# PERFORMANCE AND EMISSIONS ANALYSIS OF JATROPHA AND APHANAMIXIS POLYSTACHYA METHYL ESTERS AND INVESTIGATION OF $NO_X$ ADDITIVE IN CI DIESEL ENGINE

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# ORIGINAL LITERARY WORK DECLARATION

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Field of Study: **Energy**

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# ABSTRACT

Biodiesel fuels have the potential to become a reliable substitute for diesel which is used moderately to meet the current energy demands. This fuel can be produced from new or used vegetable oils, non-edible sources and animal fats, which are non-toxic, biodegradable and renewable. In spite of the many advantages of using biodiesel, most of the researchers have reported that biodiesel produce higher $NO_x$ emissions compared to diesel, which is a deterrent to the market expansion of these fuels. This study presents the prospect of biodiesel derived from non-edible oil *Aphanamixis polystachya* oil and Jatropha oil in diesel engine. The study deals with the physicochemical properties of *Aphanamixis polystachya* methyl ester (APME), Jatropha methyl ester (JME) and their individually blends with diesel followed by evaluation of performance and emission characteristics in a multi-cylinder diesel engine. From the literature review, it was found that the average reduction of $NO_x$ emissions by using additives, exhaust gas recirculation (EGR), water injection (WI) & emulsion technology (ET), injection timing retardation ( ITR), simultaneous technology (ST) and low temperature combustion (LTC) are in the ranges 4-45%, 26-84%, 10-38%, 9.77-37%, 22-95% and 66-93% respectively, compared to biodiesel combustion without applying $NO_x$ reduction technologies. Among all $NO_x$ reduction technologies, Fenimore mechanism explains that fuel radicals formed during the combustion process react with nitrogen from the air to form $NO_x$. It can be proposed that if these radical reactions could be terminated, $NO_x$ formation rate for biodiesel combustion would decrease. An experimental study was conducted on a four cylinder diesel engine to evaluate the performance and emission characteristics of Jatropha biodiesel blends (JB5, JB10, JB15 and JB20) with and without addition of N, N′-diphenyl-1, 4-phenylenediamine (DPPD) antioxidant.

From test results, it has been observed that the properties of biodiesel and its blends are compatible with the ASTM D 6751 and ASTM D7467 standards, respectively. It was found that, APME5 and APME10 showed an average 0.9% and 1.81% reduction in torque and 0.9% and 2.1% reduction in brake power (BP), and 0.87% and 1.78% increase in brake specific fuel consumption (BSFC) compared to diesel. In the case of engine emissions, diesel blends of APME gave an average reduction in carbon monoxide (CO) and hydrocarbon (HC) emissions but emitted higher levels of nitrous oxide compared to diesel. It was found that, JB5, JB10, JB15 and JB20 showed an average 3.92%, 4.41%, 3.86% and 4.91% reduction in torque and 0.8%, 1.68%, 2.84% and 3.68% reduction in brake power (BP), and 6.80%, 8.33%, 10.70% and 11.30% increase in brake specific fuel consumption (BSFC) compared to diesel. In the case of engine emissions, diesel blends of Jatropha biodiesel gave an average reduction in carbon monoxide (CO) and hydrocarbon (HC) emissions but emitted higher levels of nitrous oxide compared to diesel. For Jatropha biodiesel blends, the results showed that DPPD antioxidant additive could reduce $NO_x$ emission significantly with slight penalty of engine performance as well as CO and HC emissions. By addition of 0.15% (m) DPPD additive in JB5, JB10, JB15 and JB20, reduction of $NO_x$ emission were 8.03, 3.503, 13.65 and 16.54% respectively, compared to biodiesel blends without additive at full throttle position. These results suggested that the addition of antioxidant additives in biodiesel blends reduces $NO_x$ emission which can solve the barrier to its market expansion.

# ABSTRAK

Bahan api biodiesel mempunyai potensi untuk menjadi pengganti untuk memenuhi permintaan tenaga semasa. Bahan api ini boleh dihasilkan daripada minyak mentah atau terpakai sayuran, sumber-sumber yang tidak boleh dimakan dan lemak haiwan yang tidak toksik, mesra alam dan boleh diperbaharui. Walaupun banyak kelebihan boleh diperoleh daripada penggunaan biodiesel, kebanyakan penyelidik telah melaporkan bahawa biodiesel menghasilkan pelepasan $NO_x$ yang lebih tinggi berbanding diesel, yang merupakan penghalang kepada pemasaran meluas bahan api ini. Kajian ini membentangkan prospek biodiesel berasal dari minyak yang tidak boleh dimakan iaitu minyak Aphanamixis polystachya dan minyak Jatropha. Kajian ini membentangkan sifaat fizikokimia Aphanamixis polystachya methyl ester (APME), Jatropha methyl ester (JME) dan juga campuran bersama diesel, diikuti dengan penilaian prestasi dan lepasan ekzos enjin di dalam enjin berbilang-silinder. Daripada kajian literasi, didapati bahawa pengurangan purata pelepasan $NO_x$ dengan pengunaan bahan tambahan, pemusingan gas ekzos, injeksi air & teknologi emulsi, lengahan waktu injeksi, teknologi serentak dan pembakaran suhu rendah adalah dalam julat 4-45%, 26-84%, 10-38%, 9,77-37%, 22-95% dan 66-93% masing-masing, berbanding dengan pembakaran biodiesel yang tidak menggunakan teknologi pengurangan $NO_x$. Antara semua teknologi pengurangan $NO_x$, mekanisma Fenimore menjelaskan bahawa radikal bahan api yang terbentuk semasa proses pembakaran bertindak balas dengan nitrogen dari udara untuk membentuk $NO_x$. Adalah dicadangkan bahawa sekiranya reaksi radikal ini boleh ditamatkan, kadar pembentukan $NO_x$ semasa pembakaran biodiesel akan dikurangkan.  Uji kaji telah dijalankan pada enjin diesel empat silinder untuk menilai prestasi dan ciri-ciri pelepasan ekzos bagi campuran diesel-biodiesel Jatropha (JB5, JB10, JB15 dan JB20) dengan dan tanpa penambahan antioksidan N, N'-polibrominat-1, 4-phenylenediamine (DPPD). Daripada keputusan ujian, adalah diperhatikan bahawa sifat fizikokimia biodiesel dan campuran-campuran diesel-biodisel adalah seperti yang ditetapkan piawaian ASTM D 6751 dan ASTM D7467 . APME5 dan APME10 masing-masing menunjukkan pengurangan 0.9% dan 1.81% untuk purata daya tork, pengurangan 0.9% dan 2.1% pada kuasa brek (BP), peningkatan 0.87% dan 1.78% dalam penggunaan bahan api tentu brek (BSFC) berbanding diesel. Bagi lepasan ekzos enjin, campuran diesel dan APME memberi pengurangan bagi purata lepasan karbon monoksida (CO) dan hidrokarbon (HC), tetapi lepasan lebih tinggi ditunjukkan oleh nitrus oksida berbanding diesel. Juga didapati bahawa JB5, JB10, JB15 dan JB20 menunjukkan purata pengurangan 3.92%, 4.41%, 3.86% dan 4.91% bagi daya tork dan pengurangan 0.8%, 1.68%, 2.84% dan 3.68% pada kuasa brek (BP), dan peningkatan 6.80%, 8.33%, 10.70% dan 11.30% bagi brek penggunaan bahan api tertentu (BSFC) berbanding diesel. Bagi lepasan ekzos enjin, campuran diesel-biodiesel Jatropha memberi pengurangan purata karbon monoksida (CO) dan hidrokarbon (HC), kadar lepasan nitrus oksida yang lebih tinggi berbanding diesel. Untuk campuran biodiesel-diesel Jatropha, keputusan menunjukkan bahawa tambahan antioksidan DPPD dapat mengurangkan pelepasan $NO_x$ yang ketara tanpa menjejaskaskan prestasi enjin serta lepasan CO dan HC. Dengan penambahan 0.15% (m) DPPD dalam JB5, JB10, JB15 dan JB20, pengurangan lepasan $NO_x$ adalah 8.03, 3.503, 13.65 dan 16.54%, berbanding biodiesel. Keputusan ini mencadangkan bahawa penambahan bahan tambahan antioksidan dalam campuran biodiesel-diesel dapat mengurangkan pelepasan NOx dan seterusnya boleh menyelesaikan halangan untuk pengembangan pasaran.

