhaust manifold
5. BOSCH exhaust gas analyzer (model BEA-350)
6. Dynamometer
7. REO-DCA controller
8. Desktop

Figure 3.8: Schematic diagram of experimental set-up for engine test rig

Table 3.4: Details of the exhaust gas analyser

Equipment	Method	Measurement	Upper limit	Accuracy	Percentage uncertainties
BOSCH gas analyzer	Non-dispersive infrared	CO	10.00 vol.%	±0.001 vol.%	0.002 vol.%
	Non-dispersive infrared	CO_2	18.00 vol.%	±0.001 vol.%	0.150 vol.%
	Flame ionization detector (FID)	HC	9999 ppm	±1 ppm	2 ppm
	Electro-chemical transmitter	NO	5000 ppm	±1 ppm	21 ppm

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter discusses in details the results of crude oils characteristics, physical and chemical properties of biodiesels, fatty acid compositions, biodiesel blending and engine performance. Moreover, a comparison with the existing results in literature has been conducted. In thus research, the physical and chemical properties were measured using the equipment mentioned in section 3.5 (Table 3.1). The properties of biodiesel-biodiesel and biodiesel-diesel blends have been predicted using equation 3.5 in section 3.9. The engine used in this research is a Mitsubishi Pajero (model 4D56T) multi-cylinder diesel engine.

4.2 Physical and chemical properties of CCIO, CJCO, CSFO, CMOO, CCMO, CCO, CCaO, CSO, CPO, CPEO, CPaO and CMO

Table 4.1 shows the main findings of physical and chemical properties of CCIO, CJCO, CSFO, CMOO, CCMO, CCO, CCaO, CSO, CPO, CPEO, CPaO and CMO beside a comparison with some existing results in the literature. The main findings of crude oil properties show that CMO possess the highest kinematic viscosity of 132.75 mm²/s at 40 °C. However, CCMO has the best viscosity index of 224.2. CPaO possesses the lowest CFPP and highest refractive index and calorific value of 1 °C, 1.5069 and 42,986 kJ/kg respectively. CCaO possesses the highest flash point of 290.5 °C. CMOO was found to have the best oxidation stability of 41.75 h. Finally, it was found that CCO possesses the highest transmission of 91.2%. The next sections will discuss some of main the finding of this study beside a comparison with literature.

4.2.1 Kinematic viscosity (KV), dynamic viscosity and viscosity index (VI)

Kinematic viscosity is the most important property of any fuels since it affects the operation of fuel injection equipment and spray atomization, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. Moreover, high viscosity may lead to the formation of soot and engine deposits due to insufficient fuel atomization (Fernando et al., 2007).

From Table 4.1, it can be seen that CMO presented the highest kinematic viscosity of 132.75 mm^2/s and 20.624 mm^2/s at 40 °C and 100 °C, dynamic viscosity of 122.81 mpa.s at 40 °C, while CPaO possesses the lowest kinematic viscosity among all oils with viscosity of 9.8175 mm^2/s at 40 °C and 2.2151 mm^2/s at 100 °C and dynamic viscosity of 9.2933 mpa.s at 40 °C. It was also found that CCMO possesses the highest viscosity index of 224.2.

From literature, it was observed that CCIO possesses a lower kinematic viscosity compared to (Sahoo et al., 2007) of 71.98 mm^2/s. However, CSFO possesses higher kinematic viscosity compared to (Devan & Mahalakshmi, 2009a) of 49.7 mm^2/s. Whereas the viscosity of CJCO are within the limit mentioned by (Koh & Ghazi, 2011) (47-54.8 mm^2/s). While for CMOO the viscosity is slightly higher than that of (Karmakar et al., 2010; Sanford et al., 2009) of 43.2 mm^2/s. For CCMO the results obtained in this study is much lower than that presented in (Kafuku & Mbarawa, 2010) of 64 mm^2/s. The obtained viscosity of CCO in this study (27.64 mm^2/s) is slightly higher than that of (Karmakar et al., 2010; Sanford et al., 2009) of 27.26 mm^2/s. CPO possesses a viscosity of 41.932 mm^2/s lower than that presented in (Karmakar et al., 2010; Sanford et al., 2009) of 44.79 mm^2/s. The viscosity of CSO of 31.739 mm^2/s is higher than that presented in (Karmakar et al., 2010; Sanford et al., 2009) of 2.87 mm^2/s. Finally, CCaO has a viscosity of 35.706 mm^2/s which is higher than that presented in (Karmakar et al., 2010; Sanford et al., 2009) of 34.72 mm^2/s.

It can be seen that all crude oils except CPaO have very high viscosity. This is attributed to their large molecular mass and large chemical structure which indicates that all of these oils have good lubrication properties when used in CI engine. However, the high values of viscosities can negatively affect the volume flow and injection spray characteristics in the engine. At low temperature it may even compromise the mechanical integrity of the injection pump drive systems. Therefore, it is suggested that these oil should be either blended with diesel fuel or transesterified to biodiesel to reduce the viscosity and improve the lubrication properties when used in CI engines.

Table 4.1: Physical and chemical properties of CCIO, CJCO, CSFO, CMOO, CCMO, CPO, CCO, CPaO, CSO, CMO, CCaO and CPEO

	Property	**CCIO**	**CCIO**[a]	**CJCO**	**CJCO**[b]	**CSFO**	**CSFO**[c]	**CMOO**	**CMOO**[d,e]	**CCMO**	**CCMO**[f]	**CPaO**
1	Kinematic viscosity (mm²/s) at 40 °C	55.677	71.98	48.091	47-54.8	75.913	49.7	43.4680	43.2	29.8440	64	9.8175
2	Kinematic viscosity (mm²/s) at 100 °C	9.5608	-	9.1039	-	13.608	-	9.0256	-	7.2891	-	2.2151
3	Dynamic viscosity (mpa.s) at 40 °C	51.311	-	43.543	-	69.408	-	38.9970	-	27.1570	-	9.2933
4	Viscosity Index (VI)	165.4	-	174.10	-	184.80	-	195.20	-	224.20	-	-21.60
5	Flash Point (°C)	236.5	221	258.5	210-240	246.5	158	263	-	235	-	146.5
6	Cold filter plugging point (°C)	26	-	21	-	29	-	18	-	10	-	1
7	Density (g/cm³) at 40 °C	0.9216	-	0.9055	-	0.9143	-	0.8971	-	0.9100	-	0.9466
8	Acid Value (mgKOH/goil)	41.74	44	17.63	0.92-6.16	9.49	0.36	8.62	-	12.07	3.343	25.2
9	Calorific value (kJ/kg)	38,511	39,25	38,961	37,830-42,050	39,793	39,650	N/D	-	N/D	-	42,986
10	Copper strip corrosion (3 h at 50 °C)	1a	-	1a	-	1a	-	1a	-	1a	-	1a
11	Refractive Index	1.4784	-	1.4652	-	1.4651	-	1.4661	-	1.4741	-	1.5069
12	Transmission (%T)	34.7	-	61.8	-	26.6	-	69.2	-	87.5	-	71.4
13	Absorbance (Abs)	0.46	-	0.209	-	0.574	-	0.16	-	0.058	-	0.146
14	Oxidation stability (h at 110 °C)	0.23	-	0.32	15.6	0.15	-	41.75	90.8	0.14	-	0.13
15	PH at 26 °C	4.60	-	4.83	-	4.84	-	N/D	-	N/D	-	N/D

Continue

	Property	CCO	CCO[d,e]	CPO	CPO[d,e]	CSO	CSO[d,e]	CCaO	CCaO[d,e]	CPEO	CMO
1	Kinematic viscosity (mm^2/s) at 40 °C	27.640	27.26	41.932	44.79	31.7390	28.87	35.706	34.72	27.175	132.750
2	Kinematic viscosity (mm^2/s) at 100 °C	5.9404	-	8.496	-	7.6295	-	8.5180	-	6.6407	20.624
3	Dynamic viscosity (mpa.s) at 40 °C	25.123	-	37.731	-	28.796	-	32.286	-	24.393	122.810
4	Viscosity Index (VI)	168.5	-	185.0	-	223.2	-	213.5	-	216.20	179.9
5	Flash Point (°C)	264.5	-	254.5	267	280.5	254	290.5	246.5	-	192.5
6	Cold filter plugging point (°C)	22	-	23	-	13	-	15	-	-	-
7	Density (g/cm^3) at 40 °C	0.9089	-	0.8998	-	0.9073	-	0.9042	-	0.8976	0.9251
8	Acid Value (mgKOH/goil)	N/D	-	N/D	-	N/D	-	N/D	-	19.62	2.08
9	Calorific value (kJ/kg)	37,806	-	39,867	-	39,579	39,600	39,751	39,700	39,523	38,682
10	Copper strip corrosion (3 h at 50 °C)	1a	-	1a	-	1a	-	1a	-	-	-
11	Refractive Index	1.4545	-	1.4642	-	1.4725	-	1.471	-	1.4683	1.487
12	Transmission (%T)	91.2	-	63.2	-	65.2	-	62.9	-	86.1	89.3
13	Absorbance (Abs)	0.04	-	0.199	-	0.186	-	0.202	-	0.064	0.049
14	Oxidation stability (h at 110 °C)	6.93	92.23	0.08	2.7	6.09	-	5.64	14.1	0.08	0.16
15	PH at 26 °C	6.71	-	N/D	-	N/D	-	5.60	-	-	-

[a] (Sahoo et al., 2007)
[b] (Koh & Ghazi, 2011)
[c] (Devan & Mahalakshmi, 2009a)
[d] (Sanford et al., 2009)
[e] (Karmakar et al., 2010)
[f] (Kafuku & Mbarawa, 2010)

4.2.2 Flash point (FP)

Flash point is another important property for any fuel. Generally, crude oils and biodiesel have higher flash point compared to diesel which is usually more than 150 °C, while generally conventional diesel fuel has a flash point of 55-66 °C which is safe for transport, handling and storage purpose (Sanford et al., 2009).

The results from Table 4.1 show that CCaO possesses the highest flash point of 290.5 °C followed by CSO with 280 °C while CPaO possesses the lowest flash point of 146.5 °C. It can be seen except for CPaO and CMO, all of these crude oils have very high flash points (>200 °C). The high flash point makes the seed oil less flammable and ensures safer handling, storage and transportation

It has been observed that, all of the obtained results in this study are higher than those presented in literature such as; (Sahoo et al., 2007) 221 °C for CCIO, (Devan & Mahalakshmi, 2009a) 158 °C for CSFO, (Koh & Ghazi, 2011) 210-240 °C for CJCO, (Karmakar et al., 2010; Sanford et al., 2009) 254 °C for CSO and (Karmakar et al., 2010; Sanford et al., 2009) 246.5 °C for CCaO except for CPO which has a flash point of 267 °C (Karmakar et al., 2010; Sanford et al., 2009) compared to 254.5 °C of this study. The differences in the results can be attributed to the origin from which the oil was obtained.

4.2.3 Acid value (AV)

The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds (Raj & Sahayaraj, 2010).

Table 4.1 shows the results of acid value of some non-edible oils the present study. It can be seen that CCIO possesses the highest acid value of 41.74 mgKOH/g followed by CPaO with 25.2 mgKOH/, CPEO with 19.62 mgKOH/g, CJCO with 17.63 mgKOH/g, CCMO with 12.07 mgKOH/g and CSFO with 9.49 mgKOH/g, CMOO with 8.62 mgKOH/g while CMO possesses the lowest acid value of 2.08 mgKOH/g.

The comparison with existing results in the literature shows that the acid values of CCIO of 41.74 mgKOH/g is lower than that of (Sahoo et al., 2007) of 44 mgKOH/g. While the acid values of CJCO, CSFO and CCMO of 17.63 mgKOH/g, 9.49 mgKOH/g and 12.07 mgKOH/g are higher than result presented in (Koh & Ghazi, 2011), (Devan & Mahalakshmi, 2009a) and (Kafuku & Mbarawa, 2010) with 0.92-6.16 mgKOH/g, 0.36 mgKOH/g and 3.343 mgKOH/g respectively.

4.2.4 Oxidation stability (OS)

The oxidation stability is one of the major factors that helps assess the quality of any fuels. Oxidation is influenced by some factors such as presence of air, heat, traces of metal, peroxides, light, or structural features of the compounds themselves, mainly the presence of double bonds (Atadashi et al., 2010; Karmakar et al., 2010).

Table 4.1 shows the results of oxidation stabilities of the crude oils. It can be seen that CMOO possesses the highest oxidation stability 41.75 h followed by CCO with 6.93 h and CSO with 6.09 h and CCaO with 5.64 h, while CPO and CPEO possesses the lowest oxidation stability of 0.08 h. From comparison with existing results in the literature, it can be seen that the oxidation stabilities of CJCO, CMOO, CCO, CPO and CCaO of 15.6 h, 90.8 h, 92.23 h, 2.7 h and 14.1 h are much better than the obtained values in the current study of 0.32 h, 41.75 h, 6.93 h, 0.08 h and 5.64 h respectively. This may be attributed to the long and improper storage times which deteriorate the oxidation stability of some of these feedstocks.

4.2.5 Calorific value (CV)

Calorific value is an important parameter in the selection of a fuel. The caloric value of crude oils and biodiesel is generally lower than of diesel because of its higher oxygen content (Ramadhas et al., 2005a). This is proved in Table 4.1 as the calorific values of all these feedstocks are lower than diesel fuel 45,825 kJ/kg. However, it was observed that CPaO possesses the highest calorific value of 42,986 kJ/kg followed by CPO of (39,867 kJ/kg, while CCO possesses the lowest calorific value of 37,806 kJ/kg.

The obtained results for CCIO and CSO of 38,511 kJ/kg and 39,579 kJ/kg are lower than that presented in (Sahoo et al., 2007) and (Karmakar et al., 2010; Sanford et al., 2009) of 39,250 kJ/kg and 39,600 kJ/kg respectively. However, the results of CSFO and CCaO of 39,793 kJ/kg and 39,751 kJ/kg are slightly higher than that of (Devan & Mahalakshmi, 2009a) and (Karmakar et al., 2010; Sanford et al., 2009) of 39,650 kJ/kg and 39,700 kJ/kg respectively. Whereas the results of CJCO of 38,961 kJ/kg fall within the results presented in (Koh & Ghazi, 2011) of 37,830-42,050 kJ/kg.

4.2.6 Cold filter plugging point (CFPP)

Cold filter plugging point (CFPP) is the temperature at which the test filter starts to plug due to fuel components that have started to gel or crystallize. It is a commonly used as indicator of low temperature operability of fuels and reflects their cold weather performance (Sanford et al., 2009). From Table 4.1, it can be seen that CSFO possesses the highest CFPP point of 29 °C followed by CCIO with 26 °C compared to 1 °C for CPaO.

4.2.7 Refractive index (*n*)

The refractive index is a number that describes how light, or any other radiation, propagates when passing from one medium into another. More fundamentally, *n* is defined as the factor by which the wavelength and the velocity of the radiation are reduced with respect to their vacuum values. Table 4.1 shows the obtained results of refractive index. It can be seen that CPaO possesses the highest refractive index of 1.5069 followed by CMO with 1.487 while CCO has the lowest refractive index of 1.4545.

4.2.8 Transmission and Absorbance

Table 4.1 shows the obtained results of transmission and absorbance. It can be seen that CCO possesses the highest transmission of 91.2% compared to 26.6% for CSFO. Moreover, the results show that CSFO possesses the highest absorbance of 0.574 abs compared to 0.04 abs for CCO.

4.3 Fatty acid composition (FAC)

The results of fatty acid compositions of methyl esters beside a comparison with some other results in the literature are summarized in Table 4.2. The reference standard used in this study for fatty acid composition analysis was capable to identify fatty acid which are;

C6:0, C8:0, C10:0, C12:0, C14:0, C16:0, C16:1, C18:0, C18:1, C18:2, C18:3, C20:0, C20:1, C22:0, C22:1 and C24:0.

