EFFECTS OF INJECTION PARAMETERS ON PERFORMANCE OF DIESEL ENGINE RUN ON BIODIESEL FROM DIRECT TRANSESTERIFICATION

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ABSTRACT

It is well-known that energy consumption is rapidly increasing due to the population growth, higher standard of living and increased production. Significant amount of energy resources are being consumed by the transportation sector leading to the fast depletion of fossil fuels and environmental pollution. Biodiesel is one of the technically and economically feasible options to tackle the aforesaid problems.

There are more than 350 oil-bearing crops identified as potential sources for biodiesel production around the globe. The wide range of available feedstocks for biodiesel production represents one of the most significant factors for producing biodiesel. The research work is carried out on fuel properties of biodiesel prepared from the non-edible oils of *Nigella sativa*. *Nigella sativa* is believed to be investigated for the first time as a biodiesel feedstock.

Biodiesel seems to be a replacement to the diesel, can be commonly produced by esterification-transesterification. In the current research a new method i.e. direct transesterification is developed and compared it with conventional esterification-transesterification. The fuel properties of biodiesel produced by both methods are investigated and compared. Though there are no significant differences in the fuel properties obtained from either of the methods but the acid value of biodiesel and reaction time reduced significantly besides improved biodiesel yield by direct transesterification method.

The direct transesterification method was further improved to modified direct transesterification method for minimizing the time required for biodiesel separation from glycerol and blending of diesel and biodiesel.

Today’s automobiles require economy of operation, high power output and last but not the least, reduction in greenhouse gases emitted by the vehicles. Such specific demands have compelled the researchers not only to focus on the parameters affecting the performance but also on emission of the internal combustion engines. The current research has been focused and optimized the injection timing of 27^0BTDC and injection pressure of 240bar for selected diesel engine for the maximum possible efficiency and lower exhaust emissions for an internal combustion diesel engine run on biodiesel fuels.

ABSTRAK

Ia terkenal bahawa penggunaan tenaga semakin meningkat dengan pesat disebabkan oleh pertumbuhan penduduk, standard hidup yang lebih tinggi dan peningkatan pengeluaran. jumlah besar sumber tenaga yang digunakan oleh sektor pengangkutan yang membawa kepada kekurangan puasa bahan api fosil dan pencemaran alam sekitar. Biodiesel adalah salah satu teknikal dan ekonomi pilihan yang boleh dilaksanakan untuk menangani masalah tersebut di atas.

Terdapat lebih daripada 350 tanaman yang mengeluarkan minyak yang dikenal pasti sebagai sumber berpotensi untuk pengeluaran biodiesel di seluruh dunia. Pelbagai stok suapan didapati untuk pengeluaran biodiesel merupakan salah satu faktor yang paling penting untuk menghasilkan biodiesel. Kerja-kerja penyelidikan dijalankan ke atas hartanah bahan api biodiesel disediakan daripada minyak bukan makan Nigella sativa. Nigella sativa dipercayai disiasat buat kali pertama sebagai bahan mentah biodiesel.

Biodiesel seolah-olah menjadi gantian kepada diesel, boleh biasanya dihasilkan oleh pengesteran-transesterification. Dalam kajian semasa satu kaedah baru iaitu transesterification terus dibangunkan dan berbanding dengan konvensional pengesteran-transesterification. Sifat-sifat bahan api biodiesel yang dihasilkan oleh kedua-dua kaedah dikaji dan dibandingkan. Walaupun terdapat perbezaan yang signifikan dalam sifat-sifat bahan api yang diperolehi daripada salah satu daripada kaedah tetapi nilai asid biodiesel dan masa tindak balas berkurangan selain hasil biodiesel diperbaiki dengan kaedah transesterification langsung.

kaedah transesterification langsung telah dipertingkatkan lagi kepada kaedah transesterification langsung diubahsuai untuk mengurangkan masa yang diperlukan untuk pemisahan biodiesel daripada gliserol dan campuran diesel dan biodiesel.

kereta hari ini memerlukan ekonomi operasi, output kuasa tinggi dan terakhir tetapi bukan-kurangnya, pengurangan gas rumah hijau yang dikeluarkan oleh kenderaan. permintaan khusus itu telah memaksa penyelidik bukan sahaja memberi tumpuan kepada parameter menjejaskan prestasi tetapi juga pelepasan enjin pembakaran dalaman. Penyelidikan semasa telah memberi tumpuan dan dioptimumkan masa suntikan di 27^0BTDC dan tekanan suntikan 240bar untuk enjin diesel dipilih untuk kecekapan maksimum dan pelepasan ekzos yang lebih rendah untuk dalaman pembakaran diesel jangka enjin kepada bahan api biodiesel.

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NOMENCLATURE (ABBREVATIONS)

B10	Mixture of 10% biodiesel and 90% diesel
BTDC	Before top dead center
CFPP	Cold flow plug point
CO	Carbon monoxide
CP	Cloud point
CCPO	Crude ceiba pentandra oil
CNSO	Crude nigella sativa oil
CPB10	Mixture 10% of ceiba pentandra biodiesel and 90% of diesel by volume
CPME	Ceiba pentandra methyl ester
CIME	Calophyllum inophyllum methyl ester
CPME+NSME	Methyl ester prepared from the mixture of two crude oils
DT	Direct Transesterification
ET	Esterification-Transesterification
HC	Hydro carbon
JCME	Jatropha Curacus methyl ester
MDT	Modified Direct Transesterification
NSB10	Mixture 10% of nigella sativa biodiesel and 90% of diesel by volume
NSME	Nigella sativa methyl ester
NOx	Oxides of nitrogen
PP	Pour point
PPME	Pongamia pinnata methyl ester

CHAPTER 1: INTRODUCTION

1.1 Overview

Energy is most important requirement to lead a quality life. It is the most important input in all sectors of modern economies. Meeting the growing demand for energy sustainability is one of the major challenges of the twenty-first century for any nation across the globe. The increasing demand for energy around the world has grown exponentially and resulted in more fossil fuel consumption and more concentration of greenhouse gases which all have disastrous consequences for the earth's climate like rising temperature, drought, floods, famine and economic chaos (Mahlia, 2002). Oil is still the dominant source of energy around the world followed by coal and natural gas. It is anticipated that, the reserves of fossil fuels will no longer be available after few centuries. For instance coal is expected last for another 218 years, oil for 41 years and natural gas for 63 years under current scenario. The transportation sector is one of the major consumers of fossil fuels. Nearly one-third of nation's energy is now used for transportation (Agarwal, 2007). Diesel and gasoline engines are the backbone of the transportation sector today. Diesel engines are superior to gasoline engines in terms of thermal efficiency, fuel consumption and throttling losses. Furthermore, in terms of emissions diesel engines are not inferior to the gasoline engines as far as carbon monoxide is concerned. However, the fast depleting fossil fuels and formation of oxides of nitrogen deserve the attention. Hence, many of the researchers are now focusing on the domain of alternative fuels of renewability in nature. Biodiesel could be the potential source of fuel for internal combustion engines towards the reduction of emissions and dependency on the petroleum diesel (Agarwal, 2007; Demirbas, 2003;

Graboski & McCormick, 1998; Rakopoulos et al., 2006). It has been reported that a considerable amount of biodiesel is produced by edible oils (Brown, 1980). The extensive use of edible oils for biodiesel purpose might lead to negative impacts such as starvation and higher food prices in the developing countries (Balat, 2011). In Malaysia the biodiesel refineries have created shortages in the palm oil. Therefore, the price of palm oil for cooking has risen by 70% (Tenenbaum, 2008). The rising food prices may be beneficial to the poor farm producers but at the same time it is unlikely to benefit the urban poor (Thompson, 2012). Some researchers pointed out that developing the technology to convert cellulosic materials into biofuels will significantly reduce the food shortage problems (Ugarte & He, 2007). In addition to this the waste edible oil may be made primary feedstock and the fresh edible and non-edible oils should be made supplement feedstocks. This may reduce the food shortages significantly (Gui et al., 2008). Hence, the recent years have seen huge focus to find the non-edible oil feedstocks for biodiesel production (Chhetri et al, 2008).

It is widely accepted that biodiesel has emerged as a promising alternative fuel for internal combustion engines due to its comparable properties with that of fossil fuels but today's automobiles demand has been for economy of operation, high power output and last but not the least reduction in greenhouse gases emitted by the vehicle. These specific demands have forced the researchers to focus on the parameters affecting the engine performance and emissions of the internal combustion engines. The performance of internal combustion engine with biodiesel or with its blends depends mainly on the engine variables such as compression ratio, load and speed, fuel injection parameters and air turbulence (Fazal et al., 2011).

1.2 Research background

It is a known fact that the energy consumption has been on continuous rise over the years worldwide. There are many reasons for the stated problem. However, the main reasons are the population growth, increased standard of living of society and substantial increase in production of goods. From an energy consumption point of view, transportation sector is the major consumer of energy resources. The consumption of these energy resources has not only led to fast depletion of fossil fuels but also increased the harmful emissions leading to the atmospheric pollution. Many of the researchers have opined that biodiesel could be a potential alternate fuel to diesel and furthermore they have found biodiesel to be compatible on technical and economical grounds to tackle the aforesaid problems (Khan et al, 2014).

Today, edible oils are being used as the feedstocks for the production of biodiesel. It is not desirable to use since large scale consumption of edible oils is leading to the price rise and shortage of food supplies. This is a serious issue for the developing countries. Hence the focus is to look into different non-edible feedstocks for biodiesel production. Moreover, it is well known that the non-edible feedstocks could be the potential resources due to their favourable fuel properties, better performance and lower emissions.

The high viscosity, low volatility and polyunsaturated characteristics of vegetable oils make them unsuitable to be used in diesel engines. These problems could be solved to an extent by methods like pyrolysis, dilution (direct blending), Micro-emulsion, and transesterification. However, owing to the limitations of the conventional methods new technologies are starting to be developed (Khan et al., 2014).

In recent years the automotive electronics control system has advanced drastically. The primary motivation is the need to meet strict legislative exhaust emission norms imposed by different countries, provide lower fuel consumption and the most important point is to meet customer’s quality and efficient engine expectations. All of these requirements could be achieved by enabling the electronic fuel control system to a large extent especially emissions and fuel economy goals. Tomorrow’s automotive engines will feature Electronic Throttle Control (ETC), lean burn strategies, variable valve timing, variable swirl system, flexible high pressure injection system, controlled charge flow, dynamic supercharging, cam less engines, improved combustion etc. (Knecht, 2008).

1.3 Problem Statement

Biodiesel has been emerged as an alternative fuel for internal combustion engines because of its renewability and environmental friendly nature (Amani et al., 2013). Apart from these advantages biodiesel can be used in the existing compression ignition internal combustion engine without any further modifications (Canakci, 2007; Gerpen, 2005). The feedstocks for biodiesel can be broadly divided into three categories i.e. vegetable oils (edible and non-edible), animal fats and waste cooking oils (Karmakar et al., 2010). However, the attention is primarily focused towards biodiesel from non-edible feedstocks due to the food-fuel crisis and land availability problems (Atabani et al., 2013c; Bouriazos et al., 2014; Chen & Madhu, 2013; Elsheikh, 2013). In this scenario of necessity of biodiesel, one cannot oversee the wishes of manufacturer and customer, who expect highly efficient engine with lowest fuel consumption possible besides lower emissions. Thus there is a need to further explore the new sources of biodiesel to cater the ever increasing demand of energy and also to improve the presently available methods to extract biodiesel.

1.4 Objectives

Having recognized the importance of utilizing renewable energy resource, this dissertation will exhibit the way to promote biodiesel as one of the leading renewable energy sources. This research aims to achieve the following objectives:

(a) Identification and selection of promising potential oil bearing non-edible plants for biodiesel production.

(b) Development of new methods (Direct transesterification method and Modified Direct transesterification method) for biodiesel production and comparing them with conventional methods.

(c) Effects of injection parameters on performance of a biodiesel fuelled engine.

1.5 Scope of Study

Biodiesel, in particular has emerged as an alternative to fossil fuel with its reduced emissions and comparable fuel properties. Owing to fuel or food crisis, the current study is focussed on identifying the oil bearing non-edible feedstocks for biodiesel. *Nigella sativa and ceiba pentandra* could be the potential non-edible resources.

To minimize the reaction and blending time for biodiesel production, direct transesterification and modified direct transesterification methods have been developed.

The engine manufacturers and consumers wish to have a high performance engine apart from lower emission. Therefore, this research focuses to develop a high performing engine with lower emission by optimizing the injection parameters such as injection timing and injection pressure.

1.6 Organization of dissertation

This dissertation is written into five chapters. The organization of the chapters is listed as follows:

Chapter 1 gives an overview of the research topic. It starts with giving an introduction to the importance of energy, increasing prices and expected depletion of fossil fuels, impact of consumption of edible oils on food commodities, importance of biofuels and suggests it as a solution for the current world energy crisis.

Chapter 2 gives an overview of open literature on of biodiesel as an emerging energy resource, food or fuel crisis, advantages and disadvantages of biodiesel, biodiesel feedstocks, biodiesel production technologies, biodiesel standards and characterization, properties and qualities of biodiesel.

Chapter 3 explains in detail the research methodology being adopted for current work.

Chapter 4 is dedicated to show all the results which have been obtained from the experimental work and present the findings of the study followed by a detailed discussion and analysis of these findings.

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

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter gives an overview biodiesel as an emerging energy resource, advantages and disadvantages of biodiesel, biodiesel feedstocks, non-edible vegetable resources, fatty acid composition, biodiesel production technologies, biodiesel standards and characterization, properties and qualities of biodiesel as well as engine performance and emissions production of some selected non-edible biodiesel.

2.2 International trends in food demand and supply

There are concerns, whether a growing population can be fed in a sustainable manner or not (Chen, 2007). When dwarfism was introduced in wheat and rice, yields were raised by 2-3% per year during two to three decades (Tilman et al., 2002). The development of innovative technologies resulted in both improved genetic traits and advanced crop management. Despite these trends a decline of rice yields from 1985 onwards has been reported for the Indo-Gangetic Plains in India (Pathak et al., 2003). In spite of these variations in the yield of different crops still there is a gap between the growth of production and demand of supply. There may be other factors but the demand of edible feedstocks for the biofuel cannot be ruled out.

2.3 Food for poor or fuel for rich-A debate

There are many factors which cause the increase in food commodity prices (Tyner, 2013). It is difficult or impossible to separate out what are the different reasons which are responsible for the increase of commodity price rise other than biofuels. As far as biofuels are concerned, it is argued that one must distinguish between biofuels driven by market forces and biofuels driven by government policy (Tyner, 2010). However, it is accepted globally that biofuels produced from edible feedstocks cannot replace the petroleum fuels without impacting food supplies (Srinivasan, 2009).

2.4 Effects of elevated food prices on poverty

It has been reported by many researchers and non-governmental organizations that higher food commodity prices adversely affect the poor in general and urban poor in particular. The urban poor in many countries spend a much higher percentage of their income on food (Chakravorty et al., 2009; Ivanic & Will, 2008). The reason for their argument is the production of biofuels. It is therefore, for the researchers and scientists that the challenge is to produce enough food for people and biofuel in an environmentally sound manner.

2.5 Biodiesel

Biodiesel is a renewable and clean burning combustible fuel for diesel engines (Yusuf et al., 2011). It is nontoxic, biodegradable, and virtually free of aromatics and sulfur contents (Demirbas et al., 2009). This is because its primary components are domestic renewable resources such as vegetable oil and animal fats consisting of long-chain alkyl (methyl, ethyl, or propyl) esters (Ma & Hanna, 1999). Biodiesel is the mono-alkyl esters of fatty acids that result from animal fats or vegetable oils (Krawczyk, 1996). In other words, biodiesel (fatty acid ester) is the end result of the chemical reaction caused by mixing vegetable oil or animal fat with an alcohol such as methanol. Together these ingredients produce a compound recognized as a fatty acid alkyl ester. A catalyst such as sodium hydroxide is also necessary in order for the biodiesel to be considered as finished product, and is added with the new compounds to create biodiesel fuel.

Biodiesel offers many advantages such as (Basha & Raja, 2012; Borges & Diaz, 2012; Fazal et al., 2011; Mekhilef et al., 2011; Mofijur et al., 2012):

- Renewable in nature and energy efficient.
- Used in most of the diesel engines without or negligible modifications.
- Non-poisonous, biodegradable and suitable for sensitive environments.
- A fuel for diesel engines having high flash point, positive energy balance and minimised harmful emissions.

However, there are few drawbacks which should be listed down: (Murugesan et al., 2009; Shahid & Jamal, 2011)

- Biodiesel has 12% lower energy content than diesel.
- Due to the high oxygen content in biodiesel, it produces relatively higher $NO_{x.}$
- Biodiesel can cause corrosion in vehicle material.

2.6 Production technologies

The high viscosity, low volatility and polyunsaturated characteristics of vegetable oils make them unsuitable to be used in diesel engines. These problems could be solved to an extent by methods like pyrolysis, dilution (direct blending), Micro-emulsion, and transesterification. Dilution and micro-emulsion processes are not preferred due to higher viscosity and bad volatility though they are simple (Lin et al., 2011).Pyrolysis process is found to be simple, waste less and environmental friendly (Singh & Dipti, 2010). However, transesterification process is commonly used for the production of biodiesel. Transesterification is the reaction of a fat or oil with an alcohol commonly methanol to form their methyl esters and glycerol. To improve the reaction rate and yield usually sodium hydroxide or potassium hydroxide is used as catalyst. Figure 2.1 shows the different processes employed for biodiesel production.

Generally, the transesterification processes can be classified into two types depending upon the catalyst used. They are catalytic and non-catalytic transesterification. Transesterification reaction can be catalyzed by both homogeneous (alkalis and acids) and heterogeneous catalysts. Homogeneous catalysts are better in performance when the free fatty acid content in the crude oil is <1% (Karmakar et al., 2010). The expensive separation of catalyst from the mixture and formation of the unwanted by product (soap) are the limitations of the homogenous catalyst (Sharma & Singh, 2009a).

The performance of heterogeneous catalysts is found better for the transesterification reaction of vegetable oils when their free fatty acid (FFA) content is >1%. The separation of catalyst from the reaction products is easier than the homogenous catalysts. However, for the transesterification process for biodiesel production both the types of catalysts methods are found suitable (Ma & Hanna, 1999; Ranganathan et al., 2008).

In general, the use of catalyst increases the reaction rate of the transesterification and it also enhances the solubility of alcohol. When the acid value of feedstock is higher, a pre-treatment step known as esterification reaction is carried out. Basically it is an acid-catalyzed reaction and is used to reduce the higher acid value of the feedstocks. The reaction rate is relatively slower (Gerpen, 2005). A higher conversion could be achieved by increasing reaction temperature and the reaction time (Canakci & Gerpen, 1999; Meher et al., 2006).

Base-catalyzed reaction is faster than the acid-catalyzed reaction but the yield of biodiesel is lowered due to the formation of soap. In addition to this the separation of biodiesel form glycerol is quite difficult. However, it is observed that methoxide catalysts give higher yields than hydroxide catalysts (Shahid & Jamal, 2008).

The other methods such as supercritical processes, microwave and ultrasonic irradiation systems are also being used but to lesser extent. The conventional methods of transesterification with yield, reaction conditions employed for some non-edible oils are shown in table 2.1.

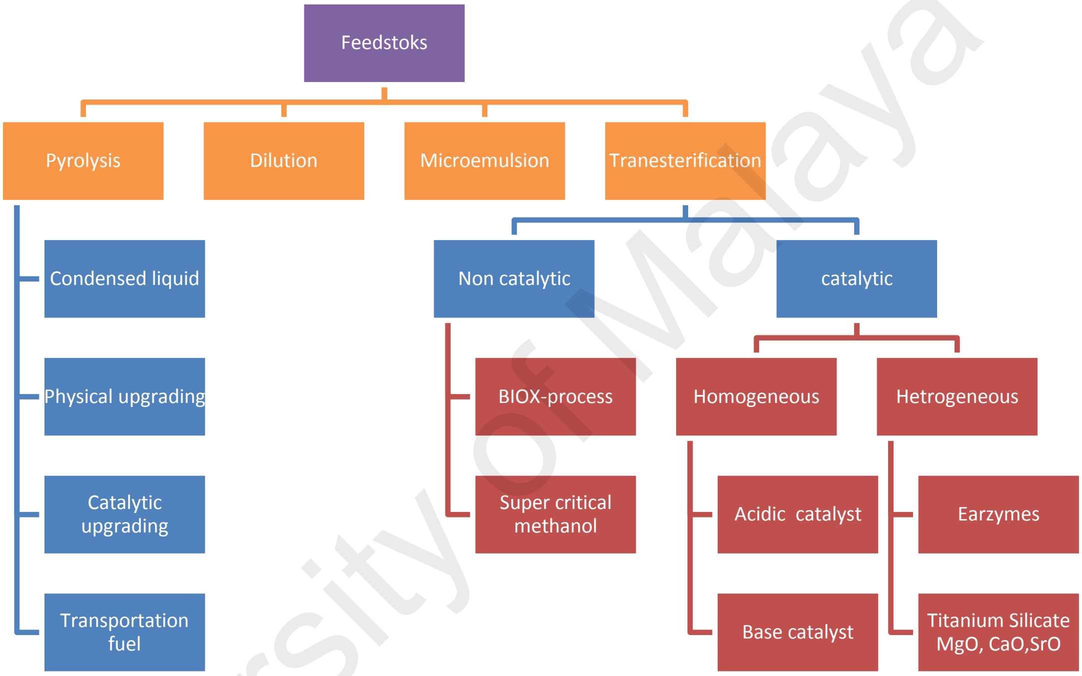


Figure 2.1: Various methods for biodiesel production (Atabani et al., 2012; Demirbas, 2011)

Table 2.1: Conventional methods available for biodiesel production

Transesterification method	Description (oil/acid/base catalyst)	Biodiesel yield %	Ref.
Homogeneous catalyzed (acids and base)	*Jatropha Curcas* oil Step 1:Esterification with 1% H_2SO_4 Step 2:Transesterification by 1% NaOH	90.1% at 6h reaction	(Jain & Sharma, 2010a; Jayed et al., 2009)
	Karanja oil Step 1:Esterification with 1.5% H_2SO_4 Step 2:Transesterification by 0.8% NaOH, 1% CH_3ONa and 1% KOH	90-95% at 2h reaction	(Sharma et al., 2009b)
	Step 1:Esterification with 0.5% H_2SO_4 Step 2:Transesterification by 2% KOH	80-85% at 1.25h reaction	(Patil & Shuguang, 2009)
	Ceiba pentandra oil Step 1:Esterification with 1.834% H_2SO_4 Step 2:Transesterification by 1% KOH	99.5% at 1.75h reaction	(Sivakumar et al., 2013)
Heterogeneous catalyzed (alkalis and acids)	*Moringa oleifera* 3% sulphated tin oxide (acid catalyst) at 150^0C	84% at 2.5h reaction	(Kafuku et al., 2010)
	Jatropha Curcas oil 7.61% sulfated zirconia loaded on alumina(acid catalyst) at 150^0C	90.32% at 4h reaction	(Yee et al., 2011)
	Jatropha Curcas oil 2% CaO/Fe_3O_4 (base catalyst) at 70^0C	95% at 80min 99% at 4h reaction	(Liu et al., 2010)
	Jatropha Curcas oil 1% Mg-Al hydrotalcites (base catalyst) at 45^0C	95.2% at 1.5h reaction	(Deng et al., 2011)

Supercritical processes	*Jatropha Curcas* oil At temperature of 320 °C and pressure of 15 MPa	84.6% at 5min reaction	(Samniang et al., 2014)
	Krating oil At temperature of 260 °C and pressure of 16 MPa	90.4% at 10min reaction	(Samniang et al., 2014)
	Jatropha Curcas oil Step 1:sub-critical water treatment at temperature of 270 °C and pressure of27 MPa for 25 min Step 2:supercritical dimethyl carbonate treatment at temperature of 300 °C and pressure 9 MPa for 15 min	97% at 40min reaction	(Ilham & Shiro, 2010)
Microwave assisted transesterification	*Camelina sativa oil* 1.5% BaO as catalyst with 9:1 methanol oil ratio	94% at 4min reaction	(Patil et al., 2011)
	Rice bran oil 0.15-0.18% NaOH as catalyst at 80^0C reaction temperature	98.82 at 20min reaction	(Kanitkar et al., 2011)
	Pongamia pinnata 0.5% NaOH or 1.5% KOH as catalyst 60^0C reaction temperature	96% at 5min reaction	Kumar et al., 2011)
	Yellow horn oil 1% heteropolyacid (HPA) as catalyst at 60^0C reaction temperature	96.22% at 10min reaction	(Zhang et al., 2010)
	Castor oil 15% cesium phosphotungstate derived catalyst at 70^0C reaction temperature	90% at 4h reaction	(Yuan & Shu, 2013)

Ultrasonic irradiation systems	Tung oil 1% CH3OH and KOH as catalyst at 20-30^{0}C reaction temperature with ultrasonic frequency of 25kHz	91.15% at 30min reaction	(Van Manh et al., 2011)
	Jatropha Curcas oil Step 1: 4% H_2SO_4catalyst used for esterification at 60^{0}C reaction temperature and power of 210W Step 2: 1.4% NaOH catalyst used for transesterification at 60^{0}C reaction temperature and power of 210W	96.4% at 1.5h reaction	(Deng et al., 2010)
Enzyme-catalyzed	*Jatropha Curcas* oil 7% water, 10% immobilized lipase and temperature of 35 °C	94% at 24h reaction	(You et al., 2013)
	Pistacia chinensis bge seed oil 20% water, 7 IU/g of oil and temperature of 37 °C	94% at 60h reaction	(Li et al., 2012)
	Babassu oil (Orbinya sp) lipase PS with productivity (7 mg of biodiesel/g h) and temperature of 45°C	90.93% at 72h reaction	(Freitas et al., 2009)
	Stillingia oil 15% Novozyme 435 with tert-butanol at and temperature of 40°C	89.5% at 10h reaction	(Liu et al., 2009)

2.7 Limitations of existing production technologies

Generally non-edible feedstocks including waste vegetable oils and fats, non-food crops are produced by conventional transesterification reaction. However owing to the limitations of the conventional methods new technologies are starting to be developed. In the previous chapters it was pointed out that, biodiesel could be produced by different technological processes mainly, transesterification using homogeneous catalyst as well as heterogeneous catalyst. All these available methods are capable of producing the biodiesel from refined oil (Atabani et al., 2013a) which is the most common source of raw material for this fuel. However, they have their own advantages and disadvantages (Marchetti, 2012).

The acid catalyzed homogeneous transesterification has not been widely investigated and employed compared to the alkali catalyzed process due to its limitations such as slower reaction rates, the need of tougher conditions (higher temperatures, methanol to oil molar ratios and quantities of catalysts) and the formation of undesired secondary products such as dialkyl or glycerol ethers. Therefore, it is less attractive to the industrial purposes (Luque et al., 2008). However, the main problem associated with the heterogeneously catalyzed transesterification is their deactivation due to the presence of water, which is normally produced from the esterification reaction (Marchetti, 2012).

Enzymes are believed to be good choice to produce biodiesel; they can easily treat fatty acid as well as triglycerides to produce biodiesel from non-edible with higher conversions (Ranganathan et al., 2008). However, their high production cost limits the employability of enzymatic methodology (Bajaj et al., 2010). This may be overcome by going for molecular technologies to enable the production of the enzymes in higher quantities as well as in a virtually purified form (Houde et al., 2004).

The most common and simple non-catalyzed biodiesel production process has been performed using supercritical methanol. The procedure has been claimed to be very effective but it is highly expensive (Luque et al., 2008; Marchetti & Errazu, 2008). Hence researches are carried out to explore the new technological methods for the production of biodiesel considering the economic viability for the industrial attraction.

2.8 Emerging technologies

Biodiesel is conventionally produced by homogeneous, heterogeneous, and enzymatic catalyzed processes, as well as by supercritical technology as described in the previous chapter. However, all of these processes have some limitations, such as waste water generation (Xie & Li, 2006) and high energy consumption etc. (Yin et al., 2008). In this context, the following methods appear to be the suitable candidates to produce biodiesel because of their ability to overcome the limitations encountered by conventional production methods. The conclusions drawn by these methods are described in table 2.2. Selection of the production method depends on several points such as quality of vegetable oil, type of process desire, quality of raw material, availability and type of oil. However, some of them might have some more promising features than other based on the outgoing research that is being done every day.

2.8.1 Low Temperature Conversion (LTC) process

The low temperature conversion LTC is basically a pyrolytic process (Demirbas & Arin, 2002; Huber et al., 2006a; Mohan et al., 2006; Yaman, 2004). It has been applied to various biomasses of urban, industrial and agricultural origin to transform them into potential biofuel products (Bayer et al., 1995; Campbell & Bridle, 1986; Lima et al., 2004; Lutz et al., 1998; Lutz et al., 2000; Ostin et al., 2007). LTC is a process for producing fuel that involves only thermal decomposition and does not use any kind of solvent or chemical reagents as utilized by other conventional methods for the production of biodiesel. The other available methods for producing alternative fuels are more sophisticated and complicated relative to the instruments required and reaction conditions. Figueiredo et al. (Figueiredo et al., 2009) reported that castor oil is a potential resource produced by LTC as an additive for diesel. They concluded that castor seeds have been found to be a useful, renewable biomass source of pyrolysis oil with high percentage of the pyrolysis oil fraction (50%). It is important to note that no organic solvents, no reagents and very simple assemblies were used in the LTC process.