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# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# LIST OF ABBREVIATIONS

| | |
|---|---|
| APME | *Aphanamixis polystachya* methyl ester |
| ASTM | American Society for Testing and Materials |
| AC | Air Cooled. |
| ASTM D6751-01 | American Society for Testing and Materials (Biodiesel Standards), USA. |
| BSFC | Brake specific fuel consumption |
| BTE | Brake thermal efficiency |
| BTDC | Before Top-Dead-Center. |
| BHT | Butylated Hydroxytoluene. |
| BP | Brake power |
| CS | Constant Speed |
| CSB | Cottonseed Biodiesel |
| CSOME | Cottonseed oil methyl ester |
| COME | Corn oil methyl ester |
| CAPO | Crude *Aphanamixis polystachya* oil |
| CCaO | Crude canola oil |
| CCIO | Crude *Calophyllum inophyllum* oil |
| CI | Compression ignition |
| CIME | *Calophyllum inophyllum* methyl ester |
| CJCO | Crude *Jatropha curcas* oil |
| CN45 | 35.3 vol% NHD with balance HMN |
| CN70 | 64.7 vol% NHD with balance HMN |
| CN45 | 35.3 vol% NHD with balance HMN |
| CO | Carbon monoxide |
| CI | Compression Ignition |

| | |
|---|---|
| CFD | Computational Fluid Dynamics. |
| COB | Corn Oil Biodiesel. |
| CB | Colza Biodiesel. |
| COME | Castor Oil Methyl Ester. |
| $C_nB$ | Canola Biodiesel |
| CaME | Canola methyl ester |
| CN | Cetane number |
| CPaO | Crude palm oil |
| CSO | Crude soybean oil |
| DMC | Dimethyl Carbonate |
| DE | Diesel engine. |
| DEE | Diethyl Ether. |
| DI | Direct Injection |
| DPPD | N,N′-diphenyl-1,4-phenylenediamine |
| EAT | Exhaust After Treatment |
| ECU | Eelectronic Control Unit. |
| EPA | Environmental Protection Agency |
| EIA | Energy Information Administration |
| EN 14213 | European Union Standards (Bio-Heating Fuels) |
| EN 14214 | European Union Standards (Biodiesel) |
| EDA | Ethylenediamine. |
| EHN | 2-Ethyl-Hexyl Nitrate |
| EGT | Exhaust gas temperature |
| FAME | Fatty acid methyl ester |
| FAC | Fatty acid composition |
| FOB | Fish Oil Biodiesel |

| | |
|---|---|
| GHG | Green House Gases |
| GC | Gas chromatography |
| HC | Hydrocarbon |
| HTC | High Temperature Combustion |
| HMN | 2,2,4,4,6,8,8-Heptamethylnonane |
| HCCI | Homogeneous Charge Compression Ignition |
| HL | High Load |
| IEA | International Energy Agency |
| IMEP | indicating mean effective pressure |
| IV | Iodine value |
| JCME | *Jatropha curcas* methyl ester |
| JME | Jatropha methyl ester |
| JOME | Jojoba oil methyl ester |
| JOB | Jojoba Biodiesel. |
| KB | Karanja Biodiesel. |
| LHR | Low Heat Rejection. |
| LL | low Load |
| ML | Medium Load |
| MJ/kg | Mega joule/kg |
| MB | Mahua Biodiesel. |
| NHD | n-hexadecane |
| $NO_x$ | Oxides of nitrogen (NO, $NO_2$) |
| NA | Naturally Aspirated. |
| NPPD | N-phenyl-1,4-phenylenedi amine. |
| NO | Nitrous oxide |
| ODA | Octylated Diphenylamine. |

| | |
|---|---|
| PM | Particulate matter |
| PCCI | Premixed or Partial Premixed Charge Compression Ignition. |
| PKB | Palm Kernel biodiesel. |
| PPD | P-Phenyle nediamine. |
| PaME | Palm oil methyl ester |
| RB | Rapeseed Biodiesel. |
| RBB | Rice bran biodiesel. |
| rpm | Revolution per minute |
| SN | Saponification number |
| SOI | Start of injection |
| SME | Soybean oil methyl ester |
| SOME | Sunflower oil methyl ester |
| SB | Soybean Biodiesel. |
| SFB | Sunflower Biodiesel. |
| TDC | Top Dead Center. |
| TC | Turbocharged. |
| $T_{ad}$ | Adiabatic flame temperature |
| TV | Tangentially Vertical. |
| TOME | Tall Oil Methyl Ester. |
| TPB | Thevitia Peruviana Biodiesel. |
| US EPA | United States Environmental Protection Agency |
| WOME | Waste cooking oil methyl ester |
| WCB | Waste Cooking Biodiesel. |
| $\Phi$ | Stoichiometric air fuel mixture |

# CHAPTER 1: INTRODUCTION

## 1.1 Overview

Petroleum-based fuels play a very significant role in the fields of industrial growth, transportation, agriculture, etc., due to their availability, combustion properties and high heating value. However, the reserves of these fuels are rapidly depleting due to increased fuel consumption. The emissions caused by the burning of petroleum-derived fuels have a serious effect on both the environment as well as human health. Fossil fuel depletion, growing carbon dioxide emissions, global warming and global environmental concerns has generated more interest in alternative, environmentally friendly sources of fuel. Therefore, it has become a global agenda to develop clean alternative fuels that are domestically available, environmentally acceptable, and technically feasible. Biodiesel is considered as a better choice of alternative fuel due to its environmentally friendly characteristics and similar functional properties of diesel fuel. Biodiesel has an immense potential to be part of the future energy mix. In developing countries, using biodiesel in internal combustion engines can play an important role in reducing the fossil fuel demand, the environmental impact, and the adverse effects on human health (A. M. Liaquat et al., 2010). Biodiesel is renewable and can be produced directly from edible and non-edible vegetable oils, recycled waste vegetable oils, and animal fats through the transesterification process (Mofijur et al., 2012).

## 1.2 Background

According to the IEA, global energy consumption will increase by about 53% by 2030 (H. Ong, Mahlia, & Masjuki, 2011). The United States' EIA has projected that the world's liquid fuel consumption will increase from 86.1 million barrels/day, to 110.6

million barrels/day by 2035 (Cecrle et al., 2012a). The emissions caused by the burning of petroleum-derived fuel also have a serious impact on both the environment and human health. Therefore, to develop clean alternative fuels that are locally available, environmentally acceptable and technically feasible has become a topic on the global agenda. Biodiesel is the better selection as an alternative fuel because of its capability to reduce GHG, it is a substitute for diesel fuel, its renewability, it is biodegradable, has better lubricity and is non-toxic and so forth (Arbab et al., 2013; G. R. Kannan & Anand, 2012; L. Lin et al., 2011; Rahman et al., 2013). However, generally, biodiesel fuels could significantly reduce the HC, CO and smoke emissions but have an adverse effect on $NO_x$ emissions (Buyukkaya, 2010; Hazar, 2011; B. Kegl, 2011a). According to the US' EPA, the $NO_x$ emissions from a biodiesel fueled engine are about 10% higher compared to conventional diesel combustion (Teixeira et al., 2012). Average emissions from biodiesel combustion in heavy-duty highway engines, as reported by EPA using statistical regression analysis, are shown in **Figure 1.1**. Though the use of biodiesel has increased tremendously, the rising trend of $NO_x$ emissions could become a significant barrier to its market expansion. Moreover, biodiesel and its blends have significant negative impacts on engine performance compared to conventional diesel combustion due to their lower heating value (Abedin et al., 2013; Ozsezen & Canakci, 2011; Jinlin Xue et al., 2011) and higher density as well as viscosity (P. K. Srivastava & Verma, 2008; Utlu & Koçak, 2008). So it is necessary to be concerned about engine performance fueled by biodiesel when applying different emission reduction technologies.

Similar reports have also been presented by other researchers (Ozsezen & Canakci, 2010, 2011b; Sivalakshmi & Balusamy, 2012). Thermal, prompt, fuel $NO_x$, nitrous oxide ($N_2O$) pathway, and NNH mechanisms are the common mechanisms for the formation of $NO_x$ emissions during combustion (Masum et al., 2013; K. Varatharajan, 2012). Among them thermal and prompt are the dominant mechanisms of $NO_x$ formation in biodiesel combustion (K. Varatharajan et al., 2011). Thermal $NO_x$ is formed by oxidation of nitrogen at elevated temperatures (above 1700 K) while prompt $NO_x$ is produced due to the formation of free radicals in the flame front of hydrocarbon flames. On the other hand, significant quantities of $NO_x$ are formed by the prompt mechanism in biodiesel combustion (G. A. Ban-Weiss et al., 2007; R.L. McCormick et al., 2006; Mueller et al., 2009). The formation of $NO_x$ by the fuel $NO_x$ mechanism for biodiesel can be considered to be negligible because it does not generally contain fuel-bound nitrogen (Moser et al., 2009). The $N_2O$ pathway mechanism is significant under elevated pressure and lean air fuel ratio conditions (WC Jr, 1999). The NNH mechanism occurs under combustion conditions where the concentration of atoms is high (K. Varatharajan, 2012). Generally, $NO_x$ is a serious cause of smog, ground level ozone, acid rain and also some human diseases, such as asthma, coughing, or nausea (Fernando et al., 2006b). $NO_x$ and PM emissions are the major toxic emissions that are being regulated as emission regulations become more and more stringent (C. Y. Lin & Lin, 2006). According to the European Union Emission Standards (Euro V and Euro VI), as shown in **Figure 1.2 (a)** and **Figure 1.2 (b)**, the amount of $NO_x$ and PM emissions must be below about 28-68% and 80%, respectively, compared to the Euro IV standard. Thus, applying different $NO_x$ mitigation technologies, CI engines are thought to be the most attractive solutions to meet emission standards. To reduce $NO_x$ emissions, many researchers have applied different technologies to the biodiesel-fueled diesel engine by modifying the engine or the fuel. Among all the technologies some were efficient and others were when assessed on engine efficiency, fuel consumption, other exhaust emissions, durability, economical operation and so forth. Moreover, recently Al-Dawody and Bhatti (Al-Dawody & Bhatti, 2013) tested a single cylinder diesel engine fueled with SB100 and its blends applying several $NO_x$ mitigation strategies. They reported that most of the one-dimensional search strategies were found to reduce one emission but increase another. Rajasekar et al. (Rajasekar et al., 2010) reviewed the $NO_x$ reduction technologies fueled with oxygenated biomass fuels, but not fully based on biodiesel. However, other than EGR, they did not elaborately discuss the impacts of using these technologies on engine performance.