Table 4.2: Fatty acid compositions of biodiesel using GC (Shidmadzu, GC-2010A series)

Name of fatty acid	**Structure**	**Chemical name of fatty acids**	**JCME**	**JCME**[a]	**JCME**[b]	**JCME**[c]	**PME**	**PME**[d]	**PME**[a]	**PME**[c]	**PEME**
Caproic	C6:0	Hexanoic	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Caprylic	C8:0	octanoic	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Capric	C10:0	Decanoic	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Lauric	C12:0	dodecanoic	N/D	N/D	N/D	N/D	0.2	0.267	0.2	N/D	N/D
Myristic	C14:0	Tetradecanoic	0.1	0.1	N/D	1.4	0.9	1.434	1.1	N/D	0.1
Palmitic	C16:0	Hexadecanoic	13	14.2	13.23	15.6	38.6	46.13	44	42.6	8.3
Palmitoliec	C16:1	cis-9-Hexadecenoic	0.7	0.7	0.85	N/D	0.2	N/D	N/D	0.3	0.1
Margaric	C17:0	Heptadecanoic	N/D	0.1	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Stearic	C18:0	Octadecanoic	5.8	7	5.4	9.7	4.4	3.684	4.5	4.4	4.0
Oleic	C18:1	cis-9-Octadecenoic	44.5	44.7	41.62	40.8	44.6	37.47	39.2	40.5	45.2
Linoleic	C18:2	cis-9,cis-12-Octadecedianoic	35.4	32.8	36.99	32.1	10.5	11.02	10.1	10.1	39.3
Linolenic	C18:3	cis-6,cis-9,cis-12-Octadecatrienoic	0.3	0.2	0.22	N/D	0.2	N/D	0.4	0.2	2.5
Stearidonic	C18:4	15-octadecatetraenoic	N/D	N/D	N/D	N/D	N/D	N/D	N/D	1.1	N/D
Arachidic	C20:0	Eicosanoic	0.2	0.2	N/D	0.4	0.4	N/D	N/D	N/D	0.2
Eicosenoic	C20:1	cis-11-Eicosenoic acid	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	0.3
Eicosadienoic acid	C20:2	11,14-eicosadienoic acid	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Behenic	C22:0	Docosanoic	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Erucic	C22:1	cis-13-docosenoic	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Lignoceric	C24:0	Tetracasanoic	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Nervonic	C24:1	15-Tetracosenoic	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Total			100	100	98.31	100	100	100	99.5	99.2	100
Unknown			0	0	1.69	0	0	0	0.5	0.8	0
Total saturation (%)			19.1	21.6	18.63	27.1	44.5	51.51	49.8	47	12.6
Total unsaturation (%)			80.9	78.4	79.68	72.9	55.5	48.49	49.7	52.2	87.4

N/D ≡ Not detected

Continue

Structure	**MOME**	**MOME**[e]	**MOME**[c]	**CoME**[f]	**CoME**	**CoME**[c]	**SME**	**SME**[a]	**SME**[c]	**MME**
C6:0	N/D	N/D	N/D	0.5	N/D	8.9	N/D	N/D	N/D	N/D
C8:0	N/D	N/D	N/D	8.6	6.3	6.2	N/D	N/D	N/D	N/D
C10:0	N/D	N/D	N/D	6.4	6	N/D	N/D	N/D	N/D	N/D
C12:0	N/D	N/D	N/D	47.2	49.2	48.8	N/D	N/D	N/D	N/D
C14:0	0.1	N/D	N/D	17.7	18.5	19.9	0.1	0.1	N/D	N/D
C16:0	6.7	7	9.1	8.7	9.1	7.8	11.3	11	12	10.5
C16:1	1.4	2	2.1	N/D	N/D	0.1	0.1	N/D	N/D	N/D
C17:0	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C18:0	6.2	4	2.7	3.1	2.7	3	4.3	4	3	N/D
C18:1	71	78	79.4	6.3	6.5	4.4	22.8	23.4	23	18.2
C18:2	2.1	1	0.7	1.2	1.7	0.8	52.7	53.2	55	43.9
C18:3	0.2	N/D	0.2	N/D	N/D	N/D	7.6	7.8	6	19.3[j]
C18:4	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C20:0	3.5	4	5.8	0.3	N/D	N/D	0.4	N/D	N/D	N/D
C20:1	1.9	N/D	N/D	N/D	N/D	N/D	0.2	N/D	N/D	0.3
C20:2	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C22:0	6	4	N/D	N/D	N/D	N/D	0.4	N/D	N/D	N/D
C22:1	0.1	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C24:0	0.8	N/D	N/D	N/D	N/D	N/D	0.1	N/D	N/D	N/D
C24:1	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Total	100	100	100	100	100	99.9	100	99.5	99	100
Unknown	0	0	0	0	0	0.1	0	0.5	1	0
Total saturation (%)	23.3	19	17.6	92.5	91.8	94.6	16.6	15.1	15	18.3
Total unsaturation (%)	76.7	81	82.4	7.5	8.2	5.3	83.4	84.4	84	81.7

N/D ≡ Not detected

Continue

Structure	**CME**	**CME**[f]	**CME**[c]	**CME**[c]	**CMME**	**CMME**[g]	**CIME**	**CIME**[h]	**CIME**[i]	**CIME**[c]
C6:0	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C8:0	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C10:0	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C12:0	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C14:0	0.1	N/D	N/D	N/D	0.1	0.1	N/D	0.09	N/D	N/D
C16:0	4	3.8	3.5	3	6.8	6.5	14.7	14.6	12.01	17.9
C16:1	N/D	0.3	N/D	N/D	0.1	0.1	0.3	N/D	N/D	2.5
C17:0	N/D	N/D	N/D	N/D	N/D	0.1	N/D	N/D	N/D	N/D
C18:0	1.7	1.9	0.9	1	4.2	3.8	13.2	19.96	12.95	18.5
C18:1	59.9	63.9	64.1	64	11.8	11.6	46.1	37.57	34.09	42.7
C18:2	22.6	19.0	22.3	22	71.2	72.7	24.7	26.33	38.26	13.7
C18:3	9.6	9.7	8.2	8	4.2	3.9	0.2	0.27	0.3	2.1
C18:4	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C20:0	0.6	0.6	N/D	N/D	0.4	N/D	0.8	N/D	N/D	N/D
C20:1	1.2	N/D	N/D	N/D	1	0.9	N/D	N/D	N/D	N/D
C20:2	N/D	N/D	N/D	N/D	N/D	0.2	N/D	N/D	N/D	N/D
C22:0	0.3	0.4	N/D	N/D	0.1	N/D	N/D	N/D	N/D	N/D
C22:1	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
C24:0	N/D	0.2	N/D	N/D	0.1	N/D	N/D	N/D	N/D	2.6
C24:1	N/D	0.2	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Total	100	100	99	98	100	99.9	100	98.82	97.61	100
Unknown	0	0	1	2	0	0.1	0	1.18	2.39	0
Total saturation (%)	6.7	6.9	4.4	4	11.7	10.50	28.7	34.65	24.96	39
Total unsaturation (%)	93.3	93.1	94.6	94	88.3	89.40	71.3	64.17	72.65	61

N/D ≡ Not detected

[a](Akbar et al., 2009)

[b] (R. Wang et al., 2011)

[c] (Singh & Singh, 2010)

[d] (Benjumea et al., 2008)

[e] (da Silva et al., 2010)

[f](Sanford et al., 2009)

[g](Kafuku & Mbarawa, 2010)

[h] (Ministry of Forestry of the Republic of Indonesia (The Forestry Research and Development Agency). 2008)

[i] (Sahoo & Das, 2009; Sahoo et al., 2007)

[j] Conjugated octadecatrienoates include eleostearic acid and other isomeric conjugated octadecatrienoates. (18:3)

4.4 Physical and chemical properties of biodiesel

Table 4.3 shows the physical and chemical properties of the produced biodiesels from different edible and non-edible oils. Moreover, Table 4.4 presents a comparison of some physical and chemical properties of edible and non-edible biodiesel relative to palm oil biodiesel as the baseline fuel. The following section will discuss some of the obtained results and compare them with each other.

4.4.1 kinematic viscosity (KV)

Table 4.3 shows the obtained results of the kinematic viscosity of CIME, JCME, SFME, PME, CoME, CME, SME, CMME, MME, PaME, PEME and MOME. It can be seen that CoME possesses the lowest kinematic viscosity of 3.1435 mm^2/s followed by CMME (4.0707 mm^2/s), SME (4.3745 mm^2/s), CME (4.5281 mm^2/s), PME (4.6889 mm^2/s), JCME (4.9476 mm^2/s), MOME (5.0735 mm^2/s), PEME (5.2296 mm^2/s), CIME (5.5377 mm^2/s), PaME (6.0567 mm^2/s), SFME (6.3717 mm^2/s) and finally MME (8.3425 mm^2/s). The kinematic viscosities of the methyl esters are all lower than those presented by their respective oils as can be seen in Table 4.2 and 4.3 respectively. This is an expected finding since biodiesel molecules are single, long chain fatty esters with higher mobility than the bigger and bulkier triglyceride molecules (Sanford et al., 2009). It can be observed that all results are in agreement with the standard specified by ASTM D6751 of (1.9-6 mm^2/s) except for MME (8.3425 mm^2/s), SFME (6.3717 mm^2/s) and PaME (6.0567 mm^2/s) which failed to pass the ASTM D6751 specification.

A comparison of some results in the present study and those in literature was also conducted. It was found that CME possesses slightly higher viscosity (4.5281 mm^2/s) than that of (Gui et al., 2008) with 4.50 mm^2/s and (Karmakar et al., 2010; Sanford et al., 2009) with 4.439 mm^2/s. CoME possesses higher viscosity (3.1435 mm^2/s) than that of (Karmakar et al., 2010; Sanford et al., 2009) with 2.726 mm^2/s. JCME possesses higher viscosity (4.9476 mm^2/s) than that of (Sanford et al., 2009) with 4.253 mm^2/s, (Oghenejoboh & Umukoro, 2011) with 4.42 mm^2/s, (Balat, 2011) with 4.84 mm^2/s and (Gui et al., 2008; Karmakar et al., 2010) with 4.80 mm^2/s but lower than that of (Balat, 2011) with 5.38 mm^2/s. MOME possesses higher viscosity (5.0735 mm^2/s) than that of (Sanford et al., 2009) with 4.008 mm^2/s, (Karmakar et al., 2010; Rashid et al., 2008) with 4.83 mm^2/s, (Kafuku et al., 2010) with 4.91 mm^2/s and (Rashid et al., 2011) with 4.80 mm^2/s. PME possesses higher viscosity (4.6889 mm^2/s) than that of (Sanford et al., 2009) with 4.570 mm^2/s, (Oghenejoboh & Umukoro, 2011) with 4.52 mm^2/s, (Balat, 2011) with 4.5 mm^2/s and of (Gui et al., 2008) with 4.42 mm^2/s but lower than that of (Karmakar et al., 2010) with 5.07 mm^2/s. SME possesses higher viscosity (4.3745 mm^2/s) than that of (Karmakar et al., 2010; Sanford et al., 2009) with 4.039 mm^2/s and (Balat, 2011; Gui et al., 2008) with 4.08 mm^2/s. SFME possesses slightly higher viscosity (6.3717 mm^2/s) than that of (Devan & Mahalakshmi, 2009c) with 6.0 mm^2/s. While, CMME possesses lower viscosity (4.0707 mm^2/s) than that of (Aliyu et al., 2011) with 4.8 mm^2/s and (Kafuku & Mbarawa, 2010) of 4.56 mm^2/s. Moreover, CIME possesses lower viscosity (5.5377 mm^2/s) than that of (Sudradjat, 2011) with 5.724 mm^2/s but higher than that of (SathyaSelvabala et al., 2011) and (Sahoo et al., 2007) of 4 mm^2/s and 4.92 mm^2/s respectively.

4.4.2 Oxidation stability (OS)

Table 4.3 shows the obtained results of oxidation stability. It can be seen that PME possesses the highest oxidation stability of 23.56 h followed by MOME (12.64 h), CoME

(8.01 h), CME (7.08 h), CIME (6.12 h), JCME (4.84 h), SME (4.08 h), SFME (1.46 h), CMME (0.71 h), PEME (0.57 h), MME (0.52 h) and PaME (0.022 h). It can be seen that PME, MOME, CoME, CME and CIME possess oxidation stabilities that agree with the range specified by ASTM D6751 standard of min 6h. However, the oxidation stability of JCME, SME, SFME, CMME, (PEME), (MME) and PaME are less than the prescribed ASTM standard. This indicates that the use of antioxidants is necessary to meet standards specifications.

The comparison with other results in literature revealed that the oxidation stability of CME (7.08 h) is comparable to that of (Karmakar et al., 2010; Sanford et al., 2009) with 7.6 h. CoME possesses lower oxidation stability (8.01 h) than that of (Karmakar et al., 2010; Sanford et al., 2009) with 35.5 h. However, the results in the present study satisfy both ASTM D6751 and EN 14214 standards of minimum 3 h and 6 h respectively. While, JCME possesses higher oxidation stability (4.84 h) than that of (Karmakar et al., 2010; Sanford et al., 2009) with only 2.3 h. Moreover, MOME possesses higher oxidation stability (12.64 h) than that of (Karmakar et al., 2010; Sanford et al., 2009) with only 2.3 h, (Rashid et al., 2008) of 3.61 h and (Rashid et al., 2011) of 3.52 h. PME possesses higher oxidation stability (23.56 h) than that of (Sanford et al., 2009) with only 0.2 h and (Karmakar et al., 2010) with 4 h. SME possesses higher oxidation stability (4.08 h) than that of (Karmakar et al., 2010; Sanford et al., 2009) with only 2.1 h.

4.4.3 Cloud (CP), pour (PP) and cold filter plugging point (CFPP)

Table 4.3 shows the obtained results of CP, PP and CFPP. It can be observed that CIME, JCME, MOME and PME have relatively higher CP, PP and CFPP than SME, PaME, CME, CoME, CMME, PEME, MME and SFME. The comparison of some results in the present study and those in literature shows that CME possess a comparable CP and CFPP of -3 °C and -10 °C compared to -3.3 °C and -13 °C of (Karmakar et al., 2010; Sanford et al., 2009). CME possesses similar CP and PP of -3 °C and -9 °C compared to -4 °C and -9 °C of (Gui et al., 2008). Same observation was drawn for SME with CP and CFPP of 1 °C and -3 °C compared to 0.9 °C and -4 °C of (Karmakar et al., 2010; Sanford et al., 2009). While CoME possesses slightly higher CP and CFPP of 1 °C and -1 °C compared to 0 °C and -4 °C of (Karmakar et al., 2010; Sanford et al., 2009). However, JCME possesses very high CP and CFPP of 10 °C compared to 2.7 °C and 0 °C of (Karmakar et al., 2010; Sanford et al., 2009). MOME possesses higher CP and CFPP of 21 °C and 18 °C compared to 13.3 °C and 13 °C of (Karmakar et al., 2010; Sanford et al., 2009) and 18 °C and 17 °C of (Rashid et al., 2011). MOME possesses slightly higher PP of 19 °C compared to 17 °C of (Rashid et al., 2011). The results of CP and CFPP for PME were similar to (Karmakar et al., 2010; Sanford et al., 2009) of 13 °C and 12 °C respectively. CIME possesses lower CP 12 °C compared to 13.2 °C but higher PP of and 13 °C compared to 4.3 °C of (Sahoo et al., 2009). CMME possesses higher CP and PP of -3 °C and -2 °C compared to -4 °C and -9 °C of (Kafuku & Mbarawa, 2010). SFME possesses slightly higher pour point of 2 °C compared to 1 °C of (Devan & Mahalakshmi, 2009c).

4.4.4 Calorific value (CV)

Table 4.3 shows the obtained results of calorific value of the produced biodiesel. It can be observed that PaME possesses the highest calorific value of 44,180 kJ/kg followed by CME (40,195 kJ/kg), MOME (40,115 kJ/kg), PME (40,009 kJ/kg), SFME (40,001 kJ/kg), SME (39,976 kJ/kg), CMME (39,786 kJ/kg), JCME (39,738 kJ/kg), PEME (39,625 kJ/kg), CIME (39,513 kJ/kg), MME (39,070 kJ/g) and finally CoME (38,300 kJ/kg).

4.4.5 Flash point (FP)

Table 4.3 shows the obtained results of flash point. It can be seen that CIME, JCME, SME, CME, SFME, PME, MOME and CMME have flash points of 162.5 °C, 186.5 °C, 202.5 °C, 186.5 °C, 130.5 °C, 214.5 °C, 176 °C and 164°C respectively. It can be seen that PME has the highest flash point of 214.5 °C followed by SME 202.5 °C while CoME and PME have the lowest flash point of 118.5 °C. These results agree with the specification of flash point in ASTM D6751 of minimum 130 °C except for CoME and PaME. The comparison with literature shows that the flash points of JCME, CME and PME obtained in this study (186.5 °C, 186.5 °C and 214.5 °C) are higher than those presented in (Gui et al., 2008) of 135 °C, 170 °C and 182 °C respectively. Moreover, the results of CIME presented in this study of 162.5 °C are higher than those presented in (Sudradjat, 2011), (SathyaSelvabala et al., 2011) and (Sahoo et al., 2007) of 151 °C, 140 °C and 140 °C respectively. The flash point of MOME (176 °C) is higher than that presented in (Rashid et al., 2011) of 162 °C. The flash point of SME (202.5 °C) is higher than that presented in (Devan & Mahalakshmi, 2009c; Karmakar et al., 2010) of 178 °C. The flash point of CoME 118.5 °C is slightly higher than that presented in (Karmakar et al., 2010) of 110 °C. For CMME the result obtained in this study (164 °C) is lower than that obtained in (Kafuku & Mbarawa, 2010) of 189 °C. Same observation was drawn for SFME which has flash point of 130.5 °C compared to 162 °C in (Devan & Mahalakshmi, 2009c).