2.8.2 Hydrothermal conversion (HTC) process

Hydrothermal conversion process is very promising method to convert biomass feedstocks into biofuels (Goudriaan & Peferoen, 1990). It is a thermo chemical process, in which biomass is de-polymerized to gaseous, aqueous, bio-oil (or bio crude) and solid by products in a heated, pressurized, and oxygen-free reactor in the presence of water for 5-15minutes.This process is conducted at lower temperatures and does not require feedstock drying. HTC bio-oil is found suitable to be used as a fuel for stationary diesel engines, burners, boilers, or turbines (Czernik & Bridgwater, 2004). It could be upgraded further to liquids similar in properties that of diesel and jet fuels via hydrodeoxygenation (Demirbas, 2011). Furthermore, HTC oils typically have much lower oxygen and moisture contents, higher hydrogen content, and consequently higher calorific value than fast pyrolysis oils (Huber & Dumesic, 2006b).

The optimum operating conditions for biofuel production from corncobs HTC and the interaction effects between these factors have been investigated by Gan and Yuan. (Gan & Yuan, 2012a).They concluded that based on RSM data and prediction models, higher bio-oil yield and carbon recovery could be achieved at low temperature and short retention time.

2.8.3 Hydrothermal liquefaction (HTL) process

Hydrothermal liquefaction (HTL) is a process in which biomass is converted in hot compressed water to a liquid bio-crude. The processing temperature and pressure are between 200-350^{0}C and 15-20Mpa respectively (Biller et al., 2012). These conditions are sufficient to break the complex molecules into desired oily compounds.

Brown and Elliott (Brown & Elliott, 2011) recently reviewed the early work in hydrothermal processing of wet biomass for both liquid and gas production. Recent reports in the literature that have described HTL and its application to algae have been primarily related to batch reactor tests (Chow et al., 2013). There have been reports of continuous flow reactor tests for hydrothermal gasification of algae, both subcritical liquid phase (Elliott et al., 2012) and super-critical vapour phase (Stucki et al., 2009). Recently algae biomass has received a very high level of interest among many researchers as a renewable biomass resource for fuel production because of their rapid photosynthetic growth rates and the high lipid content (Sayre, 2010). The primary focus has been towards the recovery of the fatty acid triglycerides produced by the algae as a feedstock for biodiesel production. Elliott et al. (Elliott et al., 2013a) reliably processed the algae feedstocks with high slurry concentrations. They achieved high yield of a bio crude product from whole algae.

2.8.4 Catalytic hydrodeoxygenation (HDO)

In the HDO process, the main concern is to upgrade the biomass-derived oil by removing the oxygen content present in the feedstocks as water. In addition to this it also removes sulphur and nitrogen present in the fuel eliminating the chances of formation of oxides of sulphur and nitrogen (Furimsky, 2000). The process includes treatment of oil at high pressures and moderate temperatures over heterogeneous catalysts. The use of vegetable oils, mainly non-edible vegetable oils, as feedstock is highly favourable for this process because their hydrocarbon content is in the same range as that of fossil fuels, such as kerosene and diesel. A study by Prasad and Bhakshi. (Prasad & Bakhshi, 1985) tried to explain the catalytic hydrodeoxygenation reaction along with the formation of by-products. The chemistry of the reaction and formation of products purely depend on the catalyst being used in the reaction (Palanisamy & Gevert, 2011). The reaction takes place with simple hydrodeoxygenation via an adsorbed enol intermediate, and the product is a hydrocarbon fuel with water and propane as the by-products.

The hydrocarbon fuel produced this hydrodeoxygenation method is characterized by its improved properties compared to conventional petroleum-based fuels. The biofuel exhibits a higher cetane number; however, the n-paraffinic fuel has poor cold flow properties. In order to improve these low-temperature properties, the n-paraffin is isomerized to isoparaffin. During the isomerization, the normal paraffin, with its high freezing point and outstanding cetane number, can be converted to isoparaffin, which has a far lower freezing point but retains a high cetane number (Krar et al., 2011; Scherzer & Gruia, 1996). Mohammad et al. concluded that hydrodeoxygenation of vegetable oil is a promising route to the production of future fuels from the non-edible feedstocks (Mohammad et al., 2013).

2.8.5 Membrane biodiesel production and refining technology

Membranes processes for the production and refining of biodiesel are being increasingly reported. Membrane technology has attracted the interest of researchers for its ability to provide high quality biodiesel fuel and its remarkable biodiesel yields as well (He et al., 2006; Saleh et al., 2010; Wang et al., 2009). Conventionally biodiesel has been produced by employing batch reactors, continuous stirred tank reactors (CSTR) and plug flow reactors. However, membrane reactor is found to be suitable in producing biodiesel due to its ability to restrict the passage of impurities in to final biodiesel product (Caro, 2008). This restriction of impurities helps in obtaining quality biodiesel from the feedstocks. The impurities mainly the unreacted triglycerides should be removed after the completion of transesterification reaction (Baroutian et al., 2011; Cao et al., 2008a). In spite of this biodiesel produced from membrane reactors do contain impurities such as glycerol, residual catalyst and excess alcohol. The removal of these impurities is done by conventional separation and purification techniques which consume large amount of water, high energy consumption, time wasting and treatment of wastewater (Ferella et al., 2010; Jaruwat et al., 2010). This problem could be solved by employing organic/inorganic separative membranes for cleaning the crude biodiesel. Furthermore, organic/inorganic separative membranes have many advantages as they consume low energy, safer, simple in operation, elimination of wastewater treatment, easy change of scale, higher mechanical, thermal and chemical stability, and resistance to corrosion (Carlson et al., 2004).

Atadashi et al. (2011) concluded that membrane technology could produce a high quality biodiesel fuel. Furthermore they reported that properties of biodiesel from membrane technology process were in confirmation with the ASTM standard specification (Atadashi et al., 2011).

The production methods of biodiesel have been undergoing through rapid technological reforms to commercialize it as a supplement or alternate fuel to the petroleum diesel. The reforms may be for higher conversion, better yield, improved fuel properties, reduced reaction and production time, optimum reaction conditions, reduction in production cost etc.

Pal and Prakash (2012) applied the new approach termed as G-fed, which was based on controlled feeding of oil into alcohol creating large interfacial area for mass transfer. They obtained more than 95% of yield at lower energy input compared to conventional methods (Pal & Prakash, 2012). Biodiesel produced by transesterification with acetone as co-solvent significantly reduced the consumption of methanol compared to conventional methods. Under optimum conditions more than 98% yield was obtained with fuel properties satisfying Japanese industrial standards (JIS K2390) (Thanh et al., 2013). This solvent technology was applied for cotton seed oil for biodiesel production and similar types of results were reported (Alhassan et al., 2014). Recently, canola oil was made to react with supercritical tert-butyl methyl ester in the absence of catalyst. Using this technique biodiesel was obtained with 94% yield within short period of time of 12 min at 400^0C and under a pressure of 10MPa (Farobie et al., 2014). Usage of methanol was replaced by dimethyl carbonate for biodiesel production. 95.8% triglycerides conversion was reported with glycerol carbonate as a by-product at optimum conditions (Dawodu et al., 2014). Furthermore, methyl acetate replaced alcohol to produce biodiesel with excellent fuel properties and yield compared to that produced by conventional method (Tan et al., 2010). A two phase solvent extraction was coupled with synthesis of biodiesel. Transesterification of methanol with oil-hexane solution in the presence of sodium hydroxide was investigated and found 98.2% of conversion at optimum reaction conditions (Shi & Bao, 2008).Under the optimal reaction conditions 96.8% yield of biodiesel was obtained when a nano catalyst was used (Wen et al., 2010). For the first time crude palm oil was converted into biodiesel with a yield of 92% by using choline chloride based deep eutectic solvent (Hayyan et al., 2014). A continuous flow integrated process gave a biodiesel yield of 95.8% theoretically and 93.7% experimentally (Hu et al., 2012).

In terms of biodiesel yield sodium methoxide (CH_3ONa) has been found better compared to sodium hydroxide (NaOH) and potassium hydroxide (KOH). It is because; sodium methoxide does not form any water particles when dissolved in methanol (Sharma, 2008). Study conducted on *Jatropha Curcas* by situ ethanolysis proved that highest yield of 99.98% biodiesel can be obtained with 2% CH_3ONa as catalyst, 30^0C reaction temperature for 2h of reaction time (Surya et al., 2012). An integrated process of catalytic composite membranes (CCMs) and sodium methoxide was developed by some researchers. The transesterification conversion was reported to be 98.1% with biodiesel satisfying the international quality standards (Shi et al., 2013). There are many researchers who have reported the biodiesel yield by using sodium methoxide as a catalyst for transesterification reaction (Chen et al., 2012; Lin et al., 2014; Sharma et al., 2009b; Srivastava & Madhumita, 2008). A direct transesterification applied for microalgae with combination acidic and basic catalysts of boron triflouride and sodium methoxide respectively was found to be more effective than each individually used (Griffiths et al., 2010). The present study intends to apply the concept of using acidic and basic catalyst sequentially termed as direct transesterification (DT) with further improvements in washing and separation methods for the production of biodiesel from crude non-edible oil.

It is evident from the discussion that the non-edible feedstocks could be the potential resources due to their favourable fuel properties, better performance and lower emissions. There are several possible methods for biodiesel production but only conventional biofuel technologies are operational on a large scale today. Technology can make the energy resources more efficient and eco-friendly

Table 2.2: Results from various non-transesterification methods

Methods	Biomass	Operating conditions	Conclusions drawn	Ref.
Low Temperature Conversion (LTC) process	Rice straw	Pyrolysis temperature of 693K	Maximum yield of 10% with higher calorific value 42.79MJ/kg with viscosity and density lower than other biofuels	(Wang et al., 2007)
	Castor seeds	Pyrolysis temperature of 653K	Maximum yield of 50% with Higher calorific value 35.656MJ/kg	(Figueiredo et al., 2009)
	Sugarcane bagasse	Pyrolysis temperature of 623K	Maximum yield of 18%. Bio yield could be upgraded by acid hydrolysis	(Cunha et al., 2011)
Hydrothermal conversion (HTC) process	Soybean oil, *Jatropha Curcas* oil, and tung oil	Temperature range of 450-475^{0}C and pressure of 210bar	Yield ranging from 40-52% were reported.	(Li et al., 2010)
	Big bluestem	Temperature of 280^{0}C and pressure of 100psi	Maximum yield of 27.2% was reported	(Gan et al., 2012b)
	Corncobs	Temperature of 280^{0}C and pressure of 100psi	Maximum yield of 41.38% was predicted	(Gan & Yuan, 2012a)

Methods	Biomass	Operating conditions	Conclusions drawn	Ref.
Hydrothermal liquefaction (HTL) process	Cornelian cherry stones	Temperature of 200-300^0C	The highest yield of 28% at both 250 and 300^0C. The higher calorific values for light and heavy bio oil are 23.86 and 28.35 MJ/kg	(Akalın et al., 2012)
	Woody eucalyptus	Temperature of 150- 300^0C	The highest yield of oil obtained with paper regeneration wastewater as solvent	(Sugano et al., 2008)
	Rice straw	Temperature of 300^0C	The highest heavy oil yield of 21.62% for 30min of hydrothermal liquefaction	(Gao et al., 2011)
Catalytic hydrodeoxygenation (HDO)	Switch grass, Eucalyptus benthamii pyrolized oil	At a temperature of 320 °C under 2100 psi H2 atmosphere for 4 h of reaction	Switch grass bio oil exhibited in terms of H2 consumption, deoxygenation efficiency	(Elkasabi et al., 2014)
	Pine sawdust pyrolized oil	At a temperature of 100 °C under 3MPa H2 atmosphere for 2 h of reaction	The calorific value of raw bio oil increased from 13.96 MJ/kg to 14.09 MJ/kg with higher contents of carbon and hydrogen	(Ying et al., 2012)
	Pine sawdust pyrolized oil	Step 1: To overcome coke formation by Ru/C as catalyst at 300 °C, 10 MPa Step 2: conventional hydrogenation setup at 400 °C, 13 MPa by NiMo/Al_2O_3 as catalyst	oxygen content decreased from 48 to 0.5% and calorific value increased from 17MJ/kg to 46MJ/kg	(Xu et al., 2013b)

Methods	Biomass	Operating conditions	Conclusions drawn	Ref.
Membrane biodiesel production and refining technology	Soybean oil	80 °C of reaction temperature, 0.27 g/mL of catalyst amount and 4.15 mL/min velocity at membrane pressure of 80 kPa	Highest yield of 84.1% with many fuel properties within EN14214 standard	(Xu et al., 2014)
	Soybean oil, canola, palm oil, yellow grease, brown grease	80 °C of reaction temperature, pressure range of 37.9-43.1kPa	Esters form each feedstocks including the low-grade lipids met the ASTM D6751 standard	(Cao et al., 2008b)
	Soybean oil	70 °C of reaction temperature, 0.531 g/cm^3 of catalyst amount and 3.16 mL/min velocity at membrane pressure of 50 kPa	The highest biodiesel yielding rate of 0.1820g/min was reported	(Xu et al., 2013a)

2.9 Biodiesel from non-edible oils

It is estimated that about 84% of the biodiesel production is obtained globally by rapeseed oil which happens to be the edible oil. Similarly other edible oils such as sunflower oil, palm oil and soybean oil are also contribute substantially (Atabani et al., 2012; Thoenes, 2006). Since more than 95% of biodiesel is produced from edible oils, many activists are claiming that it is not only conversion of edible oil into biodiesel but also conversion of food into fuel. Recently, the non-governmental organizations, social and environmental activists have started to argue the harmful effects of biodiesel production, not only from edible oils but from non-edible oils as well. They argue that usage of edible oils leading to food starvation and that of non-edible oils causing the deforestation and destruction of the ecosystem (Altieri & Bravo, 2007; Gasparatos et al., 2011; Mahapatra & Mitchell, 1999).

However, to overcome this devastating situation at least to minimize the food shortages, researches have been focused towards production of biodiesel from non-edible feedstocks. Several evergreen trees producing non-edible oils could be cultivated in non-arable land. In fact many Indian states have decided to reserve a total of 1.72 million hectares of land for cultivation of *Jatropha Curcas.* Furthermore, small quantities of *Jatropha Curcas* biodiesel are already being used successfully by state public transport buses including the railways.

2.10 Non-edible feedstocks for biodiesel production

The demand for the biodiesel has increased sharply in recent years. To meet the requirements, edible oils alone are not favourable due to various reasons stated before. Under this situation only those resources or feedstocks could be considered which are non-edible and produce oil in appreciable quantity. The following are the few non-edible feedstocks.

2.10.1 Jatropha Curcas L. (Jatropha Curcas oil)

Jatropha Curcas is a draught resistant tree mainly found in Central and South America, South-east Asia, India and Africa (Gubitz et al., 1999). It is a plant with multipurpose uses and considerable potential for biodiesel (Openshaw, 2000). The high free fatty acid contents of the *Jatropha Curcas* crude oil could be reduced by esterification. Transesterification of the esterified oil gives yield of *Jatropha Curcas* biodiesel above 99% (Kumar Tiwari et al., 2007). The biodiesel produced from *Jatropha Curcas* L. does have similar properties to that of petroleum diesel (Koh & Mohd. Ghazi, 2011).

2.10.2 Pongamia pinnata (Karanja oil)

Pongamia pinnata is a fast growing leguminous tree with a high potential for oil and to grow in marginal land (Scott et al., 2008). It is underutilized plant which grows in many parts of India. Applying dual step transesterification would result a yield of 96.6-97% biodiesel (Naik et al., 2008). The important fuel properties lie within the limit set by ASTM standards and German biodiesel standards (Karmee & Chadha, 2005). The large scale cultivation of the *pongamia pinnata* could make the non-edible feedstock cheaper for biodiesel production (Khayoon et al., 2012).

2.10.3 Madhuca Indica (Mahua)

Madhuca indica is non-edible oil with higher free fatty acid contents (19%) available largely in central and northern plains and forest of India (Ghadge & Raheman, 2005). *Madhuca* has two major species, indica and longifolia. The methyl esters of *madhuca indica* could be used as fuel for internal combustion engines in place of diesel without any modifications on the engines (Puhan et al., 2005).

2.10.4 Michelia champaca

Michelia champaca is a tall evergreen tree found in China, Burma and throughout India. It is also known as svarna champa. The seeds of *michelia* are a rich source of oil (45%). The flowers of the tree possess excellent fragrance and hence used in perfume industries also. The saponification value (SV), iodine value (IV) and cetane number (CN) of the methyl esters *michelia champaca* indicates its suitability for biodiesel production (Hosamani et al., 2009).

2.10.5 Garcinia indica

It is slender evergreen tree found in many parts of India such as Western Ghats, konkana region, north canara, south canara, Coorg etc. The seed contain around 45.5% of the oil. The properties of methyl esters of *garcinia indica* encourage to be used as the potential source for biodiesel production (Hosamani et al., 2009).

2.10.6 Azadirachta indica (Neem)

Neem tree is found in many parts of India and Bangladesh. Neem seeds contain around 30% of oil (Muthu et al., 2010). The oil is light to brown in colour. It is found useful in cosmetic and pharmaceutical industries as well (Kumar & Sharma, 2011). The esters of neem oil can be used as alternative fuel for diesel engines to avoid the food and fuel conflict (Nabi et al., 2006).

2.10.7 Nicotiana tabacum L. (Tobacco)

Tobacco seed oil is a by-product of tobacco leaf production. Tobacco cultivars can give an oil yield of 33% to 40% of mass of seed (Stanisavljevic et al., 2007). The fuel properties of biodiesel obtained from tobacco oil were well within the limit set by latest American (ASTM D 6751-02) and European (DIN EN 14214) standards (Veljkovi et al., 2006).

2.10.8 Moringa oleifera (Moringa)

Moringa is most widely known and utilized in sub-Himalayan regions of northwest India, Africa, Arabia, and Southeast Asia. The cetane number and oxidative stability of *moringa* is found to be higher than other biodiesel fuels (Rashid, 2008). The methyl esters of *moringa* could be used in diesel engines, mainly as a mixture to petro-diesel (Da Silva, 2010).

2.10.9 Rubber seed oil

Rubber seeds contain 40% to 50% of oil (Ramadhas et al., 2005). The maximum yield of oil obtained was 49% (Morshed et al., 2011). All fuel properties of biodiesel from rubber seed oil were within the range of standards including the viscosity, flash point, calorific value etc. (Ahmad et al., 2014). The highest conversion efficiency (96.9%) was seen when limestone based catalyst was used in the transesterification process to produce the biodiesel from high free fatty acid contents of rubber seed oil (Gimbun et al., 2013).

2.10.10 Calophyllum inophyllum L. (Polanga)

Calophyllum inophyllum is available in coastal regions of India, Sri Lanka, East Africa, Australia and Southern Asia (Arumugam & Ponnusami, 2014). The ester yield was found to be 98.92% and the fuel properties of the blends of *Calophyllum inophyllum* were within the limit set by ASTM standards (Ong et al., 2014a). It was reported as excellent feedstock for biodiesel production (Arumugam & Ponnusami, 2014).

2.10.11 Sterculia feotida L.

Sterculia feotida is native to east Africa, Australia, Myanmar, and Sri Lanka and to some extent India. Though, *sterculia foetida* methyl esters showed most of the fuel properties within the range of ASTM and EN specifications for biodiesel except oxidative stability and pour points (Bindhu et al., 2012).

2.10.12 Ceiba pentandra

Ceiba pentandra which is commonly known as kapok is found mainly in Southeast Asia and some parts of India. It is draught resistance tree grown naturally in humid or semi humid region.

The blend of biodiesel from *ceiba pentandra* and diesel showed remarkable improvements in all fuel properties in general and oxidation stability in particular (Silitonga et al., 2013a). The production of biodiesel from *ceiba pentandra* could add the value to the underutilized feedstock of *ceiba pentandra* (Sivakumar et al., 2013).

It has been investigated that *ceiba pentandra* could be used as feedstocks for bioethanol production as well apart from being used as biodiesel feedstock (Tye et al., 2012).

2.10.13 Rice bran

Rice bran oil is a potential source of biodiesel production which is a by-product of rice milling (Zullaikah et al., 2005). The application of two step transesterification resulted in the quality biodiesel with acceptable properties compared to the ASTM D6751-02 and DIN V51606 standards, which could be used in the engines (Lin et al., 2009). However, high yield could be obtained in shorter period with application of two step in-situ transesterification process (Shiu et al., 2010).

Figure 2.2 shows some images of non-edible feedstocks *Jatropha Curcas, pongamia pinnata, calophyllum innophylum, ceiba pentandra, nigella sativa* etc.


Kapok Tree (Ceiba pentandra) *Nigella sativa plant* *Calophyllum inophyllum*


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*

Figure 2.2: Non-edible oil feedstocks (Atabani et al., 2012)

There are some other non-edible feedstocks available, on which extensive research is being carried out. They are *Cerbera odollam* (Sea mango), *Sapindus mukorossi* (Soapnut), *Thevettia peruviana* (yellow oleander), *Crambe abyssinica* (Hochst), *Aleutites fordii* (Tung), *Sapium sebiferum* (Linn), *Roxb* (Chinese tallow), *M. azedarach* (syringe), *Putranjiva roxburghii* (Lucky bean tree), *Ricinus communis*

(Castor), *Pachira glabra*, *Euphorbia lathyris* L., *Simmondsia chinensis* (Jojoba), *Hibiscus sabdariffa* L. (Roselle), *Guizotia abyssinica*, *Argemone mexicana L.*, *Croton megalocarpus* etc.(Atabani et al., 2013a; Wang et al., 2011).

2.11 Fuel properties of biodiesel from non-edible oils

The fuel properties of biodiesel produced from a feedstock vary according to the fatty acid composition of that respective feedstock. The fuel properties of biodiesel are expected to be comparable or better than diesel in order to run the engine successfully without any expensive modifications. These properties include flash point, viscosity, cloud point and pour point, higher calorific value, oxidation stability, density and cold flow properties. Table 2.3 illustrates some of the main fuel properties of biodiesel produced from different non-edible feedstocks along with the acceptable limit set by ASTM standards. Among all the properties listed in Table 1, cold flow properties (pour point, cloud point and cold flow plug point CFPP), viscosity are among the most important properties which deserve the most attention. Based on these properties it will be decided whether the biodiesel produced could be used in an engine during cold climatic conditions or not, because currently European countries are larger consumers of biodiesel (Bozbas, 2008). Similarly viscosity of any oil indicates the resistance of a material to flow. It therefore, affects the operation of entire fuel supply system mainly the fuel injection and spray atomization, particularly at lower temperatures (Atabani et al., 2013a; Atabani et al., 2012). Oxidation stability is one more important property which describes the degradation tendency of biodiesel and is of great importance in the smooth running of engine parts (Karavalakis et al., 2010).

Table 2.3: fuel properties of biodiesel from different non-edible oil resources (Ahmad et al., 2014; Ahmad et al., 2011; Atabani et al., 2013b; El Boulifi et al., 2013; Kapilan & Reddy, 2008; Karmakar et al., 2010; Mofijur et al., 2013; Nabi et al., 2009; Ragit et al., 2011; Saravanan et al., 2013; Sarin et al., 2009)

	Non-edible oils									
Fuel properties	***Jatropha Curcas***	***Pongamia Pinnata***	***Madhuca Indica***	***Azadirachta indica***	***Moringa oleifera***	***Calophyllum inophyllum***	***Sterculia foetida***	**Rice bran**	**Rubber seed**	**ASTM D6751–08 standards**
Viscosity at 40 $^{\circ}$C (mm^2/s)	4.723	4.2	5.10	5.213	5.0735	5.5377	6.3717	3.522	3.89	1.9–6.0
Density at 40 $^{\circ}$C(g/cm^3)	0.8642	0.860	0.850	0.8845	0.8597	0.8776	0.8776	-	-	-
Oxidation stability (h at 110 $^{\circ}$C)	3.02	2.54	-	7.1	12.64	6.12	1.46	1.70	8.54	Min. 3 h
CFPP (^{0}C)	-	-7	6	11	18	11	2	0	0	-
Cloud point(^{0}C)	3	-1	4	14.4	21	12	1	-10	3.2	-
Pour point(^{0}C)	3	-6	-	2	19	13	2	-11	-2	-
Flash point(^{0}C)	182.5	180	129	76	176	162.2	130.5	169	152	Min.130
Higher calorific value(kJ/kg)	40536	40750	36914	39810	40115	39513	40001	38853	39700	-

2.12 Performance and emissions of biodiesel from non-edible oils

The demand for combustion engines continuously growing. On one side the customer wants more power and torque and on other side one cannot lose sight of fuel economy and increasingly stringent emissions laws. The main findings of the previous literature on the performance of biodiesel fuelled internal combustion engine showed that the biodiesel have comparable power, brake specific fuel consumption and brake thermal efficiency (Tesfa et al., 2013). However, the formation of oxides of nitrogen is a matter of concern (Subramanian & Lahane, 2011). Table 2.4 shows the performance and emissions tests of some of the biodiesel prepared from non-edible oils. It is evident from the discussion that the non-edible feedstocks could be the potential resources due to their favourable fuel properties, better performance and lower emissions.

Table 2.4: Test results of biodiesel (non-edible oils) fuelled engines

Biodiesel	Operating conditions	Performance	Emissions	Ref.
Jatropha Curcas	Full load-variable speed	B(10) gave reduced fuel consumption with complete combustion compared to other biodiesel blends	Reduced exhaust emissions except NOx	(Mofijur et al., 2013; Ong et al., 2014b)
Pongamia Pinnata	Gradually variable load Constant speed	3-5% lower brake thermal efficiency for different blends compared to diesel	Reduced unburned hydrocarbon, CO,CO_2 With increased NOx than diesel	(Chauhan et al., 2013; Sureshkumar et al., 2008)
Madhuca Indica	Gradually variable load Constant speed	B(20) resulted slightly better in thermal efficiency than diesel	Reduced hydrocarbon, CO with increased NOx than diesel	(Godiganur et al., 2009)
			However 4% lesser NOx is reported by Saravanan et al. compared to diesel	(Saravanan et al., 2010a)
Azadirachta indica	Variable load-Constant speed	Brake specific fuel consumption and thermal efficiency was found to be higher than mineral diesel	Reduced hydrocarbon, CO with increased NOx than diesel	(Dhar et al., 2012)
Moringa oleifera	Variable speed and full load condition	Reduced brake power with increased fuel consumption for B(10) and B(20) than diesel	Reduced hydrocarbon, CO with slightly increased NOx than diesel	(Mofijur et al., 2014; Rahman et al., 2014)

Calophyllum inophyllum	Variable speed and full load condition	Higher thermal efficiency and lower specific fuel consumption and exhaust temperature than diesel for B(10)	Reduced CO and smoke with slight increase in NOx	(Ong et al., 2014a)
	High idling conditions	Negligible fuel consumption increment compared to diesel	CO and HC were lower, with higher NOx emissions	(Rahman et al., 2013)
Sterculia foetida	Variable load-Constant speed	Power output and fuel consumption were almost same for low biodiesel blend and diesel	Low smoke and CO for low biodiesel concentrated blends. However 4% reduction in NOx for B(20) was seen	(Devan & Mahalakshmi., 2009a)
		B(40) blend showed 2.13% more thermal efficiency than diesel at full load	11% reduction in NOx for B(20) 7.4% increment for B(40) at full load. Reduction in HC and smoke for B(40)	(Devan & Mahalakshmi, 2009b)
Ceiba pentandra	Variable speed and full throttle condition	B(10) resulted in the best engine torque, brake power and fuel consumption than diesel at 1900 rpm with full throttle	CO, HC and smoke capacity lower compared to diesel except for CO2 and NOx	(Silitonga et al., 2013b)
	Constant speed variable load condition	B(25) claimed 4% increase in thermal efficiency than conventional diesel	comparable emissions of HC, CO, NOx and smoke with diesel	(Vedharaj et al., 2013)
Rice bran	Constant speed variable load condition	B(20) exhibited marginal fuel consumption difference compared to diesel.	Lower smoke and higher NOx were reported	(Saravanan et al., 2010b)
Castor oil	Constant speed variable load condition	Increased thermal efficiency with lower fuel consumption for lower biodiesel blends	NOx emissions were same as that of diesel for low loads. Slightly higher NOx for full load condition	(Kulkarni & Kore 2013; Panwar et al., 2010)
Cotton oil	Variable speed and full throttle condition	No significant differences in performance of B(5), B(20) and diesel fuel	Lesser CO was reported for all blends. NOx was found to be less for all blends except B(5).	(Aydin & Bayindir 2010)

2.13 Performance parameters of an IC engine

The engine manufacturers and consumers wish to have a high performance engine apart from lower emission. Therefore, the focus should be to develop a high performing engine with lower emissions apart from minimizing the dependency on fossil diesel. Biodiesel, especially the low concentrated blends with diesel perform more or less same as that of diesel fuelled engines (Datta & Mandal, 2012).

Power, torque, specific fuel consumption, exhaust gas temperature are the main parameters of practical interest. These parameters have both brake and indicated values. The difference between these two is the frictional power between the moving parts of the engine and the ratio is termed as mechanical efficiency of the engine.

2.14 Variables affecting the performance of an IC engine

There are many variables which affect the performance and emission of biodiesel fuelled engines. The key influencing variables are compression ratio, load and speed, fuel injection parameters (injection pressure, injection timing and injection duration), air swirl, piston design etc.