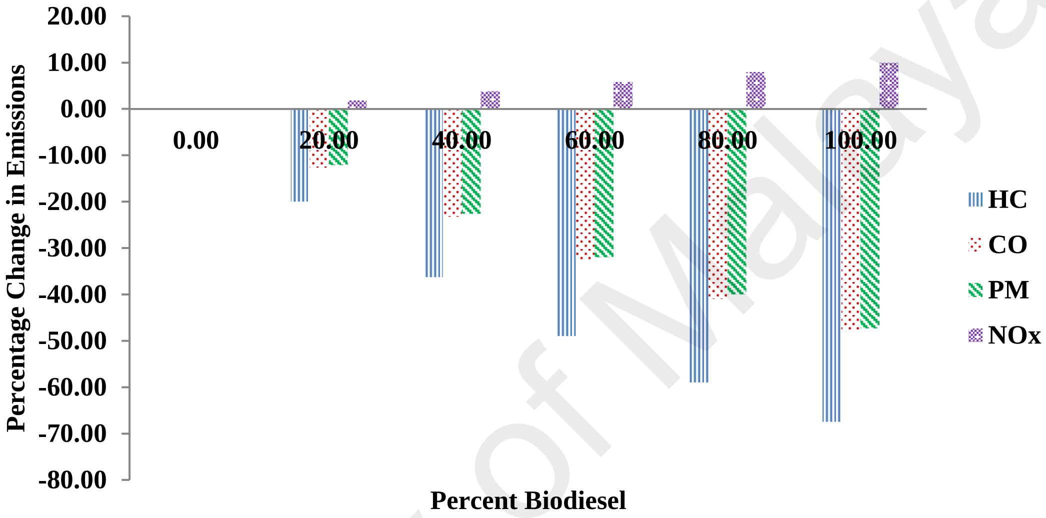


**Figure 1.1:** Emissions from biodiesel combustion in heavy-duty highway engine averagely (Teixeira et al., 2012).

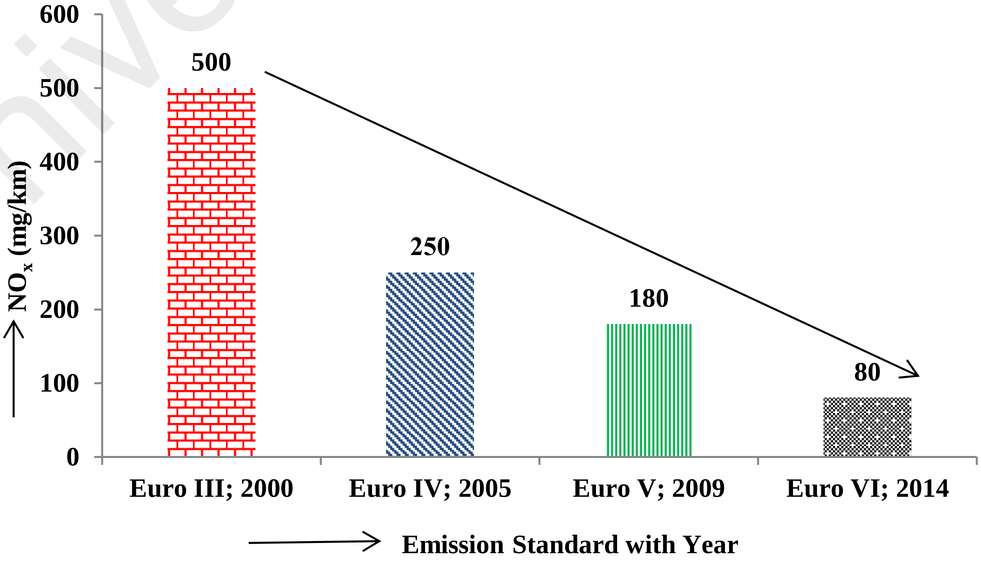


**Figure 1.2 (a)**

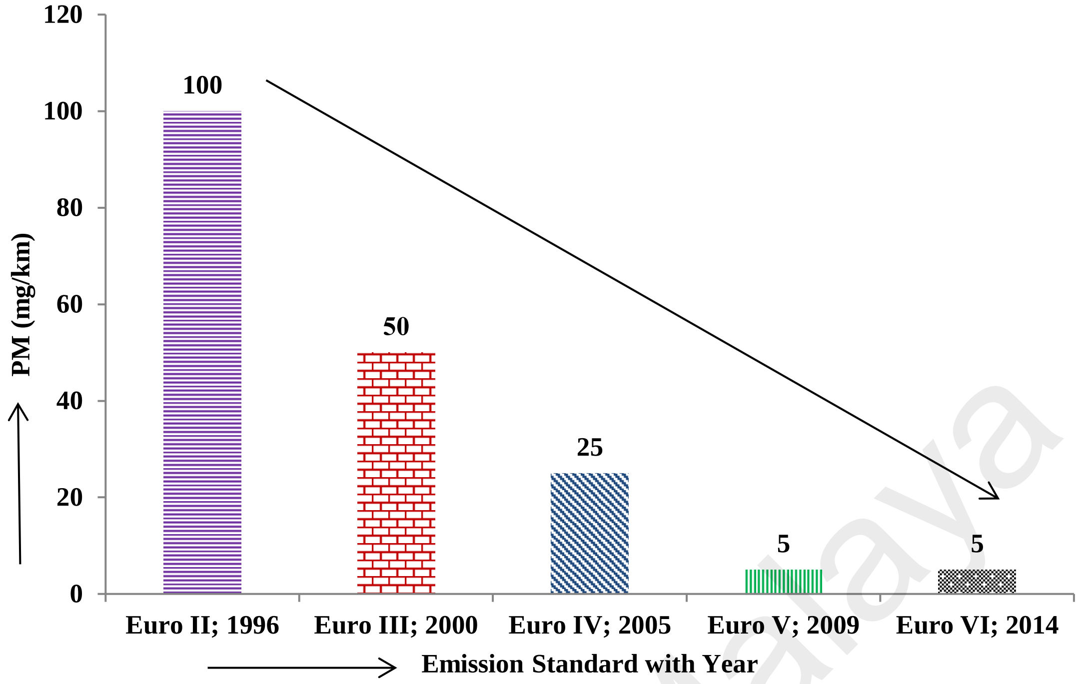


**Figure 1.2 (b)**

**Figure 1.2 (a) & (b)** Passenger cars $NO_x$ and PM emissions overview of past and future requirements (V. Subramanian et al., 2007; Tesfa et al., 2012)

## 1.3 Objectives of study

This study presents the prospect of biodiesel derived from *Aphanamixis polystachya* and Jatropha non edible oils in diesel engine. The study deals with the physicochemical properties of *Aphanamixis polystachya* methyl ester (APME), Jatropha methyl ester (JME) and their individually blends with diesel followed by evaluation of performance and emission characteristics in a multi-cylinder diesel engine. The N, N′-diphenyl-1, 4-phenylenediamine (DPPD) antioxidant additive is used as $NO_x$ reduction technology for Jatropha biodiesel blends. The considered aims of study are as follows:

- To investigate fuel properties of *Aphanamixis polystachya*, Jatropha methyl esters and their individually blends with diesel.

- To analyze engine performance and emission at different engine speeds using several blends of *Aphanamixis polystachya* and Jatropha methyl esters with diesel.
- To investigate the engine performance and emissions in a four cylinder diesel engine fueled with Jatropha biodiesel blends addition of $NO_x$ reducing antioxidant additive.

## 1.4 Scope of work

This study aims to find out the better $NO_x$ reduction technology for biodiesel blends in diesel engine without any engine modification. First this study presents the prospect of biodiesel derived from *Aphanamixis polystachya* oil in diesel engine. The study deals with the physicochemical properties of *Aphanamixis polystachya* methyl ester (APME) and its blends followed by evaluation of performance and emission characteristics of APME5 and APME10 in a multi-cylinder diesel engine. An experimental study was conducted on a multi cylinder diesel engine to evaluate the performance and emission characteristics of Jatropha biodiesel blends (JB5, JB10, JB15 and JB20) with and without addition of N, N′-diphenyl-1, 4-phenylenediamine (DPPD) antioxidant where this antioxidant additive selected as better $NO_x$ reduction technology because of no need any engine modification.

## 1.5 Organization of dissertation

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

**Chapter 1** gives a short overview of the research topic together with specific goals to be achieved. This section comprises of requirement of energy, problems of fossil fuel, its viable alternative, and advantages and disadvantages of biodiesel as an alternative fuel of diesel. This is followed by a background that shows the importance about the research on biodiesel. After that, different paths to reduce biodiesel $NO_x$ emission are discussed. Finally, objectives and scopes of this study are discussed.

**Chapter 2** gives a brief of the biodiesel as an alternative fuel. At first, the physicochemical properties of biodiesel and their blends with diesel are described. $NO_x$ formation mechanism with factors affecting biodiesel $NO_x$ emissions are described elaborately. Also different $NO_x$ reduction technologies with their effect on engine performance and emissions are explained.