Table 4.3: Physical and chemical properties of the produced biodiesel

No	Property	CIME	JCME	SME	CME	SFME	PME	CoME	MOME	CMME	PaME	PEME	MME	ASTM D6751 limit
1	Kinematic viscosity at 40 °C (mm^2/s)	5.5377	4.9476	4.3745	4.5281	6.3717	4.6889	3.1435	5.0735	4.0707	6.0567	5.2296	8.3425	1.9-6.0.
2	Dynamic Viscosity at 40 °C (mpa.s)	4.8599	4.2758	3.8014	3.9212	5.5916	4.0284	2.705	4.3618	3.453	5.5848	4.5551	7.4067	-
3	Density at 40 °C (kg/cm^3)	0.8776	0.8642	0.869	0.866	0.8776	0.8591	0.8605	0.8597	0.8704	0.9221	0.8710	0.8878	-
4	Oxidation stability (h at 110 °C)	6.12	4.84	4.08	7.08	1.46	23.56	8.01	12.64	0.71	0.022	0.57	0.52	3h min
5	CFPP (°C)	11	10	-3	-10	2	12	-1	18	-4	-17	-8	5	-
6	Cloud point (°C)	12	10	1	-3	1	13	1	21	-3	<-33	-6	1	Report
7	Pour point (°C)	13	10	1	-9	2	15	-4	19	-2	<-33	-4	3	-
8	Flash point (°C)	162.5	186.5	202.5	186.5	130.5	214.5	118.5	176	164	118.5	N/D	N/D	130 min
9	Copper strip corrosion (3h at 50 °C)	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	No.3 max
10	Caloric value (kJ/kg)	39,513	39,738	39,976	40,195	40,001	40,009	38,300	40,115	39,786	44,180	39,625	39,070	-
11	CCR (m/m%)	0.4069	0.0440	0.0204	0.0291	0.2911	0.0118	0.0114	0.022	0.028	0.385	N/D	N/D	0.050% mass max
12	Saponification value	201.3	201.5	201.2	199.25	N/D	206.7	272.5	196.5	200.4	N/D	200.8	201.7	-
13	Iodine value	87	105.7	137	122.1	N/D	59.9	7.8	71.224	152	N/D	119.2	149.2	-
14	Cetane number	53.8	49.6	42.6	46.2	N/D	59.2	64.6	90.1	39.3	N/D	46.7	39.8	47 min
15	Total Sulfur (ppm)	4.11	3.84	0.86	0.83	7.02	1.81	0.94	N/D	N/D	77.1	N/D	N/D	15 Max (S15) 500 Max (S500)
16	Absorbance (abs) at WL 656.1	0.057	0.045	0.037	0.041	0.057	0.05	0.035	0.046	0.041	3	0.160	0.146	-
17	Transmission (%) at WL 656.1	87.7	90.3	92	91.1	87.9	89.1	92.3	90	91.1	0	69.2	71.5	-
18	Refractive index (RI) at 25 °C	1.4574	1.4513	1.4553	1.4544	1.4557	1.4468	1.4357	1.4494	1.4569	1.5032	1.4551	1.4698	-
19	Viscosity Index	183.2	194.6	257.8	236.9	174.4	203.6	230.8	206.7	276.3	61.8	211.8	176	-
20	Viscosity at 100 °C (mm^2/s)	1.998	1.8557	1.764	1.7864	2.1954	1.7921	1.3116	1.9108	1.6781	1.8223	1.9651	2.6683	-

N/D ≡ Not determined

N/S ≡ Not specified

Table 4.4: A comparison of some physical and chemical properties of edible and non-edible biodiesel relative to palm oil biodiesel (PME)

No	**Property**	**CIME**	**JCME**	**SFME**	**MOME**	**CMME**	**PaME**	**PEME**	**PME**	**SME**	**CME**	**CoME**	**MME**
		NE1	**NE2**	**NE3**	**NE4**	**NE5**	**NE6**	**NE7**	**E1 (Ref)**	**E2**	**E3**	**E4**	**E5**
1	Kinematic viscosity at 40 °C (mm²/s)	+18.1%	+5.5%	+35.9%	+8.2%	-13.2%	+29.2%	+11.5%	**0.0%**	-6.7%	-3.4%	-33.0%	+77.9%
2	Dynamic Viscosity at 40 °C (mpa.s)	+20.6%	+6.1%	+38.8%	+8.3%	-14.3%	+38.6%	+13.1%	**0.0%**	-5.6%	-2.7%	-32.9%	+83.9%
3	Density at 40 °C (kg/cm³)	+2.2%	+0.6%	+2.2%	+0.1%	+1.3%	+7.3%	+1.4%	**0.0%**	+1.2%	+0.8%	+0.2%	+3.3%
4	Oxidation stability (h at 110 °C)	-74.0%	-79.5%	-93.8%	-46.3%	-97.0%	-99.9%	-97.6%	**0.0%**	-82.7%	-69.9%	-66.0%	-97.8%
5	CFPP (°C)	-8.3%	-16.7%	-83.3%	+50.0%	-133.3%	-241.7%	-166.7%	**0.0%**	-125.0%	-183.3%	-108.3%	-58.3%
6	Cloud point (°C)	-7.7%	-23.1%	-92.3%	+61.5%	-123.1%	>-353.8%	-146.2%	**0.0%**	-92.3%	-123.1%	-92.3%	-92.3%
7	Pour point (°C)	-13.3%	-33.3%	-86.7%	+26.7%	-113.3%	>-320.0%	-126.7%	**0.0%**	-93.3%	-160.0%	-126.7%	-80.0%
8	Flash point (°C)	-24.2%	-13.1%	-39.2%	-17.9%	-23.5%	-44.8%	N/D	**0.0%**	-5.6%	-13.1%	-44.8%	N/D
9	Caloric value (kJ/kg)	-1.2%	-0.7%	+0.0%	+0.3%	-0.6%	+10.4%	-1.0%	**0.0%**	-0.1%	+0.5%	-4.3%	-2.3%
10	Absorbance (abs) at WL 656.1	+14.0%	-10.0%	+14.0%	-8.0%	-18.0%	+5900.0%	+220.0%	**0.0%**	-26.0%	-18.0%	-30.0%	+192.0%
11	Transmission (%) at WL 656.1	-1.6%	+1.3%	-1.3%	+1.0%	+2.2%	-100.0%	-22.3%	**0.0%**	+3.3%	+2.2%	+3.6%	-19.8%
12	Refractive index (RI) at 25 °C	+0.7%	+0.3%	+0.6%	+0.2%	+0.7%	+3.9%	+0.6%	**0.0%**	+0.6%	+0.5%	-0.8%	+1.6%
13	Viscosity Index	-10.0%	-4.4%	-14.3%	+1.5%	+35.7%	-69.6%	+4.0%	**0.0%**	+26.6%	+16.4%	+13.4%	-13.6%
14	Viscosity at 100 °C (mm²/s)	+11.5%	+3.5%	+22.5%	+6.6%	-6.4%	+1.7%	+9.7%	**0.0%**	-1.6%	-0.3%	-26.8%	+48.9%

N/A ≡ Not determined

NE ≡ Non-edible

E ≡ Edible

4.5 Effect of biodiesel-biodiesel blending on some physical and chemical properties

4.5.1 Effect of CoME, PME and SFME blending on KV

The effect of blending of CoME and PME with SFME on kinematic viscosity has been studied. Blending of PME with SFME improved the viscosity of SFME from 6.3717 mm^2/s to 6.0482 mm^2/s (3:1), 5.5995 mm^2/s (1:1) and 5.3254 mm^2/s (1:3) respectively as can be seen in Figure 4.1(a). Moreover, the following equation has been developed from this figure to predict the viscosity at any PME-SFME blends as follow:

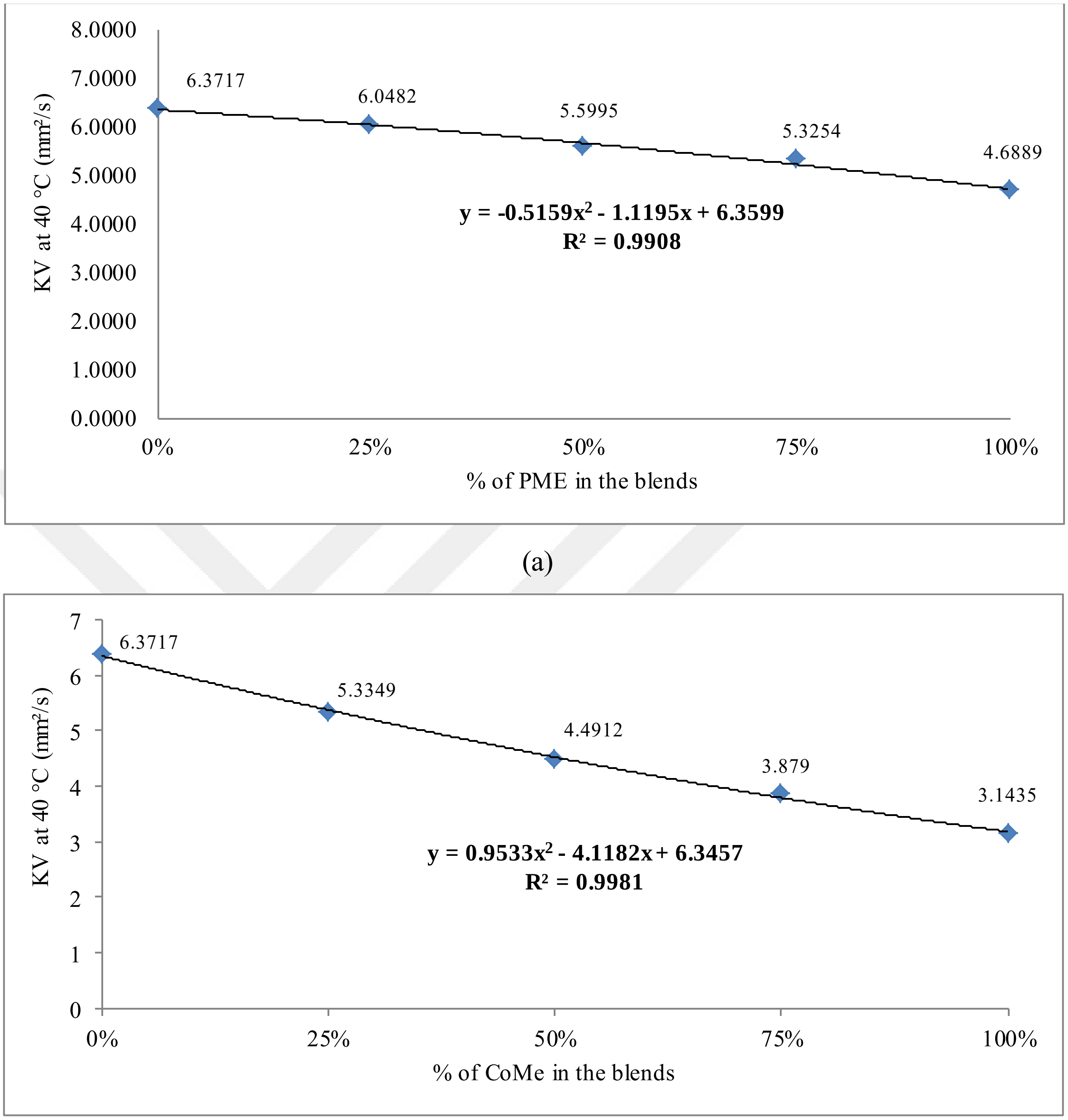
$$\text{Viscosity (SFME-PME)} = -0.5159x^2 - 1.1195x + 6.3599 \quad 0 \leq x \geq 100 \quad (x \equiv \%\text{PME}) \quad (4.1)$$

$(R^2 = 0.9908)$

Blending of CoME with SFME improved the viscosity of SFME from 6.3717 mm^2/s to 5.3349 mm^2/s (3:1), 4.4912 mm^2/s (1:1) and 3.879 mm^2/s (1:3) respectively as can be seen in Figure 4.1(b). Moreover, the following equation has been developed from this figure to predict the viscosity at any CoME-SFME blends as follow:

$$\text{Viscosity (SFME-CoME)} = 0.9533x^2 - 4.1182x + 6.3457 \quad 0 \leq x \geq 100 \quad (x \equiv \%\text{CoME}) \quad (4.2)$$

$(R^2 = 0.9981)$



(a)

(b)

Figure 4.1: Prediction of KV (a) PME and SFME blends (b) CoME and SFME blends

Table 4.5 shows the predicted results of kinematic viscosities of CoME-SFME and POME-SFME blends.

Table 4.5: Predicted KV of CoME-SFME and PME-SFME blends

Blends	**Predicted KV (mm^2/s)**
75% SFME 25% PME	6.0478
50% SFME 50% PME	5.6712
25% SFME 75% PME	5.2301
75% SFME 25% CoME	5.3757
50% SFME 50% CoME	4.5249
25% SFME 75% CoME	3.7933

4.5.2 Effect of CME, PME, JCME and CIME blending on CP, PP and CFPP

The effect of blending of CME with PME, JCME and CIME on the cloud, pour and cold filter plugging point has been studied. As can be seen in Figures 4.2-4.4, blending of CME with PME, JCME and CIME improved the cold flow properties of PME, CIME and JCME respectively. The developed equation in these figures can be used to predict the CFPP, CP and PP of these blends at any blending ratio based on CME% in the blends.

4.5.2.1 Prediction of CP, PP and CFPP of PME-CME blends

$$CP = 3.4286x^2 - 20.629x + 13.429 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.9704 \qquad (4.3)$$

$$PP = -2.2857x^2 - 20.114x + 14.114 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.9784 \qquad (4.4)$$

$$CFPP = -6.8571x^2 - 15.543x + 11.943 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.9843 \qquad (4.5)$$

4.5.2.2 Prediction of CP, PP and CFPP of JCME-CME blends

$$CP = -1.1429x^2 - 12.857x + 10.457 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.979 \qquad (4.6)$$

$$PP = -13.714x^2 - 6.2857x + 10.286 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.9785 \qquad (4.7)$$

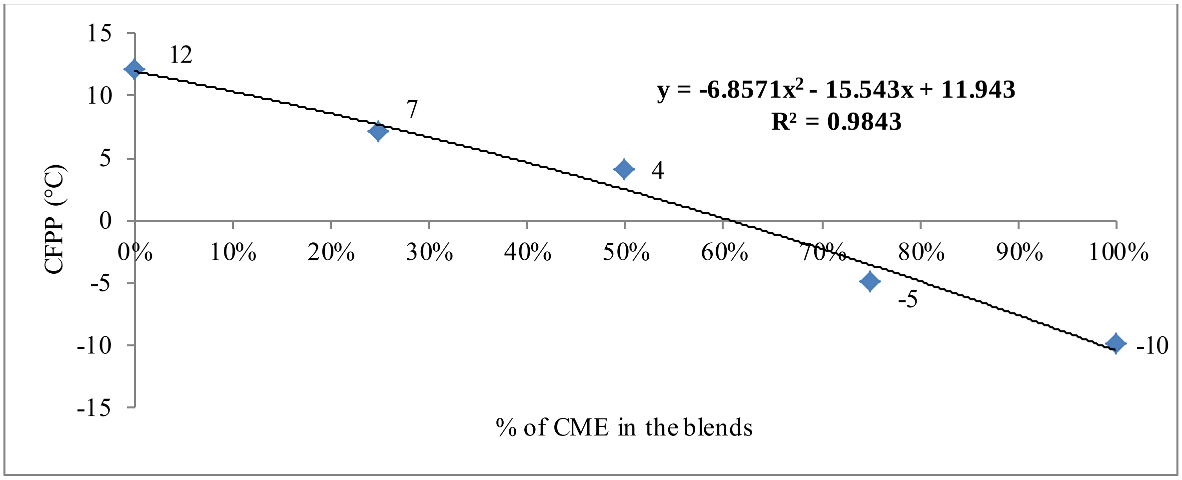
$$CFPP = -6.8571x^2 - 14.743x + 10.543 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.9639 \qquad (4.8)$$

4.5.2.3 Prediction of CP, PP and CFPP of CIME-CME blends

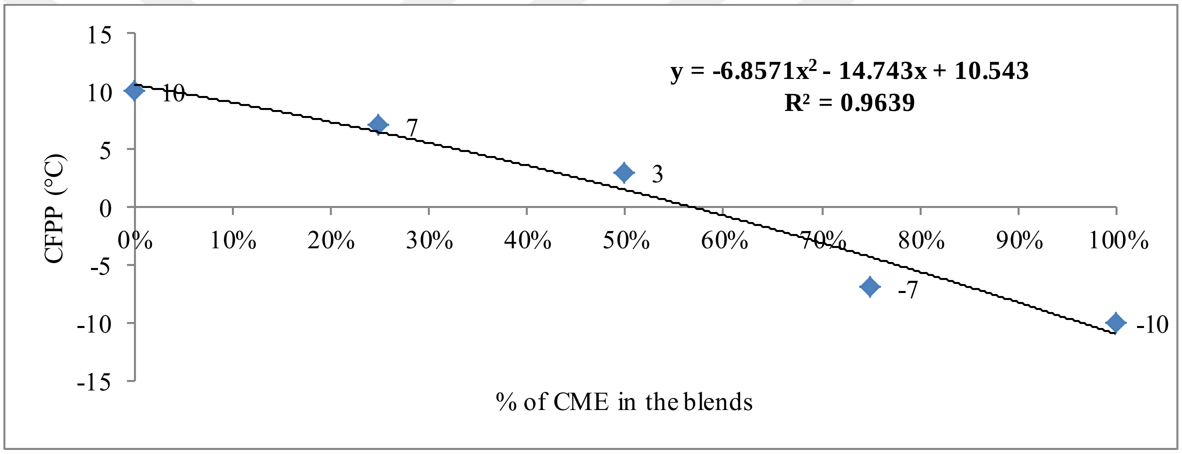
$$CP = -3.4286x^2 - 12.171x + 12.171 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.9867 \qquad (4.9)$$

$$PP = -13.714x^2 - 8.6857x + 13.286 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.9972 \qquad (4.10)$$