2.14.1 Compression ratio

It is the ratio of sum of the swept and clearance volumes to the clearance volume. The CR (compression ratio) of an engine depends on the fuel to be used. For most of the engines it ranges from 8:1-12:1. For high performance cars CR may be of 15:1. However, diesel engine cars could be operated at higher CR17:1 (Raman & Ram, 2013).The performance test conducted on Ricardo E6 engine by using madhuca indica biodiesel showed reduction in performance with increase in biodiesel percentage in the blend. However, increasing the compression ratio and injection timing the performance of biodiesel fuelled engine could be made comparable with that of diesel engines. Furthermore, it is concluded that pure madhuca indica biodiesel could be used as fuel at CR of 20 and injection timing of 40^0 without compromising on performance with that of diesel (Raheman & Ghadage, 2008). The B40 blend of waste cooking oil and diesel gave the maximum brake power of 2.07kW compared to that of 2.12kW from the pure diesel at a CR of 21. At the same CR of 21, the emissions such as oxides of nitrogen (NOx) and CO were more compared to the diesel engine (Muralidharan & Vasudevan, 2011). The engine torque was increased by 11.1% than diesel engine (CR=14) when the CR of engine, fuelled by waste cooking oil biodiesel (B50) was 18. Similarly 6% increase in brake thermal efficiency was obtained (Ibrahim et al., 2013). 19.2% increase in brake thermal efficiency, 52% reduction in hydro carbon (HC), 37.5% reduction in CO emissions and 36.84% more NOx were reported for biodiesel from waste cooking oil B(50) from restaurants (El_Kassaby et al., 2013). Maximum brake thermal efficiency and better fuel economy were found for a CR of 17.5 for *Jatropha Curcas* (B10), Karanja (B10) and compressed natural gas blended with honge oil (Balajee et al., 2013; Banapurmath et al., 2013; Kumar et al., 2013). At higher CR both *Jatropha Curcas* and karanja biodiesel engines gave lesser emissions than diesel engine (Amarnath et al., 2013). The optimum CR of 20 and 19 were found to be suitable for better performance and lower emissions for the engine running on biodiesel from rubber seed oil and palm oil respectively (Jose et al., 2014; Nagaraja et al., 2012). The performance of engine was found to be maximum at an optimum CR of 20 for preheated (90^0C) palm oil-diesel blend (B20) (Nagaraja et al., 2013). The CR of 16 yielded optimum performances in terms torque and power for marula oil fuel and diesel fuelled engines (Gandure & Clever, 2011). The maximum brake power of 3.51 kW, 0.24 kg/kW-hr of specific fuel consumption and 30.57% of brake thermal efficiency were obtained for a CR of 18 for a variable compression ratio engine running on tamanu biodiesel beside lower exhaust gas temperature (Mohanraj et al., 2013). Diesel engine fuelled with pungam methyl ester (B20) found to better in performance than diesel engine for CR of 19 and injection pressure of 240 bar (Venkatraman & Devaradjane, 2010).

Heat transfer does have the effects on performance of an internal combustion engines. As the heat transfer decreases, the exhaust gas temperature increases including increase in work output and thermal efficiency (Parlak, 2005). Increase in compression ratio resulted in decrease in ignition delay and increase in heat release rate with minimum emissions in a biogas fuelled engine (Porpatham et al., 2012). The heat release rate of higher biodiesel concentrated fuel indicated was found to be less due to the lower heating value of biodiesel. This heat release rate could be increased by increasing the compression ratio (Gumus, 2010). However, it is predicted that ceramic coated biodiesel fuelled engines reduces the heat transfer improving the brake thermal efficiency marginally (Rajendra et al., 2010).

2.14.2 Injection parameters

Fuel injection parameters such as injection timing and injection pressure beside injection rate, nozzle design (including number of holes) play vital role towards reduction of emissions (Sayin et al., 2010). Basically the biodiesel is used in the unmodified diesel engine; hence same performance as that of diesel fuelled engine cannot be expected (Agarwal, 2007; Devan & Mahalakshmi, 2009c; Lapuerta et al., 2008; Mohibbe Azam et al., 2005; Rao et al., 2008; Subramanian et al., 2005).

2.14.2.1 Injection pressure

In addition to reduced emissions the higher injection pressure resulted in improved performance of the *Jatropha Curcas* biodiesel fuelled engine (Jindal et al., 2010). Puhan et al. (Puhan et al., 2009) conducted the performance test on direct injection diesel engine at constant speed operated on linseed oil methyl esters with varied injection pressure (220bar, 240bar and 240bar). They concluded that 240bar is the optimum injection pressure. Furthermore, at this optimum injection pressure the thermal efficiency was similar to that of diesel engine with lower carbon monoxide but increased NOx. The effect of injection pressure demonstrated improved brake specific fuel consumption for higher percentage biodiesel–diesel blends (such as B20, B50, and B100) and lower emissions of smoke capacity, unburned hydrocarbon, carbon monoxide but higher emissions of carbon dioxide and NOx (Gumus et al., 2012). The engine used in this study is shown in figure 2.3. Experiments conducted with different injection pressures 205, 220, 240, 260 and 280 bars, on a single cylinder direct injection engine with honge methyl ester (B20) gave overall better performance at a pressure of 220bar (Banapurmath et al., 2009a). The maximum torque of 191Nm, 185Nm and 179Nm were reported for diesel, rapeseed and soybean biodiesel respectively at an injection pressure of 250bar. Similar trends for specific fuel consumption were reported as stated before. Smoke and carbon monoxide reduced drastically by increasing the injection pressure from 250 to 350 bars. However, there was 20% increase in the NOx at higher injection pressure (Celikten et al., 2010). The optimum injection pressure and injection timing of 225 bar and 27^0 BTDC respectively, were found for the single cylinder constant speed diesel engine fuelled with the methyl esters of *thevetia peruviana* seed oil (Balusamy & Marappan, 2010).

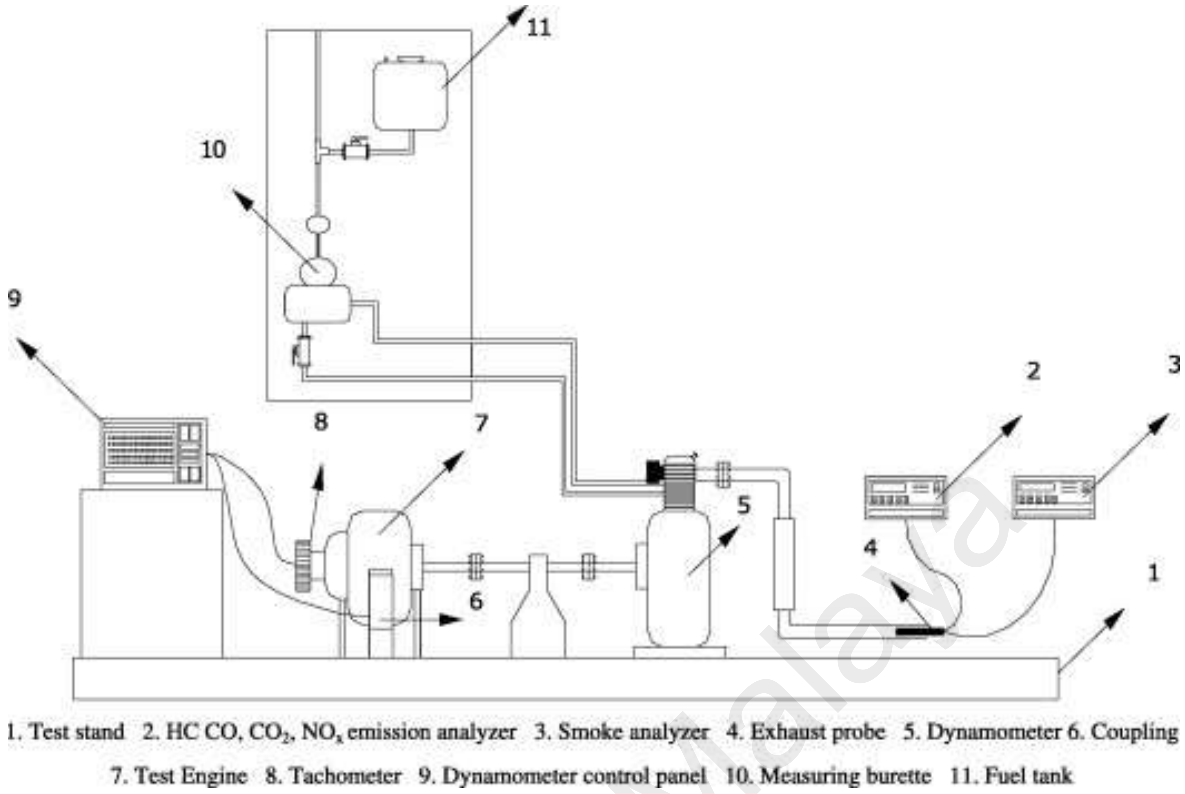


Figure 2.3: Experimental set up of engine used by Gumus et al. (Gumus et al., 2012)

2.14.2.2 Injection timing

The effect of injection timing is quite significant on the performance of internal combustion engine and it is studied by many researchers. Alternative fuels exhibit longer delay period resulting in lower burning rate and late combustion. Therefore, advancing the injection timing could compensate these effects (Nwafor et al., 2000). The best injection timing for single cylinder four stroke air cooled engine running on *Jatropha Curcas* biodiesel was reported to be 340 crank angle degrees for minimum fuel consumption and emissions with maximum thermal efficiency and heat release rate. Nevertheless, minimum NOx were reported at 350 crank angle degrees (Ganapathy et al., 2011). Advancing the injection timing by 4^0 from 15^0before top dead centre (BTDC), the diesel engine gave 1.6% more thermal efficiency, 9.9% reduction in carbon monoxide but 76.6% more NOx emissions when fuelled with waste cooking oil (Bari et al., 2004). Mani and Nagarajan

(Mani & Nagarajan, 2009) retarded the injection timing from 23°BTDC to 20, 17 and 14° BTDC for a diesel engine running on waste plastic oil as fuel. They found reduction in oxides of nitrogen (NOx), carbon monoxide (25%) and unburned hydrocarbon (30%) while increase in brake thermal efficiency and carbon dioxide at all test conditions. Direct injection diesel engine fuelled with soybean oil also showed lesser contents of oxides of nitrogen with slight increase in fuel consumption when the main injection timing was retarded (Qi et al., 2011).

The performance of an engine is also influenced by the combined effect of injection parameters (Heywood, 1988). Kannan and Anand (Kannan & Anand, 2012a) investigated the combined effect of the injection pressure and injection timing on performance, emission and heat release of diesel engine fuelled with waste cooking oil running at constant speed. They found significant improvements in thermal efficiency, gas pressure and heat release rate at 280bar and 25.5°BTDC injection pressure and injection timing respectively (Kannan & Anand, 2012a). They observed reduction in nitric oxide and smoke too. Pandian et al (2011) designed the experiments for performance test on an engine of 7.5kW at 1500rpm operated with pongamia biodiesel blend based on response surface methodology. The results reported lower brake specific energy consumption, carbon monoxide and smoke with higher brake thermal efficiency and more NOx at 225bar and 30° BTDC of injection pressure and injection timing respectively. However, an injection pressure of 225 bar, injection timing of 21° BTDC and 2.5 mm nozzle tip protrusion found to be optimum values (Pandian et al., 2011).

Many researchers do agree that biodiesel can reduce carbon monoxide, particulate matters and hydrocarbon but not NOx emissions (Hamdan & Khalil, 2010; Kannan et al., 2012b; Labeckas & Stasys, 2013; Qi et al., 2010; Rakopoulos et al., 2007; Rakopoulos et al., 2008a; Rakopoulos et al., 2008b; Ushakov et al., 2013). However, using multidimensional optimization gave 50.26% reduction in NOx emissions for B20 soybean methyl esters (Al-Dawody & Bhatti, 2013).

2.15 Spray behaviour

The performance and emission parameters of diesel engine are dependent on the inner nozzle flow and spray behaviour because these processes control the better mixing of fuel with air and ultimately better combustion process (Som et al., 2010). Spray characteristics such as Injection delay, spray penetration, spray angle, spray projected area and spray volume were studied by Wang (Wang et al., 2010). They reported longer injection delay and spray tip penetration for biodiesel. The spray angle, projected area and volume of biodiesel were found to be smaller than those for petro-diesel fuel. The injection delay for the biodiesel and B75 fuel found to be lesser for higher injection pressure (Bang & Lee, 2010). The atomization performance of biodiesel also found to be effective by increasing ambient pressure. The spray tip penetration and spray area decreased as the ambient pressure increased (Kim et al., 2010). Similar type of opinion is reported for undiluted soybean biodiesel (Park et al., 2009). The spray area of biodiesel decreased with increase in the ambient pressure. Som (Som et al., 2010) observed that the biodiesel needs to be injected at about 60K higher than temperature of diesel for improvements in injection velocity, discharge coefficient and mass flow rate. Furthermore, they recommended changes in the piston bowl design for biodiesel to be used in existing engines. Similar types of observations were made by some researchers. Atomization and vaporization depend on the viscosity and density of fuel. They are temperature dependent hence; increasing the inlet temperature will enhance atomization (Pandey et al., 2012). The spray visualization system for biodiesel is shown in figure 2.4

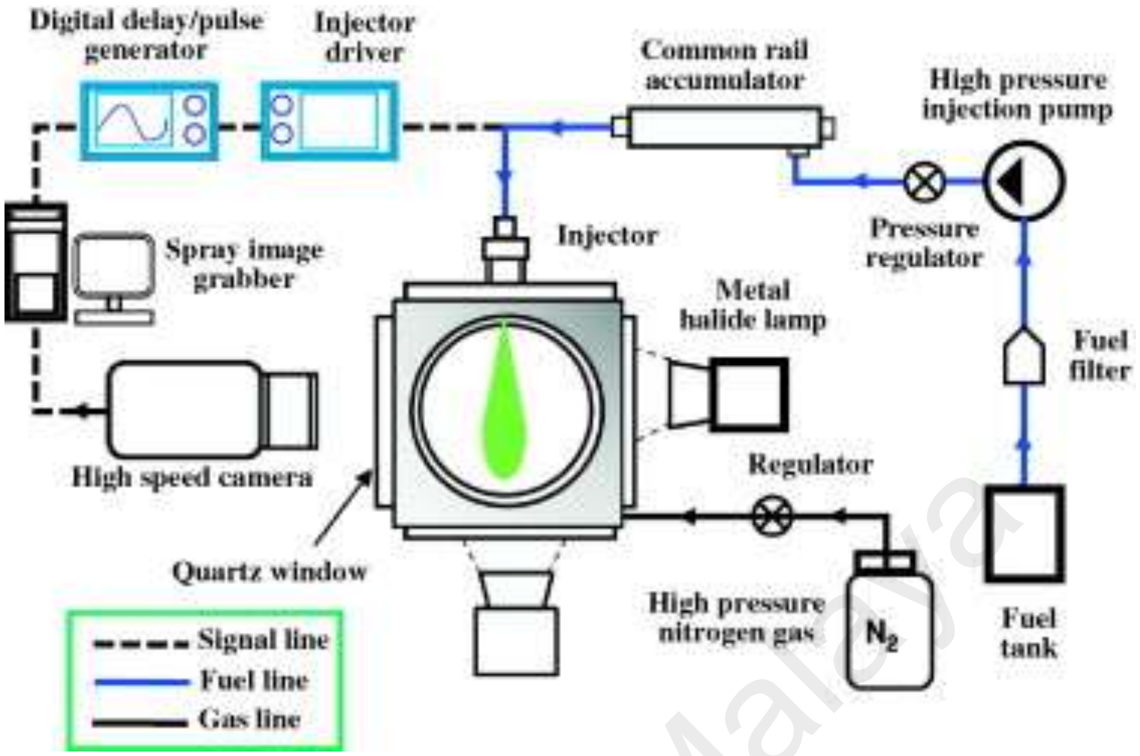


Figure 2.4: Experimental device for spray visualization of biodiesel fuel (Park et al., 2011)

2.16 Exhausts gas recycle (EGR)

When the combustion chamber temperature exceeds the critical temperature then the molecules of the oxygen try to combine with the molecules of nitrogen leading to the formation of oxides of nitrogen (NOx). The exhaust gas recirculation is the most effective solution for the reduction of NOx emissions (Jacobs et al., 2003; Pfeifer et al., 2002). Figure 2.5 shows the schematic diagram for EGR (Agarwal et al., 2011). Saleh (Saleh, 2009) studied the effect of EGR on constant speed, two cylinders, naturally aspirated internal combustion engine running on jojoba biodiesel. He concluded that EGR rate of 5-15% could be a better trade-off between CO, HC and NOx for all operating conditions. Simultaneous reduction of NOx and soot formation was achieved with EGR in modern production diesel engines with biodiesel as fuel (Zheng et al., 2008). The use of EGR was found to be most promising in case of diesel engine running on rapeseed methyl esters. The NOx emissions were reduced to that of emission levels of ultra-low sulphur diesel (Tsolakis et al., 2007). Experiments conducted on a single cylinder, four-stroke, direct injection, water-cooled compression ignition engine using diesel, honge methyl esters and neem methyl esters proved that 10% EGR is the best of the range from 5 to 20%for better performance and trade-off between NOx, CO and HC (Banapurmath & Tewari, 2009b).From 50-60% reduction in NOx and other emissions were reported for eucalyptus oil and diesel fuel blends with 15% exhaust gas recirculation (Anandavelu et al., 2011). For the same 15% EGR rate the NOx emissions were reduced but the performance also reduced for the tests carried on kirloskar diesel engine operated on palm oil biodiesel (Kumar & Vijayaraj, 2005).5% EGR has been recommended for the engine running on neat mahua methyl esters for most of the situations (Prasad et al., 2009). However, 10% EGR reduced the fuel consumption and 20% EGR reduced NOx emissions for B20 madhuca indica biodiesel (Manieniyan & Sivaprakasam, 2013). The NOx and soot emissions were reduced by 27% and 11.3% respectively, for *Jatropha Curcas* blended biodiesel for 5% EGR rate (Gomaa, 2010). The combined effect of retarding injection timing, higher injection pressure and EGR was studied by Suryawanshi and Deshpande (Suryawanshi & Deshpande, 2005). The NOx emissions were drastically reduced for combination of 20% EGR, 4° retarded injection timing and 30 MPa fuel injection pressure in addition to better performance. The test conducted for sunflower biodiesel fuelled engine, showed increase in the NOx emissions when the biodiesel contents increased in the fuel. Similar trends were reported for higher load when the EGR rate was lesser. Hence, it is concluded that the performance and emissions of an engine depend on fuel injection and EGR strategy during transient conditions (Armas et al., 2009).The marginal improvement in thermal efficiency was observed for single cylinder, indirect diesel engine fuelled with rubber seed biodiesel-diesel blend and liquefied petroleum gas in dual fuel mode operation with exhaust gas recirculation (Ramadhas & Jayaraj, 2010). Karra (Karra et al., 2008) showed that injecting shift is not the reason for the NOx emissions; however, use of EGR would reduce the NOx emissions for all the fuels. An effective method of supplying higher EGR rates is EGR at lower pressure. When a low pressure system was used for EGR, decreases in NOx, N2O and fuel consumption were observed. However, increases in CO and HC were noted (Bermudez et al., 2011). Rapeseed methyl ester (B100) was used in diesel engine equipped with high pressure EGR system and low pressure EGR system. Low pressure EGR found to better than high pressure EGR in reducing CO and NOx emissions. Furthermore, an increase in low pressure EGR rate led to reduction of both NOx and smoke emissions (Kawano et al., 2007). A combination of EGR and ethyl hexyl nitrate (cetane improver) is used to conduct the performance and emissions test on single cylinder, air cooled diesel engine run on *Jatropha Curcas* biodiesel. The results showed that increase in EGR rate increases brake thermal efficiency, decrease in brake specific fuel consumption and exhaust gas temperature. In addition to this biodiesel with cetane improver for 20% EGR reduced NOx emissions by 33% (Venkateswarlu et al., 2012).

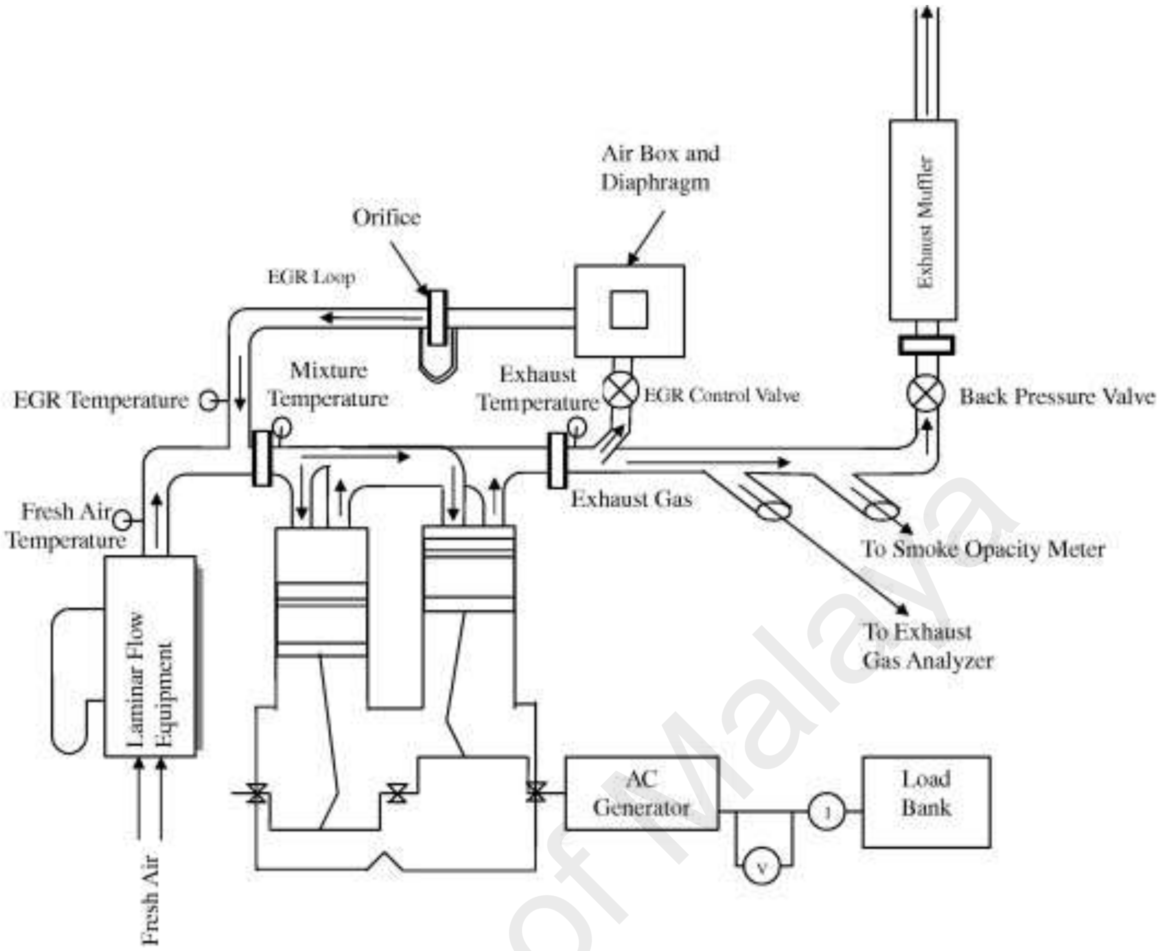
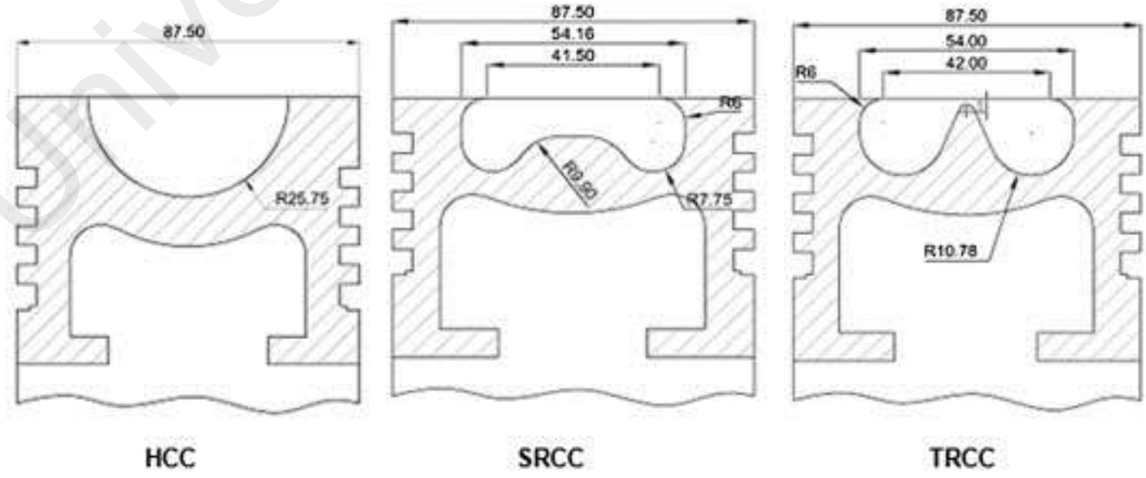


Figure 2.5: Schematic diagram of engine setup using EGR (Agarwal et al., 2011)

2.17 Combustion chamber geometry

Engine manufacturers are putting a lot of effort in reduction of both soot and NOx due to stringent emission norms. One of the feasible solutions is to optimize the combustion chamber design and injection strategies. In order to obtain better fuel air mixing, evaporation of fuel in short available time and higher combustion efficiency, the combustion chamber should be designed to achieve better air movement, swirl and turbulence (Jaichandar & Annamalai, 2013). Experiments conducted on engine with pistons having hemispherical and toroidal re-entrant combustion chamber geometries are shown in figure 2.6 and figure 2.7, with *pongamia pinnata* biodiesel (B20) as fuel. The results showed an improvement of 5.64% of brake thermal efficiency and 4.6%

reduction in brake specific fuel consumption in toroidal re-entrant combustion chamber compared to baseline engine run on diesel. However, 11% increment was found in NOx emission due to higher combustion chamber temperature beside maximum heat release and peak pressure (Jaichandar et al., 2012). The tests conducted by employing the same (B20) pongamia biodiesel on engines having hemispherical, toroidal and shallow depth combustion chamber showed promising improvement in brake thermal efficiency for toroidal combustion chamber compared to other two combustion chambers. The oxides of nitrogen were higher for toroidal combustion chamber. The heat release rate was slightly lesser compared to the baseline diesel engine (Jaichandar & Annamalai, 2012). Similar types of results were reported for *Jatropha Curcas* (B20) biodiesel fuelled engine, but *Jatropha Curcas* biodiesel showed higher heat release rate than diesel in last phase of the combustion possibly late burning of higher fatty acid components of biodiesel for all blends (Mamilla et al., 2013). A numerical study on the effect of piston bowl geometry on the performance of engine favoured shallow depth combustion chamber for low speed engine, whereas omega combustion chamber was preferred for higher engine speed. Both resulted in higher NOx for their respective low and high engine speed (Li et al., 2014).



All dimensions are in 'mm'

Figure 2.6: Schematic diagram different combustion chambers employed (Jaichandar & Annamalai, 2012).

Figure 2.7: Photographic view of different combustion chambers employed (Jaichandar & Annamalai, 2012)

2.18 Load and speed

At higher speeds the brake specific fuel consumption (BSFC) increases due to increase in friction losses. Similarly the BSFC increases at lower speed because of the increased heat transfer time from the gas to cylinder wall. Hence, there is a minimum in BSFC versus engine speed curve. An et al found some differences and even opposite conclusions regarding the performance and emission test in some of the research articles. They attributed this to the external factors such as injection parameters, biodiesel feedstocks, engine speed and load etc. The investigations on common rail diesel injection engine run on biodiesel and its blends showed increased BSFC and lower thermal efficiency with decreased load and speed but the opposite trends were observed for high loads (An et al., 2012). Recently, tests conducted on multi cylinder diesel engine using moringa oleifera biodiesel (B10) and (B20) at various speeds (1000-4000rpm) and full load conditions. It is revealed that for entire range of speed the brake power was less and BSFC was more for both (B10) and (B20) biodiesel compared to diesel (Mofijur et al., 2014). Performance, emission and heat release rate of karanja biodiesel and its blends based engine were compared to that with diesel engine. The results showed brake thermal efficiency for all the blends of karanja were same as that of diesel at higher engine load. However, the higher biodiesel blends showed lower thermal efficiency at lower engine load. At higher engine speed and load the CO emissions for biodiesel engine were less but at lower engine load the CO emissions found to be more for higher biodiesel blends. The heat release found to be maximum at higher engine load (Dhar & Agarwal, 2014). Engine running on low load and low speed (high idling condition) is a matter of concern to the transportation industry. At high idling condition, the fuel consumption and NOx from biodiesel were increased compared to diesel but reduced CO and HC emissions were reported for *Jatropha Curcas* based biodiesel engine (Rahman et al., 2014b).

2.19 Low heat rejection engines

The concept of low heat rejection engines is to minimize the heat transfer to coolant and hence improve the thermal efficiency. The combustion chamber elements are usually coated by thermal barrier coatings to minimize the heat transfer as shown in figure 2.8 and figure 2.9. Mohamed conducted the performance and emission test on fly ash coated single cylinder diesel engine fuelled with biodiesel (B20) from rice bran and pongamia oils. They found an increase of 6.8% and 4.9% in brake thermal efficiency for rice bran and pongamia biodiesel (B20) respectively, compared to that of uncoated diesel engine. The specific fuel consumption was found to decrease by 16.8% and 13.7% for rice bran and pongamia biodiesel (B20) respectively. Similar trend was observed for emissions except NOx (Mohamed et al., 2011).

Figure 2.8: Photographic view of piston, cylinder head and cylinder liner before coating (Rajendra et al., 2010)

Figure 2.9: Photographic view of piston, cylinder head and cylinder liner after coating (Rajendra et al., 2010)

Similar type of performance tests have been carried out with piston and both intake and exhaust valves coated with ZrO_2 layer. The different performance parameters such as power and torque were found to increase beside reduction in fuel consumption and emission (Iscan & Aydin, 2012). Turbocharged diesel engine converted into low heat rejection engines with inclusion of thermal barrier coating resulted in better fuel economy and improved thermal efficiency. The engine power and torque were found to be more due to the increased exhaust gas temperatures before the inlet of turbocharger (Hasimoglu et al., 2008).