**Chapter 3** explains in detail the materials and experimental techniques to achieve the objectives of this study.

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

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

# CHAPTER 2: LITERATURE REVIEW

## 2.1 Introduction

Biodiesel is renewable and can be produced directly from edible and non-edible vegetable oils, recycled waste vegetable oils, and animal fats through the transesterification process (Mofijur et al., 2012). Generally, biodiesel fuels offer reduction of harmful pollutant emissions such as CO, HC and PM, but it produces higher $NO_x$ emissions (B.S. Chauhan et al., 2011; Fazal et al., 2011; J. Sun et al., 2010; Szulczyk & McCarl, 2010; J. Xue et al., 2011). The $NO_x$ emissions are the most harmful parameters that affect the environment through acid rain, human disease, etc. Furthermore, CO and NO are primary pollutants in the formation of tropospheric ozone, which is an important greenhouse gas (Latha & Badarinath, 2004). The United States Environmental Protection Agency (EPA) estimated an average 10% increase in $NO_x$ emissions for a pure (100%) biodiesel fuel compared to conventional diesel fuel ((EPA), 2002; Cecrle et al., 2012b). Wu et al., (2009) found that the reduction of exhaust emissions fuelled with five types of biodiesel individually as a range such as PM, dry soot, HC and CO to be about 53–69%, 79–83%, 45–67%, 4–16%, respectively, but an increase in $NO_x$ of 10–23% compared with petroleum diesel. Very few authors have found reduced the NOx emissions for biodiesel fuels combustion (Gongping et al., 2011; M. Nabi, 2010; Sendzikiene et al., 2006). Sun et al. (J. Sun et al., 2010) reported that biodiesel fuel gives higher $NO_x$ due to: the advancement of injection timing, the higher adiabatic flame temperature ($T_{ad}$), less radiative heat transfer, increase in ignition delay, higher degree of unsaturation, and high oxygen content, etc. As use of biodiesel in diesel engine has increased tremendously, higher $NO_x$ emissions could become a significant barrier to its spread in the market. Therefore researchers are persistently looking for a reliable and economically viable solution to this problem. Some of them have already managed to establish some techniques. This will help end users to overcome the problem of biodiesel expansion. This study presents a comprehensive review on the effects biodiesel combustion on $NO_x$ emissions of biodiesel fuelled engines, in order to provide useful information to engineers, policy makers, industrialists and researchers. Articles from highly rated journals as well as SAE technical papers are reviewed to discuss the notable factors affecting $NO_x$ emissions of biodiesel fuel. Finally, reduction techniques of the $NO_x$ emissions (both pre and post combustion) are described for biodiesel fuelled engine.

## 2.2 Biodiesel as an Alternative Fuel

Biodiesel is defined as the mono alkyl esters of long-chain fatty acids produced from renewable lipid feed stocks, such as vegetable oils or animal fats (Testing & Materials, 2009). Vegetable oils and animal fats are mainly composed of triacyl-glycerols (TAG) consisting of long-chain fatty acids chemically bound to a glycerol (1, 2, 3-propanetriol) backbone (Koh & Mohd Ghazi, 2011; H. Ong et al., 2011). Some edible vegetable oils like palm, soybean, rapeseed, sunflower and corn, and some non-edible oils such as Madhuca indica, cottonseed, Jatropha curcas and Pongamia pinnata have been used for biodiesel production. Vegetable oils are becoming a promising substitute for diesel fuel because of having nearly same amount of energy content compared to diesel fuel after undergoing chemical modification. However, the viscosity of vegetable oils is higher (about ten times) than diesel fuel and contributes to poor atomization of the fuel, incomplete combustion and coking of the fuel injectors and so on. As a result, the use of unsaturated vegetable oils may cause engine damage, which can be solved by chemically modifying them into biodiesel, which has similar characteristics to diesel (Barnwal & Sharma, 2005). There are lots of processes available to improve the fuel properties of edible and non-edible oils for use as alternative fuels in diesel engines. The blending of crude oils, micro-emulsions, pyrolysis and transesterification are the primary ways to convert vegetable oils into diesel substitute (Jain & Sharma, 2010; Koh & Mohd Ghazi, 2011; Leung et al., 2010). However, except for transesterification, blending, pyrolysis and emulsification do not improve the vegetable oils' properties properly (M. Gumus & Kasifoglu, 2010). As reported in Global Data, in a report entitled "Global Biodiesel Market Analysis and Forecasts to 2020" (Global Data:, 03/2010) Germany, the US, France, Argentina and Brazil are the top five biodiesel producing countries in the world. From this report, it has been found that the US is the second largest biodiesel producing country in the world and expects its biodiesel market to be about 6,453 million liters by 2020, whereas, globally, the expectation is about 45,291 million liters to fulfill energy demand. Hence, more research and effort are needed to overcome all the drawbacks against biodiesel combustion whether by fuel or engine modification. The advantages and disadvantages of biodiesel over diesel fuel are shown in Table 2.1a.

**Table 2.1a**

Advantages and disadvantages of biodiesel as an alternative fuels over diesel fuel

| Advantages | Reference | Disadvantages | Reference |
|---|---|---|---|
| Higher viscosity which increases it's lubricity properties | (Tate et al., 2006) | Higher production cost, Limited feedstock availability | (Abbaszaadeh et al., 2012) |
| High nontoxicity & biodegradability implies less impact on environment pollution | (Pantoja et al., 2013) | Produces higher $NO_x$ emissions in unmodified diesel engine | (Debnath et al., 2013) |
| Higher Cetane number hence produces less HC | (Buyukkaya et al., 2013b) | Coking, Filter plugging, Auto-oxidation, Corrosive nature | (Fazal et al., 2013) |
| Low sulfur content and no aromatic components results low PM, $SO_2$ and HC | (Chang et al., 2013) | Most of the biodiesel feedstock are from edible source results increase the price of food. | (Koizumi, 2013) |
| Safer to handle, store, and transport as high flash point | (Demirbas, 2009) | Higher BSFC due to lower heating value. Higher density and viscosity of biodiesel leads to poor atomization. | (Al-Dawody & Bhatti, 2013) |

## 2.3 $NO_x$ formation mechanisms

Nitrogen oxide is the generalized term for NO and $NO_2$ given with the formulae of $NO_x$ (Rizwanul Fattah et al., 2013a). Understanding the kinetics behind the $NO_x$ forming reaction is important for taking attempt to reduce the $NO_x$ emissions. The thermal (Zeldovich), prompt (Fenimore), $N_2O$ pathway and fuel-bound nitrogen mechanism are the most common mechanisms for NO formation in diesel combustion (K.

Varatharajan, 2012). Among them thermal and prompt are the dominant mechanisms of $NO_x$ formation in biodiesel combustion (K. Varatharajan et al., 2011). The atmospheric or molecular nitrogen is the main source of nitrogen for $NO_x$ formation during conventional combustion of typical petroleum and bio-based fuels. Based on literatures, the general $NO_x$ formation mechanisms are summarized below.

### 2.3.1. Zeldovich mechanism

$NO_x$ formation occurs at temperature above 1700K by this mechanism (S.K. Hoekman & C. Robbins, 2012). At this temperature nitrogen ($N_2$) and oxygen ($O_2$) react through a series of chemical steps known as Zeldovich mechanism. The rate of formation increases rapidly with temperature. This mechanism of thermal NOx formation is believed to be the predominant contributor of total NOx. The basic kinetic equations for thermal $NO_x$ formation are described by the following chemical reactions (1) to (3).

$N_2 + O \leftrightarrow NO + N$ -------------------------- (1)

$N + O_2 \leftrightarrow NO + O$ ------------------------- (2)

$N + OH \leftrightarrow NO + H$ ------------------------- (3)

The first step is rate limiting, and due to its high activation energy (314 KJ/mole), requires high temperatures to proceed. Reaction (3) is only significant under reducing conditions. Residence time and the concentration of nitrogen and oxygen also have an influence on the production of thermal NO (K. Varatharajan & Cheralathan, 2012b). Hu and Hung (Hu & Huang, 2011) theoretically proved that $NO_x$ formation depends directly on two factors: the concentration of reactants, and temperature.

### 2.3.2. Prompt or Fenimore mechanism

The presence of a second mechanism leading to $NO_x$ formation was first identified by Fenimore and was termed “prompt $NO_x$”. There is a good evidence that prompt $NO_x$ can be formed in a significant quantity in some combustion environments; such as in low-temperature, fuel rich conditions and where residence time is short (C. Fenimore, 1971; Fluent, 2001-11-29). Prompt $NO_x$ is most prevalent in rich flames. The actual formation involves a comply series of reactions and many possible intermediate species. Prompt $NO_x$ is produced when hydrocarbon fragments react with nitrogen in the combustion chamber to form fixed nitrogen species such as HCN (Fernando, Hall, & Jha, 2006a). After that these nitrogen-containing fragments react with atmospheric nitrogen. Prompt $NO_x$ is more sensitive than thermal $NO_x$ in fuel chemistry because of the dependence on hydrocarbon fragments. Miller and Bowman (Miller & Bowman, 1989) studied the mechanism and modeling of nitrogen chemistry in combustion and stated that in order to estimate the total $NO_x$, the prompt $NO_x$ must be considered, which was also verified by the recent study by Ren and Li (Ren & Li, 2011). The prompt $NO_x$ is generally formed through the following reactions (4) to (8).

$$CH + N_2 \leftrightarrow HCN + N \text{ -------------------------- } (4)$$

$$CH_2 + N_2 \leftrightarrow HCN + NH \text{ ------------------------ } (5)$$

$$N + O_2 \leftrightarrow NO + O \text{ -------------------------------- } (6)$$

$$HCN + OH \leftrightarrow CN + H_2O \text{ ------------------------ } (7)$$

$$CN + O_2 \leftrightarrow NO + CO \text{ ------------------------ } (8)$$

Here, CH and $CH_2$ are the significant contributors to form prompt $NO_x$ (eqs 4 and 5). The formation of prompt $NO_x$ is proportional to the number of carbon atoms in each unit volume. Prompt $NO_x$ is independent of the parent hydrocarbon. The amount of HCN increases with increasing the concentration of hydrocarbon radicals which enhances with increasing equivalence ratio. Prompt $NO_x$ formation increases with an increasing equivalence ratio and then reaches a peak and decreases because of a shortage of oxygen.