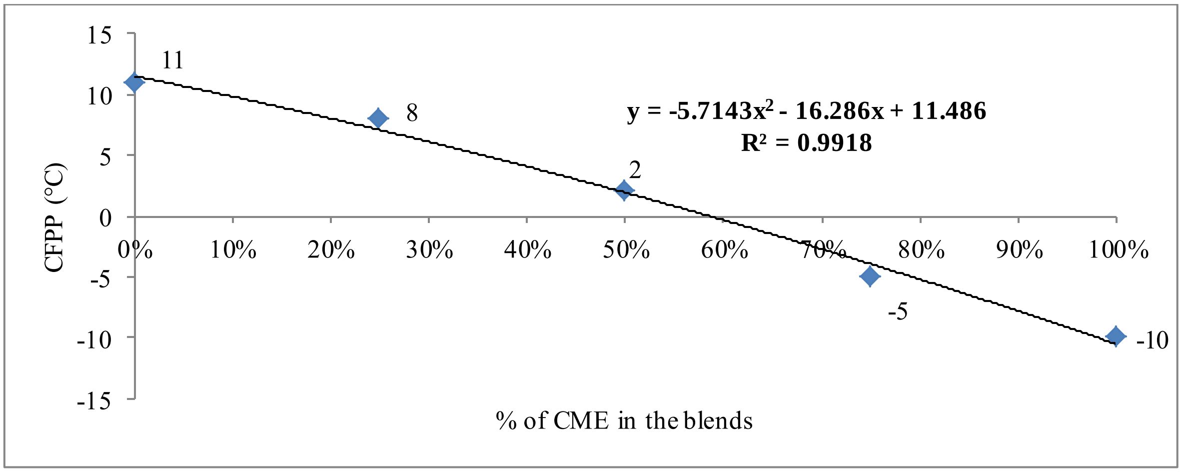
$$CFPP = -5.7143x^2 - 16.286x + 11.486 \qquad 0 \leq x \geq 100 \qquad R^2 = 0.9918 \qquad (4.11)$$



(a)

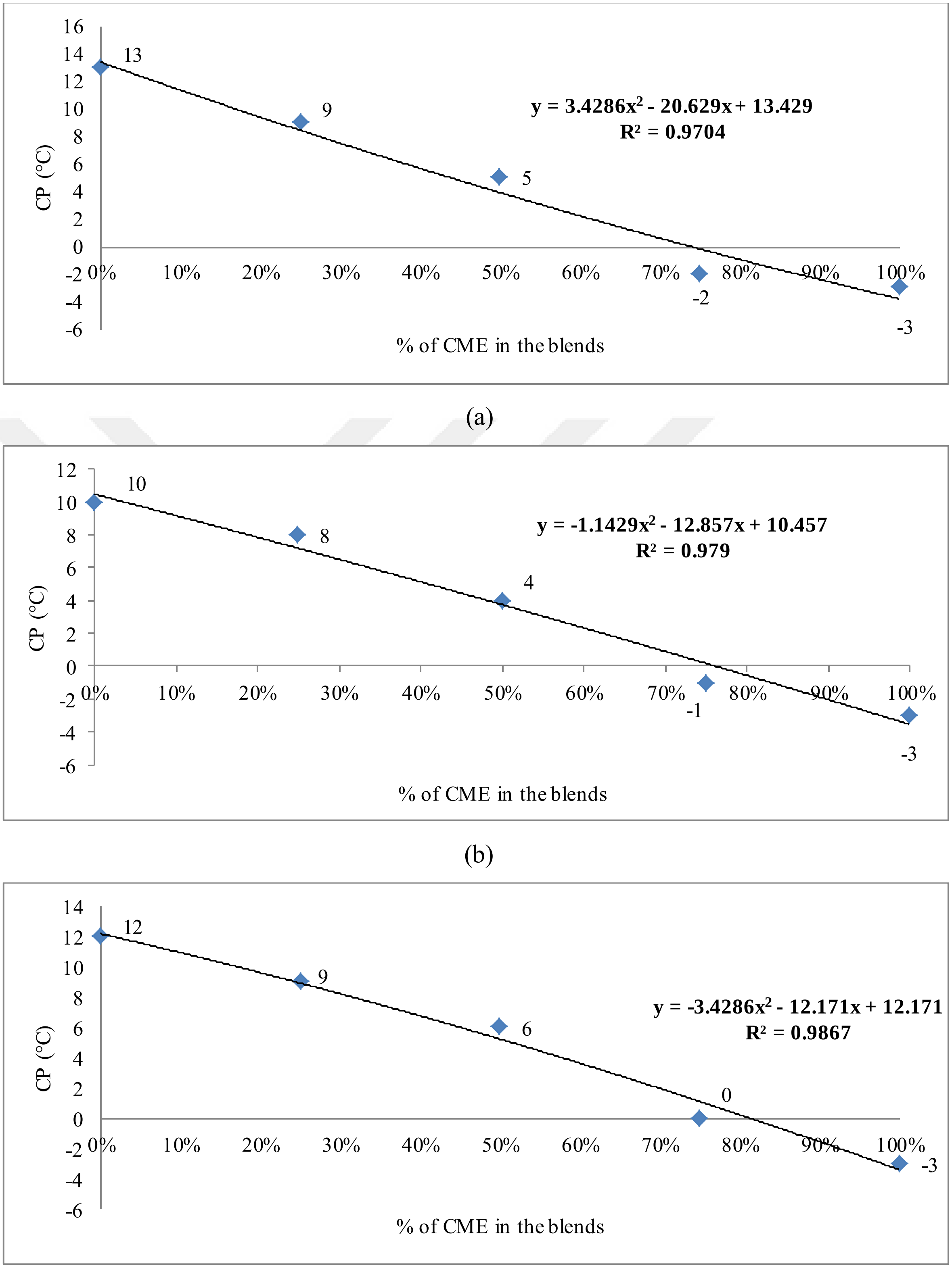


(b)



(c)

Figure 4.2: Prediction of CFPP (a) CME and PME blends (b) CME and JCME blends (c) CME and CIME blends

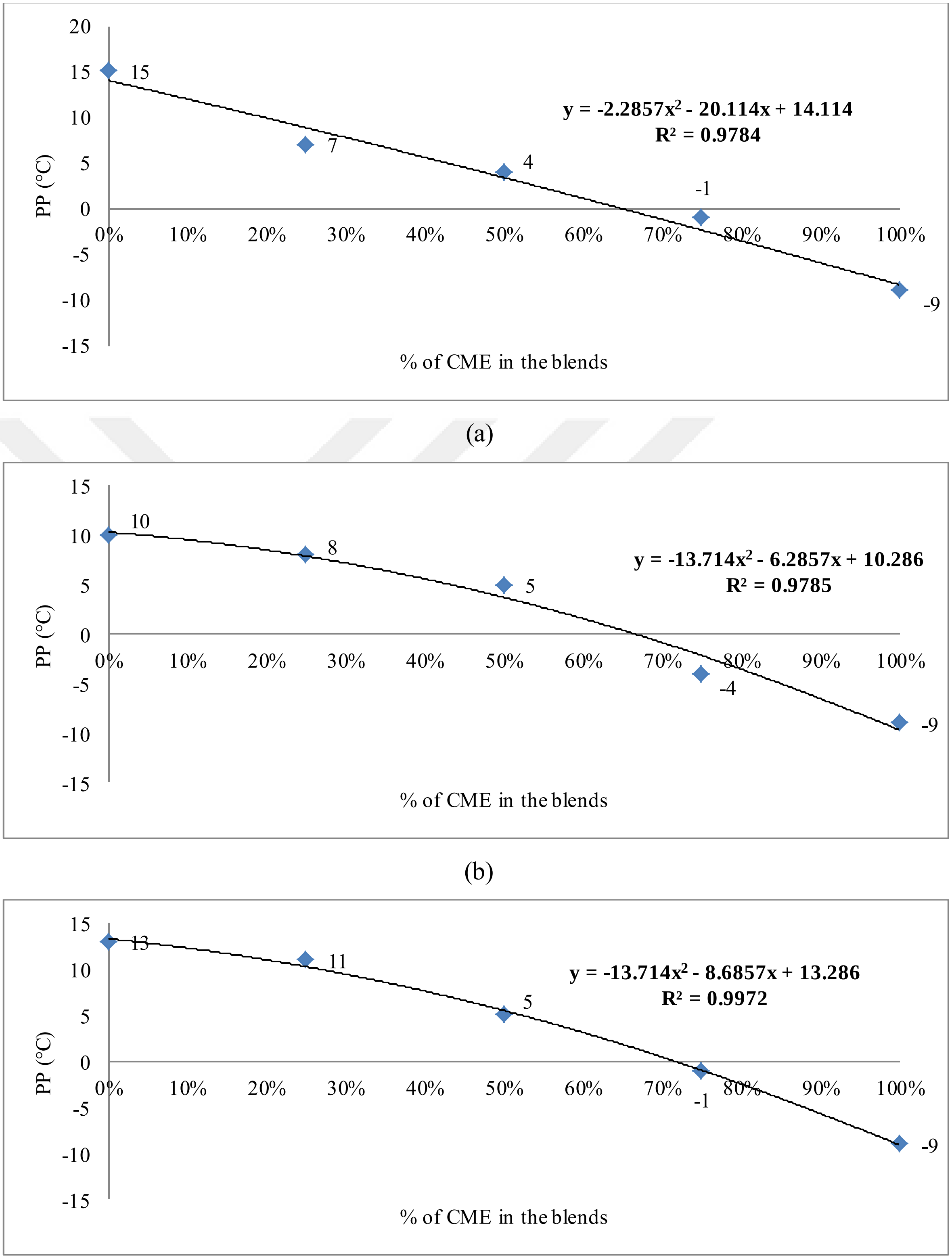


(a)

(b)

(c)

Figure 4.3: Prediction of CP (a) CME and PME blends (b) CME and JCME blends (c) CME and CIME blends



(a)

(b)

(c)

Figure 4.4: Prediction of PP (a) CME and PME blends (b) CME and JCME blends (c) CME and CIME blends

Table 4.6 shows the predicted results of CFPP, CP and PP of CME-PME, CME-JCME and CME-CIME blends.

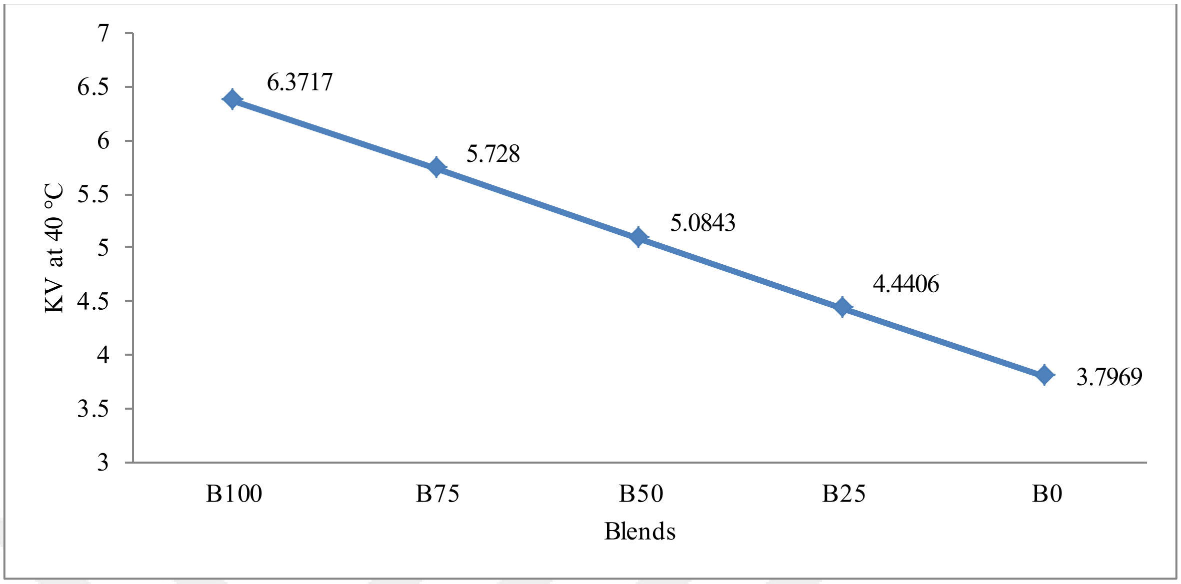
Table 4.6: Predicted CFPP, CP and PP of CME-PME, CME-JCME and CME-CIME blends

Blends	**CFPP (°C)**	**CP (°C)**	**PP (°C)**
75% CME 25% PME	-4	0	-2
50% CME 50% PME	2	4	3
25% CME 75% PME	8	8	9
75% CME 25% CIME	-4	1	-1
50% CME 50% CIME	2	5	6
25% CME 75% CIME	7	9	10
75% CME 25% JCME	-4	0	-2
50% CME 50% JCME	1	4	4
25% CME 75% JCME	6	7	8

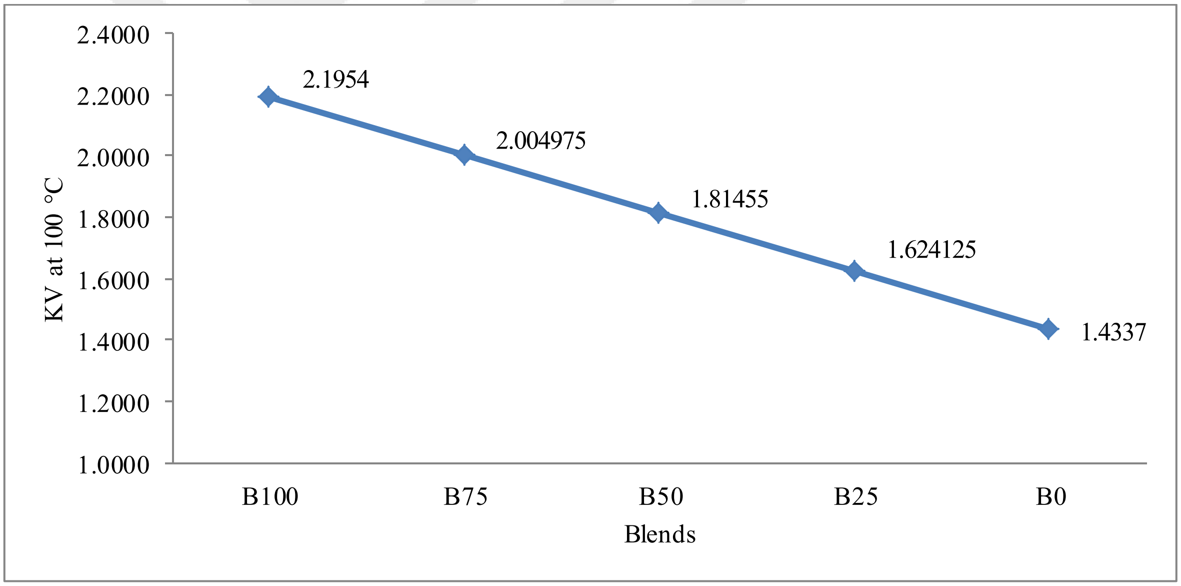
4.6 Effect of biodiesel-diesel blending on some physical and chemical properties

4.6.1 Effect of SFME-diesel blending on KV and VI

The effect blending of SFME with diesel on kinematic viscosity at 40 °C and 100 °C and viscosity index has been studied and presented in Figure 4.5 and 4.6 respectively. It can be seen that blending with diesel will result in an improvement in kinematic viscosity from 6.3717 mm^2/s (B_{100}) to 6.0548 mm^2/s (B_{75}) and 5.4007 mm^2/s (B_{50}) and 4.9574 mm^2/s (B_{25}). Moreover, blending will improve the viscosity index of diesel from 120.2 to 133.7 (B_{25}) to 144.2 (B_{50}) and 149.8 (B_{75}).