The performance of internal combustion engine with biodiesel or with its blends depends mainly on the engine variables such as compression ratio, load and speed, fuel injection parameters, air turbulence etc. (Fazal et al., 2011).

Therefore, an attempt has been made to investigate and analyze effects of varying injection parameters such as injection pressure and injection timing on performance, heat transfer and emissions of *ceiba pentandra* and *nigella sativa* biodiesel run engines.

2.20 Summary

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

From this literature review, it was understood that developing new methods for biodiesel production is vital. Moreover, the automotive engine's manufacturers and consumers wish to have highly efficient engine with lower emissions, which of course depend on the engine variables. Therefore, this research will focus on development of new methods of biodiesel production from different non-edible oil feedstocks. Apart from this to fulfil the demands of consumers (performance) and legislation (emissions) an effort has been made to find the optimum injection parameters for engine for better performance and lower emissions.

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 crude oils characteristics, biodiesel production; physical and chemical properties of biodiesel, engine performance and emissions were conducted. The opportunities of biodiesel-diesel blending too were also studied in this research. The equipment list and the apparatus used are discussed 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 the research where ET refers to two steps esterification-transesterification, DT refers to direct transesterification and MDT refers to modified direct transesterification method.

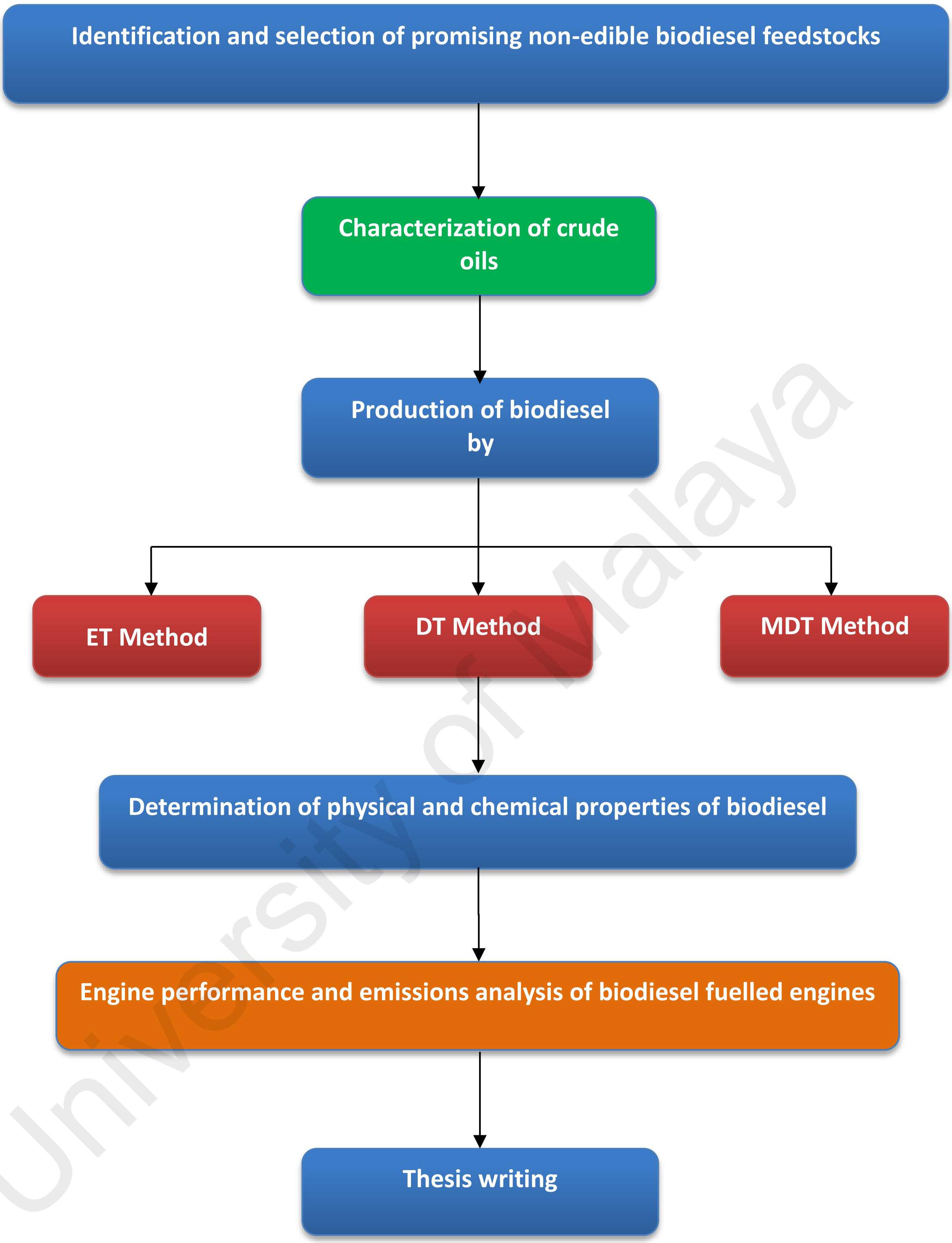


Figure 3.1: Flow chart of the research methodology

3.3 Materials and methods

3.3.1 Materials

The crude oils of *pongamia pinnata (CPPO)* (karanja), *Jatropha Curcas (CJCO)*, calophyllum innophylum (CCIO) were purchased from India. While the crude oil of *Nigella sativa (CNSO)* (Black cumin) was purchased from Bangladesh through personal communications. *Ceiba pentandra (CCPO)* was purchased from Indonesia. Chemicals required for the chemical reactions such as methanol, sodium methoxide (0.1N), boron triflouride (BF_3), petroleum ether 60^0C-80^0C (spectroscopic grade), sulfuric acid, hydrochloric acid, potassium hydroxide, anhydrous sodium sulphate etc. were purchased from the local markets of Kuala Lumpur, Malaysia. Figure 3.2 shows pictures of non-edible feedstocks *ceiba pentandra*, *nigella sativa*.

Kapok Tree (Ceiba pentandra) *Nigella sativa plant*

Figure 3.2: Ceiba pentandra and nigella sativa (Khan et al., 2015)

3.3.2 Equipment list and Properties for analysis

The quality of any fuel is expressed in terms of the fuel properties such as kinematic viscosity, calorific value, 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 ASTMD6751 standard. These properties include; viscosities, viscosity index, density, flash point, CP (cloud point), PP (pour point), CFPP (cold filter plugging point), calorific value, oxidation stability, beside some other non-ASTM properties such as transmission, absorbance and refractive index. Table 3.1shows the equipment used to analyse these properties, their manufacturers and the standards used to measure these properties.

Table 3.1: Equipment list

	Property	**Equipment**	**Manufacturer**	**ASTM D6751**
1	Kinematic viscosity	NVB classic	(Normalab, France)	D 445
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	CFPP	Cold filter plugging point – automatic NTL 450	(Normalab, France)	D 6371
6	Density	SVM 3000	(Anton Paar, UK)	D 1298
7	Dynamic viscosity	SVM 3000	(Anton Paar, UK)	N/S
8	Viscosity Index (VI)	SVM 3000	(Anton Paar, UK)	N/S
9	Caloric value	C2000 basic calorimeter	(IKA, UK)	N/S
10	Refractive Index	RM 40 Refractometer	(Mettler Toledo, Switzerland)	N/S
11	Transmission	Spekol 1500	(Analytical Jena, Germany)	N/S
12	Absorbance	Spekol 1500	(Analytical Jena, Germany)	N/S

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

3.3.3 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 detailed procedure to find the acid values of different non-edible oils is explained in the following sections.

3.3.3.1 Procedure to prepare phenolphthalein indicator (phph)

Phenolphthalein is a commonly used chemical having a formula $C_{20}H_{14}O_4$. Its property is to turn into colourless when the solution is acidic and turn itself into pink when the solution is basic. The titration solution was prepared by dissolving 0.5 g of phenolphthalein in 50% ethanol (50ml of ethanol and 50ml of water).

3.3.3.2 Titration procedure

Firstly, a measured quantity of the crude oil was taken into a beaker or Erlenmeyer flask. 50ml of 2-Propanol was added to the beaker containing the crude measured quantity of crude oil. The mixture was then heated for to around 50-55°C. It was made sure that the crude oil was well mixed and diluted with the 2-Propanol. 1-3 drops of phph indicator were added to the mixture. The titration started by the addition of base titrant potassium hydroxide (KOH solution) with a known normality (0.1N) from the burette drop by drop to the mixture until the indicator changes. When the endpoint of the reaction was reached i.e. the colour changed from colourless to pink, addition of KOH solution was stopped. The volume of reactant consumed was measured and further, the acid value of the crude oil calculated by using the following relationship.

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

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 3.3 shows the procedure to conduct titration.

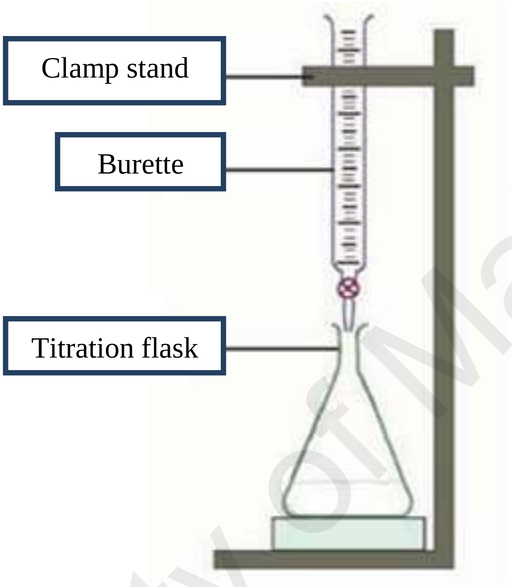


Figure 3.3: Titration procedures

3.4 Apparatus for biodiesel production

The biodiesel from different non-edible crude oils was prepared in a small scale laboratory reactor. It consists 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 shown in the figure 3.4.

Figure 3.4: 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.

3.5 Biodiesel from nigella sativa by esterification-transesterification (ET)

It is the process of producing biodiesel from the feedstock followed by chemical reactions known as esterification and transesterification. The transesterification is regarded as best method compared to others due to its simplicity and lower cost (Atabani et al., 2012). However employment of the esterification reaction depends on the acid value of the respective crude oil.

In esterification process the crude oil was mixed with methanol in the ratio of 2:1 by volume. In this study, 37% concentrated hydrochloric acid (1% v/v oil) was used as acid catalyst in the production of the biodiesel from crude oil of *Nigella sativa (CNSO)* owing to its higher acid value. Other details of the process are same as explained in section 3.6.

3.6 Biodiesel production by esterification-transesterification (ET)

Biodiesel was produced from the crude non-edible feedstocks (crude oils) of *pongamia pinnata (CPPO), ceiba pentandra (CCPO), Jatropha Curcas (CJCO)* and *Calophyllum inophyllum (CCIO)* by 2-step transesterification method. In this, a pre-treatment acid esterification and followed by base-transesterification reactions were employed for biodiesel production.

In esterification process the crude oil was mixed with methanol in the ratio of 2:1 by volume. 98% concentrated sulphuric acid (1% v/v crude oil) was added as a catalyst to enhance the esterification reaction to the mixture. The mixture of crude oil, methanol and the catalyst were reacted in the reactor at 60 ^{0}C for 3 hours under the stirrer speed of 700 rpm approximately.

The reaction was stopped after 3 hours. The mixture obtained, consisting of two layers, the upper layer of methanol and sulphuric acid and the lower layer consisting the esterified oil. With the help of separating funnel the esterified oil was separated from the methanol and other impurities.

The transesterification reaction was carried out with the mixture of esterified oil and methanol in the ratio of 4:1 by volume in the reactor. 1% of potassium hydroxide by weight was added to the mixture of esterified oil and methanol. The reaction was allowed to take place at a temperature of 60 ^{0}C and stirrer speed of 700 rpm for 2 hours less than an hour to that of esterification reaction.

The reaction was stopped after two hours. The upper layer of the methyl ester (biodiesel) was separated from the lower layer of methanol including other impurities, with the help of separating funnel. This was followed by the post treatment processes.

Finally, sodium sulphate was added to methyl ester to remove water vapours and then filtered with a filter paper.

Apart from above mentioned conventional methods two more methods that are newly developed during the current study are adopted. The details of those methods are discussed in results and discussion chapter.

3.7 Biodiesel production

The biodiesel production from *nigella sativa* by esterification-transesterification (ET) has been explained in section 3.5. Similarly biodiesel production from other feedstocks such as *pongamia pinnata*, *ceiba pentandra*, *Jatropha Curcas* and *calophyllum inophyllum* by esterification-transesterification (ET) has been explained in section 3.6.

The current research yielded a new method which produces biodiesel in one step of transesterification eliminating two-steps of ET method. This method has many advantages compared to ET method. The details of those methods (DT & MDT method) are provided in section 4.2 and 4.3 respectively.

3.8 Performance and emissions testing

Different sets of experiments were conducted on single cylinder four stroke diesel engine as shown in figure 3.5. The specifications of the engine are given in table 3.2. To measure the emissions from the engine exhaust, exhaust gas analyser and smoke meter were employed in the current research and are shown in figure 3.6 and figure 3.7 respectively. The technical specifications of the same are shown in table 3.3 and 3.4 respectively.

Engine performance and emission testing were carried out for the biodiesel-diesel blends of *ceiba pentandra* and *nigella sativa*. The biodiesel-diesel blends of

CPB10 (blend of 10% of *ceiba pentandra* biodiesel and 90% of diesel) and NSB10 (blend of 10% of *nigella sativa* biodiesel and 90% of diesel) were obtained from modified direct transesterification method as explained in detail in section 4.3. The 10% blends of ceiba *pentandra* and *nigella sativa* with diesel were selected because of their comparable fuel properties with diesel.

All the experiments were carried out at engine rated speed of 1500 rpm and different load conditions. Readings were always taken after the engine attained stability of operation. Exhaust gas analyzers were switched ON and allowed to stabilize before measurements. Instruments were periodically calibrated.

Figure 3.5: Compression ignition (CI) engine test rig

Figure 3.6: Exhaust gas analyzer

Figure 3.7: Smoke meter

The engine was operated with diesel, CPB10 and NSB10 as fuels. Diesel was run with optimum injection timing and injection pressure of 23^0BTDC (Before top dead centre) and 205 bar respectively. CPB10 and NSB10 were run at three injection timings of 19^0, 23^0, 27^0 BTDC and injection pressures were varied from 220 bar to 250 bar.

The heat release rate of the fuel causes a variation of gas pressure and temperature within the engine cylinder, and strongly affects the fuel economy, power output and emissions of the engine. It provides a good insight into the combustion process that takes place in the engine. So finding the optimum heat release rate is particularly important in engine research. During this work a computer program was developed to obtain the heat release rate. The heat release rate at each crank angle was calculated by using a first law analysis of the average pressure versus crank angle variation obtained from 100 cycles.

The cylinder pressure and top dead centre (TDC) position signals obtained from sensors were recorded with the aid of AD-convertor. The data acquisition frequency and data length were selected depending on the engine speed, number of cycles of data to be processed, number of signals and resolution required. The signals were recorded with a resolution of one sample/degree of crank angle.

Table 3.2: Specification of the engine

Sl. No.	Parameters	Specification
1	Type	TV1 (Kirlosker made)
2	Nozzle opening pressure	200–250 bar
3	No. of cylinders	Single cylinder
4	No. of strokes	Four stroke
5	Rated power	5.2kW (7 HP) at 1500 rpm
6	Cylinder diameter (bore)	87.5mm
7	Stroke length	110mm
8	Compression ratio	17.5:1

Table 3.3: Specification of the exhaust gas analyzer

Sl. No.	Type	Delta 1600S
1	Object of measurement	Carbon monoxide (CO), Nitrous oxide (NOx) and hydrocarbons (HC)
2	Range of measurement	HC= 0- 20,000 ppm, CO = 0-10%, NOx = 0-5000 ppm (as nitric oxide)
3	Accuracy	HC=±30 ppm HC, CO±0.2% CO, NOx±10 ppm NO,
4	Warm up time	10 min (self-controlled) at 20^0C
5	Speed of response time	Within 15 s for 90% response
6	Power source	100-240 V AC/50 Hz
7	Weight	800 g
8	Sampling	Directly sampled from tail pipe
9	Size	100 mm x 210 mm x 50 mm

Table 3.4: Specification of the smoke meter

Sl. No.	Type	Delta 1600S
1	Object of measurement	Smoke
2	Range of measurement	0-100%
3	Accuracy	±2% relative
4	Warm up time	10 min (self-controlled) at 20^0C
5	Speed of response time	Within 15 s for 90% response
6	Power source	100-240 V AC/50 HZ, 10-16 V DC @15 amps
7	Smoke length	0.43m
8	Sampling	Directly sampled from tail pipe
9	Size	100 mm x 210 mm x 50 mm

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction

This chapter discusses the biodiesel production methods of newly developed direct transesterification and modified direct transesterification in section 4.2 and 4.3 respectively. Section 4.4 discusses in detail the results of crude oils' characteristics, physical and chemical properties of biodiesels of *nigella sativa, ceiba pentandra* and their mixture obtained. Similarly section 4.5 discusses the results obtained for fuel properties of biodiesel-diesel blending for *nigella sativa, ceiba pentandra* and their mixture. These results are obtained by conventional ET method

Section 4.6 explains the results acquired by applying the new method i.e. direct transesterification and also comparison with conventional ET method. Initially the direct transesterification method is applied and tested for *pongamia pinnata* oil alone and expanded the same to other non-edible oils such as *nigella sativa*, *ceiba pentandra, Jatropha Curcas* and *calophyllum inophyllum*. Sections 4.7 and 4.8 are for the results obtained for blends of *pongamia pinnata* by esterification-transesterification and direct transesterification respectively.

Section 4.9 exclusively explains the results obtained by application of modified direct transesterification method which is applied and tested for *nigella sativa* and *ceiba pentandra.*

4.2 Biodiesel production by direct transesterification (DT)

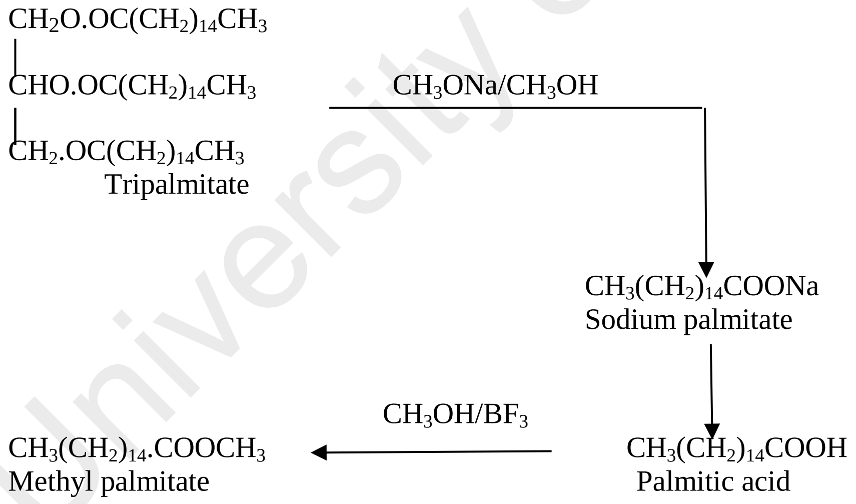
It is seen that the production of biodiesel has been obtained in general by following two step esterification-transesterification methods. However, this method has some critical disadvantages such as high reaction time, high acid value and low biodiesel yield besides problems associated with separation of glycerine from the biodiesel. Thus there have been efforts going on to improve the biodiesel production methods. This has motivated us to try and develop a new method which is named as direct transesterification that uses acid and base catalysts sequentially. This method is applied to produce the biodiesel to all the feedstocks (*Pongamia pinnata*, *nigella sativa*, *ceiba pentandra*, *Jatropha Curcas* and calophyllum inophyllum) considered in the current research. The method works as mentioned below.

Biodiesel was produced from the crude oils (*Pongamia pinnata*, *nigella sativa*, *ceiba pentandra*, *Jatropha Curcas* and calophyllum inophyllum) by chemical reaction known as direct transesterification. The mixture of methanol and sodium methoxide a base catalyst was taken in the reactor. This mixture was shaken well for better mixing. After that boron triflouride as acid catalyst was added carefully. Finally, the neat crude oil was added into the mixture containing the above chemicals. The crude oil, methanol, sodium methoxide and boron triflouride were taken in the ratio 1:4:0.1:0.1 by volume respectively. The direct transesterification (DT) reaction was carried out at 50 ^{0}C for 2hrs under the stirrer speed of 700 rpm approximately. It is worth mentioning that two-step esterification-transesterification takes about 2hrs for esterification and 3hrs for transesterification making it altogether 5hrs process (Khan et al., 2014). Thus the current method (DT) has reduced the production time by 150% to arrive at the final biodiesel product.

After 2hrs, the reaction was stopped. The reaction was believed to be completed after 2hrs based on the kinetics of transesterification reaction. The mixture obtained had two layers, the upper layer of methyl esters with fatty acids and lower layer that of glycerol. Distilled water was added to the mixture for cleaning and washing purposes besides petroleum ether (same quantity as that of methanol) was added to the same mixture to extract methyl esters. The petroleum ether extracts the biodiesel at a very fast rate and gets separated quickly from the glycerol layer, whereas in two-step esterification-transesterification method the mixture normally takes substantially more time for the separation of two layers of biodiesel and glycerol.

The methyl ester (biodiesel) with petroleum ether forms one organic layer while lower layer forms the glycerol, excess water, sodium ions etc. However, lower layer was removed and separated from the methyl ester and petroleum ether mixture. The petroleum ether was separated from the esters by allowing it to evaporate and petroleum ether was condensed back to liquid form for recirculation.

Finally, the methyl ester was further dried with sodium sulphate and filtered on a filter paper to get the biodiesel with minimum impurities. The chemical reaction is as shown in the following reaction.



Glycerine is produced as the by-product which is not mentioned in the scheme. Treating fat with NaOH (Sodium hydroxide) or KOH (Potassium hydroxide) is a basic reaction of the category of saponification. Though the reaction is carried out with absolute methanol it is very difficult to obtain sodium methoxide. It can only be obtained with the reaction between methanol and sodium metal, where there is a formation of sodium methoxide. Our reaction is based on this principle only. We have directly used analytical grade sodium methoxide instead of preparing sodium methoxide in the laboratory. However, the preparation of sodium methoxide can be incorporated in our existing scheme.

The direct transesterification method still had some disadvantages especially while using petroleum ether. The method described was not economical and was consuming more time while evaporation and condensation of petroleum ether. It was decided to avoid usage of petroleum ether itself. Hence, after 2 hrs of chemical reaction, the mixture obtained had two layers, the upper layer of methyl esters with fatty acids and lower layer that of glycerol. The reaction mixture was washed with distilled water without petroleum ether. The biodiesel was separated from water. Sufficient quantity of sodium sulphate was added to remove the moisture contents. The mixture was filtered. Finally biodiesel was obtained. However, in this method the separation of biodiesel from water was difficult and biodiesel yield was not appreciable. There was wastage of biodiesel during separation. Hence, the method further improved with some modifications. The details of the modified method have been explained in section 4.3.

4.3 Modified Direct-Transesterification (MDT)

In the modified direct transesterification method instead of petroleum ether direct diesel was mixed.

By using the diesel in place of petroleum ether, usage of petroleum ether was avoided. Hence, evaporation and condensation time of petroleum ether was eliminated. In direct transesterification method the yield of biodiesel was noted. Based on the yield, the quantity of biodiesel present in the reaction mixture was known. Now, the proportionate volume of diesel to make the B10 blend with biodiesel was decided and added to the reaction mixture instead of petroleum ether. The reaction mixture which contains B10 biodiesel-diesel blend was separated from the other glycerol layer in the same way as did for petroleum ether. The cleaning and separation processes remained same. Potassium carbonate was added to reaction mixture to minimise the formation of moisture contents. It is important to note that the modified DT method yields the required biodiesel-diesel blends directly by mixing diesel into reaction mixture containing biodiesel. However, this is not the case with conventional ET method and DT method. These methods require that the biodiesel be first separated from the reaction mixture and then clean the biodiesel. After that required quantity of diesel is added to arrive at the biodiesel blend.

It is worth mentioning that evaporation and condensation problems and separation timing associated with the petroleum ether in case of direct transesterification method is totally eliminated. The blending time of biodiesel with diesel also eliminated. However, there were no significant differences in fuel properties obtained from B10 biodiesel-diesel blend by direct-transesterification and modified direct-transesterification.

4.4 Characterization of crude oil and its methyl esters of nigella sativa and ceiba pentandra

It is well known that the world is facing dual problem of energy scarcity and environmental related issues. That has motivated the scientific community to look into ways that can address the energy crisis and protecting the environment from harmful emissions. The best alternate to this crisis could be to use renewable energy resources. Thus many researchers are trying to find new feedstocks that can replace the fossil fuels. This has encouraged us too to search new non-edible feedstocks. In the process we found new non-edible oil by name nigella sativa. To the best of our knowledge, it is worth mentioning that this oil has not been tested for its fuel properties and engine suitability. Apart from nigella sativa, ceiba pentandra is also tested for its fuel properties and engine performance to have a comparison of new feedstock i.e. nigella sativa. The following paragraph deals with the results obtained for nigella sativa, ceiba pentandra and mixture of nigella sativa and ceiba pentandra.

4.5 Fatty acid composition of biodiesel

The free fatty acid composition of the biodiesel is shown in table 4.1. It can be seen that the main constituents are palmitic acid, oleic acid and linoleic acid. Biodiesel from *Nigella sativa* possesses the highest contents of linoleic and oleic acids (43.1% and 25.8%) followed by the mixture of feedstock (41.0% and 23.2%) and *Ceiba pentandra* (38.1% and 20.1%), while *Ceiba pentandra* biodiesel possesses the highest contents of palmitic acid (20.8%) followed by the mixture of feedstock (15.3%) and *Nigella sativa* (10.2%).

Table 4.1: The fatty acid composition of different biodiesel

Fatty acid	**Structure**	**NSME**	**CPME**	**CPME+NSME**
Caprylic	C8:0	< 0.1	< 0.1	< 0.1
Capric	C10:0	< 0.1	< 0.1	< 0.1
Lauric	C12:0	< 0.1	< 0.1	< 0.1
Myristic	C14:0	0.1	0.1	0.1
Palmitic	C16:0	10.2	20.8	15.3
Palmitoleic	C16:1	0.2	0.3	0.3
Margaric	C17:0	0.1	0.1	0.1
Stearic	C18:0	3.7	2.7	3.1
Oleic	C18:1	25.8	20.1	23.2
Linoleic	C18:2	43.1	38.1	41.0
C18:2 isomer	C18:2 isomer	< 0.1	3.5	1.2
Linolenic	C18:3	1.4	1.7	1.6
Arachidic	C20:0	0.6	0.5	0.6

Gondoic	C20:1	1.4	0.1	0.8
C20:0 isomer	C20:0 isomer	1.5	1.1	0.8
Behenic	C22:0	0.6	0.4	0.5
Erucic	C22:1	9.0	0.1	4.5
Lignoceric	C24:0	0.3	0.1	0.3

The different properties of crude *nigella sativa* oil (CNSO), *ceiba pentandra* oil (CCPO), mixture of crude oils of *nigella sativa* and *ceiba pentandra* (CCPO+CNSO) along with their respective methyl esters NSME, CPME and NSME+CPME are represented in table 4.2. All the fuel properties fit well with the ASTM D6751 standards. Biodiesel from *nigella sativa* was prepared as explained in the section 3.5. Similarly ceiba pentandra biodiesel was prepared as explained in the section 3.6.

The main findings of this table indicate that *Nigella sativa* has (39,251 kJ/kg) comparatively lower calorific value than *Ceiba pentandra* (39,498 kJ/kg) and the feedstock mixture (39,372 kJ/kg). However, they have marginal difference in calorific value in terms of their respective methyl esters. Kinematic viscosity of *Ceiba pentandra* methyl ester is (4.4180 mm^2/s) better compared to other methyl esters though its crude oil has highest viscosity than other two. The cold flow properties of *Nigella sativa* methyl ester seem to be better than other two types of methyl esters. After observing the different properties of the methyl esters of *Ceiba pentandra* and *Nigella sativa*, it can be concluded that these two biodiesel have some advantages as well as limitations as far as fuel properties are concerned.