### 2.3.3. Fuel $NO_x$ mechanism

Fuel $NO_x$ is formed when nitrogen that is chemically bound in the fuel combines with excess oxygen during the combustion process. The type of $NO_x$ is negligible for both diesel and biodiesel because of low nitrogen levels (S.K. Hoekman & C. Robbins, 2012). Biodiesel has an average nitrogen concentration of only 0.02% (Fernando et al., 2006a). Addition of additives containing nitrogen atoms e.g. pyridine, pyrrole etc. may lead to more fuel $NO_x$ formation. This can be attributed to weaker C-N bond compared to N-N bond. The C-N bond in pyridine and pyrrole are shown in **Figure 2.1**. The main pathway for this type of $NO_x$ formation involves the creation of intermediate nitrogen containing species such as HCN, $NH_3$, NH, or CN. These molecules can then be oxidized to form $NO_x$ (Fluent, 2001-11-29).

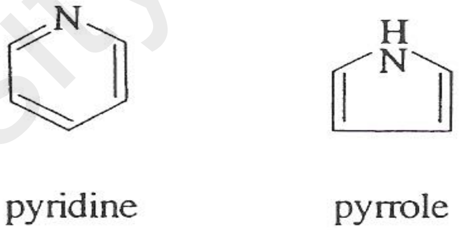


**Figure 2.1:** Organic, fuel bound nitrogen compounds in solid fuels.

### 2.3.4. $N_2O$ pathway mechanism

The $NO_x$ formation due to the $N_2O$ pathway is another essential mechanism in a combustion process under high pressure and lean air-fuel ratio compared with Fenimore NO, and a minor contribution to the formation of $NO_x$ related to the thermal NO mechanism (Gardiner, 2000). In this mechanism, the reaction occurs between $N_2$ and atomic oxygen to form $N_2O$ by a three-body reaction.

$O + N_2 + M \leftrightarrow N_2O + M$ -------------------------------- (9)

Here, the molecule M is required to execute this reaction. The $N_2O$ formed in reaction (9) can then react to form NO which is shown in equation (10).

$N_2O + O \leftrightarrow NO + NO$ --------------------------------- (10)

## 2.4. Effect of Biodiesel on $NO_x$ Emissions

In general, the formation of $NO_x$ emissions by biodiesel and its blends is higher than that of diesel combustion reported in much of the literature (Keskin et al., 2010; Ozsezen & Canakci, 2011b; D. H. Qi et al., 2010a; Serrano et al., 2012). Biodiesel fuel properties are not only the main contributor to increasing emissions, but also to a number of coupled mechanisms whose effects may tend to reinforce or cancel one another under different conditions, depending on the specific combustion and fuel characteristics (Mueller et al., 2009). **Table 2.1b** shows some of the main physical and chemical properties of diesel and commonly used biodiesel fuels. There are multitudinous theories that try to explain the biodiesel $NO_x$ effect, including cetane number (Devan & Mahalakshmi, 2009), soot radiation (G. A. Ban-Weiss et al., 2007), bulk modulus (Baiju et al., 2009), prompt $NO_x$ formation (Robert L. McCormick et al., 2001) and changes in fuel composition that affect fuel spray or ignition patterns within the combustion chamber, and adiabatic flame temperature (G. A. Ban-Weiss et al., 2007; W. Eckerle et al., 2008; Jha et al., 2008; M. Nabi et al., 2004).

The higher bulk modulus of compressibility of biodiesel causes pressure waves in the fuel line of the engine to move faster and, therefore, the fuel injector will open earlier in the engine cycle while injecting biodiesel. This advance injection timing leads to earlier combustion and a subsequent longer residence time at high temperatures, hence increases the formation of thermal $NO_x$ (R.L. McCormick et al., 2006; Mueller et al., 2009; J.P. Szybist et al., 2005). On the other hand, high-pressure common rail injection systems do not see an injection timing advance when biodiesel is used (Altın et al., 2001), while some $NO_x$ increase still occurs in these systems.

Graboski et al. (2003) showed that the iodine number increases with the increasing number of double bonds in the ester molecule. They also reported an increase in $NO_x$ emissions with the increase in unsaturation and the decrease in mean carbon chain length. The lesser the compressibility of biodiesel fuel, the faster the fuel injection pressure develops and the fuel is injected sooner. With the earlier start of the injection in most engines, the exhaust $NO_x$ increases (Monyem et al., 2001; Zhu et al., 2010). An increase in $NO_x$ emissions with the increase in iodine number was reported earlier by Peterson et al. (2000). The US EPA (U.S.EPA, 2002) and Wyatt et al. (2005) have confirmed a direct relationship between $NO_x$ emissions and molecular unsaturation. It has been suggested that the double bonds can contribute to the formation of higher levels of certain hydrocarbon radicals in the pre-mixed fuel-rich mixture, which results in more prompt $NO_x$ formation during subsequent combustion (McCormick et al., 2001).

Biodiesels have a higher distillation temperature; hence, they do not vaporize as readily as diesel. Therefore, much more fuel is vaporized and mixed with air in the diffusion stage rather than pre-mixed stage. In the diffusion stage, the equivalence ratio at the flame front is essentially always at a stoichiometric value (Lapuerta et al., 2008b). Therefore, once the fuel is largely being consumed in a diffusion flame, it is more relevant to consider the oxygen fraction within it. It is well-known that higher oxygen fractions yield higher combustion temperatures and $NO_x$ formation rates for diffusion flames (Nakayama et al., 2003; Ogawa et al., 2006).

## 2.5. Factors affecting $NO_x$ emissions

Many researchers have proposed many possible reasons for the increase of $NO_x$ emissions when biodiesel is used in diesel engine (S.K. Hoekman & C. Robbins, 2012; J. Sun et al., 2010; K. Varatharajan & Cheralathan, 2012b). Summarizing of the review on factors affecting biodiesel $NO_x$ as well as other criteria emissions are presented in **Table 2.2**. On the other hand few of them also found reduced $NO_x$ emissions using biodiesel fuels (Nagarhalli et al., 2010; Saqib et al., 2012). They have also proposed other mechanisms. No single factor is responsible for these $NO_x$ effects. However the exact cause is still under investigation. The possible causes that have been proposed by the researchers to explain the biodiesel $NO_x$ increase are presented in this section.

**Table 2.1b**

Comparative physical and thermal properties of fossil diesel, edible and non-edible biodiesels (Anand et al., 2011; Ganapathy et al., 2011; Hazar & Ozturk, 2010; Johansson et al., 2011; Y. C. Lin et al., 2011; Raheman & Ghadge, 2007; H. Raheman & A. Phadatare, 2004; Rizwanul Fattah et al., 2013b; Saleh, 2009; Solaimuthu et al., 2012; Subbaiah & Gopal, 2011; Suryanarayanan et al., 2008; F. Wu et al., 2009)

| **Fuel / standard Name** | **Properties** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Calorific Value (MJ/kg) | Density at 288K (kg/m$^3$) | Flash point (K) | Pour point (K) | Kinematic viscosity at 313K (mm$^2$/s) | Carbon residue %, w/w | Cetane Number | Iodine value (g iodine/100 g)$^b$ | Oxygen content (wt%) |
| **Diesel** | 43.2-45.2 | 830-839 | 318-353 | 253-264 | 3.11-4 | - | 49 - 57.9 | 6 | 0 |
| **Palm Biodiesel (PB)** | 37.4–40.1 | 864–878 | 408 | 287–289 | 4.05–5.1 | - | 58–65.5 | 59 | 11.2 |
| **Rapeseed Biodiesel (RB)** | 37-39.8 | 873–930 | 420–443 | 261 | 3.5–5.0 | - | 50–56.6 | 108.05 | 10.5 |
| **Waste Cooking Biodiesel (WCB)** | 40.1-41.2 | 870-880 | 442 | 272 | 4.31 | - | 54-56 | - | 11.3 |
| **Cottonseed Biodiesel (CSB)** | 39.8–40.8 | 872–885 | 343–473 | 258–279 | 3.6–5.94$^a$ | 0.3 | 55–60 | 90–119 | 10.6 |
| **Soybean Biodiesel (SB)** | 39–40.5 | 873-885 | 414–440 | 266–272 | 3.9–4.65 | 0.2 | 46–56 | 120.52 | 9.8 |
| **Sunflower Biodiesel (SFB)** | 39.7 | 882 | 451 | 258 | 6.74$^a$ | - | 49-52 | 136 | - |
| **Corn oil Biodiesel (COB)** | 39.12 | 890 | 361 | - | 4.21 | - | - | 119.41 | - |
| **Karanja Biodiesel (KB)** | 36.12 | 876-889 | 454-460 | - | 5.71 | - | 53 | 85 | - |
| **Jatropha Biodiesel (JB)** | 37.2–43.0 | 862–886 | 453–553$^a$ | 267–279 | 3.0–5.65 | - | 53–70 | 105 | - |
| **Rice Bran Biodiesel (RBB)** | 38.73 | 874 | 438 | 276 | 4.63 | - | 56.2 | 102 | 11.25 |
| **Thevitia Peruviana Biodiesel (TPB)** | 41 | 860 | 433 | 269 | 6.0 | - | 50 | - | - |
| **Jojoba Biodiesel (JOB)** | 47.38 | 866 | 334 | - | - | 0.5 | 63.5 | - | - |
| **Mahua Biodiesel (MB)** | 36.9 | 880 | 443-481 | 279 | 3.98-6.04 | 0.20 | 52.4 | 80 | - |
| **Colza Biodiesel (CB)** | 40.2 | 883.4 | | | 4.6 | | 52.6 | | |
| **EN 14213$^c$** | 35.0 | 860-900 | 393 (LL) | 273 (UL) | 3.5-5.0 | 0.3 (UL) | | 130 (UL) | - |
| **ASTM D6751-01$^c$** | - | - | 403 (LL) | - | 1.9–6.0 | 0.05(UL) | 47 (LL) | - | - |
| **EN 14214$^c$** | - | 860–900 | 374 (LL) | - | 3.5–5.0 | 0.3 (UL) | 51 (LL) | 120 (UL) | - |