(a) At 40 °C



(b) At 100 °C

Figure 4.5: Effect of blending SFME with diesel on KV (a) at 40 °C (b) 100 °C

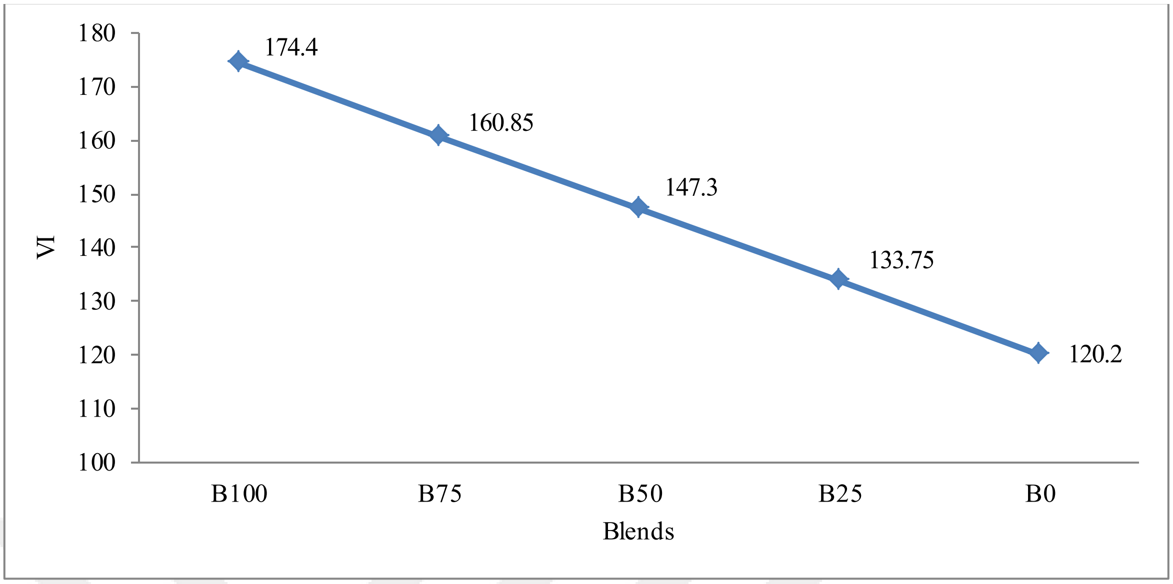


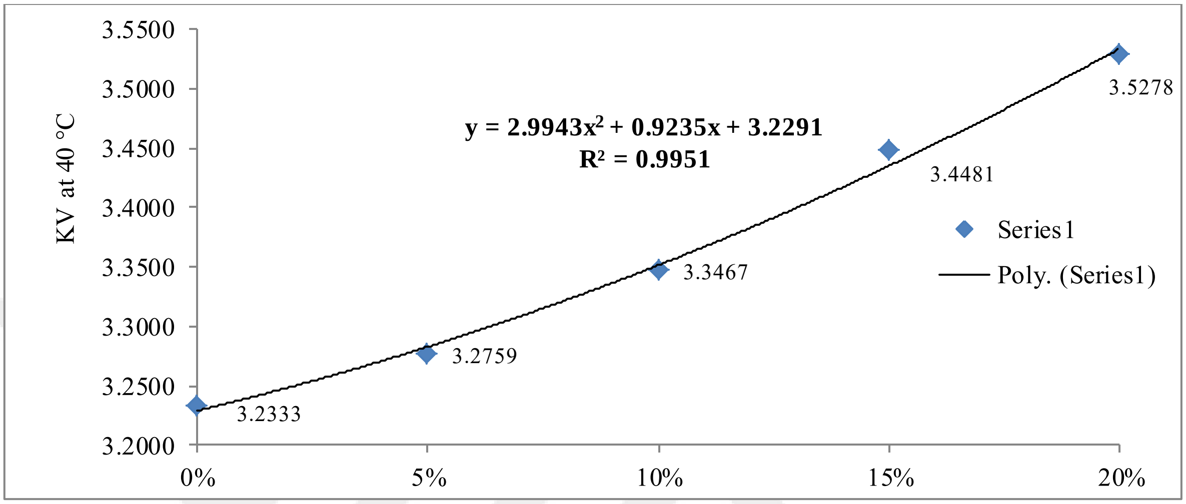
Figure 4.6: Effect of blending SFME with diesel on VI

4.6.2 Effect of PEME-diesel blending on physical and chemical properties

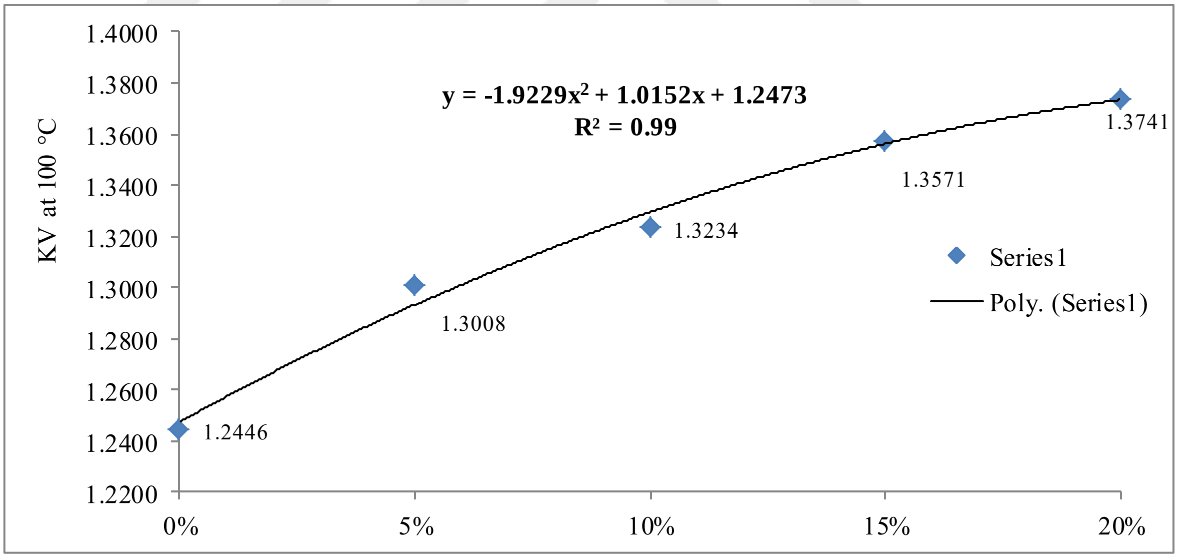
The effect of blending PEME and conventional petroleum-derived diesel fuel on kinematic viscosity (KV), density, calorific value (CV), cloud point (CP), pour point (PP), cold filter lugging point (CFPP), flash point (FP), oxidation stability (OS) and viscosity index (VI) was also investigated**.** Table 4.7 shows the obtained results of physico-chemical properties of PEME-diesel blends of 5%, 10%, 15% and 20% respectively beside a comparison with ASTM 6751 and EN 14214 specifications for (B_{100}), ASTM D975 specifications for diesel fuel and blends up to 5% by volume (B_5) and ASTM 7467 for blends (B_6-B_{20}). It can be seen that blending with diesel improves remarkably kinematic viscosity, density, oxidation stability and calorific value of PEME. However, cloud and pour point increase slightly.

Figure 4.7(a-d) shows the effect of blending PEME and diesel on kinematic viscosity (KV), density, calorific value (CV) and oxidation stability (OS). Moreover, the following table

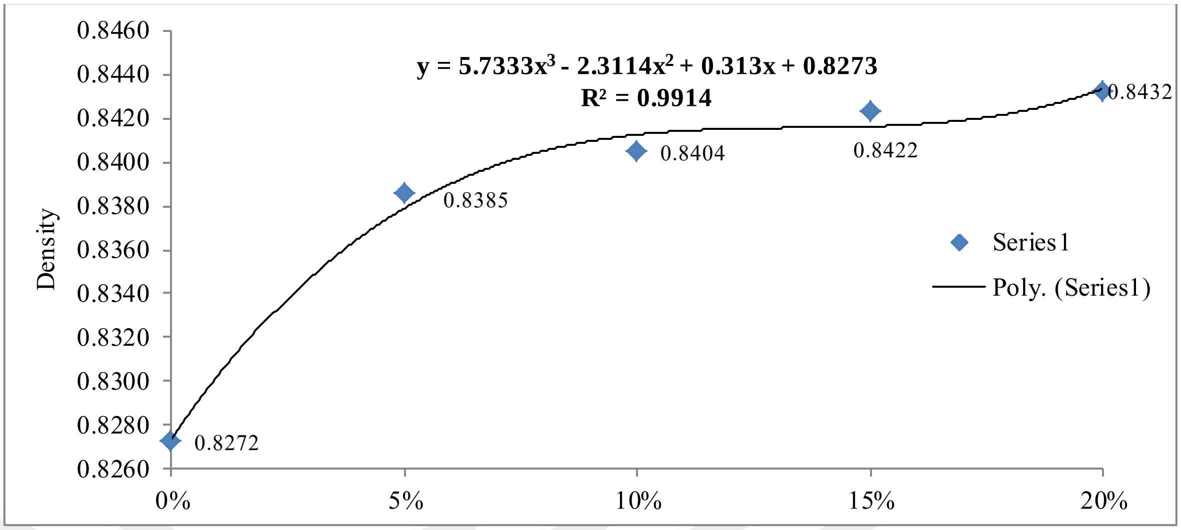
(Table 4.8) shows the equations that have been developed from Figure 4.7 to predict the properties of PEME-diesel blends (in the range of 0-20% blends).



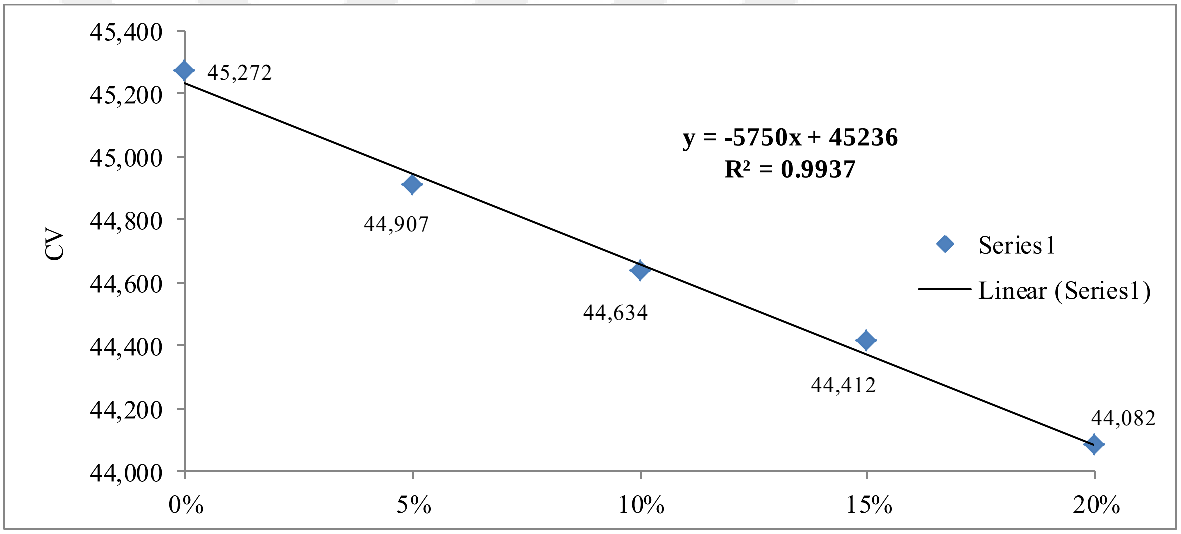
(a) KV at 40 °C (mm^2/s)



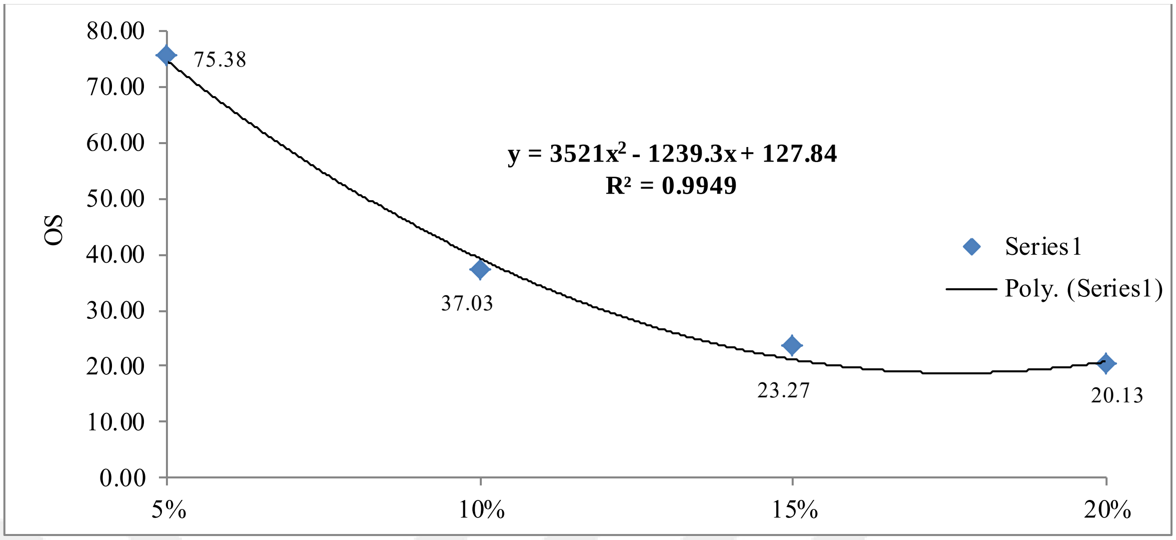
(b) KV at 100 °C (mm^2/s)



(c) Density at 40 °C (kg/m^3)



(d) CV (kJ/kg)



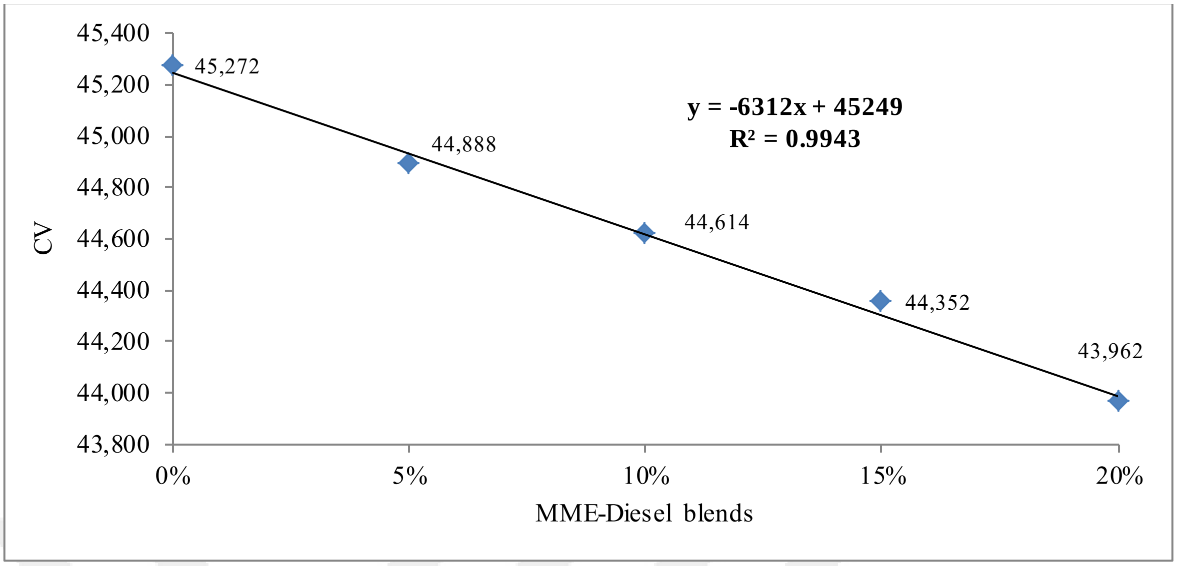
(e) OS (h at 110 °C)

Figure 4.7: Effect of blending PEME and diesel on KV, density, CV and OS

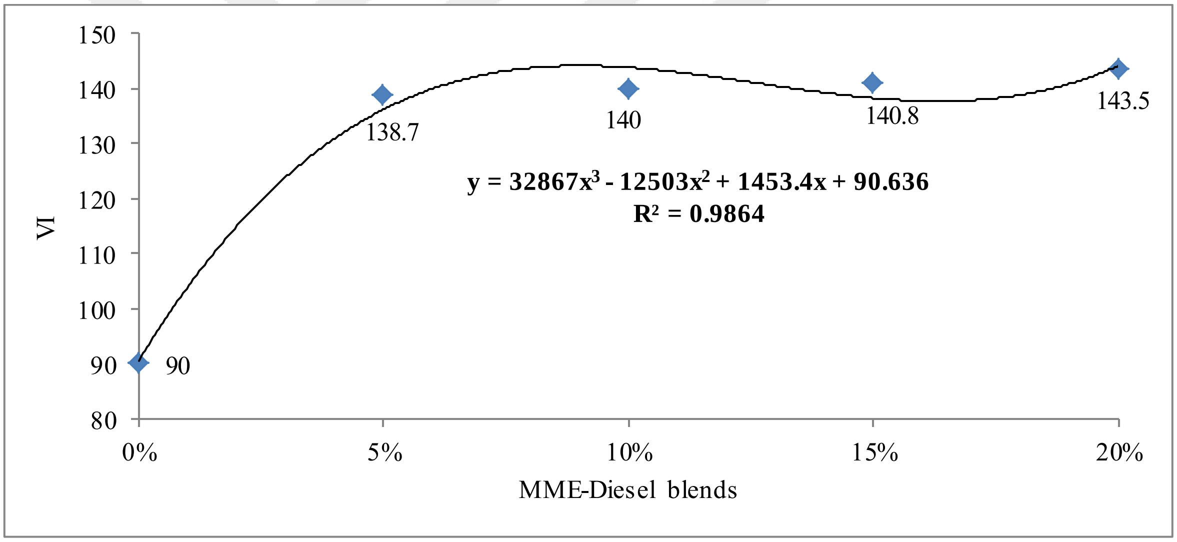
4.6.3 Effect of MME-diesel blending on physical and chemical properties

Table 4.9 shows the physico-chemical properties of (MME)-diesel blends of 5%, 10%, 15% and 20% respectively beside a comparison with ASTM D975 specifications for diesel fuel and blends up to 5% by volume (B_5) and ASTM 7467 for blends (B_6-B_{20}). From this table it can be seen that blending of manketti methyl esters (MME) with diesel has resulted in a remarkable improvement in the viscosity, calorific value, density and oxidation stability of (MME). However, viscosity index and flash point dropped as the percentage of diesel increases in the blends.