Table 4.2: The properties of crude oils and their methyl esters (biodiesel)

Fuel properties	**CCPO**	**CPME**	**CNSO**	**NSME**	**CCPO+CNSO**	**CPME+NSME**
Calorific value (kJ/kg)	39,498	40,064	39,251	39,967	39,372	39,945
Kinematic viscosity (mm^2/s) at 40 °C	34.592	4.4180	32.3680	4.5026	33.375	4.4421
Dynamic viscosity (mPa.s) at 40 °C	31.286	3.8264	29.3880	3.9067	30.243	3.8509
Flash point (^{0}C)	282.5	202.5	150.5	172.5	184.5	186.5
Density (kg/m^3) at 15 °C	0.9216	0.8844	0.9247	0.8861	0.9230	0.8848
Specific gravity at 15 °C	0.9224	0.8852	0.9255	0.8869	0.9238	0.8856
Density (kg/m^3) at 40 °C	0.9044	0.8661	0.9079	0.8677	0.9062	0.8669
Kinematic viscosity at 100 °C	7.6958	1.7260	7.1132	1.7457	7.3935	1.7527
Acid value	22.73	0.16	40.706	0.26	25.690	0.14
Oxidation stability (h at 110^{0}C)	4.23	1.14	8.24	1.32	10.49	3.27
Cloud point (^{0}C)	-7	3	7	-1	-4	0
Pour point (^{0}C)	-3	5	-7	-1	-2	-1
CFPP (^{0}C)	44	4	29	-4	32	-1
Viscosity index (VI)	201.6	216.5	191.6	232.6	197.4	231.6
Refractive index	1.4691	1.4526	1.4718	1.4554	1.4704	1.4540
Transmission (%T)	80.2	89.1	8.2	46.3	25.3	66.5
Absorbance (Abs)	0.096	0.050	1.087	0.335	0.598	0.177

4.6 Physical and chemical properties of biodiesel with their respective blends

Biodiesel is seen as the most acceptable alternative fuel for diesel engines with little or no modifications on the engines apart from its technical and environmental benefits. In addition to this, they are completely soluble in petroleum diesel. However, differences in the chemical structure of biodiesel and diesel fuel make a difference in the basic properties of biodiesel blend such as viscosity, calorific value, flash point, cloud and pour point etc. which further affect the engine performance and emission (Benjumea et al., 2008). The fuel properties of biodiesel, either physical or chemical are strongly influenced by the properties of their respective fatty ester in biodiesel (Knothe, 2005). Hence, it is important to know the basic properties of the biodiesel before using them into engines as fuel. Table 4.3 to table 4.5 shows the detailed properties of blends of diesel and methyl esters produced from *Ceiba pentandra*, *Nigella sativa* and mixture of *Ceiba pentandra* and *Nigella sativa* feedstocks respectively. It is found that, the methyl ester from the feedstock mixture possesses excellent properties including the calorific value, viscosity, cold flow properties, oxidation stability etc.

Table 4.3: The properties of *ceiba pentandra* methyl ester and its blends

Fuel properties	**B0**	**B10**	**B20**	**B40**	**B60**	**B80**
Calorific value (kJ/kg)	45,369	44,900	44,155	43,245	42,007	40,952
Kinematic viscosity (mm^2/s) at 40 °C	3.6056	3.6572	3.7089	3.8594	4.0245	4.2251
Dynamic viscosity (mPa.s) at 40 °C	3.0095	3.0634	3.1183	3.2688	3.435	3.6338
Flash point (^{0}C)	81.5	87.5	91.5	89.5	108.5	128.5
Density (kg/m^3) at 15 °C	0.8518	0.8553	0.8579	0.8645	0.8712	0.8780
Specific gravity at 15 °C	0.8526	0.8561	0.8587	0.8653	0.872	0.8788
Density (kg/m^3) at 40 °C	0.8347	0.8376	0.8408	0.847	0.8535	0.8601
Kinematic viscosity at 100 °C	1.3845	1.4043	1.4333	1.4988	1.5716	1.6519
Oxidation stability (hr at 110^{0}C)	N/R	4.96	3.49	1.73	1.48	1.26
Cloud point (^{0}C)	7	7	5	7	4	2
Pour point (^{0}C)	2	2	3	3	0	3
CFPP (^{0}C)	0	5	4	3	3	0
Viscosity index (VI)	120.3	129.5	145	166.4	189.1	204.7

Table 4.4: The properties of *nigella sativa* methyl ester and its blends

Fuel properties	**B0**	**B10**	**B20**	**B40**	**B60**	**B80**
Calorific value (kJ/kg)	45,369	44,887	44,131	43,197	41,814	41,027
Kinematic viscosity (mm^2/s) at 40 °C	3.6056	3.645	3.7016	3.8897	4.0603	4.2418
Dynamic viscosity (mPa.s) at 40 °C	3.0095	3.0534	3.1132	3.2969	3.4648	3.6532
Flash point (^{0}C)	81.5	85.5	88.5	95.5	106.5	122.5
Density (kg/m^3) at 15 °C	0.8518	0.8554	0.8592	0.8651	0.8725	0.8804
Specific gravity at 15 °C	0.8526	0.8562	0.86	0.8659	0.8733	0.8812
Density (kg/m^3) at 40 °C	0.8347	0.8377	0.841	0.8476	0.8542	0.8613
Kinematic viscosity at 100 °C	1.3845	1.39	1.4316	1.5082	1.5643	1.6747
Oxidation stability (hr at 110^{0}C)	N/R	10.35	7.32	2.58	2.33	1.26
Cloud point (^{0}C)	7	7	6	6	5	1
Pour point (^{0}C)	2	3	3	-2	0	0
CFPP (^{0}C)	0	7	7	6	2	-3
Viscosity index (VI)	120.3	138.7	144.5	166.5	188.1	212.6

Table 4.5: The properties of methyl ester from the feedstock mixture and its blends

Fuel properties	**B0**	**B10**	**B20**	**B40**	**B60**	**B80**
Calorific value (kJ/kg)	45,369	44,921	44,283	43,046	42,041	40,923
Kinematic viscosity (mm^2/s) at 40 °C	3.6056	3.7038	3.753	3.8615	4.0256	4.2441
Dynamic viscosity (mPa.s) at 40 °C	3.0095	3.1054	3.1586	3.2733	3.4386	3.6540
Flash point (^{0}C)	81.5	87.5	90.5	97.5	106.5	124.5
Density (kg/m^3) at 15 °C	0.8518	0.856	0.8588	0.865	0.8718	0.8791
Specific gravity at 15 °C	0.8526	0.8568	0.8596	0.8658	0.8726	0.8799
Density (kg/m^3) at 40 °C	0.8347	0.8384	0.8416	0.8477	0.8542	0.861
Kinematic viscosity at 100 °C	1.3845	1.4205	1.4446	1.5	1.5735	1.6605
Oxidation stability (hr at 110^{0}C)	N/R	15.12	7.53	3.16	1.41	1.03
Cloud point (^{0}C)	7	7	7	5	4	1
Pour point (^{0}C)	2	2	2	5	2	-1
CFPP (^{0}C)	0	5	5	3	2	-2
Viscosity index (VI)	120.3	128.6	143.1	168.6	190.2	207.3

4.6.1 Calorific value

The calorific value is generally termed as the energy content or the energy per unit mass of the fuel. The calorific value of biodiesel is lower compared to diesel due to the presence of higher oxygen contents (Atabani et al., 2013c).

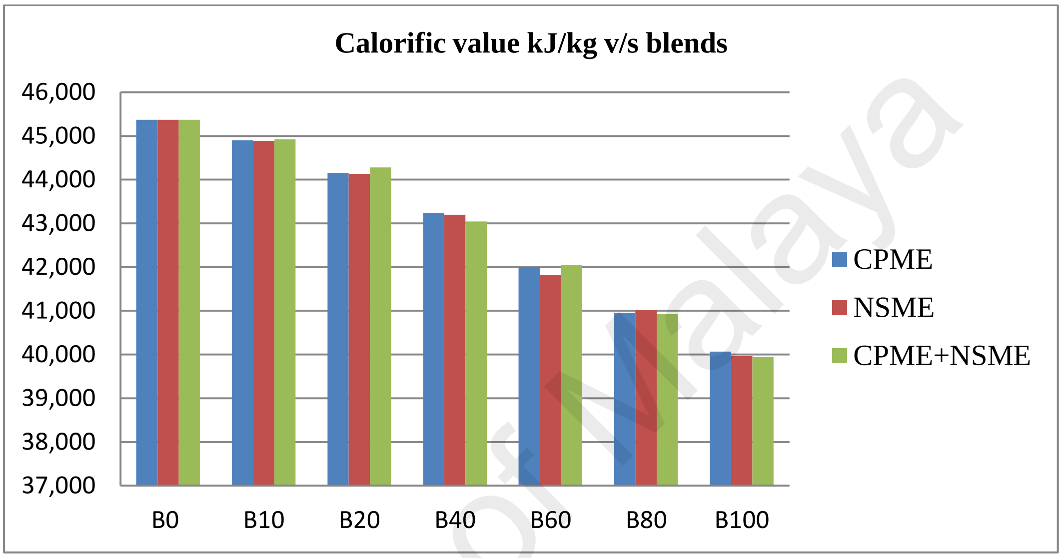


Figure 4.1: Calorific value of different biodiesel with different blends

Figure 4.1 shows the variation of calorific value with the variation in blends. Obviously, diesel (B0) possesses the highest calorific value as compared to biodiesel. The observation on the biodiesel shows that there is a marginal difference in the calorific value of *Ceiba pentandra* and *Nigella sativa*. However, especially B10 and B20 blends from the mixture of feed stocks (CPME+NSME) gave slightly higher calorific value of 44,921 kJ/kg and 44,283kJ/kg than their respective individual methyl ester blends CPME (B10 & B20) and NSME (B10 & B20) i.e. 44,900kJ/kg, 44,155kJ/kg and 44,887kJ/kg, 44,131kJ/kg respectively.

4.6.2 Kinematic viscosity

Kinematic viscosity is an important property of any fuel, because high viscosity could cause excessive fuel injection pressure during engine warm-up (Tat et al., 1999). Though the viscosity of biodiesel is higher than the petro diesel (Knothe et al., 2007), but still it can be observed that all the methyl esters and their blends have acceptable viscosities according to the limit specified by ASTM D6751of (1.9-6 mm^2 /s).

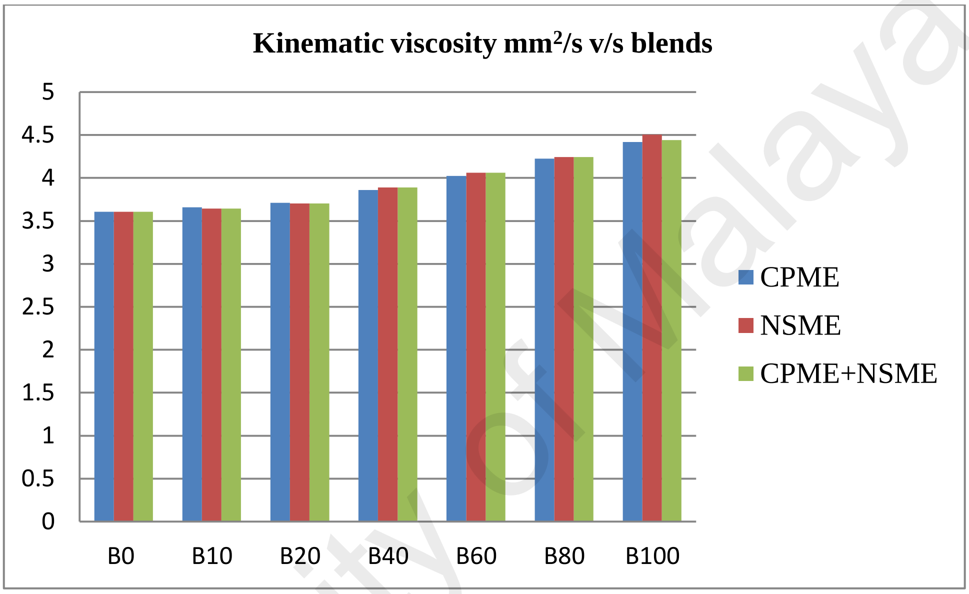


Figure 4.2: Kinematic viscosity of different biodiesel with different blends

From figure 4.2, it is evident that the viscosity increases with the quantity of biodiesel in the blend. However, for B10 and B20 in contrast to calorific value, viscosity of *Nigella sativa* (3.6056mm^2/s and 3.645mm^2/s) is marginally better than the other two esters. Furthermore, as the quantity of biodiesel was increased, it was found that *Ceiba pentandra* (4.0245mm^2/s) and the methyl ester from the mixture (4.0256mm^2/s) possessed slightly better viscosity than *Nigella sativa* (4.0603mm^2/s).

4.6.3 Flash point

The flash point of any fuel is the lowest temperature at which it possesses enough vapors to ignite in the presence of a source of ignition. It is the important parameter as far as storage and handling issues are concerned (Elliott, 2013b).

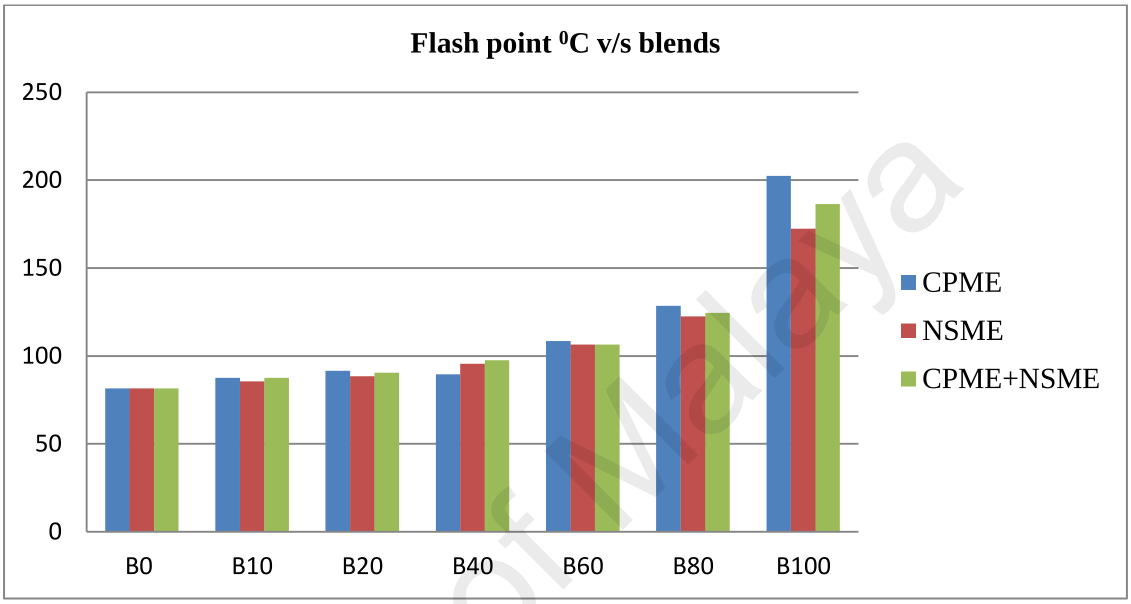


Figure 4.3: Flash point of different biodiesel with different blends

The flash point of *Ceiba pentandra* is more for almost all of its blends than the *Nigella sativa* and the feed stock mixture methyl ester. Especially for B100 it is (202.5 ^{0}C) much more than the flash point of *Nigella sativa* (172.5^{0}C). However, the mixture gives the flash point of 186.5^{0}C which is in between the values obtained by other two methyl ester. Figure 4.3 shows the variation of flash point with the blends .It is interesting to note that the flash point of all the biodiesel are within the limit set by ASTM D6751 of minimum of 130^{0}C.

4.6.4 Oxidation Stability

Oxidation stability is one of the important biodiesel quality parameters. The auto oxidation process of the fuel during its storage makes the fuel unsuitable to be used in engines (Sendzikiene et al., 2005).ASTM D6751standard specifies a minimum of 3hours of the induction period for the oxidation stability.

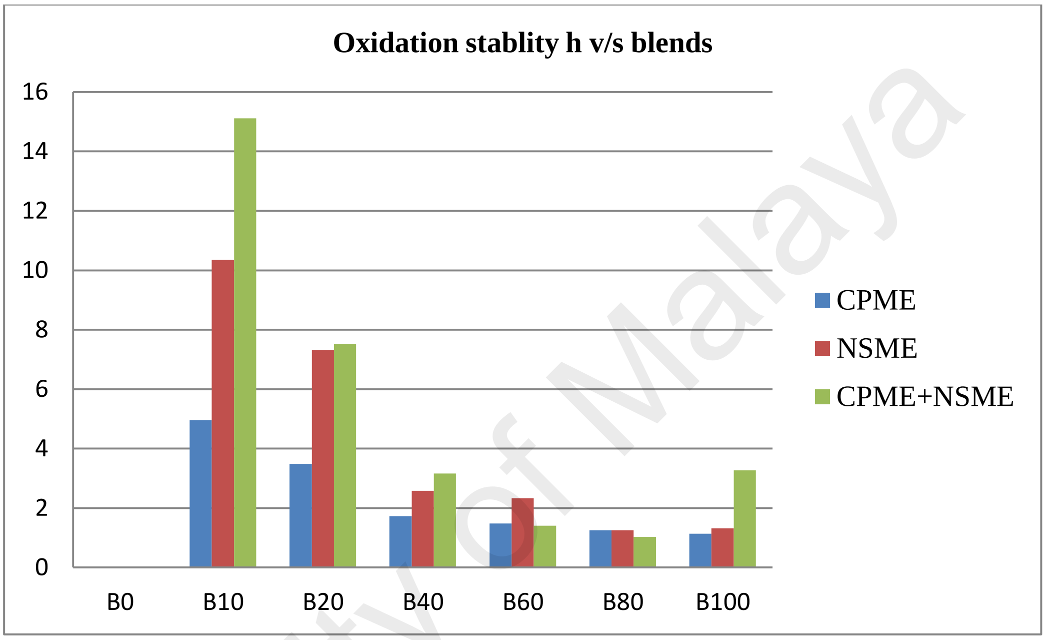


Figure 4.4: Oxidation stability of different biodiesel with different blends

The oxidation stability of the different blends illustrates some interesting results as shown in Figure 4.4. Except for B80 and B60 the oxidation stability of biodiesel from the mixture is found to be better than their individual biodiesel. The oxidation stability of biodiesel from the mixture B10, B20 and B40 are 15.12h, 7.53h and 3.16h respectively. The oxidation stability of *Nigella sativa* seems to be better than *Ceiba pentandra* for all of the blends. Especially for B10 and B20, the oxidation stability of *Nigella sativa* is superior to the *ceiba pentandra*. Nevertheless, for B10 and B20 the oxidation stability of all the biodiesel is within the limit set by ASTM D6751standard.

4.6.5 Cloud, Pour and Cold filter plugging point (CFPP)

It is the tendency of fuel to jelling or to solidify at lower temperatures. At lower temperature the biodiesel may crystallize or solidify and cause the engine to stop. Hence, it is important to know the lowest temperature at which the biodiesel can be used. This could be known in terms of cloud point, pour point and cold filter plugging point temperature (Atabani et al., 2013b).

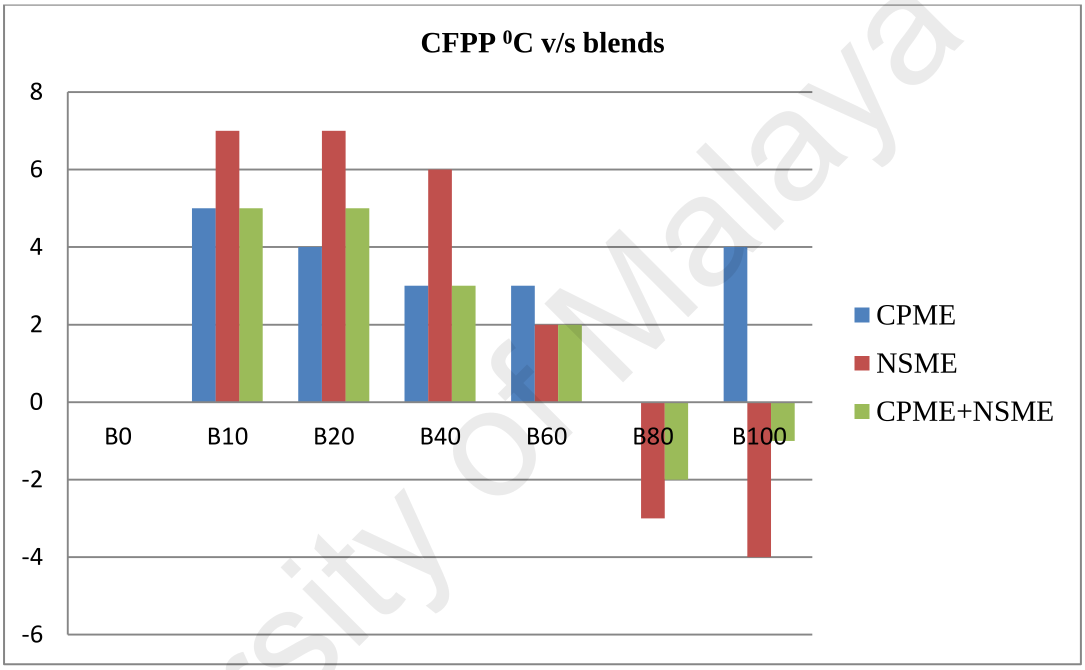


Figure 4.5: CFPP of different biodiesel with different blends

The B10, B20 and B40 of *Ceiba pentandra* possess better CFPP (5^0C, 4^0C and 3^0C respectively) than its counterpart *Nigella sativa* (7^0C, 7^0C, 6^0C respectively). However, it is evident from Figure 4.5 that the biodiesel from the mixture possess the same CFPP (5^0C) value for B10 as that of *Ceiba pentandra*(5^0C) and better CFPP (5^0C) than *Nigella sativa*(7^0C) for B20. Furthermore, it can be concluded that *nigella sativa* could be a potential feedstock for the biodiesel production.

4.7 Characterization of crude pongamia pinnata and its methyl esters

This section presents the fuel properties of biodiesel prepared by direct transesterification (DT) and two step esterification and transesterification (ET) methods. The fuel properties obtained by both the methods have been studied and compared. Initially, to study the DT method crude *pongamia pinnata* oil (CPPO) was used. Later, the same method was applied for other feedstocks as well and explained in subsequent sections. The details of DT method are given in section 4.2. The different fuel properties such as Calorific value, Kinematic viscosity, Flash point, Density of crude *pongamia pinnata* and its methyl ester (PPME) obtained from both ET and DT methods are shown in the table 4.6.

4.7.1 Calorific value

The calorific value of (39,951 kJ/kg) CCPO is found to be higher than calorific value of the methyl esters produced by ET method (39,738kJ/kJ) and DT method (39,505 kJ/kg) as well. This calorific value is less than 42,133 kJ/kg and more than 37,980 kJ/kg compared to previous results available on *pongamia pinnata* biodiesel (Dhar & Agarwal, 2014; Sahoo & Das, 2009). There is no significant difference between the calorific value obtained by ET and DT methods however, by DT method the calorific value is found to be low by 233 kJ/kg.

Table 4.6: The fuel properties of crude oil and its methyl esters (biodiesel)

Fuel properties	**CPPO**	**PPME (ET)**	**PPME (DT)**
Calorific value (kJ/kg)	39,951	39,738	39,505
Kinematic viscosity (mm2/s)at 40 °C	42.8620	4.9907	5.1067
Flash point (^{0}C)	224.5	196.5	200.5
Density (g/cc) at 40 °C	0.9213	0.8740	0.8827
Kinematic viscosity at 100 °C	8.5319	1.8578	2.3351
Acid value mg KOH/g	8.384	0.25	0.10
Oxidation stability(h at 110^{0}C)	0.07	13.32	13.22
Cloud point (^{0}C)	8	18	17
Pour point (^{0}C)	8	11	10
CFPP (^{0}C)	N/D	16	16
Viscosity index (VI)	181.3	191.1	254.5
Yield (%)	--	90	94

4.7.2 Kinematic viscosity

Kinematic viscosity is an important property expected from a fuel for its better supply and atomization for efficient combustion. Though the kinematic viscosity (4.9907 mm^2/s) of *pongamia pinnata* biodiesel prepared by ET method was better compared to viscosity (5.1067 mm^2/s) by DT method but both the results fit within the limit of 1.9-6.0 mm^2/s prescribed by ASTM D6751. The kinematic viscosity of fuel obtained was higher than the results available in the literature (Chauhan et al., 2013; Dhar & Agarwal, 2014; Naik et al., 2008; Sahoo & Das, 2009; Thiruvengadaravi et al., 2012).

4.7.3 Flash Point

The flash point of any fuel is the lowest temperature at which it possesses enough vapours to ignite in the presence of a source of ignition. Flash point of biodiesel fuel is usually higher than 150^0C (Atabani et al., 2012). Furthermore, the vegetable oils or crude oils have higher flash point than their respective methyl esters (Demirbas, 2009). The flash point obtained by ET and DT methods is 196.5^0C and 200.5^0C respectively which were lower than the flash point of CCPO of 224.5^0C.

4.7.4 Density

Density is one of the fuel properties which affect the performance of an engine (Bahadur et al., 1995; Tat et al., 2000). The density of biodiesel prepared by ET is 0.874g/cc is less than the density of biodiesel prepared from DT method i.e. 0.8827g/cc.

4.7.5 Acid value

Acid value is a measure of free fatty acids contained in a fresh fuel sample. High acid value may cause severe corrosion problems in the automotive fuel supply systems.

Hence, 0.5 mg KOH/g is the limit set by both ASTM D664 and EN 14104 standards. The fuel properties stated above slightly favoured the ET method over DT method but the acid value (0.1 mg KOH/g) of biodiesel prepared from DT method was found to be less than the acid value (0.25 mg KOH/g) of biodiesel prepared by ET method. The acid value so obtained by DT is less compared to 0.12, 0.23 and 0.42 reported by different researchers (Atabani et al., 2012; Chauhan et al., 2013; Naik et al., 2008).

4.7.6 Yield

Yield is an important aspect of biodiesel production. Higher values of yield represent lesser quantities of free glycerol present in the final product of biodiesel. In case of DT method the partial saponification which results in % loss of yield is skipped. Hence, the % yield of biodiesel obtained was higher in case of DT (94%) method than in ET (90%) method.

4.8 Fuel properties of biodiesel-diesel blends (ET)

The different fuel properties of diesel and biodiesel-diesel blends are mentioned in the table 4.7 in which biodiesel was prepared by ET method. All the mentioned properties have been found experimentally with the instruments shown in table 3.1.

Table 4.7: The fuel properties of *pongamia pinnata* methyl ester and its blends by ET

Fuel properties	**B0**	**B10**	**B20**	**B40**	**B60**	**B80**
Calorific value (kJ/kg)	45,369	44,888	44,183	43,052	41,920	40,737
Kinematic viscosity (mm^2/s)at 40 °C	3.6056	3.7380	3.8430	4.0615	4.3480	4.6745
Flash point (^{0}C)	81.5	92.5	95.5	100.5	113.5	131.5
Density (g/cc) at 40 °C	0.8347	0.8384	0.8425	0.8500	0.8583	0.8664
Acid value mg KOH/g	0.33	-	-	-	-	-
Yield %	90	-	-	-	-	-
Kinematic viscosity at 100 °C	1.3845	1.4149	1.4570	1.5408	1.6447	1.7514
Viscosity index (VI)	120.3	123.4	130.2	152.4	170.1	178.4

4.9 Fuel properties of biodiesel-diesel blends (DT)

The fuel properties of B100 (Biodiesel) which was prepared by DT method are found experimentally. However, the fuel properties of B10, B20, B40, B60, and B80 have been predicted by linear mathematical equations 4.1 to 4.6 with the help of fuel properties at two points B0 (diesel) and B100. Table 4.8 shows the fuel properties of different biodiesel-diesel blends for DT method.

The following equations are used to predict the different fuel properties.

Calorific value $y = 45369 - 58.64x$ (4.1)

Kinematic Viscosity at 40°C $y = 3.6056 + 0.015004x$ (4.2)

Density at 40 °C $y = 0.8347 + 0.00048x$ (4.3)

Flash point $y = 81.5 + 1.19x$ (4.4)

Kinematic viscosity at 100°C $y = 1.3845 + 0.0095x$ (4.5)

Viscosity index $y = 120.3 + 1.3420x$ (4.6)

Where y is the fuel property and x is the blend percentage.