$^a$ At 300 K, $^b$Data obtained from ref. (Gopinath, Puhan, & Nagarajan, 2009), $^c$Data obtained from ref. (Seta Biofuel Testing), LL= Lower Limit, UL= Upper Limit

## Table 2.2

Summarizing the review on factors affecting biodiesel $NO_x$ as well as other criteria emissions

| Fuel | Engine used & Condition | Results compared to diesel fuel (%) | | Explanation for higher NOx | Source |
|---|---|---|---|---|---|
| | | **$NO_x$** | **Others emission** | | |
| **POME25** | IRLOSKAR TV-1, 1C, DI, NA, WC, DE, Max power output: 5.2 kW, IT 23.51bTDC CR 17.5 IP: 19.6 MP, full load, CS= 1500 rpm | ↑ high | CO↓21.4, HC↑9.52, Smoke↑9.8, | Fuel burn during the late phase of combustion resulting in higher exhaust temperature because of having higher molecular weights. | (Sharon et al., 2012) |
| **POME50** | | ↑ little | CO↓35.2, HC↓9.53 | | |
| **POME75** | | ↑ little | CO↓35.2, HC↓19.05, Smoke↓10, | | |
| **POME100** | | ↑ little | CO↓52.9, HC↓38.09, Smoke↓19, | | |
| **POME20** | 3C, 2.5 L Perkins AD 3–152 Max engine power of 44 kW at 2132 rpm, 8-mode cycle | Max ↑24 | CO↓20(avg.) | The higher the number of double bounds in the biodiesel molecular structure. | (Redel-Macías et al., 2012) |
| **POME50** | | ↑(0.32 -25) | CO↓27(avg.) | | |
| **ROME100** | Lister Petter 1C, DI, CR 15.5, Max power 8.6 kW at 2500 rpm, CS=1500 rpm, VL: 2 bar, 4 bar and 5 bar EGR variation at each load: 0 and 30% | ↑(7-11) | CO↓, HC↓23 (0% EGR) & HC↓41 (30% EGR), smoke(BSN)↓52, PM↑ with ↑ load, | The higher cylinder pressures, injection timing advance and high amount of fuel injection. | (Rounce et al., 2012) |
| **ROME100** | MAN D2566 MUM 6C, bus engine, CR 17.5 Mechanically controlled DI, Max power 162 kW at 2200 rpm | ↑ | CO↓, HC↑, Smoke↓ & (- ) (CO, HC & smoke) with (+) speed for both fuel | Higher oxygen content into biodiesel fuel | (B. Kegl, 2011b) |
| **ROME80** | Juling SD-1110 1C, CR 16.5, Rated power 20 HP (14.7 kW) | ↑(4.17 ±0.1) | CO↓(32.47±0.4), PM↓(27.7 ± 1.6) | Biodiesel has low sulphur content and presence of high fuel bound oxygen. | (Saqib et al., 2012) |
| **ROME100** | | ↑(6.27±0.2) | CO↓ (30.57±1.1), PM↓(39.8 ± 2.0) | | |
| **ROME50** | 4C, 46 kW DI, CR 16.1 Max power 46 kW at 2400 rpm, full load, speed+(1200-2100) rpm | ↑7.82 (avg.) | CO↓15.53, $CO_2$↑ 2.9, smoke ↓46.29 | The high oxygen content and higer density of ROME fuel results higher combustion temperature | (İ. Çelikten et al., 2012) |
| **WOME5, WOME10, WOME20, WOME30** | Cummins B5.9-160, DI, IP= 250 bar, IT= 12.3 BTDC CR:17.9: 1, Max$^m$ power 118 kW at 2500 rpm, a Max$^m$ torque of 534 Nm at 1600 rpm | ↑(0.73-2.19) | CO↓(3.33-13.1), HC↓(10.5-36.0), $CO_2$↑(0.117-1.06), PM↓(5.29-8.53), PAHs↓(7.53-37.5) | Not mention | (Y. C. Lin et al., 2011) |
| **WOME25, WOME50, WOME75** | MWMD229/4, 50 kW, NA, 4S, 4C, mechanically controlled DI fuel system, VL= 0 to 25 kW, | ↑7.1(WCB25), ↑4.8(WCB50), ↑6.5(WCB75), Max variation occurred at | CO↑19.2(WCB25), ↑20.1(WCB50),↑46.1(WCB75);HC↑0.6(WCB25), ↑ 23.5 (WCB50); $CO_2$↑5.3(WCB25), ↑8.5(WCB50),↑13.3(WCB75), Max variation occurred at HL | NOx increases with increasing engine load, cylinder pressure and temperature are increased as a result of larger fuel amount being burned in the combustion chamber. | (Valente et al., 2012) |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
|  |  | LL |  |  |  |
| **SME5** | 4S, NA, 4C,DI diesel engine, 1600 rpm, full load | same | CO↓2.8, smoke↓6.6 | Higher oxygen content and lower calorific value of SME fuel. | (Gokalp et al., 2011) |
| **SME20** |  | ↑8.26 | CO↓8.5, smoke↓19.6 |  |  |
| **SME50** |  | ↑10.5 | CO↓18.4, smoke↓31.28 |  |  |
| **SME100** |  | ↑18.34 | CO↓32.1, smoke↓54.5 |  |  |
| **SME100** | Yanmar L100V, vertical DI, CI Engine, NA, AC, 4S, 1C, rated power 6.2 kW at 3600 rpm | ↑56 (LL) ↓4 (ML) ↓20 (HL) | CO↓8(LL) ↓34 (ML) ↓27 (HL), HC↓64(LL) ↓14(ML) ↓2.5 (HL), PM↓56 (after 1 hour test) | - | (Cecrle et al., 2012b) |
| **JME5, JME10, JME20, JME50 & JME100** | 3.3-L 4C, DI, TC, intercooled, HPCRS, Rated power output 79 kW at 3200 rpm, VL: 10%, 25%, 50% & 75% full load, CS: 2000 rpm | ↑(1.02, 2.06, 4.74, 5.71 & 13.9 with increasing JME blends at HL) | (CO↑ at LL, CO↓ at HL, smoke↓4.54 for JME5); (CO↑ at LL, CO↓ at HL, smoke↓14.1 avg. for JME10); (CO↑ at LL, CO↓ at HL, smoke↓24.9 avg. for JME20); (CO↑ at LL, CO↓ at HL, smoke↓54.0 avg. for JME50) & CO↑(2.3-17.6) at LL, CO↓ (15- 23.1) at HL, HC↓( 26.5-27.6) at LL, HC↓( 30.9-46.7) at HL, smoke↓80.5(avg.) for JME100 | The higher bulk modulus and sound velocity and viscosity, lead to an advanced start of injection. This, jointly with any cetane number increase, may slightly advance the start of combustion. | (Tan et al., 2012) |
| **JME5, JME10, JME20, JME30, JME100,** | Kirloskar 1C, AC, DI, NA diesel engine, VL: 0%, 20%, 40%, 60%, 80% & 100% load | NOx↑ with ↑(load and blend ratio) | CO↓ with ↑blend ratio, $CO_2$↑ with ↑(blend ratio and load), HC↓ with ↑(blend ratio and load), smoke↓ | The shorter ignition delay and the increased amount of biodiesel undergoing premixed combustion results in higher cylinder pressure and hence temperature. | (B.S. Chauhan et al., 2011) |
| **JME5, JME10, JME20, JME30, JME40 & JME50** | Kirloskar 1C, DI, AC diesel engine CR 17.5 speed 1500rpm rated power 4.4 kW IP= 200 bar, Variable load | NOx↑ with ↑ load | CO↓ with ↑ blend ratio, Smoke↑ with ↑(load and blend ratio) | The higher exhaust gas temperature is an important cause for biodiesel higher NOx | (Elango & Senthilkumar, 2011) |
| **JME5** | Yanmar 1C, NA Engine CR 17.7 Max. Power 7.7 kW IT 171 BDTC, CS: 2300 rpm, Throttle position (TP): 100% and 80% | ↑(4-9.5) | CO↓(17.26-20.7), HC↓(8.96-16.28) | Higher fuel borne oxygen and higher burned gas temperature | (A. Liaquat et al., 2012) |
| **JME10** |  | ↑(6.25-17) | CO↓(25.92-33.24), HC↓(11.25-30.23) |  |  |
| **Rice bran biodiesel (RBB100)** | Kirloskar model AV1, 4S, 1C,Vertical, WC, CR:16.5:1, Rated power 3.72 kW | ↑4 (NOx↑ with ↑ engine load) | CO↓25.8, $CO_2$↑, HC↓54, smoke↑27.93; all emission increases with ↑ engine load | Higher combustion temperature as well as the $O_2$ content of the biodiesel fuel | (Subbaiah & Gopal, 2011) |
| **TPOME100** | 1C, CR= 16.5:1, Rated power= 3.7KW, Rated speed= 1500 rpm, full load | ↑9.44 | CO↓12.5, HC↓8.75, smoke↑8.5 | Higher exhaust gas temperature due to heavier molecules of biodiesel | (T. Kannan & Marappan, 2011) |