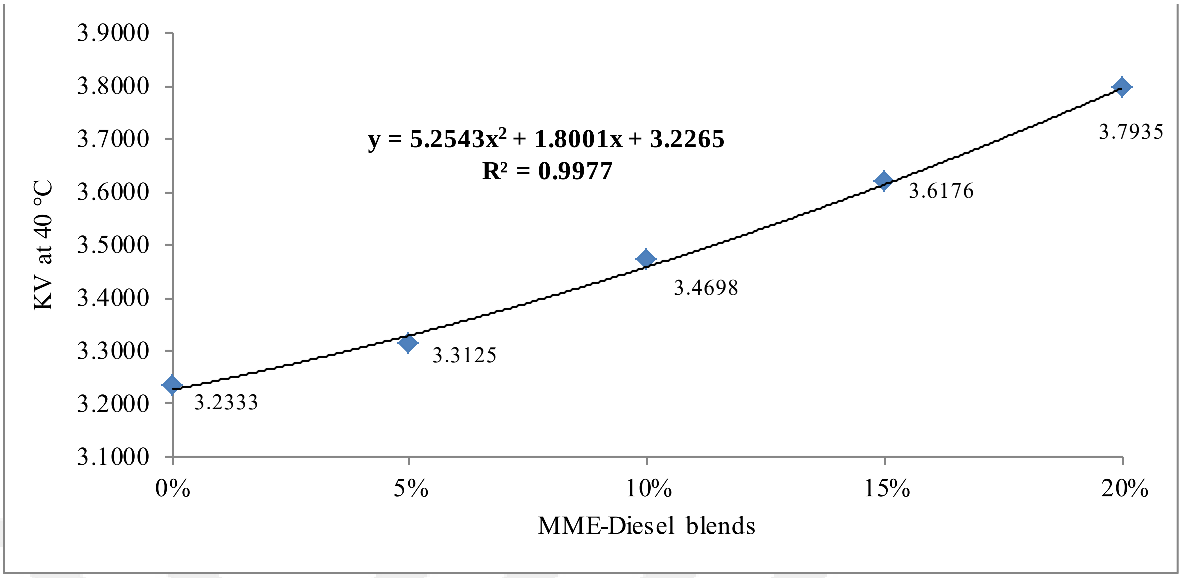
Figure 4.8(a-d) shows the effect of blending MME and diesel on kinematic viscosity (KV), density, viscosity index (VI) and calorific value (CV). Moreover, the following table (Table 4.10) shows the equations that have been developed from Figure 4.8 to predict the properties of MME-diesel blends (in the range of 0-20% blends).


45,400
45,200
45,000
44,800
44,600
44,400
44,200
44,000
43,800
CV
45,272
44,888
44,614
44,352
43,962
y = -6312x + 45249
R² = 0.9943
0%
5%
10%
15%
20%
MME-Diesel blends

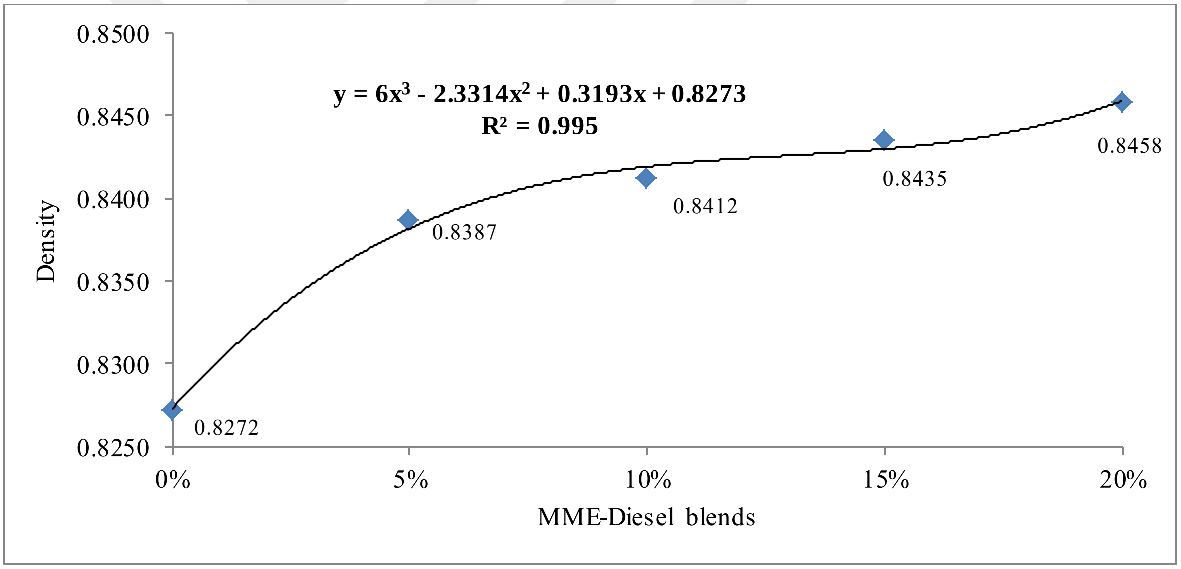
(a) CV (kJ/kg)


150
140
130
120
110
100
90
80
VI
90
138.7
140
140.8
143.5
y = 32867x³ - 12503x² + 1453.4x + 90.636
R² = 0.9864
0%
5%
10%
15%
20%
MME-Diesel blends

(b) VI



(c) KV at 40 °C (mm^2/s)



(d) Density at 40 °C (kg/m^3)

Figure 4.8: Effect of blending MME and diesel on CV, VI, KV and density

Table 4.7: Physico-chemical properties of diesel and PEME-diesel blends (5-20%)

No	**Property**	**unit**	**Diesel**	**PEME (5%)**	**ASTM D975**	**PEME (10%)**	**PEME (15%)**	**PEME (20%)**	**ASTM D7467**
1	KV at 40 ℃	mm²/s	3.2333	3.2759	1.9-4.1	3.3467	3.4481	3.5278	1.9-4.1
2	KV at 100 ℃	mm²/s	1.2446	1.3008	N/A	1.3234	1.3234	1.3571	N/A
3	Dynamic viscosity at 40 ℃	mpa.s	2.6996	2.747	N/A	2.8126	2.9038	2.9746	N/A
4	Viscosity Index (VI)	N/A	90	134.6	N/A	137.1	143.5	149.9	N/A
5	Cloud Point (CP)	℃	8	7	Report	8	6	6	Report
6	Pour Point (PP)	℃	0	0	Report	0	0	-3	Report
7	Cold filter plugging point	℃	8	8	Report	7	8	8	Report
8	Flash point (FP)	℃	68.5	73.5	52min	74.5	76.5	79.5	52min
9	Density at 40 ℃	kg/m³	0.8272	0.8385	N/A	0.8404	0.8422	0.8432	N/A
10	Calorific value (CV)	kJ/kg	45,272	44,907	N/A	44,634	44,412	44,082	N/A
11	Oxidation stability (OS)	h at 110 ℃	N/D	75.38	N/A	37.03	23.27	20.13	6 (min)

Table 4.8: Prediction of properties of PEME-diesel blends (0-20%)

Property	**Blend ratio**[a]	**Predicted equation**	$\mathbf{R^2}$
KV at 40 ℃	$0 \leq x \geq 20$	KV (40 ℃) = $2.9943x^2 + 0.9235x + 3.2291$	0.9951
KV at 100 ℃	$0 \leq x \geq 20$	KV (100 ℃) = $-1.9229x^2 + 1.0152x + 1.2473$	0.99
Density at 40 ℃	$0 \leq x \geq 20$	Density = $5.7333x^3 - 2.3114x^2 + 0.313x + 0.8273$	0.9914
CV	$0 \leq x \geq 20$	CV = $-5750x + 45236$	0.9937
OS	$5 \leq x \geq 20$	OS = $3521x^2 - 1239.3x + 127.84$	0.9949

[a] x≡% of PEME in the blends

Table 4.9: Physico-chemical properties of diesel and MME-diesel blends (5-20%)

No	Property	unit	Diesel	MME (5%)	ASTM D975	MME (10%)	MME (15%)	MME (20%)	ASTM D7467
1	Calorific value (CV)	kJ/kg	45,272	44,888	N/A	44,614	44,352	43,962	N/A
2	Cloud Point (CP)	°C	8	6	Report	7	6	7	Report
3	Pour Point (PP)	°C	0	2	Report	4	1	1	Report
4	Cold filter plugging point	°C	8	8	Report	8	8	7	Report
5	KV at 40 °C	mm^2/s	3.2333	3.3125	1.9-4.1	3.4698	3.6176	3.7935	1.9-4.1
6	Dynamic viscosity at 40 °C	mpa.s	2.6996	2.7781	N/A	2.9188	3.0516	3.2086	N/A
7	Density at 40 °C	kg/m^3	0.8272	0.8387	N/A	0.8412	0.8435	0.8458	N/A
8	KV at 100 °C	mm^2/s	1.2446	1.3143	N/A	1.3617	1.4035	1.4559	N/A
9	Viscosity Index (VI)	N/A	90	138.7	N/A	140	140.8	143.5	N/A
10	Flash point (FP)	°C	68.5	73.5	52 (min)	74.5	74.5	75.5	52 (min)
11	Oxidation stability (OS)	h at 110°C	-	0.54	N/A	0.32	0.36	0.37	6h (min)

Table 4.10: Prediction of properties of MME-diesel blends (0-20%)

Property	Blend ratio[a]	Predicted equation	R^2
KV at 40 °C	$0 \leq x \geq 20$	$KV (40 °C) = 5.2543x^2 + 1.8001x + 3.2265$	0.9977
CV	$0 \leq x \geq 20$	$CV = -6312x + 45249$	0.9943
Density at 40 °C	$0 \leq x \geq 20$	$Density = 6x^3 - 2.3314x^2 + 0.3193x + 0.8273$	0.995
VI	$0 \leq x \geq 20$	$VI = 32867x^3 - 12503x^2 + 1453.4x + 90.636$	0.9864

[a] x≡% of MME in the blends

4.7 Engine performance

The fuel properties of any fuel play a significant role in the engine performance. Biodiesel has a major influence on engine performance due to its higher oxygen contents, higher heat of vaporization, higher density, higher viscosity, lower heating values and higher cetane number (Özener et al., 2012).

According to (Abdullah et al., 2014), the higher peak in-cylinder pressure with biodiesel compared to diesel is attributed to the higher cetane number and reduced ignition delay. This is also attributed to the higher oxygen content of the biodiesel that lead to the improved combustion. (Fontaras et al., 2009), (Mofijur et al., 2013) and (Ng et al., 2012) attributed the higher brake specific fuel consumption (BSFC) of biodiesel compared to diesel to the lower energy contents and higher density of biodiesel fuel. While (Muralidharan et al., 2011) attributed the reduction in brake power (BP) of biodiesel compared to diesel to the lower heating values and higher viscosities of biodiesel.

In this research, the effect of *Croton megalocarpus,* Coconut and *Calophyllum inophyllum* methyl esters on engine performance in terms of torque, brake power (BP), and brake specific fuel consumption (BSFC) was assessed. The following section will discuss the obtained results of these parameters.

4.7.1 Engine Torque

Figure 4.9 shows the variation of torque of diesel, B_{10} and B_{20} at different engine speeds and full load condition. It has been observed that all torque results of B_{10} and B_{20} are lower compared to diesel. These results are in agreement with literature such as (Liaquat et al., 2012; Murillo et al., 2007). It has been found that $COME_{10}$ gives the highest torque value of 130.9 N-m at 1500 rpm. While $CIME_{20}$ gives the lowest torque value of 77.6 N-m at 4000 rpm. Over the whole range of speed, the average torque values for $CMME_{10}$, $CMME_{20}$, $CIME_{10}$, $CIME_{20}$, $COME_{10}$, $COME_{20}$ and diesel were found 111.12, 108.92, 109.98, 107.98, 112.7, 110.21 and 115.82 N-m respectively. Thus, $CMME_{10}$, $CMME_{20}$, $CIME_{10}$, $CIME_{20}$, $COME_{10}$, $COME_{20}$ give an average reduction in torque of 4.05%, 5.95%, 5.04%, 6.77%, 2.70% and 4.84% respectively compared to that of diesel. The reduction in torque values for the blends may be due to the combined effect of the lower calorific value and higher viscosity and density of biodiesel.

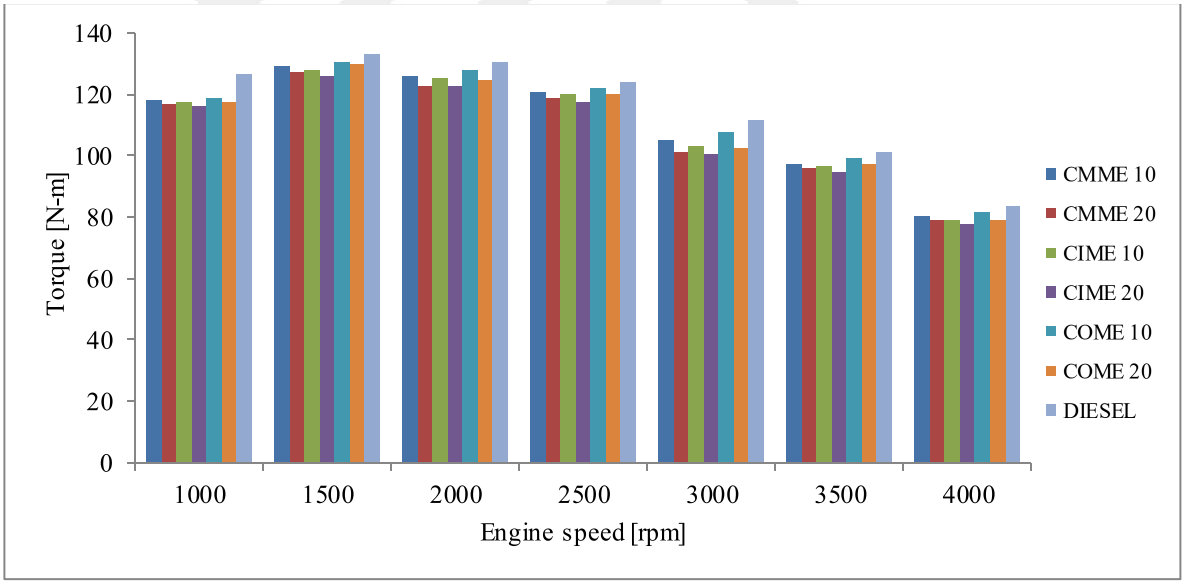


Figure 4.9: Variation of torque at different engine speeds and full load condition

4.7.2 Brake Power (BP)

Figure 4.10 shows the variation of brake power (BP) of diesel, B_{10} and B_{20} at different engine speeds and full load condition. In general, biodiesel-diesel blends produce lower brake power compared to that of diesel fuel. It has been found that $COME_{20}$ gives the highest brake power (BP) value of 36.48 kW at 3500 rpm. While CIME$_{20}$ gives the lowest brake power (BP) of 12.14 kW at 1000 rpm. It can also be seen that the brake power increased gradually with engine speed. Over the entire range of speed, the average brake power for CMME$_{10}$, CMME$_{20}$, CIME$_{10}$, CIME$_{20}$, COME$_{10}$, COME$_{20}$ and diesel was found 27.59, 27.01, 27.27, 26.75, 28.02, 27.32 and 28.72 kW respectively. CMME$_{10}$, CMME$_{20}$, CIME$_{10}$, CIME$_{20}$, COME$_{10}$, COME$_{20}$ lowered the brake power by 3.94%, 5.95%, 5.06%, 6.85%, 2.43% and 4.88% than diesel. This reduction is mainly owed to their lower heating values and higher viscosities compared to diesel (Muralidharan et al., 2011).