Table 4.8: The fuel properties of *pongamia pinnata* methyl ester and its blends by DT

Fuel properties	**B0**	**B10**	**B20**	**B40**	**B60**	**B80**
Calorific value (kJ/kg)	45,369	44782	44196	43023	41850	40677
Kinematic viscosity (mm^2/s)at 40 °C	3.6056	3.7556	3.9056	4.2057	4.5058	4.8059
Flash point (^0C)	81.5	93.4	105.3	129.1	152.9	176.7
Density (g/cc) at 40 °C	0.8347	0.8395	0.8443	0.8539	0.8635	0.8731
Acid value mg KOH/g	0.12	-	-	-	-	-
Yield %	92%	-	-	-	-	-
Kinematic viscosity at 100 °C	1.3845	1.4796	1.5746	1.7647	1.9549	2.1450
Viscosity index (VI)	120.3	133.72	147.14	173.98	200.82	227.66

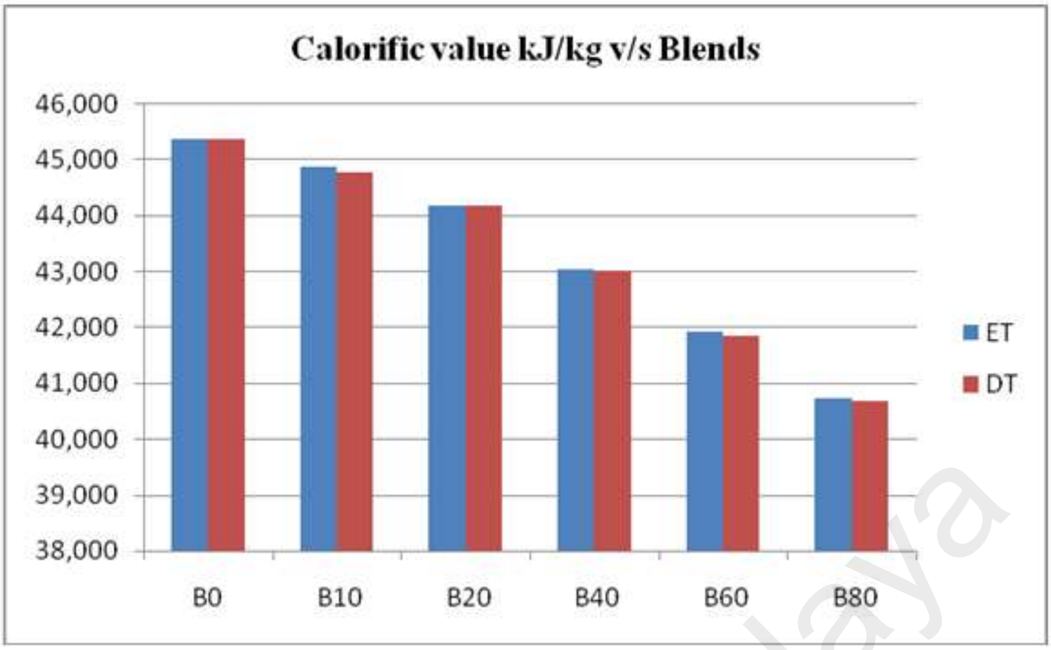


Figure 4.6: Calorific value of different biodiesel-diesel blends

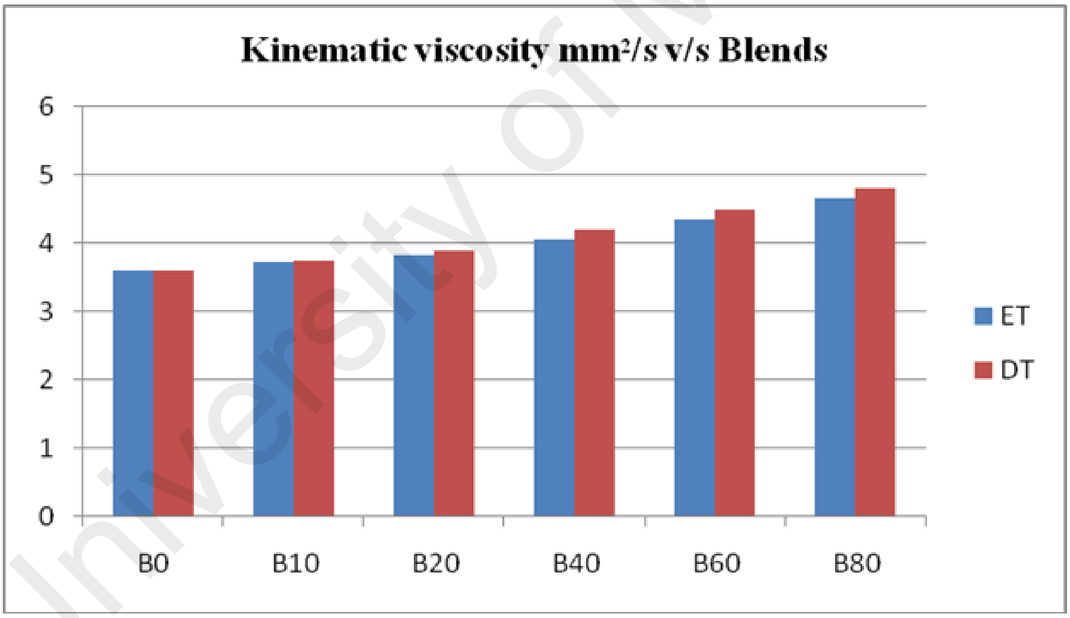


Figure 4.7: Kinematic viscosity of different biodiesel-diesel blends

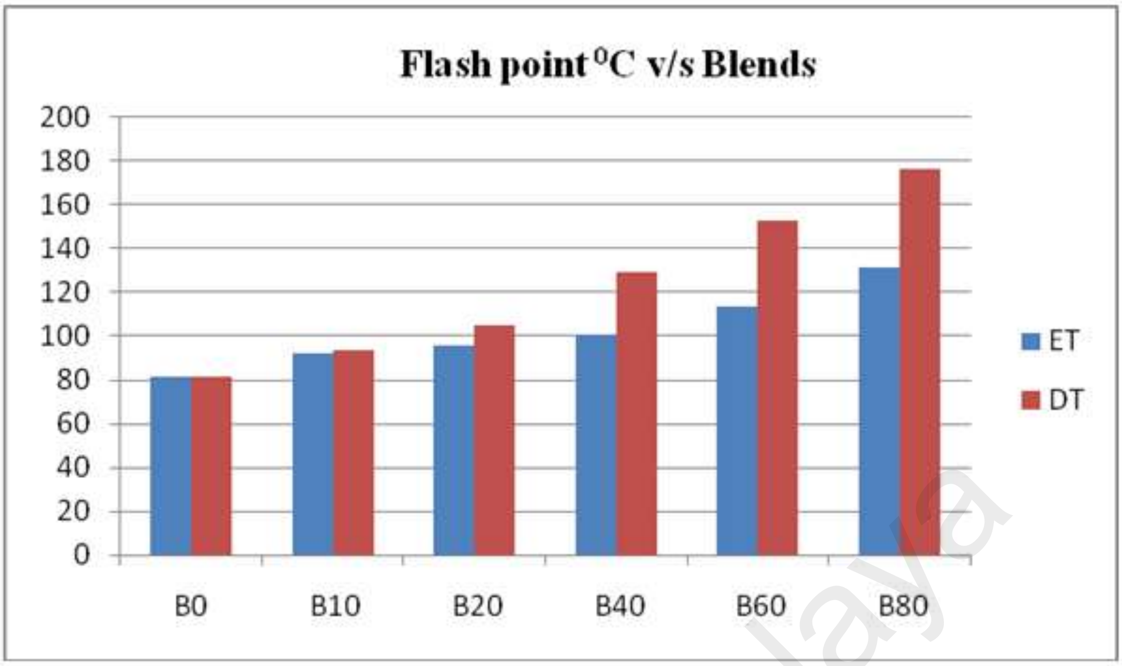


Figure 4.8: Flash point of different biodiesel-diesel blends

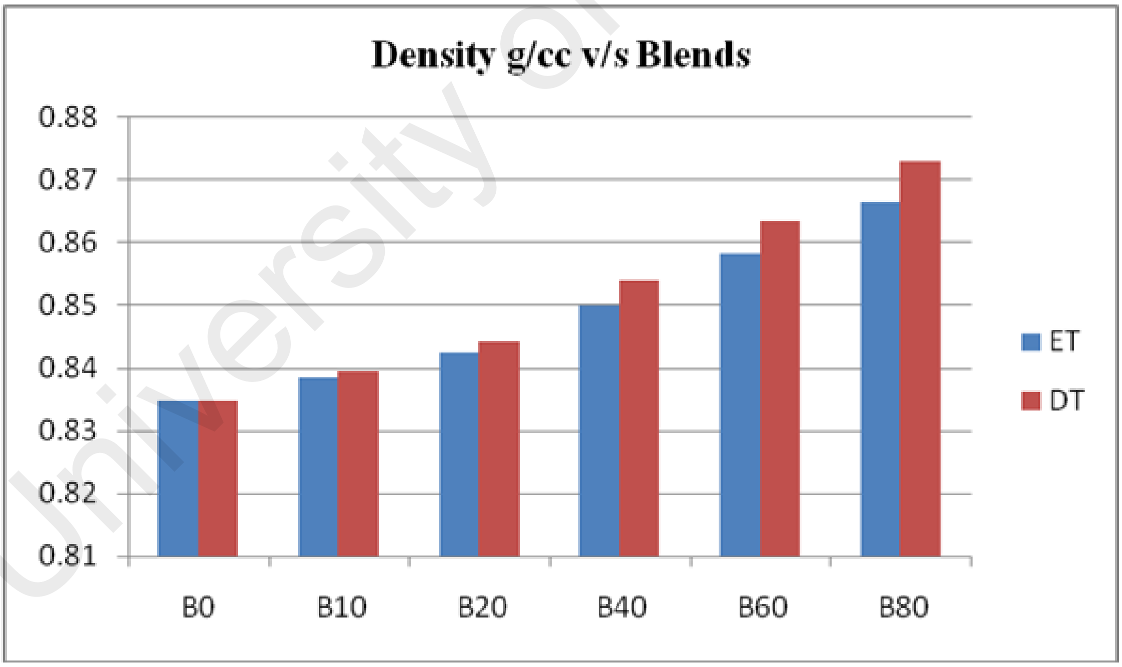


Figure 4.9: Density of different biodiesel-diesel blends

The variation of different fuel properties with the variation of blends for both ET and DT methods are shown in figure 4.6 to figure 4.9. There were no significant differences between the fuel properties of the biodiesel obtained from ET and DT methods except for acid value. Therefore, there is no significant difference in the fuel properties of all of their respective blends of ET and DT method. However, the limitations associated with the ET method cannot be neglected. The ET method also known as acid-alkaline catalyzed transesterification produces high biodiesel yield but 5 hrs of reaction time and higher production cost are the problems associated with it (Wang et al., 2007). In some results reported yield to ester is normal but purification of glycerol and ester is difficult besides high cost of equipment and more reaction time (Bankovic-Ilic et al., 2012; Jain & Sharma, 2010b; Khan et al., 2014; Marchetti, 2012). Boron triflouride catalyzed transesterification often utilized as a rapid means of esterifying free fatty acids. Similarly the reaction between sodium methoxide in methanol and a vegetable oil is very rapid (Demirbas, 2008). Hence, in the present research work it can be noted that less time is required for DT to complete the reaction with higher biodiesel yield. This encouraged us to apply the DT method to other non-edible feedstocks. Hence, same method was applied to produce the biodiesel from *Jatropha Curcas* (JCME), *nigella sativa* (NSME), *ceiba pentandra* (CPME) and calophyllum innophylum (CIME). The fuel properties of JCME, NSME, CPME, and CIME are shown in table 4.9.

Table 4.9: Fuel properties of different biodiesel prepared from DT method

Fuel properties	**JCME**	**NSME**	**CPME**	**CIME**
Calorific value (kJ/kg)	39740	39970	40067	39520
Kinematic viscosity (mm2/s)at 40 °C	4.9586	4.5036	4.4119	5.5387
Flash point (^{0}C)	187.5	174.5	204.5	164.5
Density (g/cc) at 40 °C	0.8632	0.8680	0.8665	0.8785
Kinematic viscosity at 100 °C	1.8558	1.7459	1.728	1.990
Acid value mg KOH/g	0.12	0.26	0.16	0.11
Oxidation stability(h at 1100C)	4.85	1.35	1.15	6.15
Cloud point (0C)	11	-1	5	11
Pour point (0C)	11	-1	3	12
CFPP (0C)	11	-5	4	10
Viscosity index (VI)	194.5	232.5	216.5	183.4
Yield (%)	95	92	93	95

4.10 Modified direct transesterification (MDT)

The modified direct transesterification method was applied to two non-edible feedstocks of *nigella sativa* and *ceiba pentandra*. The method used to get the B10 blend of both respective biodiesel. The detailed procedure was same as explained in section 4.3. The B10 blends of both biodiesel characterised and found the fuel properties. Table 4.10 shows the fuel properties of B10 *nigella sativa* (NSB10) and *ceiba pentandra* (CPB10). The properties obtained by MDT applied to nigella sativa and ceiba pentandra clearly show that there is not much difference in the fuel properties obtained by all three methods i.e. ET, DT and MDT methods. Thus it can be confidently said that the MDT and DT are well qualified to be adopted as biodiesel production techniques. The MDT and DT are particularly encouraging since they have plenty of advantages (already mentioned in previous sections) over conventional ET method.

Table 4.10: Fuel properties of biodiesel-diesel blend B10 (MDT)

Fuel properties	NSB10	CPB10	Diesel
Calorific value (kJ/kg)	44,890	44,904	45,369
Kinematic viscosity (mm^2/s) at 40 °C	3.655	3.6568	3.6056
Dynamic viscosity (mPa.s) at 40 °C	3.0535	3.0636	3.0095
Flash point (°C)	85.7	87.6	81.5
Density (g/cc) at 40 °C	0.8441	0.8377	0.8347
Oxidation stability(h at 110 °C)	10.25	4.98	N/R
Cloud point (°C)	7	7	7
Pour point (°C)	3	2	2
CFPP (°C)	7	5	0

N/R= Not required

4.11 Engine performance tests

The previous sections have described the biodiesel production methods along with characterization in terms of biodiesel fuel properties of new as well as existing oils. However, the study would not be complete if the developed biodiesel is not tested in the engine. Thus, the engine testing was carried out for the biodiesel-diesel blend (10%) produced by MDT method of nigella sativa and ceiba pentandra feedstocks. It should be note that only two of the five oils considered in the current research are subjected to engine testing. The reason being that the nigella sativa is a new feedstock that deserves to be tested, on the engine to establish its authority as a potential biodiesel feedstock. The other oil considered for engine testing is ceiba pentandra for the reason that there is not much work done on this oil with respect to its behaviour in the engine due to variations in injection parameters.

4.11.1 Performance characteristics with variable injection timing

The diesel engine was run with diesel at a known optimum injection timing of 23^0 BTDC (Before top dead centre) and an injection pressure of 205bar for different loading conditions (Banapurmath et al., 2008). However, the biodiesel-diesel blended (CPB10 and NSB10) fuelled engine was run at three different injection timings of 19^0 BTDC, 23^0 BTDC and 27^0 BTDC at fixed injection pressure of 205bar at different loading conditions.

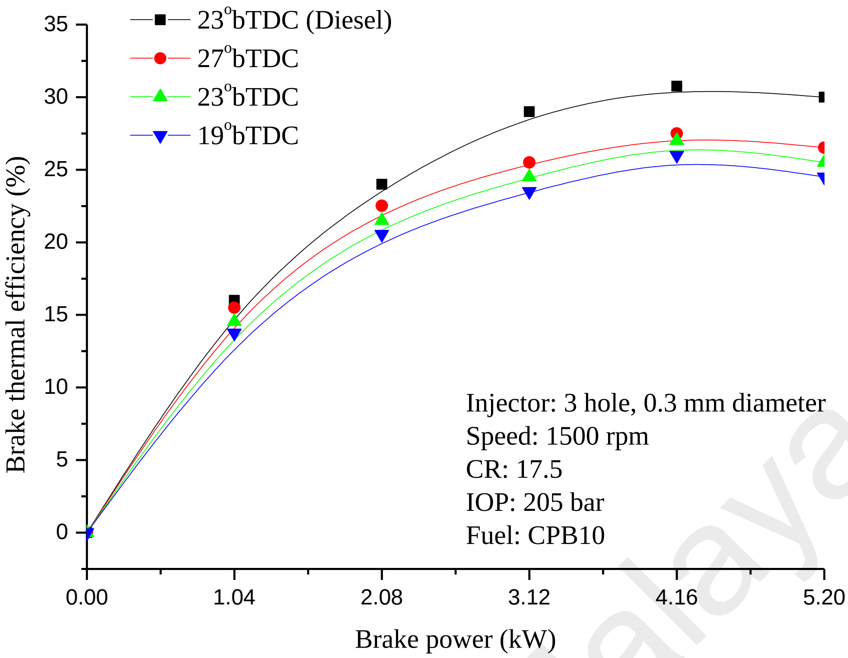


Figure 4.10: Effect of brake power on brake thermal efficiency (CPB10)

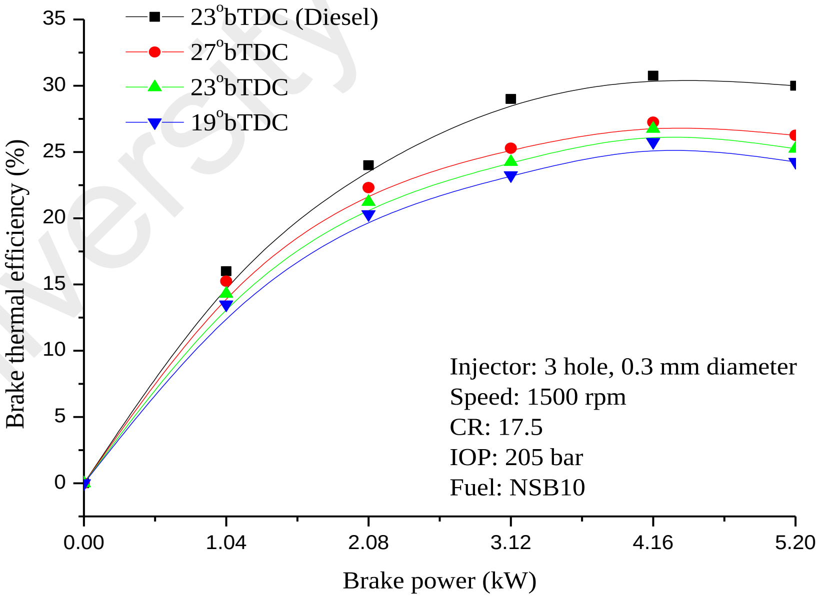


Figure 4.11: Effect of brake power on brake thermal efficiency (NSB10)

4.11.1.1 Brake thermal efficiency

Brake thermal efficiency is one of the important performance characteristics of an internal combustion engine (IC engine). It is defined as the ratio of brake power produced at the crankshaft to the energy in the fuel burned to produce this power. The brake thermal efficiency of diesel, CPB10 and NSB10 is shown in figure 4.10 and figure 4.11. The brake thermal efficiency of all the fuels increases with increase in the brake power steadily and fuel injection advancements. The combustion is slow in case of biodiesel-diesel blend due to its high viscosity than diesel. High viscosity offers more resistance to flow that intern slows down the fluid movement thus, the atomization is poorer. The lower atomization leads to weak combustion thus reducing the heat release rate leading to low brake thermal efficiency. This effect can be compensated by advancing the fuel injection. The advance fuel injection provides more time to fuel to get mixed with air and better atomization thus increasing the combustion rate. Hence, the brake thermal efficiency increases with fuel injection advancements. The brake thermal efficiency is found to be maximum for both diesel and biodiesel-diesel blends at 80% load as expected. However, brake thermal efficiency for diesel, CPB10 and NSB10 is 30.75%, 27% and 26.75% respectively at an injection timing of 23^0 BTDC and injection pressure of 205bar. This is expected since the calorific value of all the biodiesel fuels reported in open literature is lesser than that of diesel. However, it can be concluded from figure 4.10 and figure 4.11 that one can slightly increase the brake thermal efficiency biodiesel-diesel blends (i.e. 27.5% and 27.25% for CPB10 and NSB10 respectively) if injection timing for biodiesel-diesel blends is advanced to 27^0BTDC. It is known that there is always optimum injection timing for an engine for best possible efficiency with lowest emissions. The higher brake thermal efficiency for CPB10 is attributed to its higher calorific value and lower viscosity than NSB10.

4.11.1.2 Emission characteristics

There are many fuels available that can be used in IC engines but current policies have put stringent regulations to control the harmful emissions and these policies are essential to safe guard the environment. Thus any new fuel discovered has to meet emission legislation standards. Thus the current study is further explored to know the emissions characteristics of CPB10 and NSB10.

The effects of injection timing and brake power on the emissions such as carbon monoxide (CO), hydrocarbon (HC), oxides of nitrogen (NO_x) and smoke are shown for diesel, CPB10 and NSB10 in figure 4.12 to figure 4.19.

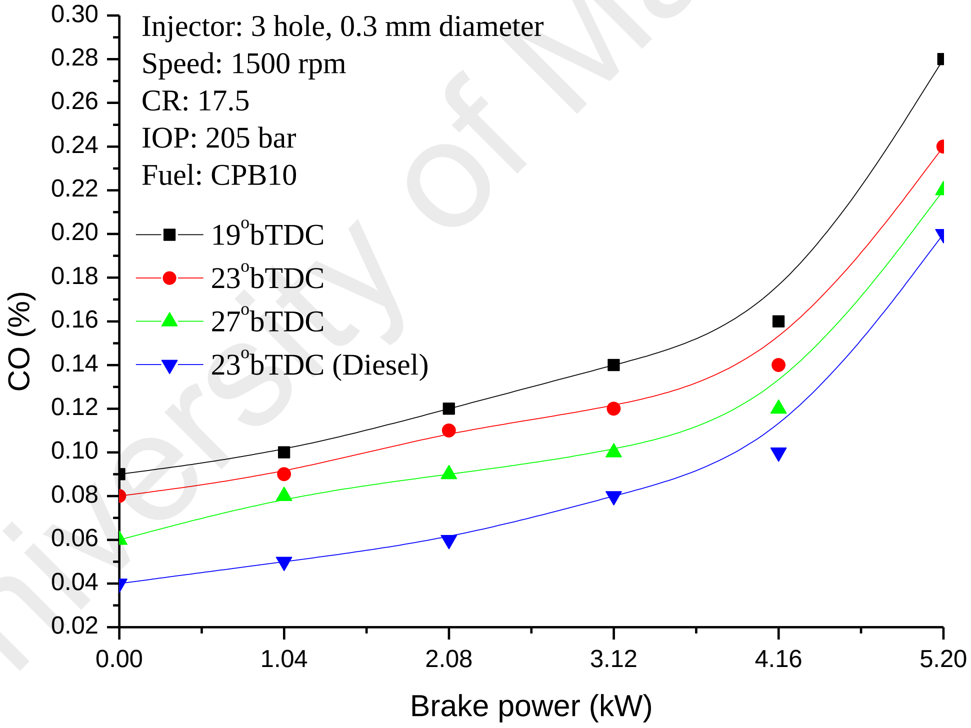


Figure 4.12: Effect of brake power on CO emission (CPB10)

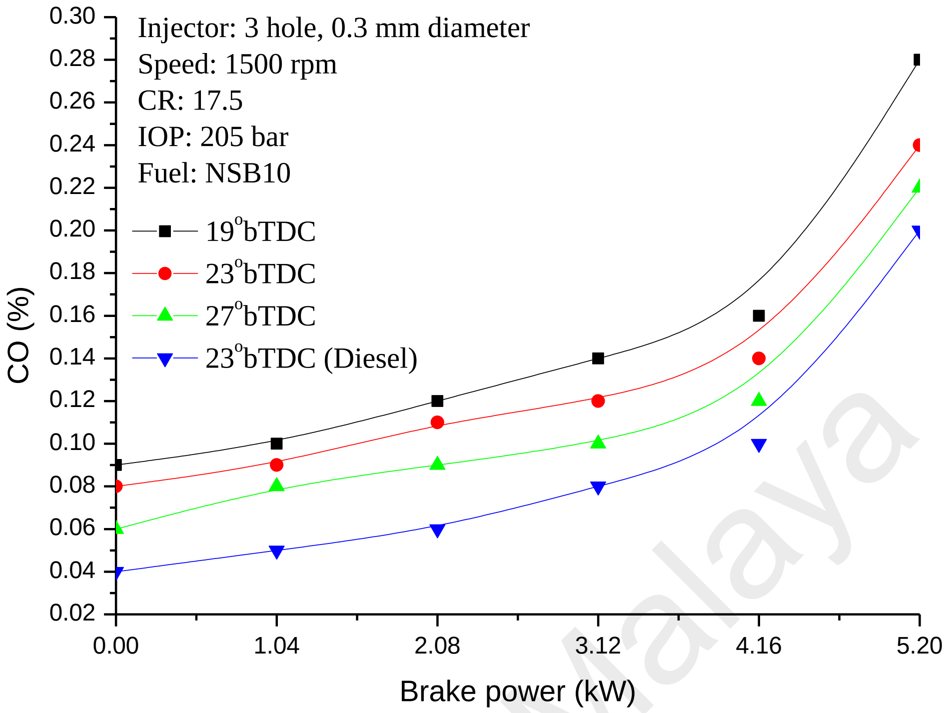


Figure 4.13: Effect of brake power on CO emission (NSB10)

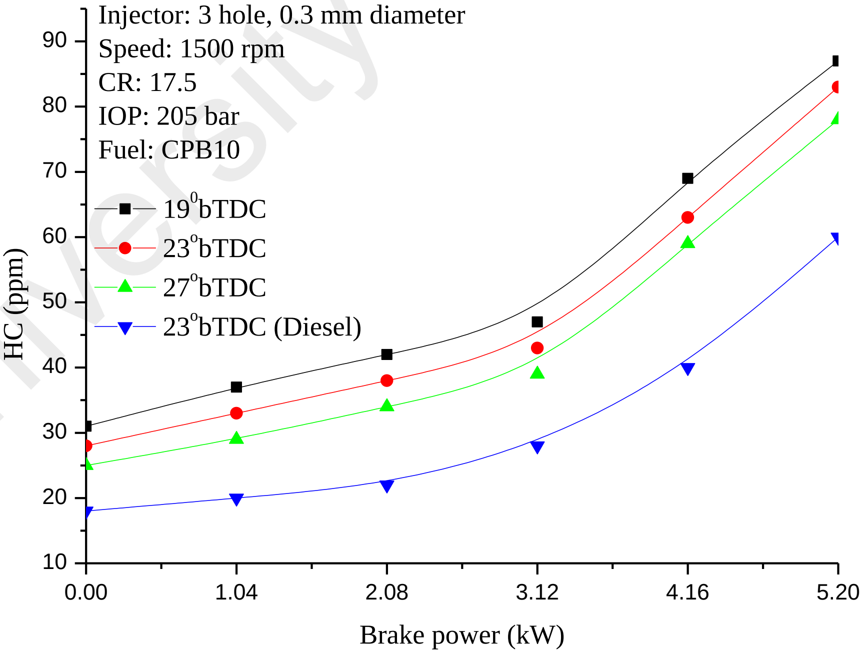


Figure 4.14: Effect of brake power on HC emission (CPB10)

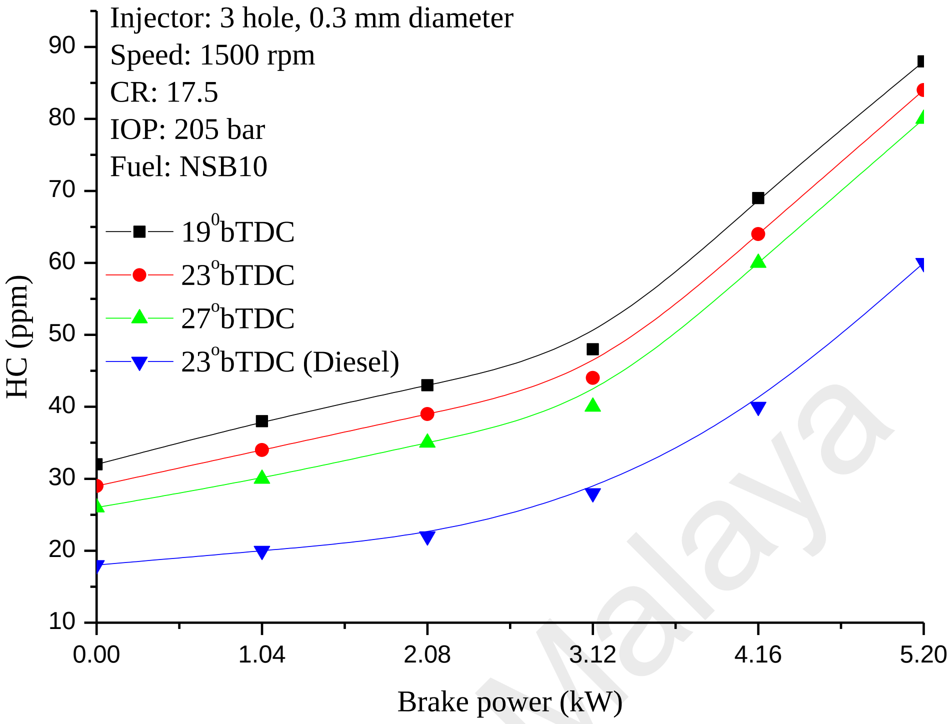


Figure 4.15: Effect of brake power on HC emission (NSB10)

The effects of brake power on CO and HC emissions for diesel, CPB10 and NSB10 are shown in figure 4.12 to figure 4.15. CO and HC emissions are found to be more in case of biodiesel compared to diesel. Poor atomization and low volatility are the reasons responsible for these higher CO and HC in case of biodiesel. The brake thermal efficiency was found to be more at 80% load hence; the emissions released at 80% load are discussed henceforth.

The formation of CO and HC in exhaust decreased by advancing the injection timing. It is due to improved combustion and improved brake thermal efficiency at advanced injection timing. The CO for diesel, CPB10 and NSB10 is found to have the same trend. 0.1% of CO for diesel and 0.14% of CO were obtained for both CPB10 and NSB10 at 23^{0}BTDC and 80% load. The formation of CO decreases by 0.2% in case of CPB10 and NSB10 by advancing injection timing by 4^0 (at 27^{0}BTDC).

HC produced by CPB10 is slightly less than the HC produced by NSB10. At 80% load and 23^0BTDC the HC for CPB10 and NSB10 are 63ppm and 64ppm respectively, whereas for diesel it was found to be 40ppm. The formation of CO and HC decreases to 59ppm and 60ppm respectively by advancing the injection timing by 4^0 (at 27^0BTDC).