Note: ↑ indicates increase, ↓ indicates reduced, HPCRS = High-pressure common rail fuel system

**Table 2.3**

Typical fatty acid (FA) groups with composition in biodiesel. Source: (Glaude et al., 2010; Hoekman et al., 2011; Schönborn et al., 2009; Shahabuddin et al., 2013; A. Srivastava & Prasad, 2000)

| **Common name** | **Formal name** | **C:N** | **Molecular formula** | **FAME composition (EN14103) (m/m %) for different biodiesel** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | **ROME** | **POME** | **JME** | **Tallow** | **CNOME** | **SME** | **SOME** | **Peanut** | **CME** |
| Lauric acid | Dodecanoic acid | 12:0 | $C_{12}H_{24}O_2$ | 0.0 | 0.2 | 0.0 | 0.1 | 45.6 | - | | | |
| Myristic acid | Tetradecanoic acid | 14:0 | $C_{14}H_{28}O_2$ | 0.1 | 1.1 | 0.0 | 3.3 | 22.1 | 0.1 | 0.1 | | 0.1 |
| Palmitic acid | Hexadecanoic acid | 16:0 | $C_{16}H_{32}O_2$ | 4.6 | 43.0 | 12.6 | 25.2 | 10.2 | 10.3 | 6.0 | 10.4 | 3.9 |
| Palmitoleic acid | cis-9-Hexadecanoic acid | 16:1 | $C_{16}H_{30}O_2$ | 0.3 | 0.2 | 0.8 | | - | | | | |
| Stearic acid | Octadecanoic acid | 18:0 | $C_{18}H_{36}O_2$ | 1.8 | 4.7 | 5.9 | 19.2 | 3.6 | 4.7 | 5.9 | 8.5 | 3.1 |
| Oleic acid | cis-9-Octadecenoic acid | 18:1 | $C_{18}H_{34}O_2$ | 60.7 | 40.1 | 35.8 | 48.9 | 8.2 | 22.3 | 20.43 | 47.1 | 60.2 |
| Linoleic acid | cis-9,12-Octadecadienoic acid | 18:2 | $C_{18}H_{32}O_2$ | 19.1 | 9.5 | 28.8 | 2.7 | 2.7 | 54.1 | 66.2 | 32.9 | 21.1 |
| Linolenic acid | cis-9,12,15-Octadecatrienoic acid | 18:3 | $C_{18}H_{30}O_2$ | 8.3 | 0.2 | 0.2 | 0.5 | 0.0 | 8.3 | 0.6 | 0.5 | 11.1 |
| Others | | | | 5.1 | 1.0 | 15.9 | 0.1 | 7.6 | 0.2 | | 0.6 | 0.5 |
| Saturated fatty acids (%) | | | | 6.5 | 50.2 | 18.5 | 47.8 | 81.5 | 37.4 | 32.43 | 66 | 67.3 |
| Unsaturated fatty acids (%) | | | | 88.4 | 48.8 | 65.6 | 52.1 | 10.9 | 62.6 | 67.57 | 34 | 32.7 |

Note: C:N, C the number of carbons and N the number of double bonds of carbons in the fatty acid chain.

### 2.5.1. Physicochemical properties of biodiesel

The physical and chemical properties of biodiesel such as: viscosity, density, bulk modulus of compressibility, sound velocity, cetane number, iodine value, surface tension, thermal conductivity, chain length, heat capacity and fuel composition etc. have a significant effect on $NO_x$ emissions. The Physicochemical properties of diesel and some commonly used biodiesel fuels are presented in **Table 2.1b**.

Fuel viscosity has significant effect on $NO_x$ emissions. Anderson and Olsen (Nettles-Anderson & Olsen, 2009) analyzed $NO_x$ emissions as a function of viscosity and found an increase in $NO_x$ with increasing viscosity at low temperatures. Generally the kinematic viscosity of biodiesel is greater than that of diesel fuel (Table 2.1b), which reduces fuel leakage during injection and leads to increased pressure as well as advanced injection timing (Breda Kegl, 2006). The advance in injection timing facilitates increased fuel mass injected which in turn results in increased $NO_x$ emissions. Moreover, Yuan and Hansen (Wenqiao Yuan & Hansen, 2009) observed reduced $NO_x$ emissions of about 3.52% with reduced viscosity of soy methyl ester to a level of petroleum diesel fuel.

The $NO_x$ emissions increase with increasing fuel density as well as decreasing cetane number (CN) (Alptekin & Canakci, 2008; G.A. Ban-Weiss et al., 2007; Robert L. McCormick et al., 2001). The start of injection (SOI), the injection pressure, and the fuel spray characteristics are affected by the fuel density, which influences combustion as well as emissions. In modern diesel engine, fuel injection systems measure the fuel by volume. As a result, the changes in the fuel density will greatly act upon mass of fuel injected and corresponding $NO_x$ emissions (Alptekin & Canakci, 2008). Moreover Boehman et al.

(2004) found the relationships between FAME density and $NO_x$ emissions as increased $NO_x$ emissions with increasing FAME density.

Tat et al. (2000) reported that, vegetable oils and their methyl esters are less compressible and have greater speed of sound, which means they have a higher bulk modulus of compressibility than diesel fuel. As a result, the fuel injection pressure develops faster and the fuel is injected sooner. Earlier start of injection delivers increased fuel mass delivery in most engines. Combustion of higher quantity mass develops an elevated temperature, which causes more $NO_x$ formation. Tat and Van Gerpen (2003) studied the effect of fuel property changes on injection timing and finally reported advanced injection timing of about 1° due to the high value of bulk modulus and the speed of sound which may be partially responsible for increasing the $NO_x$ emissions. It was also found that 60 vol % blend of biodiesel and a paraffinic solvent (Norpar-13) displays the same bulk modulus of compressibility as a diesel fuel (Boehman et al., 2004). Hence, one scheme for combating the "biodiesel NOx effect" is to use highly paraffinic diesel fuels, such as F-T diesel as the diesel basestock.

The higher cetane number of biodiesel implies shorter ignition delay which reduces the combustion temperature as well as residence time, consequently less $NO_x$ formation (Bora & Baruah, 2012; Z. Zhu et al., 2012). In general, higher saturated fatty acids biodiesel such as coconut, palm and tallow shown in **Table 2.3**, produce less $NO_x$ than mineral diesel and have a higher cetane number (Giakoumis et al., 2012; Ono et al., 2009). Despite of having a high cetane number, it produces higher $NO_x$ than diesel fuel usually. Wang et al. (2000) gave suggestion of this regard that, high CN of biodiesel tend to increase peak pressure and temperature due to shortened ignition delay which leads to enhanced $NO_x$ formation.

Mueller et al. (2009) also investigated the biodiesel $NO_x$ effect and reported that somewhat higher cetane number of biodiesel relative to diesel causes ignition to occur earlier in the cycle. This allows the combustion products to have a longer residence time at high temperatures, which increases $NO_x$ emissions.

The Iodine value (IV) of biodiesel directly impacts on $NO_x$ emissions. The emissions of $NO_x$ increase with an increasing iodine value of biodiesel, which was investigated by McCormick et al. (Robert L. McCormick et al., 2001). The measurement of the degree of unsaturation of fatty acid is indicative of the iodine value. Thus, a higher degree of unsaturation indicates a higher iodine value. Wyatt et al. (2005) carried on emission tests with the TOME (IV:  53.6), lard methyl ester (IV: 62.5) and chicken fat esters (IV: 77.4) and compared with SOME (IV: 129.1) and found that $NO_x$ emissions are linearly correlated with an IV of fatty acid ester. Moreover, Peterson et al. (2000) conducted emission tests with several FAME fuels and reported that with increase in IV from 7.88 to 129.5, the $NO_x$ emissions were raised by 29.3%.

The surface tension of biodiesel is more than 22% compared to diesel (K. Varatharajan & Cheralathan, 2012b). In diesel spray properties, specifically the droplet size distribution and Sauter mean diameter (SMD), are influenced by fuel surface tension and viscosity. The SMD has been shown to increase with increasing surface tension and viscosity. As noted, increased droplet size can reduce the fraction of fuel burned in the premixed combustion phase and lead to increased duration of diffusion flame combustion (Michael S. Graboski & McCormick, 1998). The surface tension of biodiesel is more than 22% compared to diesel (K. Varatharajan & Cheralathan, 2012b). As a result, the SMD of biodiesel fuels varies from 5 to 40% higher than diesel fuel, hence increases the $NO_x$ concentration. Therefore, the $NO_x$ concentration may be considered as a strong function of fuel surface tension (Gopinath, Puhan, & Nagarajan, 2010).

Other physical properties of biodiesel such as liquid thermal conductivity, radiative heat loss and vapor heat capacity are slightly lower than diesel fuel which allows to rise its temperature at a faster rate once injected, resulting in evaporated droplets sooner than petroleum diesel. Sun et al. (J. Sun et al., 2010) reported that biodiesel combustion inside cylinder has less radiative heat transfer due to less soot formation which can be ascribed as a cause of $NO_x$ emissions. So variations of these properties have significant influences on $NO_x$ formation rate.