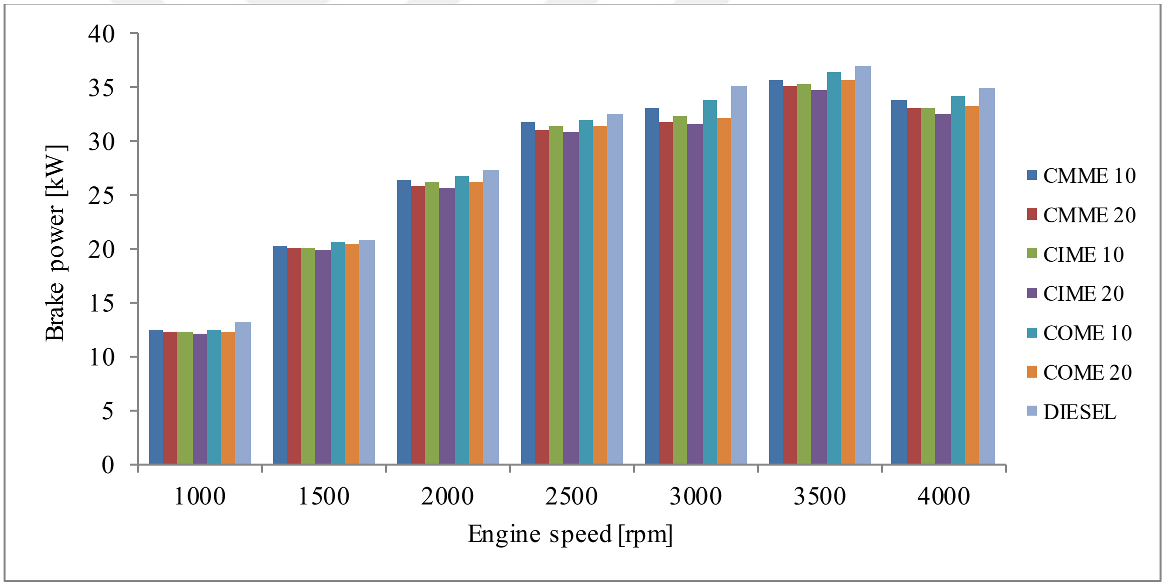


Figure 4.10: Variation of brake power at different engine speeds and full load condition

4.7.3 Brake Specific Fuel Consumption (BSFC)

The BSFC of diesel engine depends mainly on the relationship among volumetric fuel injection system, fuel density, viscosity and energy content (Qi, Chen, Geng, & Bian, 2010). Figure 4.11 shows the variation of brake specific fuel consumption (BSFC) of diesel, B$_{10}$ and B$_{20}$ blends at different engine speeds and full load condition. It can be observed that the BSFC values are higher when biodiesel blends are used. These findings are in agreement with those in literature such as (Chauhan et al., 2012; Shahabuddin et al., 2012; X. Wang et al., 2013). Moreover, it has been found that $COME_{10}$ gives the lowest BSFC value of 338.5 g/kWh at 1500 rpm. While $CIME_{20}$ gives the highest BSFC value of 523.5 g/kWh at 4000 rpm. Over the entire range of speeds, the average BSFC for $CMME_{10}$, $CMME_{20}$, $CIME_{10}$, $CIME_{20}$, $COME_{10}$, $COME_{20}$ and diesel was found 407.38, 421.34, 413.38, 434.58, 398.44, 419.44 and 386.85 g/kWh respectively. $CMME_{10}$, $CMME_{20}$, $CIME_{10}$, $CIME_{20}$, $COME_{10}$, $COME_{20}$ increased the BSFC by 5.3%, 8.9%, 6.85%, 12.33%, 2.99% and 8.31% than diesel fuel. The reason for the higher BSFC of biodiesels blends is mainly due to the higher density and lower energy content of biodiesel-diesel blends (Fontaras et al., 2009; Mofijur et al., 2013; Ng et al., 2012). Any fuel is delivered to the engine on a volumetric basis. For the same fuel volume, an increase in fuel density would imply a larger mass flow rate to the cylinders and this would increase the BSFC to produce the same power (Tsolakis et al., 2007).

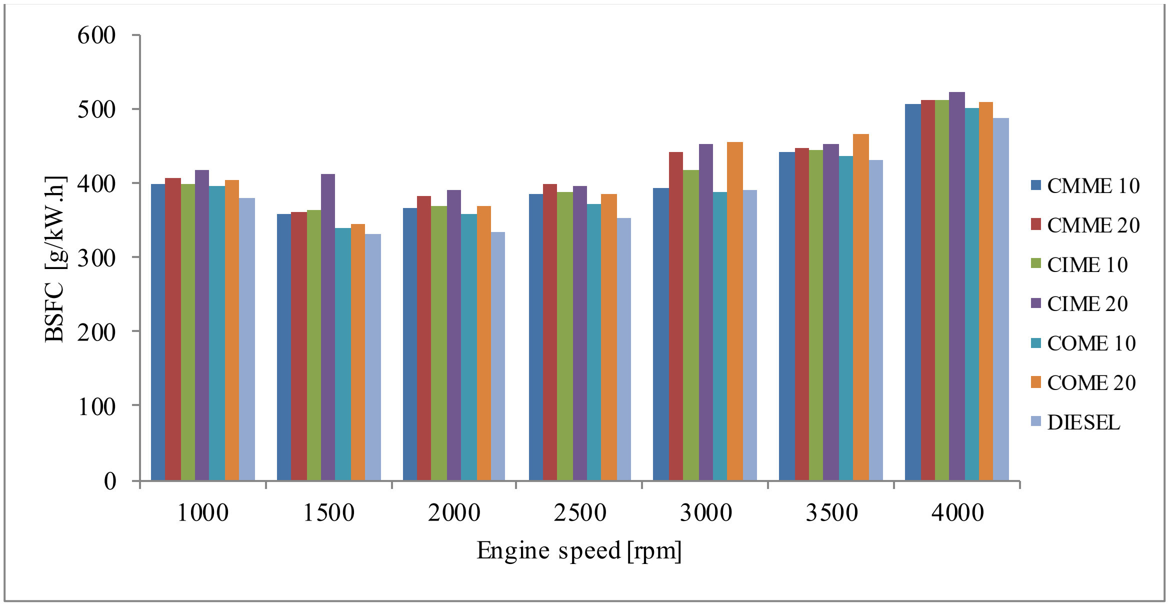


Figure 4.11: Variation of BSFC at different engine speeds and full load condition

4.8 Emissions analysis

4.8.1 CO emission

Carbon monoxide (CO) is a toxic gas formed due to the incomplete combustion of any fuel which does not contain oxygen. Several factors such as engine speed, air-fuel ratio, injection pressure, injection timing and type of fuel used have an effect on CO emission (Gumus et al., 2012). Figure 4.12 shows the variation of CO emissions of diesel (B_0), B_{10} and B_{20} at different engine speeds and full load condition. Over the entire range of speeds, the fuel samples $CMME_{10}$, $CMME_{20}$, $CIME_{10}$, $CIME_{20}$, $COME_{10}$ and $COME_{20}$ give an average reduction of CO emission by 8.89%, 29.04%, 16.81%, 34.49%, 15.44% and 34.72% than B_0 fuel. These results are supported by literature such as (Hirkude & Padalkar, 2012; Kim & Choi, 2010; Lapuerta et al., 2008; Nabi et al., 2009). This is due to the higher oxygen content (10-12% higher oxygen than diesel fuel) of biodiesel which resulted in complete combustion. Therefore, 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. Moreover, low aromatics in the blends may be an additional reason for reducing CO emission.

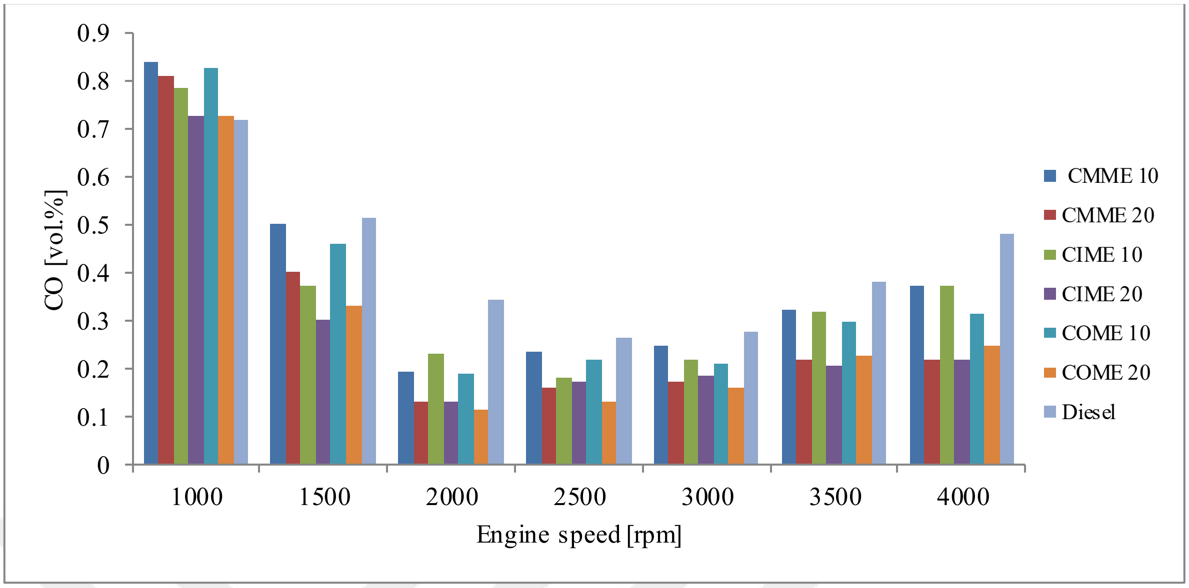


Figure 4.12: Variation of CO emissions at different engine speeds and full load condition

4.8.2 HC emission

Unburned hydrocarbons (HC) are mainly resulted from the incomplete combustion of fuel and the flame quenching in crevice regions and at cylinder walls (Mofijur et al., 2013). Figure 4.13 shows the variation of HC emission values of diesel (B_0), B_{10} and B_{20} at different engine speeds and full load condition. It is evident that unburned hydrocarbons for biodiesel-diesel blends are lower than that of diesel. Over the entire range of speed, the average reductions in HC emission for $CMME_{10}$, $CMME_{20}$, $CIME_{10}$, $CIME_{20}$, $COME_{10}$ and $COME_{20}$ compared to diesel fuel are 3.89%, 11.68%, 5.19%, 19.48%, 3.89% and 15.58% respectively. It can be also seen that HC emissions are reduced as the percentage of biodiesel in the blends increases. This can be attributed to the higher oxygen content and lower carbon and hydrogen of biodiesel than diesel which resulted in a complete combustion (B.-F. Lin et al., 2009; Qi, Chen, Geng, Bian, et al., 2010).

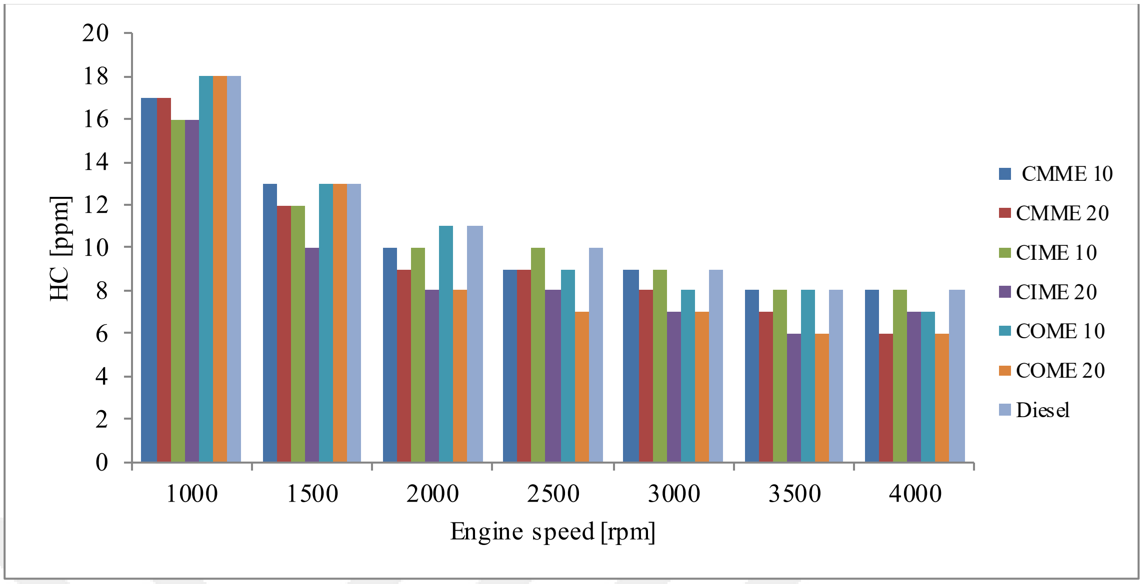


Figure 4.13: Variation of HC emissions at different engine speeds and full load condition

4.8.3 NO emission

Figure 4.14 shows the variation of NO emission of diesel and biodiesel-diesel blends. It is seen that the NO values are little bit higher when $CMME_{10}$, $CMME_{20}$, $COME_{10}$ and $COME_{20}$ are used. Same observation was observed in literature such as (El-Kasaby & Nemit-allah, 2013). In contrary, using *Calophyllum inophyllum* biodiesel blends has resulted in lower NO emission. Same observation was reported by (Sahoo et al., 2007). Over the entire range of speed, the average increase in NO emission for $CMME_{10}$, $CMME_{20}$, $COME_{10}$ and $COME_{20}$ compared to diesel are 7.31%, 8.06%, 1.55% and 6.16% respectively. This can be attributed to the lean air/fuel ratio, as biodiesel is an oxygenated fuel and contains 11-12% more oxygen in its molecular structure which causes higher chamber temperature by improving combustion at warmed-up condition (Devan & Mahalakshmi, 2009b). Adiabatic flame temperature can be also considered as another reason of increasing NO/NO_x. Biodiesel fuel contains higher percentages of unsaturated fatty acids that have higher adiabatic flame temperature which causes higher NO/NO_x

emission (El-Kasaby & Nemit-allah, 2013). The average NO emissions for $CIME_{10}$ and $CIME_{20}$ blends were 0.54% and 1.49% lower than diesel fuel. This may be due to the lower combustion chamber temperatures using *Calophyllum* biodiesel as was observed by (Sahoo et al., 2007).

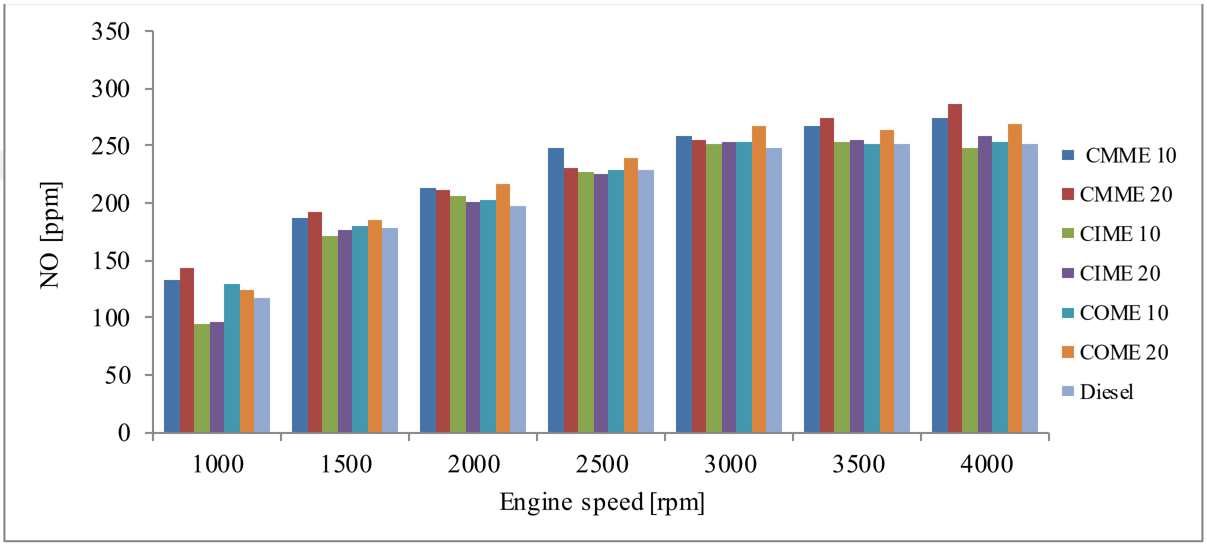


Figure 4.14: Variation of NO emissions at different engine speeds and full load condition

4.9 Summary of engine performance and emissions analysis

Table 4.11 gives a summary of engine performance and emissions of *Croton megalocarpus* (non-edible), Coconut (edible) and *Calophyllum inophyllum* (non-edible) methyl esters relative to diesel and possible causes. It can be seen that all biodiesel-diesel blends have lower torque, brake power, CO and HC and higher BSFC. However, *Croton megalocarpus* (non-edible), Coconut (edible) have higher NO while *Calophyllum inophyllum* (non-edible) has lower NO compared to diesel.