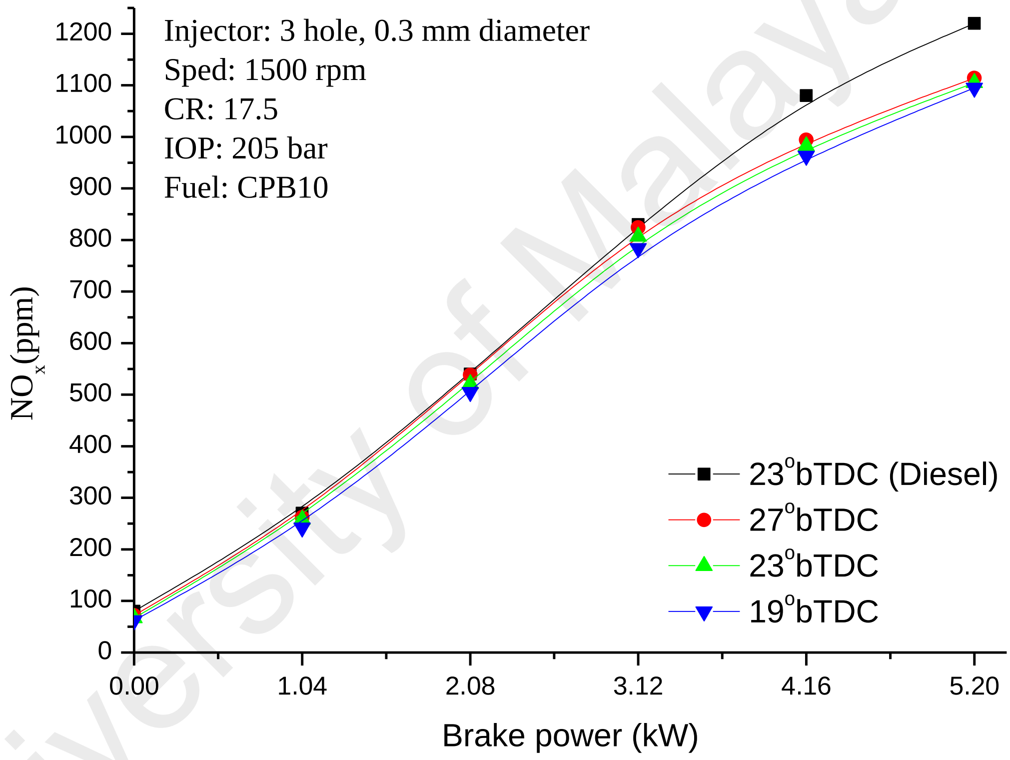


Figure 4.16: Effect of brake power on NOx emission (CPB10)

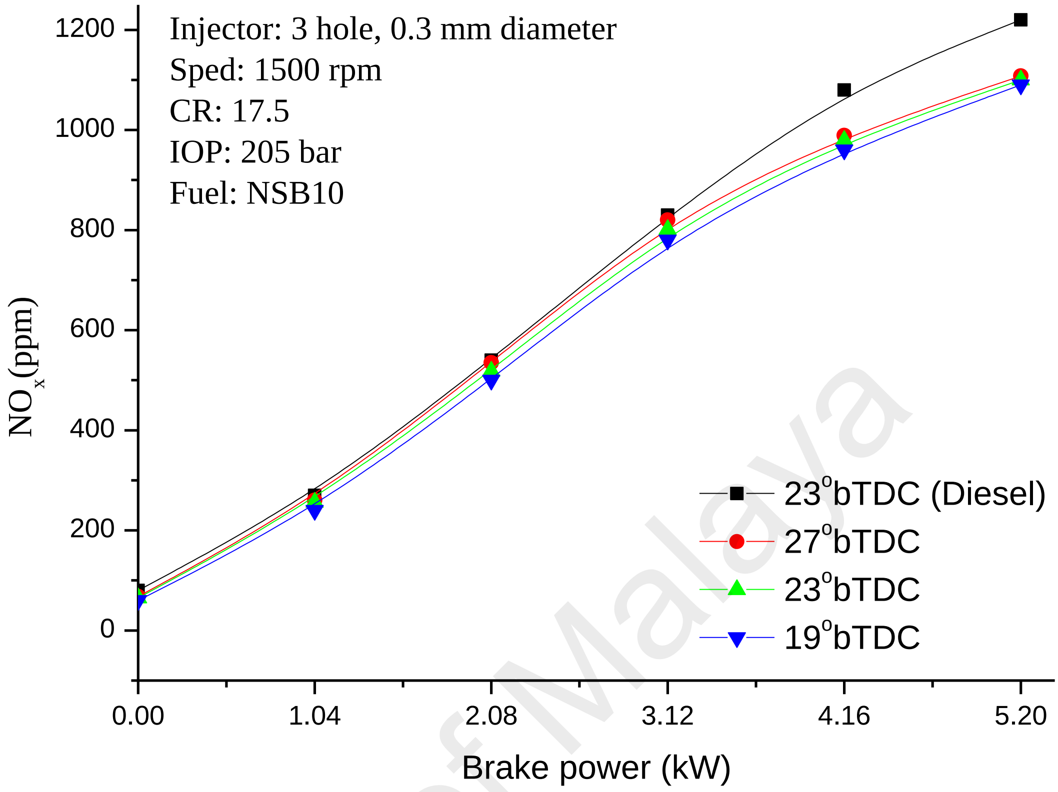


Figure 4.17: Effect of brake power on NOx emission (NSB10)

The effect of brake power on nitrogen oxides emissions is shown in figure 4.16 and figure 4.17. It is observed that NOx emissions are higher for diesel compared to the two biodiesel. The maximum amount of NOx for diesel, CPB10 and NSB10 is found to be 1080 ppm, 982 ppm and 979 ppm respectively at 80% load at 23^{0}BTDC. However, the formation of NOx reduced slightly with retarding the injection timing. Retarding the injection timing reduces the NOx due to poor combustion leading to low cylinder gas temperature. The lower heat released by the biodiesel might be another reason for lower NOx emissions.

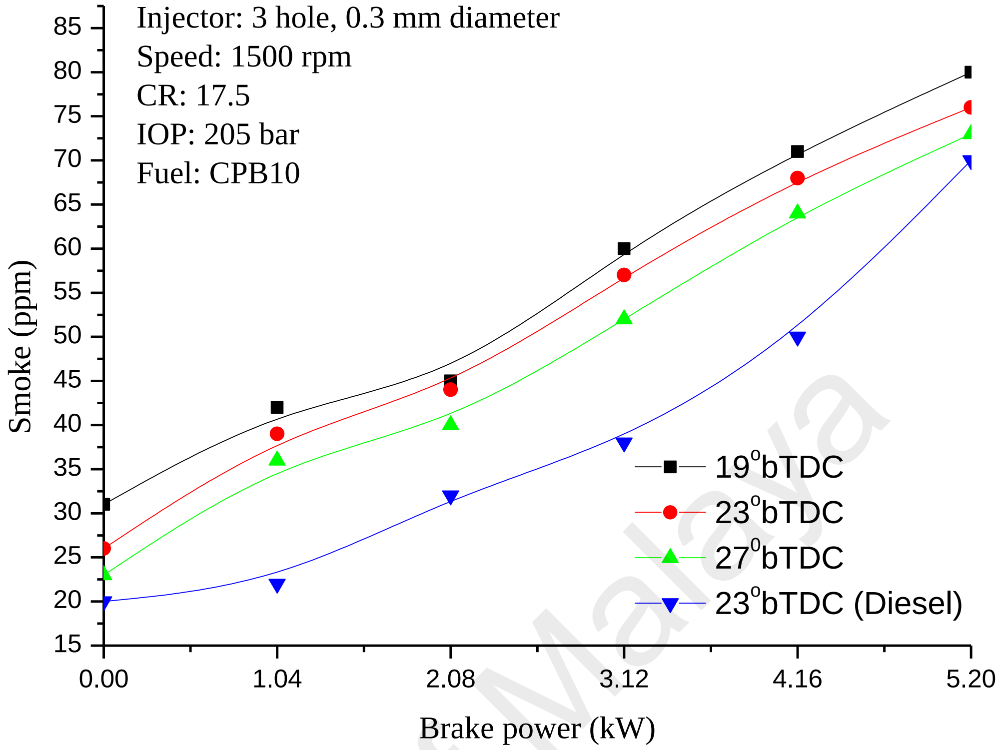


Figure 4.18: Effect of brake power on smoke capacity (CPB10)

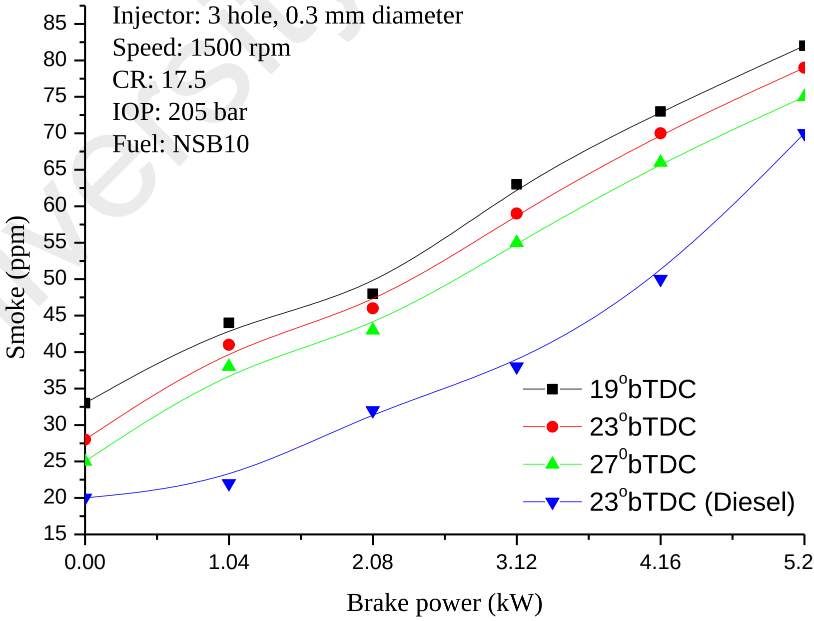


Figure 4.19: Effect of brake power on smoke capacity (NSB10)

Higher smoke capacity is observed for biodiesel compared with diesel at all loads. At 80% load and 23^0 BTDC injection timing, smoke for CPB10 and NSB10 is found to be 68ppm and 70ppm respectively as shown in figure 4.18 and figure 4.19. For diesel 50ppm of smoke is found at same engine operating conditions. The smoke decreases by advancing the injection timing due to dominance of premixed combustion phase. The mass particulate emissions also decrease as injection is advanced due to better combustion. Smoke for CPB10 is reduced from 68ppm to 64ppm and for NSB10 it is reduced from 70ppm to 66ppm by advancing the injection timing to 27^0 BTDC.

4.11.2 Performance characteristics with variable injection pressure

It is observed from previous discussion (section 4.11.1) that the performance of the biodiesel is optimum at advanced injection timing i.e. 27^0BTDC. It is known that injection timing more advanced than this results in early combustion before the piston reaches top dead centre (TDC). Similarly more retarded than this results in late combustion of the fuel. Hence, the performance tests were conducted for a fixed injection timing of 27^0BTDC and different injection pressure from 220bar to 250bar in the interval of 10bar at various loading conditions. It should be noted that the tests are conducted by varying the injection pressure only for biodiesel-diesel blends of CPB10 and NSB10.

4.11.2.1 Brake thermal efficiency

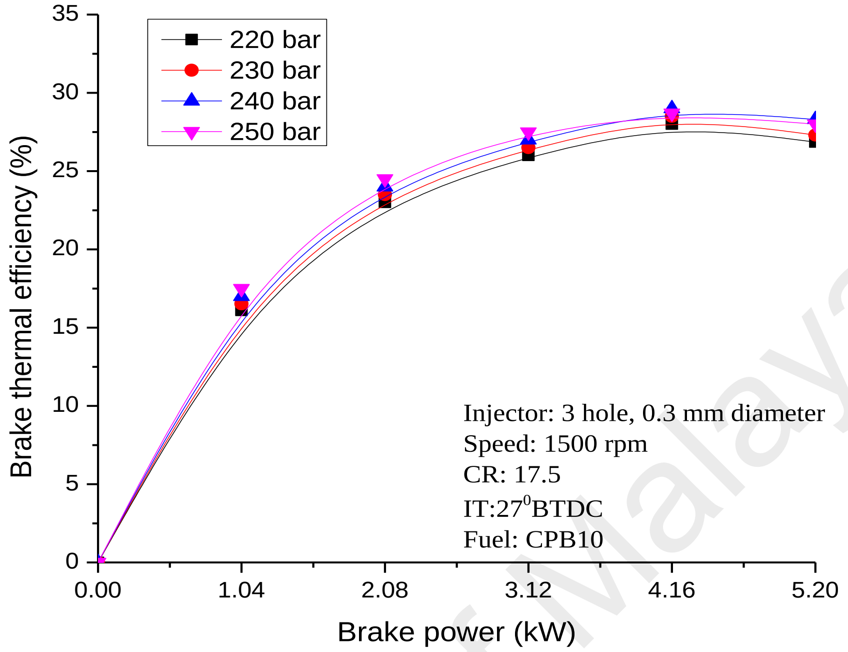


Figure 4.20: Effect of brake power on brake thermal efficiency (CPB10)

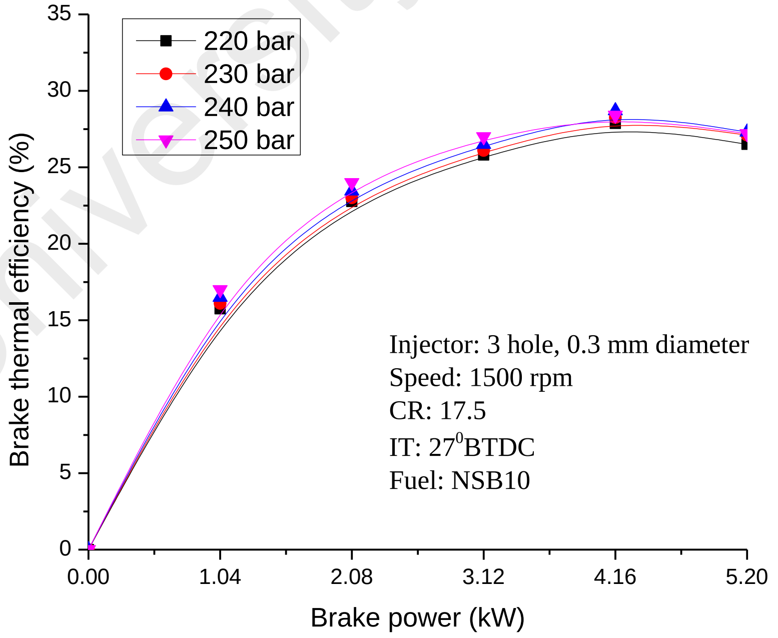


Figure 4.21: Effect of brake power on brake thermal efficiency (NSB10)

The brake thermal efficiency of both the biodiesel increased with increase in the injection pressure from 220bar to 240bar as shown in Figure 4.20 and Figure 4.21. Increasing the injection pressure increases the better fuel spray and hence, better atomization and mixing of fuel with air that leads to better combustion. However, further increase in injection pressure decreases the brake thermal efficiency. Maximum brake thermal efficiency obtained for CPB10 and NSB10 is 29% and 28.7% respectively at an injection pressure of 240bar, fixed injection timing of 27^0BTDC and 80% load. The efficiencies obtained by the respective biodiesel-diesel blends CPB10 and NSB10 (29% and 28.7%) is very close to the brake thermal efficiency obtained by diesel (30.75%) at 205bar and 23^0BTDC. Therefore, by increasing the injection pressure by 35bar and advancing the injection timing by 4^0BTDC for biodiesel-diesel blend (10%) run engine, same performance as that of diesel engine at 205bar injection pressure and 23^0BTDC injection timing can be achieved.

4.11.2.2 Emission characteristics

The effect of injection pressure and brake power at an injection timing of 27^0BTDC on the emissions such as CO, HC, NOx and smoke are shown for CPB10 and NSB10 in Figure 4.22 to Figure 4.29.

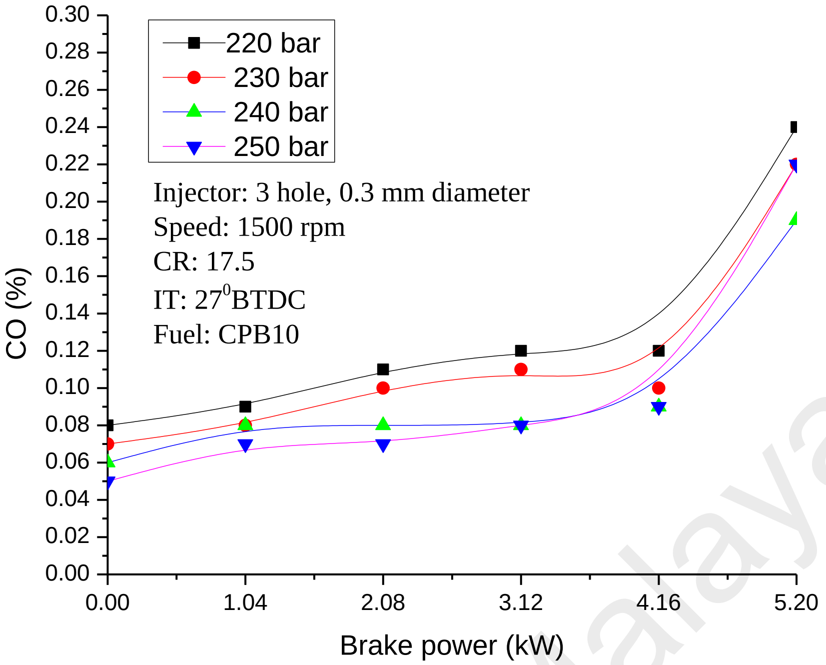


Figure 4.22: Effect of brake power on CO emission (CPB10)

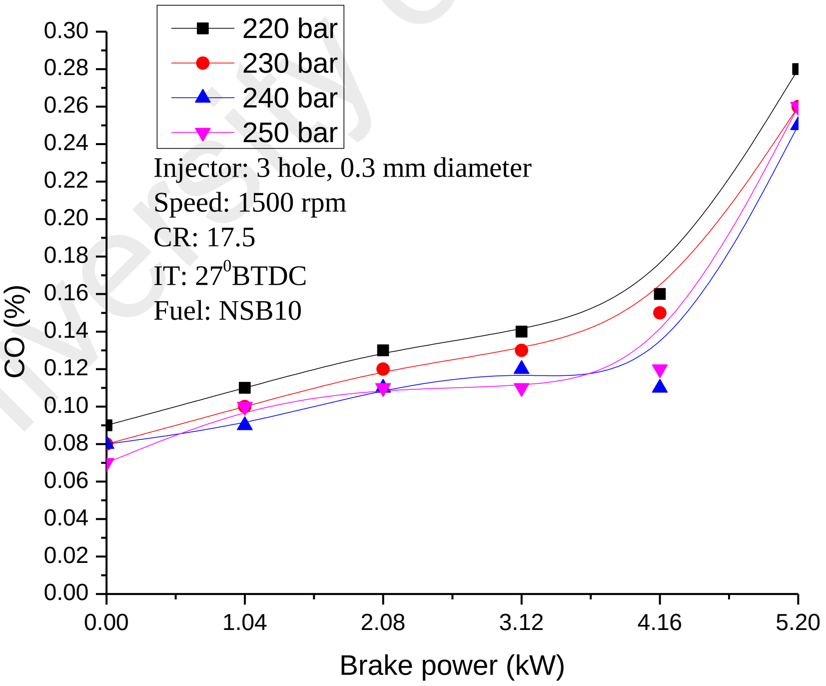


Figure 4.23: Effect of brake power on CO emission (NSB10)

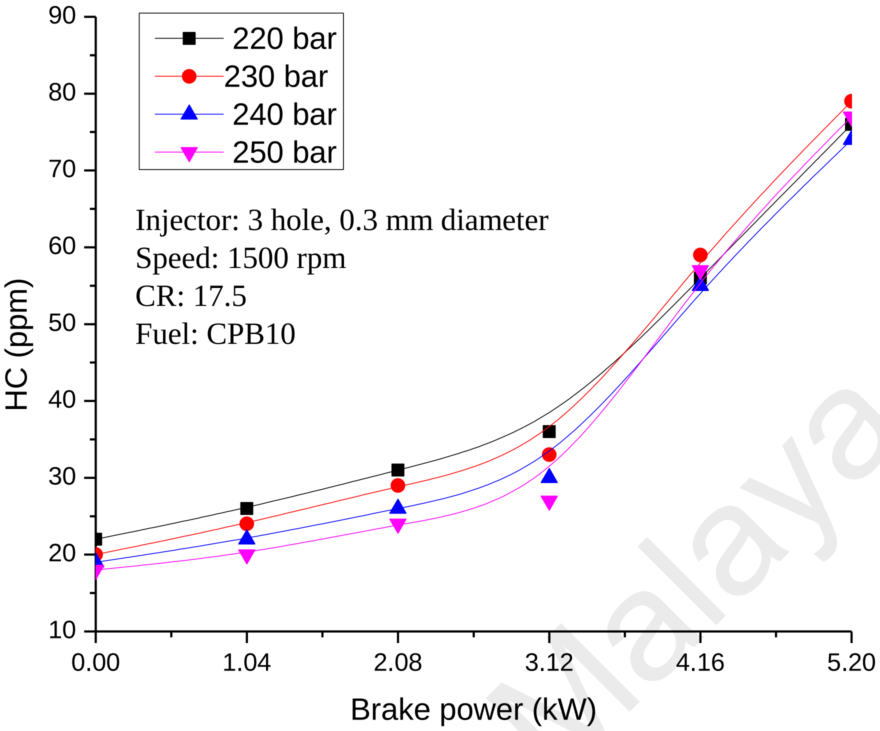


Figure 4.24: Effect of brake power on HC emission (CPB10)

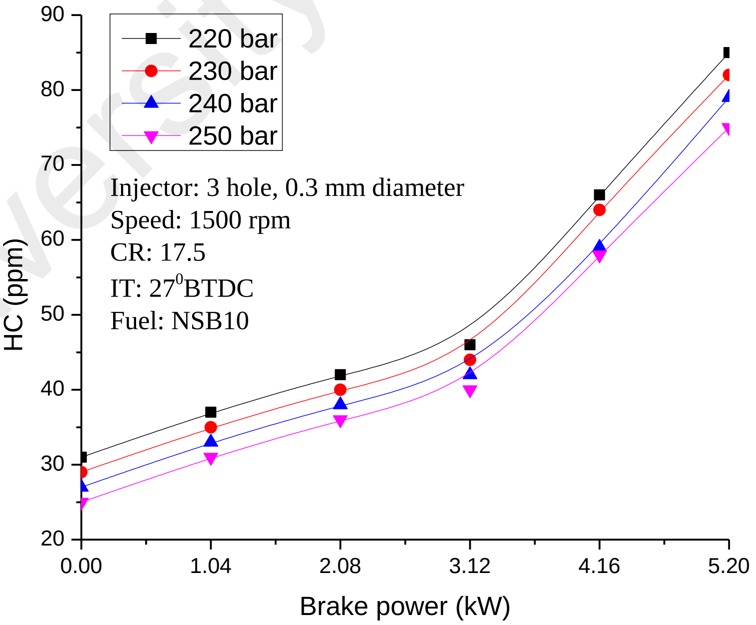


Figure 4.25: Effect of brake power on HC emission (NSB10)

Formation of CO and HC is found to decrease with increase in the injection pressure as shown from Figure 4.22 to Figure 4.25. The significant drop in CO and HC emissions at higher injection pressures are due to improved fuel vaporization and combustion. It is noted that the optimum condition for biodiesel-diesel blends is 240bar injection pressure and 27^0BTDC injection timing. The corresponding optimum conditions for diesel are 205bar and 23^0BTDC respectively. Thus the CO emission for CPB10 and NSB10 at optimum condition is found to be 0.09% and 0.11% respectively whereas for diesel it is 0.1%. Similarly HC for CPB10 and NSB10 are found to be 55ppm and 59ppm at 240bar and 80% load while for diesel it is 40ppm. Thus it can be concluded that the CO emission is very much comparable to that of the diesel at corresponding optimum conditions. However, this cannot be said about HC since biodiesel produces higher HC than the diesel at optimum conditions.

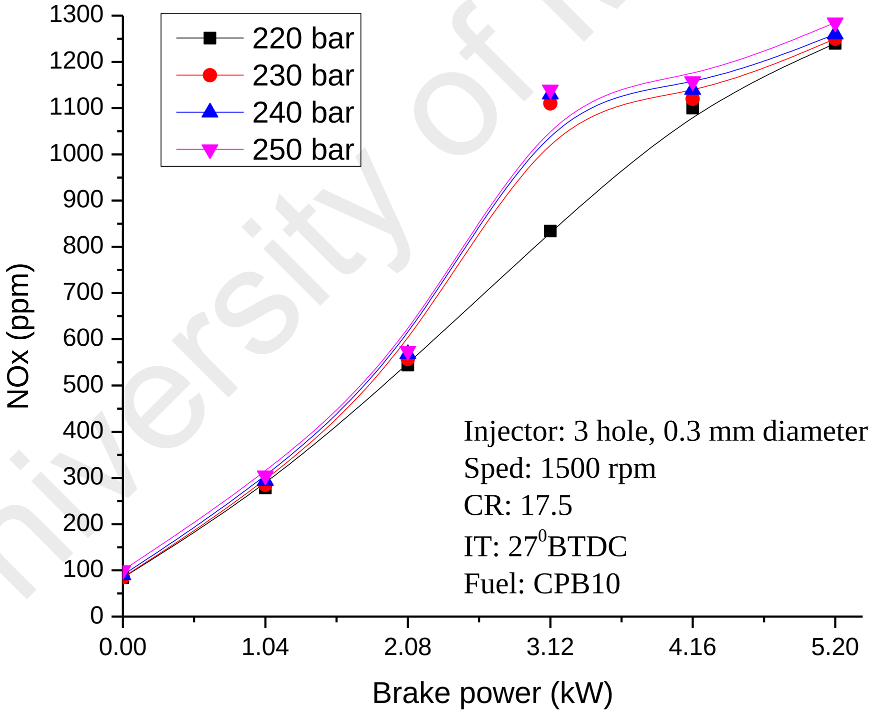


Figure 4.26: Effect of brake power on NOx emission (CPB10)

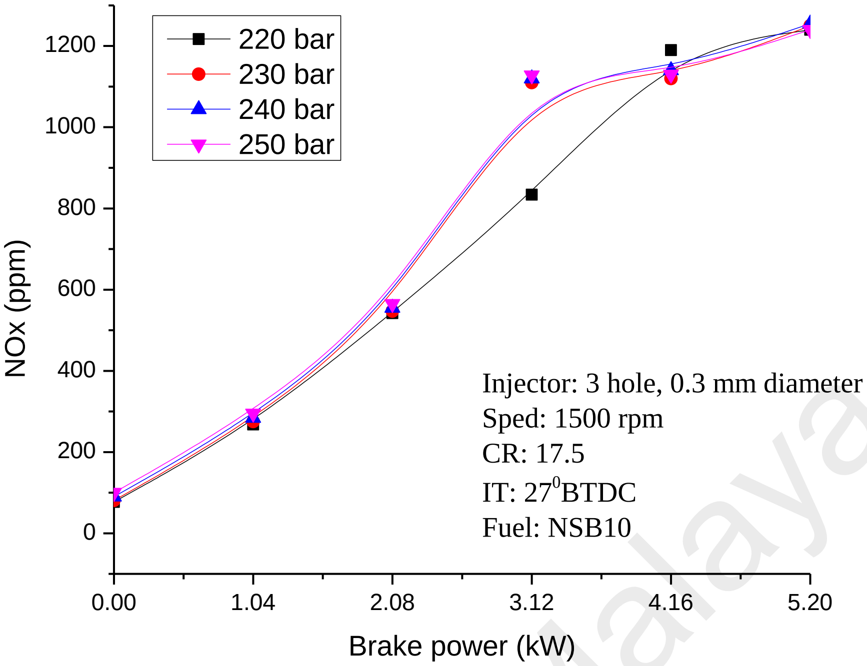


Figure 4.27: Effect of brake power on NOx emission (NSB10)

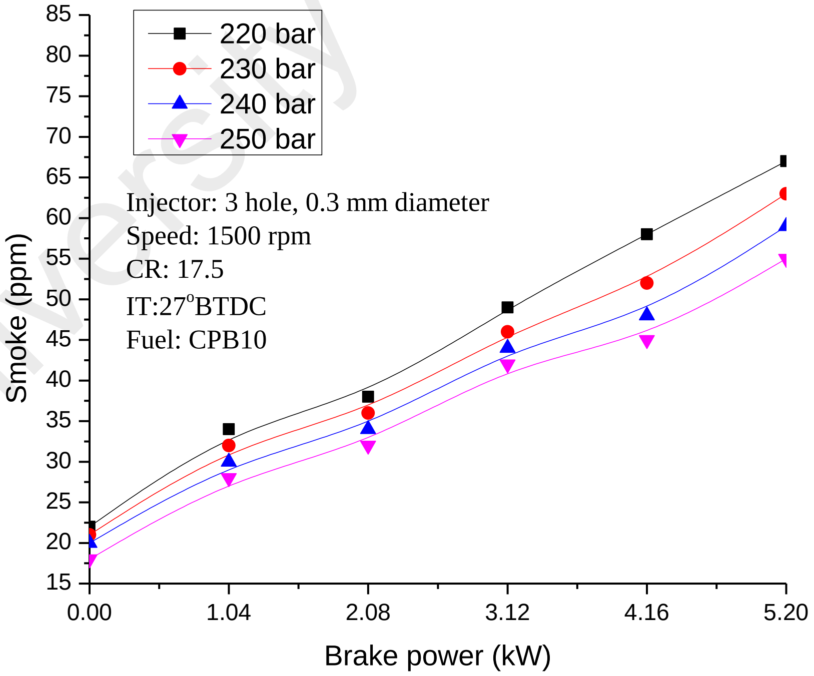


Figure 4.28: Effect of brake power on smoke capacity (CPB10)

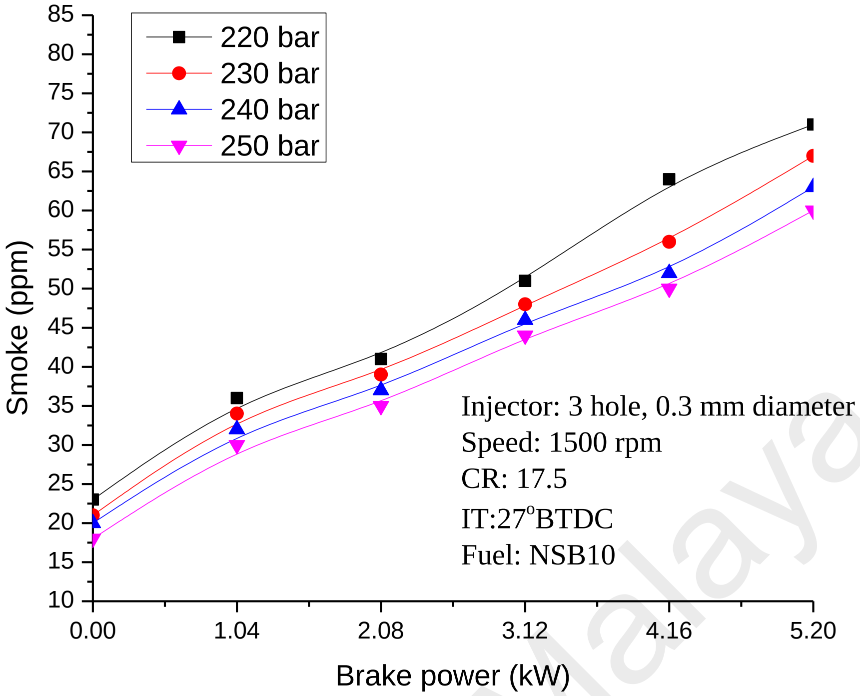


Figure 4.29: Effect of brake power on smoke capacity (NSB10)

Formation of NOx which is a function of combustion temperature found to increase with the injection pressure. The NOx formation behaviour of biodiesel-diesel is shown in Figure 4.26 and Figure 4.27. In contrast the smoke is found to decrease with higher injection pressure due to better fuel spray at higher injection pressure as shown in figure 4.28 and figure 4.29 respectively. 1140 ppm of NOx was found for both CPB10 and NSB10 biodiesel at 240 bar and 80% load. It was 1080ppm in case of diesel run engine. Smoke formed was less in case of CPB10 i.e. 48 ppm, while it was 52 ppm in case of NSB10 at 240 bar and 80% load. 50ppm of smoke was found in case of the diesel engine at 205bar and 23^0BTDC.