Table 4.11 Summary of engine performance and emissions test of biodiesel-diesel blends of CMME, CIME and COME (B10 and B20) relative to diesel

	CMME 10	**CMMW20**	**CIME10**	**CIME20**	**COME10**	**COME20**	**Possible causes**
Engine performance							
Torque	-4.05%	-5.95%	-5.04%	-6.77%	-2.7%	-4.84%	(1) Lower calorific value of biodiesel (2) higher viscosity and density of biodiesel
BP	-3.94%	-5.95%	-5.06%	-6.85%	-2.43%	-4.88%	(1) lower heating value of biodiesel (2) higher viscosity of biodiesel
BSFC	+5.3%	+8.9%	+6.85%	+12.33%	+2.99%	+8.31%	(1) higher density of biodiesel (2)lower energy content of biodiesel
Emissions analysis							
CO	-8.89%	-29.04%	-16.81%	-34.49%	-15.44%	-34.72%	(1) higher oxygen content of biodiesel
HC	-3.89%	-11.68%	-5.19%	-19.48%	-3.89%	-15.58%	(2) lower carbon and hydrogen of biodiesel
NO	+7.31%	+8.06%	-0.54%	-1.55%	+1.55%	+6.16%	For CMME and COME (1) the lean air/fuel ratio, as biodiesel is an oxygenated fuel which causes higher chamber temperature by improving combustion at warmed-up condition (2) Adiabatic flame temperature can be also considered as another reason of increasing NO/NOx. Biodiesel fuel contains higher percentages of unsaturated fatty acids that have higher adiabatic flame temperature which causes higher NO/NOx emission For CIME (1) Lower combustion chamber temperatures using CIME.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Biodiesel has attracted attention as a viable renewable energy source due to its lower greenhouse gas emission and its potential to reduce dependence on imported fossil fuels as well as meet the global energy demand. Traditionally, biodiesel has been produced from edible oils due to their low free fatty acids. However, their use has elevated some issues such as food versus fuel and many other problems that have negatively affected their economic viability. Therefore, exploration of non-edible oils may significantly reduce the cost of biodiesel especially in poor countries which can barely afford the high cost of edible oils.

This research aims to produce biodiesel from some potential edible and non-edible feedstocks. These oils include; crude *Calophyllum inophyllum* L. (CCIO), *Jatropha curcas* L. (CJCO), *Sterculia foetida* L. (CSFO), *Croton megalocarpus* L. (CCMO), *Moringa oleifera* L. (CMOO), *Patchouli* (CPO), Coconut (CCO), Palm (CPaO), Canola (CCaO), Soybean (CSO), Manketti (CMO) and *Pangium edule* (CPEO) oils. Several physical and chemical properties of the crude oils and their respective methyl esters such as kinematic viscosity, density, calorific value, acid value, flash point, cold filter plugging point, viscosity index and oxidation stability were determined and compared with the existing literature.

This research also discusses the concept of biodiesel-biodiesel and biodiesel-diesel blending to improve some properties such as kinematic viscosity, cloud, pour and cold filter plugging point. Moreover, the effect of biodiesel-diesel blends of 10% and 20% (by volume) of coconut, *Calophyllum inophyllum* and *Croton megalocarpus* methyl esters on engine performance and emissions was evaluated in a multi-cylinder Mitsubishi Pajero turbocharged diesel engine.

Based on the experimental study and the main findings of this research, the following conclusions can be drawn:

(1) The findings of physical and chemical properties of crude oils show that CMO possess the highest kinematic viscosity of 132.75 mm²/s at 40 °C. CCMO has the best viscosity index of 224.2. CPaO possesses the lowest CFPP and highest refractive index and calorific value of 1 °C, 1.5069 and 42,986 kJ/kg respectively. CCaO possesses the highest flash point of 290.5 °C while CPO possesses the lowest flash point of 146.5 °C. CMOO have the best oxidation stability of 41.75 h compared to 0.08 h only of CPaO. CSFO possesses the highest CFPP point of 29 °C. CCIO possesses the highest acid value of 41.74 mgKOH/g. Finally, it was found that CCO possesses the highest transmission of 91.2%.

(2) The findings of physical and chemical properties of biodiesels show that (CoME) possesses the lowest kinematic viscosity of 3.1435 mm^2/s followed by CMME of 4.0707 mm^2/s. While MME possesses the highest kinematic viscosity of 8.3425

mm^2/s). PME possesses the highest oxidation stability of 23.56 h followed by MOME of 12.64 h, while PaME possesses the lowest oxidation stability of only 0.022 h. PaME possesses the highest calorific value of 44,180 kJ/kg followed by CME of 40,195 kJ/kg. However, CoME has the lowest calorific value of 38,300 kJ/kg. PME has the highest flash point of 214.5 °C followed by SME 202.5 °C while CoME and PaME have the lowest flash point of 118.5 °C.

(3) Biodiesel-biodiesel blending has resulted in remarkable improvement in some properties such as kinematic viscosity, cloud point, pour point and cold filter plugging point. For instance, blending of SFME and CoME improves the viscosity of SFME from 6.3717 mm^2/s to 5.3349 mm^2/s (3:1), 4.4912 mm^2/s (1:1) and 3.879 mm^2/s (1:3). It was also found that blending has improved the cold flow properties of PME, CIME and JCME respectively.

(4) Blending of SFME with diesel resulted in an improvement in kinematic viscosity from 6.3717 mm^2/s (B_{100}) to 6.0548 mm^2/s (B_{75}) and 5.4007 mm^2/s (B_{50}) and 4.9574mm^2/s (B_{25}). Moreover, blending improved the viscosity index of diesel from 120.2 to 133.7 (B_{25}) to 144.2 (B_{50}) and 149.8 (B_{75}). Moreover, blending of PEME of MME with diesel improves remarkably kinematic viscosity, density, oxidation stability and calorific value of PEME and MME. However, viscosity index and flash point dropped as the percentage of diesel increases in the blends.

(5) Over the entire range of speed, B_{10} and B_{20} of CMME, CIME and COME give average reduction in torque, brake power (BP) and increased brake specific fuel

consumption (BSFC) compared to B_0. In case of engine emission, the fuel blends give an average reduction in carbon monoxide (CO) and hydrocarbon (HC) emissions. However, CMME and COME blends increased nitrous oxides (NO) emission while CIME emits lower NO compared to B_0.

5.2 Recommendations

Based on the conclusion, the following recommendations can be drawn:

(1) Optimization of biodiesel production from *Pangium edule*, *Patchouli* as promising biodiesel feedstocks using response surface methodology (RSM) should be considered in the future studies.

(2) Engine performance using additives to improve engine performance and emission of these feedstocks should be considered.

(3) Several non-technical limiting factors of biodiesel production cost from these feedstocks such as feedstock price and production cost should be considered by conducting a techno-economic, sensitivity analysis and life cycle cost (LCC).

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APPENDIX A

SAMPLE OF CALCULATIONS OF SAPONIFICATION NUMBER, IODINE VALUE AND CETANE NUMBER OF PME

The saponification numbers (SN), iodine value (IV) and cetane number (CN) of PME were calculated empirically with the help of the following equation:

$$SN = SUM\left(\frac{560 \times A_i}{MW_i}\right)$$

$$IV = SUM\left(\frac{254 \times D \times A_i}{MW_i}\right)$$

$$CN = \left(46.3 + \left(\frac{5458}{SN}\right) - (0.225 \times IV)\right)$$

The following table shows the detailed calculations of SN and IV.

Structure	Name of fatty acid	Formula	MW	D	A	SN	IV
C6:0	Caproic	$C_6H_{12}O_2$	116.15828	0	0	0	0
C8:0	Caprylic	$C_8H_{16}O_2$	144.21144	0	0	0	0
C10:0	Capric	$C_{10}H_{20}O_2$	172.2646	0	0	0	0
C12:0	Lauric	$C_{12}H_{24}O_2$	200.31776	0	0.2	0.559	0
C14:0	Myristic	$C_{14}H_{28}O_2$	228.37092	0	0.9	2.2069	0
C16:0	Palmitic	$C_{16}H_{32}O_2$	256.42408	0	38.6	84.297	0
C16:1	Palmitoliec	$C_{16}H_{30}O_2$	254.4082	1	0.2	0.440	0.199
C17:0	Margaric	$C_{17}H_{34}O_2$	270.45066	0	0	0	0
C18:0	Stearic	$C_{18}H_{36}O_2$	284.47724	0	4.4	8.661	0
C18:1	Oleic	$C_{18}H_{34}O_2$	282.46136	1	44.6	88.422	40.106
C18:2	Linoleic	$C_{18}H_{32}O_2$	280.44548	2	10.5	20.966	19.019
C18:3	Linolenic	$C_{18}H_{30}O_2$	278.4296	3	0.2	0.402	0.547
C20:0	Arachidic	$C_{20}H_{40}O_2$	312.5304	0	0.4	0.716	0
C20:1	Eicosenoic	$C_{20}H_{38}O_2$	310.51452	1	0	0	0
C20:2	Eicosadienoic acid	$C_{20}H_{36}O_2$	308.49864	2	0	0	0
C22:0	Behenic	$C_{22}H_{44}O_2$	340.58356	0	0	0	0
C22:1	Erucle	$C_{22}H_{42}O_2$	338.56768	1	0	0	0
C24:0	Lignoceric	$C_{24}H_{48}O_2$	368.63672	0	0	0	0
C24:1	Nervonic	$C_{24}H_{46}O_2$	366.62084	1	0	0	0
		Total Sum				**206.674**	**59.873**

SN= **206.675**

IV=**59.8728**

$$CN = \left(46.3 + \left(\frac{5458}{206.674}\right) - \ (0.225\ \times 59.8728)\right) = \underline{\mathbf{59.237}}$$

APPENDIX B

SAMPLE OF CALCULATIONS FOR THE PREDICTION OF VISCOSITY OF PME AND SFME BLENDS

From **Figure 4.1(a)** and based on **Equation 4.1** in section **4.5.1**, it can be seen that the viscosity of PME and SFME blends can be predicted using the following equation:

Viscosity (SFME-PME) = $-0.5159x^2 - 1.1195x + 6.3599$ $0 \leq x \geq 100$ (x=%PME)

($R^2 = 0.9908$)

Therefore, the predicted viscosity of (75%PME and 25%SFME) [x(75%)] and (25%PME and 75%SFME) [x(25%)] biodiesels blend can be estimated based on the above equation as follow:

x(75%) = **-0.5159*(75%^)^2 - 1.1195*(75%) + 6.3599 = <u>5.2301 mm^2/s</u>**

x(25%) = **-0.5159* (25%^)^2 - 1.1195*(25%) + 6.3599 = <u>6.0478 mm^2/s</u>**

Based on Equation 3.6, the percentage error of the viscosity of PME and SFME can be calculated as follow:

$$Percentage\ Error\ (x75\%) = \frac{|5.2301 - 5.3254|}{|5.3254|} \times 100 \qquad = \underline{\mathbf{1.7895\%}}$$

$$Percentage\ Error\ (x25\%) = \frac{|6.0478 - 6.0482|}{|6.0482|} \times 100 \qquad = \underline{\mathbf{0.0066\%}}$$

The following table shows the calculation of percentage error of kinematic viscosity for all PME-SFME blends.

Blends	**Predicted KV (mm^2/s)**	**Percentage Error**
75% SFME 25% PME	6.0478	0.0066%
50% SFME 50% PME	5.6712	1.2805%
25% SFME 75% PME	5.2301	1.7895%
75% SFME 25% CoME	5.3757	0.7648%
50% SFME 50% CoME	4.5249	0.7504%
25% SFME 75% CoME	3.7933	2.2093%

APPENDIX C

LIST OF PUBLICATIONS

(1) **Atabani, A.E.,** Mahlia, T.M.I., Masjuki, H.H., Irfan Anjum Badruddin, Hafizuddin Wan Yussof, Chong, W.T., & Lee., K.T. (2013). A comparative evaluation of physical and chemical properties of biodiesel synthesized from edible and non-edible oils and study on the effect of biodiesel blending. Energy, 58(September), 296-304.

(2) **Atabani, A.E.,** Mahlia, T.M.I., Badruddin, I.A., Masjuki, H.H., Chong, W.T., & Teong, L. K. (2013). Investigation of physical and chemical properties of potential edible and non-edible feedstocks for biodiesel production, a comparative analysis. Renewable and Sustainable Energy Reviews, 21(May), 749-755.

(3) **Atabani, A.E.,** Silitonga, A.S., Irfan Anjum Badruddin, Mahlia, T.M.I., Masjuki, H.H., & Mekhilef, S. (2012). A comprehensive review on biodiesel as an alternative energy resource and its characteristics. Renewable and Sustainable Energy Reviews, 16(4), 2070-2093.

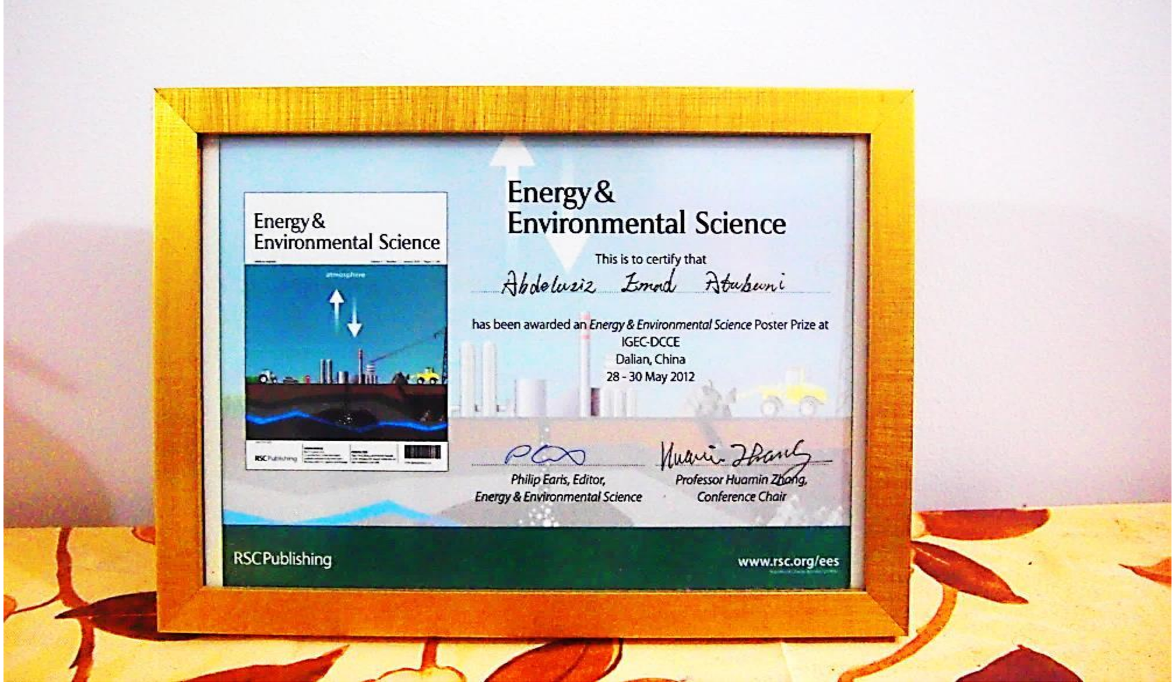
(4) **Atabani, A.E.,** Silitonga, A.S., Ong, H.C., Mahlia, T.M.I., Masjuki, H.H., Irfan Anjum Badruddin, & Fayaz, H. (2013). Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. Renewable and Sustainable Energy Reviews, 18(February), 211-245.

(5) **Atabani**, A.E., Irfan Anjum Badruddin, Mahlia, T.M.I., Masjuki, H.H., Mofijur, M., Lee, K.T., Chong, W.T. (2013). Fuel Properties of Croton megalocarpus, Calophyllum inophyllum, and Cocos nucifera (coconut) Methyl Esters and their Performance in a Multicylinder Diesel Engine. Energy Technology 1 (11), 685-694.

APPENDIX D

PRIZE

EES (Energy Environmental Science) Best Poster Prize, 7th International Green Energy & 1st DNL Conference on Clean Energy (IGEC-DCCE), Dalian-China May 2012.



Energy &
Environmental Science

This is to certify that

Abdelaziz Emad Atabani

has been awarded an *Energy & Environmental Science* Poster Prize at
IGEC-DCCE
Dalian, China
28 - 30 May 2012

Huamin Zhang

Philip Earis, Editor,
Energy & Environmental Science

Professor Huamin Zhang,
Conference Chair

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