4.11.3 Heat transfer analysis

Acceptable amount of heat transfer from the engine cylinder to the atmosphere is very much essential for the engine performance, efficiency and emissions besides material temperature limits and lubricant performance limits. Higher the heat transfer rate to the combustion chamber walls lower the in-cylinder pressure, combustion temperature and hence, reduction in the power output from the engine. The changes in combustion gas temperature due to heat transfer also affect the formation of emissions. The engine heat transfer is a critical issue not only about performance and emissions but also the exhaust gas recovery by the turbocharger, governing the piston, liner distortion and ring lubricating oil film temperature and viscosity.

The engine heat transfer rate depends on the coolant temperature, engine size and engine variables. Furthermore, there are complex interactions between different operational parameters of an engine.

4.11.4 Heat release rate

There are two approaches which are commonly used to get the information on combustion with the help of pressure data. They are heat release analysis and fuel mass burning rate analysis (Chun & Heywood, 1987). Furthermore, heat release rate and fuel mass burning rate can be employed in knowing the completeness of combustion. The heat release due to the combustion of fuel causes variations in pressure and temperature within the combustion chamber. The heat release analysis is carried out within the limits of first law of thermodynamics assuming single zone model with uniform cylinder contents from 100 cycles.

The effects of injection pressure on performance and emissions are discussed in section 4.11.2. Among all the injection pressure tested, the highest brake thermal efficiency obtained is at 240bar. Therefore, in case of cylinder pressure and heat release rate studies, the injection pressure of 240bar is fixed. The effects of injection timing on heat release rate for CPB10 and NSB10 are shown in figure 4.30.and figure 4.31 respectively with crank angle at full load operation have been studied.

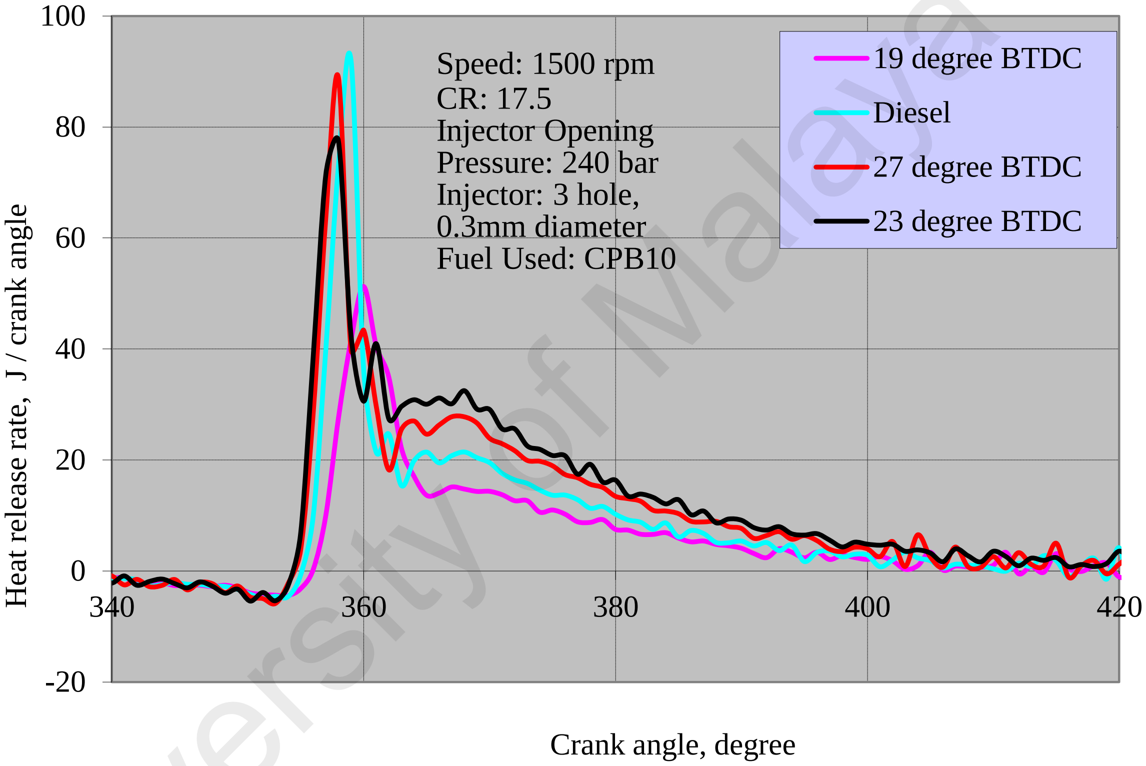


Figure 4.30: Effect of injection timing on the variation of Heat Release Rate (HRR) with crank angle at full load operation (CPB10)

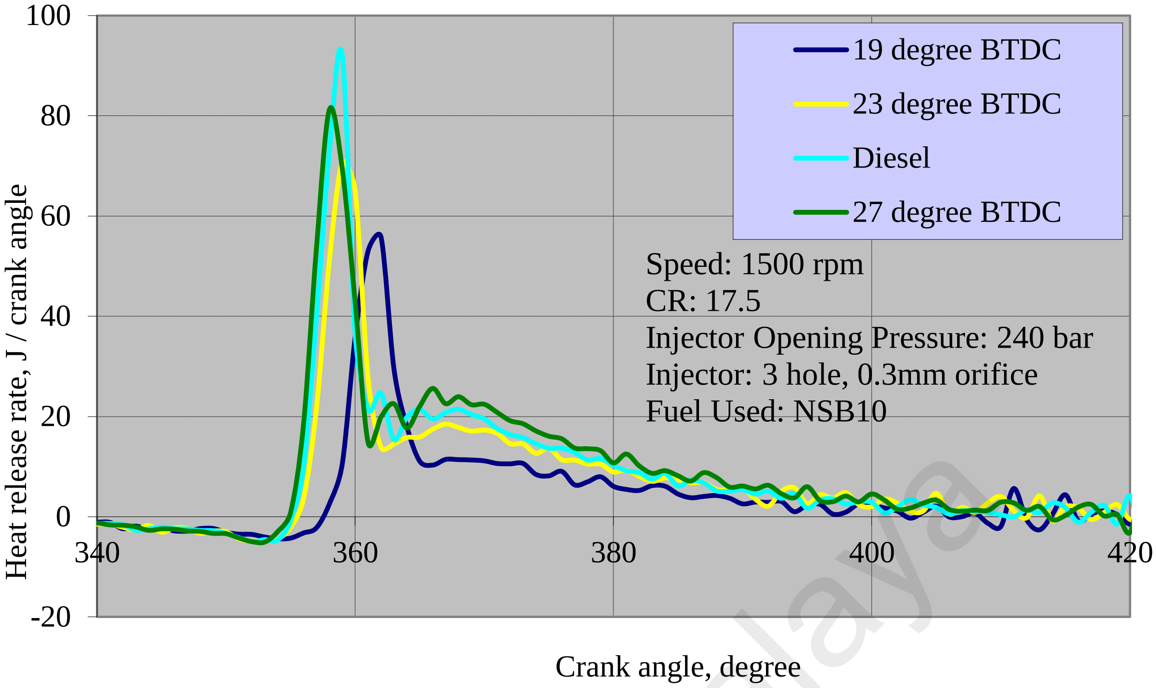


Figure 4.31: Effect of injection timing on the variation of Heat Release Rate (HRR) with crank angle at full load operation (NSB10)

The combustion started in both biodiesel-diesel blends of CPB10 and NSB10, 2^0 before that of diesel for the case of optimum condition i.e. 27^0BTDC injection timing, 240bar injection pressure for biodiesel and 23^0BTDC injection timing, 205bar injection pressure for diesel. The combustion started at 16^0 BTDC for CPB10 and NSB10 compared to diesel for which combustion started 14^0 BTDC. The maximum heat release for CPB10 and NSB10 are 83 J/deg (5^0 BTDC) and 81 J/deg (5^0 BTDC) respectively. For diesel it is found to be 86 J/deg (2^0 BTDC) at an injection timing of 23^0BTDC. The peak heat release rate increases with advancing the injection timing due to the accumulation of more quantity of fuel before start of the combustion and leads to prominent initial phase of combustion. The difference of heat release rate of biodiesel and diesel is found to be negligible. It may be noted that the optimum injection timing for biodiesel fuelled engine is 27^0BTDC at an injection pressure of 240bar.

4.11.5 Cylinder pressure

Diagnosis of combustion is necessary to know the combustion quality and to control it with the information of available cylinder pressure data. The in-cylinder pressure is not only important factor for combustion alone but also important for analyzing the factors affecting the performance of an engine Furthermore, the cylinder pressure has been used in misfire detection and noise estimation.

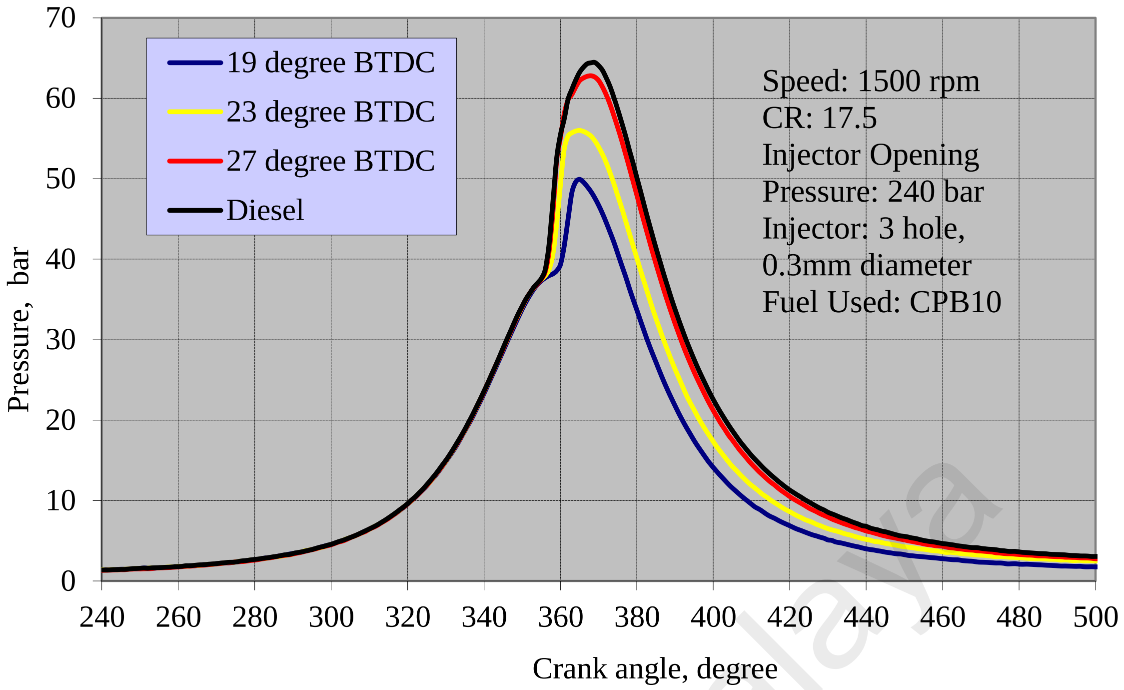


Figure 4.32: Effect of injection timing on the variation of Pressure with crank angle at full load operation (CPB10)

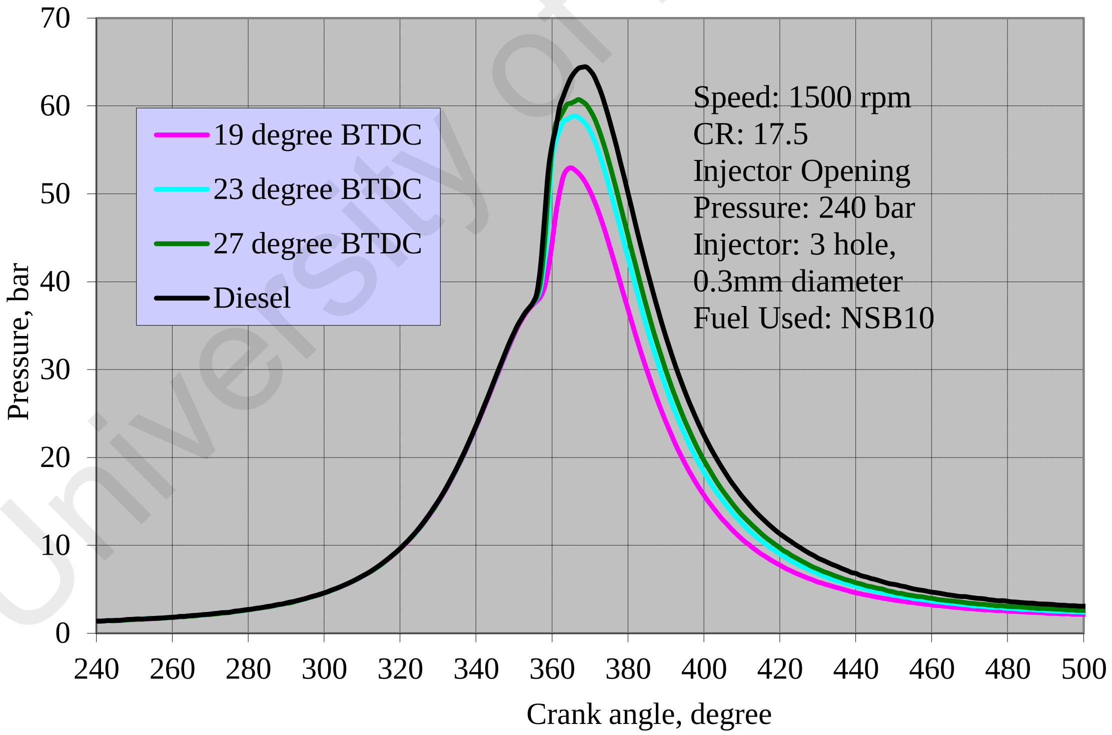


Figure 4.33: Effect of injection timing on the variation of Pressure with crank angle at full operation (NSB10)

Figure 4.32 and figure 4.33 show the variation of cylinder pressure with crank angle for CPB10 and NSB10 at full load respectively. It is evident that a slightly lesser peak cylinder pressure is obtained for both biodiesel-diesel blends compared to that of diesel (64.44bar). Furthermore, peak cylinder pressure for CPB10 is marginally more than that of NSB10. The peak cylinder pressure for CPB10 and NSB10 were found be 62.79bar and 62.75bar respectively at an injection timing of 27^0BTDC, at 10^0 after top dead centre (ATDC) for full applied load condition. The retardation of injection timing reduces the peak cylinder pressure due to late start of combustion. With the available information from cylinder pressure data it could be concluded that smooth combustion takes place for both biodiesel-diesel blends.

4.11.6 Ignition delay

The fuel is directly injected into the cylinder at the end of compression stroke. The liquid fuel atomizes and penetrates deep into combustion chamber. The fuel vaporizes and mixes with air and hence combustion starts. There are four phases of combustion in diesel engines. They are ignition delay, premixed combustion phase, mixing controlled combustion phase, late combustion phase. The first phase i.e. ignition delay is defined as the time or crank angle from when fuel injection starts to the onset of combustion. Both physical and chemical processes must take place before a significant fraction of chemical energy of injected fuel is released. The ignition delay in diesel engine is affected by injection timing and injection pressure.

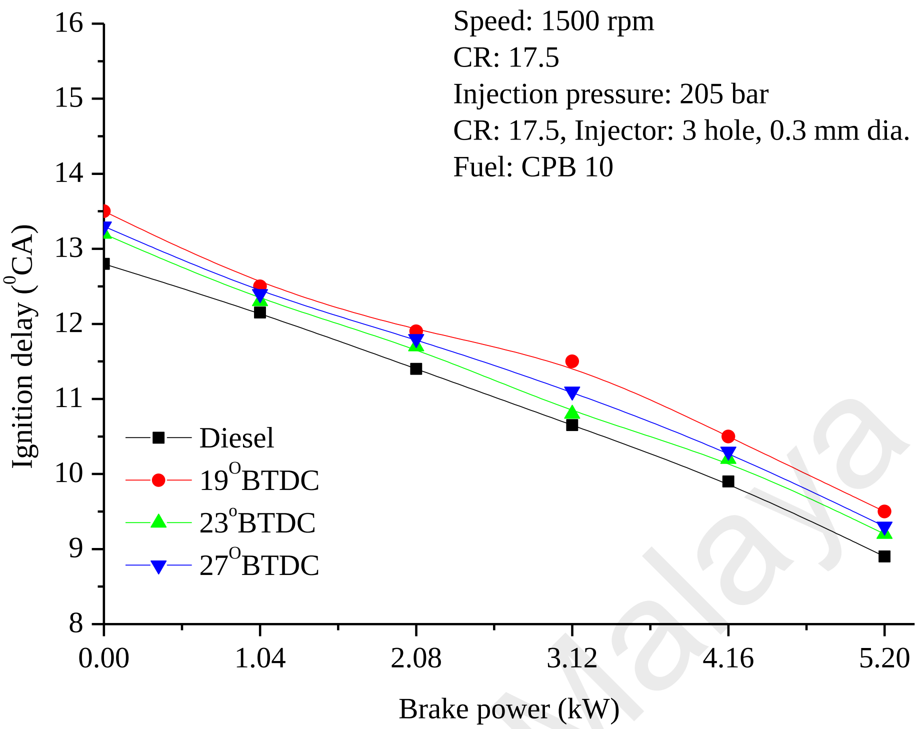


Figure 4.34: Effect of injection timing on ignition delay (CPB10)

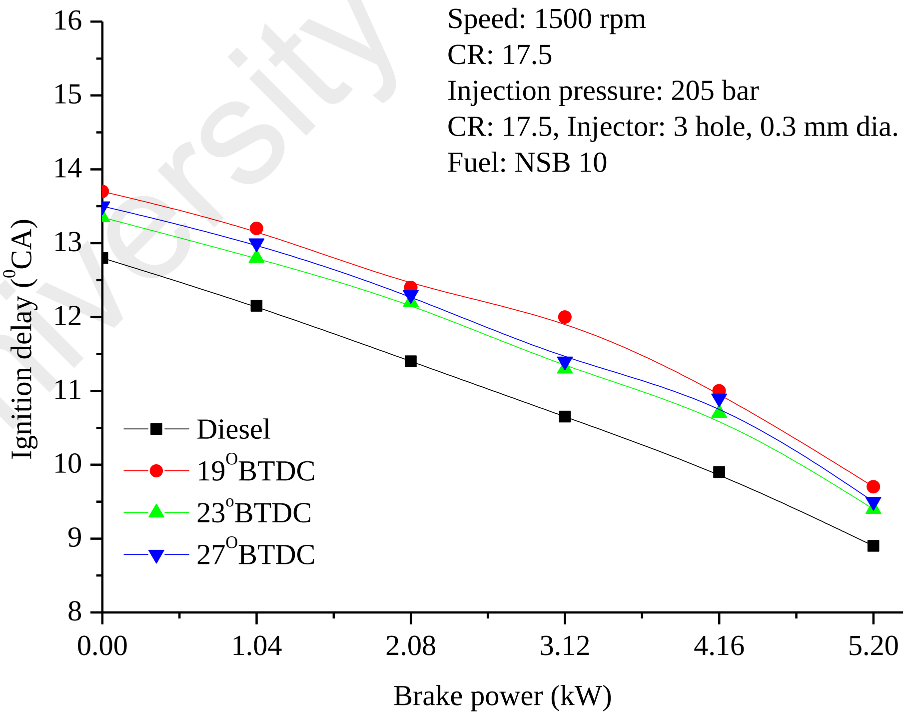


Figure 4.35: Effect of injection timing on ignition delay (NSB10)

The effect of injection timing on ignition delay for CPB10 and NSB10 are shown in figure 4.34 and figure 4.35 respectively. The ignition delay for biodiesel-diesel blends is longer than the diesel due to high cetane number of diesel. The ignition delay decreases with increase in load. For effective combustion to take place the ignition delay should be shorter. The optimum injection timing of 23^0BTDC was obtained for both CPB10 and NSB10 from the perspective of ignition delay. If the injection timing is too advanced then initial temperature and pressure are low. Hence, delay period will increase. Similarly if the injection timing is retarded the initial temperature and pressure increase initially then decrease as the delay proceeds. The minimum delay periods are found to be 9.4^0 crank angle (CA) and 9.6^0 CA for CPB10 and NSB10 respectively at 23^0BTDC and full load condition.

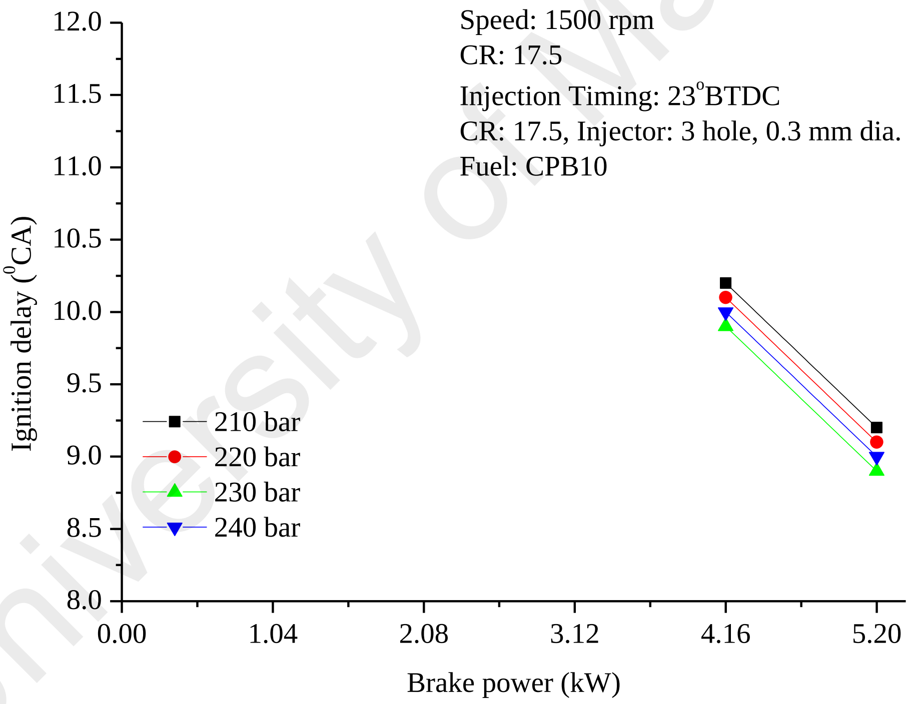


Figure 4.36: Effect of injection pressure on ignition delay (CPB10)

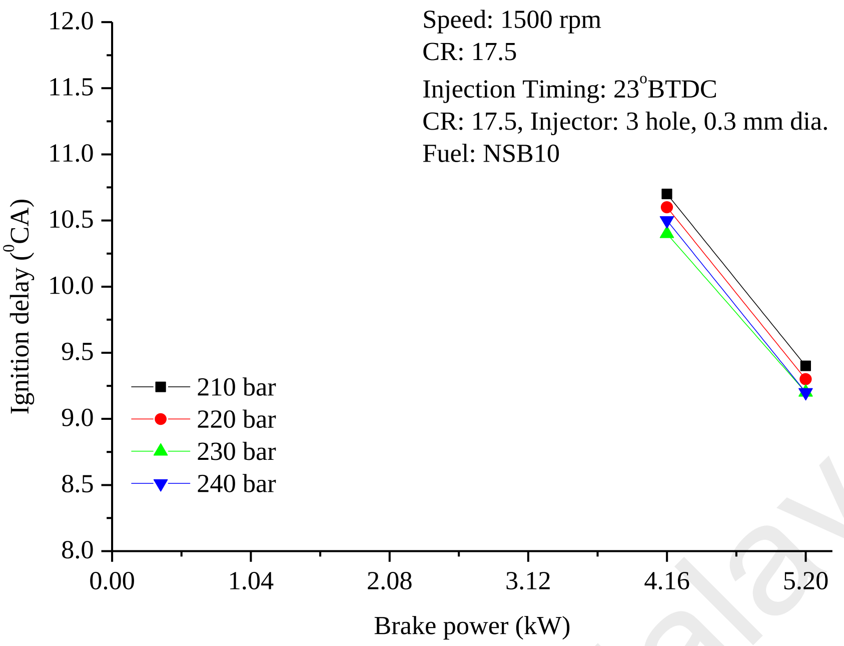


Figure 4.37: Effect of injection pressure on ignition delay (NSB10)

The fuel injection pressure affects the delay period. Figure 4.36 and figure 4.37 show the effect of injection pressure on ignition delay for CPB10 and NSB10 respectively as a function of load. Thus, an increase in injection pressure decreases the ignition delay. The higher the injection pressures the shorter the delay period. Shortest delay periods of 8.7^0 CA and 9^0 CA for CPB10 and NSB10 respectively are obtained at an injection pressure of 230bar at full load.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The world is changing fast. Innovations in every field are the order of the day. In the present scenario, biodiesel has emerged as an alternate fuel to the fossil diesel. Its importance cannot be overlooked as the sources of fossil diesel are drying up and moreover biodiesel does not cause harmful emissions. Secondly, it can be produced conventionally by various methods but esterification-transesterification (ET) reactions are commonly used today. These methods have advantages and disadvantages. Formation of glycerine and its separation from biodiesel are the biggest issues besides longer reaction and separation time in these methods. Hence, this work was aimed at identifying the new non-edible feedstocks for biodiesel production, development of new transesterification methods, developing an efficient diesel engine by optimizing the fuel injection parameters. Based on the comprehensive experimental investigations following conclusions have been drawn.

- Nigella sativa can be used as a feedstock for biodiesel production and its low concentration blend may be used in diesel engine.
- Direct transesterification (DT) certainly would solve the problems associated with glycerine separation to a large extent. Though, fuel properties of biodiesel prepared from both DT and esterification-transesterification (ET) methods were more or less similar but, the acid value reduced considerably and reaction time reduced from 5 hours to just 2 hours. Yield of biodiesel which is another important property, certainly increased from 2% to 5% in DT method for all the feedstocks used in the current research.

- The Modified direct transesterification (MDT) eliminates problems associated with petroleum ether and blending. The blending time for diesel and biodiesel is totally eliminated.
- The diesel run engine gave 30.75% brake thermal efficiency at 23^0 BTDC, 205bar injection pressure and at 80% load. By advancing the injection timing to 27^0 BTDC, increasing the injection pressure to 240bar and at a load of 80%, CPB10 fuelled engine gave a maximum brake thermal efficiency of 29% while NSB10 fuelled engine gave a brake thermal efficiency of 28.7%.
- CO, HC, NOx and Smoke for CPB10 were 0.09%, 55ppm, 1140ppm and 48ppm respectively, whereas for NSB10 they are 0.11%, 59ppm, 1140ppm and 52ppm at 27^0 BTDC of injection timing, 240 bar injection pressure and 80% load, which are comparable with the diesel run engine at 23^0 BTDC, 205bar injection pressure and at 80% load. CO, HC, NOx and Smoke for diesel engine at stated operating conditions are 0.1%, 40ppm, 1080ppm, 52ppm. Infact NOx is more in diesel run engine.
- Heat release rate in NSB10 run engine is 82 $J/^0$ crank angle, 90 82 $J/^0$ crank angle for CPB10 at 27^0 BTDC of injection timing, 240 bar injection pressure and 80% load. This is nearer to 92 $J/^0$ crank angle for diesel engine at 23^0 BTDC, 205bar injection pressure and at full load.
- The peak cylinder pressure for CPB10 and NSB10 were 62 bar and 60 bar respectively at 27^0 BTDC, 240 bar injection pressure and at full load. . Whereas for diesel it was 65 bar at 23^0 BTDC, 205bar injection pressure and at full load.

5.2 Recommendations

- The present work can be extended to study the effect of swirl on engine performance and emissions.
- Further work can be taken up to study effect of ultra-high injection pressure on engine performance and emissions.
- The results of the present work could be used for validating results of computer simulation models.

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