### 2.5.2. High oxygen content

Biodiesel is an oxygenated fuel and it contains oxygen of about 11% by weight (M.S. Graboski et al., 1999; K. Varatharajan & Cheralathan, 2012b). Several scientists (B.S. Chauhan et al., 2011; Janaun & Ellis, 2010; D. Qi et al., 2010; J. Sun et al., 2010; J. Xue et al., 2011) have investigated the effects of biodiesel fuel on exhaust emissions, and found a significant reduction in CO, sulfur, smoke, PM, and noise emissions. They explained these attributing to the high oxygen content leading to complete combustion. The presence of oxygen in biodiesel fuel results in higher heat release during the premixed phase combustion. Rapid breakage of hydrocarbon contributes to a hotter combustion process, which can be regarded as the main contributor to increased $NO_x$ emissions (Mueller et al., 2009; Ye & Boehman, 2010). Nabi et al. (2009) tested a four-stroke diesel engine with KOME biodiesel and observed that $NO_x$ increased by about 15% under high load conditions, because of the 12% oxygen content of B100, which resulted in a higher gas temperature in the combustion chamber. In contrast, Lapuerta et al. (2005) inferred that the oxygen content of biodiesel could not be the cause for an increase in $NO_x$ because the oxygen/fuel mass ratio of biodiesel (2.81) is less than that of the diesel (3.58). Lapuerta et al. (2008) also showed that there was no significant difference between the diesel and biodiesel $NO_x$ emissions. They tested different blends of waste cooking oil methyl and ethyl esters in a 2.2 L, CRDI diesel engine and found a very slight difference in $NO_x$ emissions between the biodiesel and diesel fuel.

### 2.5.3. Molecular structure of biodiesel fuel

Many researchers (Hoekman et al., 2011; Pandey et al., 2012; Rizwanul Fattah et al., 2013a) observed that, the biodiesel molecular structure has a substantial impact on combustion and hence emissions. The structural formula and fatty acid composition of some biodiesel fuels are presented in **Table 2.3**. Shahabuddin et al. (2013) reported that the cetane number, heat of combustion, melting point, and viscosity of neat fatty compounds increase with increasing chain length and decrease with increasing unsaturation of the FAME molecule. Furthermore, the heating value, melting point, cetane number, viscosity and oxidation stability decrease whereas density, bulk modulus, fuel lubricity and iodine value increase as the degree of unsaturation increases. McCormick et al. (2001) investigated the impact of biodiesel chemical structure on $NO_x$ emission; specifically fatty acid chain length and number of double bonds, and found that $NO_x$ increases with an increasing number of double bonds of the fuel, which can be quantified as the iodine value. McCormick et al. (2005) studied various biodiesel with different degrees of unsaturation and reported that progressively increasing $NO_x$ emissions due to the use of biodiesel fuels with higher degrees of unsaturation, which correlates with higher $T_{ad}$. Ban-Weiss et al. (2007) investigated numerically to show the biodiesel $NO_x$ effect and found enhanced the

$NO_x$ emissions of about 21% due to higher peak flame temperature of the double bonded methyl trans-2-butanoate about 14°K than the single- bonded methyl butanoate. Pattamaprom et al. (2011) analyzed the performance and emissions using palm olein and palm stearin (co-products of palm oil refining processes) biodiesel fuels and reported that palm olein has a slightly higher degree of unsaturation than palm stearin, which leads to a lower cetane number and thus, a higher combustion temperature, which implies greater $NO_x$ formation.

#### 2.5.4. Premixed-burn fraction

Because of having oxygen into biodiesel, it premixes more fully during the ignition delay, and a larger fraction of its heat release occurs during the premixed-burn phase of combustion at ignition. The combustion that is more premixes has higher oxygen concentrations and therefore produces more $NO_x$. The difference in $NO_x$ produced during the premixed burn is responsible for the biodiesel $NO_x$ increase.

#### 2.5.5. Ignition delay time

The time between the injection start and onset of combustion is called the ignition delay time. Ban-Weiss et al. (2007) reported that in a combustion chamber, the reactants are rapidly preheated due to a longer ignition delay time, which results in an increase of the flame temperature and corresponding $NO_x$ emissions. Benjumea et al. (2011) reported that biodiesel fuels, having higher degree of unsaturation have longer ignition delay time which results in higher $T_{ad}$. Therefore, $NO_x$ emissions increase according to the thermal $NO_x$ mechanism. But in general case, the ignition delay of biodiesel is shorter than that for conventional diesel fuel at all load condition investigated by many researchers (A. K.

Agarwal, 2007; R.L. McCormick et al., 2006; Nagaraju et al., 2008; Schönborn et al., 2009; Shahabuddin et al., 2013; J. Sun et al., 2010). They reported that the contribution of some fuel properties of biodiesel, such as; the high cetane number, high ignition quality, increased chain length and degree of unsaturation etc., advance the combustion timing lead to shorter ignition delay and consequently, higher $NO_x$ formation. Schönbornet al., 2009 investigated the effect of molecular structure of natural biodiesel (NB) and single molecule fatty acid esters (SMFAE) on the combustion behavior under diesel engine conditions. They reported that for a shorter ignition delay time, the relationship between $NO_x$ emissions and the $T_{ad}$ becomes gradually steeper.

### 2.5.6. Injection timing (IT)

In combustion systems, injection timing is also an important parameter that affects combustion temperature and hence $NO_x$ emissions. The start of fuel injection is advanced for biodiesel compared with petroleum diesel in rotary/distributor-style fuel injection systems, which has been reported by several authors (G.A. Ban-Weiss et al., 2007; Canakci, 2007; R. McCormick et al., 2005; James P. Szybist et al., 2007). Monyem et al. (2001) carried out an experiment with a diesel engine fuelled by biodiesel without changing the setting of the injection timing and observed that B100 and B20 fuel injects about 2.3° and 0.25–0.75° earlier, respectively than the studied petroleum diesel fuel. This injection timing advance can be attributed due to several properties of biodiesel e.g. high density, higher bulk modulus of compressibility, and greater speed of sound (Schönborn et al., 2009; Xiaoming et al., 2005). The higher bulk density and viscosity move the pressure wave inside the fuel pipe lines more quickly and an earlier needle lift results in advanced injection. Szybist et al. (2005) studied injection and combustion processes of soy-derived biodiesel blends and Fischer-Tropsch (FT) diesel fuel. Their results showed that soy-derived biodiesel blends produced advance SOI timing of about 1.1° crank angle relative to diesel fuel because of the lower compressibility (higher bulk modulus). From the information in **Table 2.4**, it can be seen that increasing $NO_x$ emissions with biodiesel is mainly caused by the advancement of injection timing, which has also been described by other researchers (Lapuerta et al., 2008a; Xiaoming et al., 2005; W. Yuan et al., 2007). Injection timing advance generally lengthens the ignition delay; this permits additional time for premixing the fuel and air, which normally increases the premix portion of diesel combustion that increases the reaction temperature. Finally, it reaches an elevated diffusion reaction temperature to post-flame gas temperature. An increase in post-flame gas temperature enhances the $NO_x$ formation rate. An advance of injection timing also typically progresses the onset of combustion, which can increase the reaction time and generally increase the overall gas temperatures (J. Sun et al., 2010; J.P. Szybist et al., 2005; James P. Szybist et al., 2007).

**Table 2.4**

Effect of advance injection timing of biodiesel fuel compared to diesel fuel on $NO_x$ emission

| Engine Specification | Fuel | Advance SOI timing | NOx emission compared to diesel combustion | Reference |
|---|---|---|---|---|
| A John Deere DE | Vegetable derived B100, B20 | B100 (2.3°CA)<br>B20 (0.25°) 0.75°CA | ↑ | (Monyem et al., 2001) |
| A John Deere 4276T, Cyl: 4, 4S, TC, DI, DE | Soybean biodiesel B100, B20 | B100 (2.28° CA)<br>B20 (0.4-0.6°) CA | B100 (10-24.5%)↑<br>B20 (0.62-16.6%)↑ | (Canakci, 2007) |
| Yanmar L70 EE, AC, 4S, Cyl: 1, DI, DE | soy-derived biodiesel | 1.1°CA | ↑ 6-9% | (J.P. Szybist, Kirby, et al., 2005) |
| Lombardini 6 LD 400, Cyl:1, IOP: 20 MPa, SOI timing: 20 (deg CA BTDC), CR: 18:1 | (COME+ Diesel) | 5°CA | B5 ↑3.03%, B20 ↑8.6%, B50 ↑9.14,B100 ↑ 12.92 | (C. Sayin, Gumus, & Canakci, 2010b) |

Note: AC= Air Cooled, NS= Number of stroke, Cyl. = number of cylinder, CA= crank angle, TC= turbocharged.

## 2.6. $NO_x$ Mitigation Technologies

Logically $NO_x$ mitigation technologies are classified by three major categories: (1) pre-combustion (treating the fuel and applying some techniques), (2) during combustion (minimizing the formation of $NO_x$ at the source), and (3) post-combustion (removing $NO_x$ by some means before expelling them into the atmosphere) (Ayoub et al., 2011). Based on modification, Hoekman et al. (S. Kent Hoekman & Curtis Robbins, 2012) classified the $NO_x$ reduction technology as (1) fuel modification and (2) engine modification. However, pre-combustion and during combustion techniques greatly impact on the engine combustion characteristics, while post-combustion technique has no effect. Here, based on duration of application, $NO_x$ mitigation technology can be classified into two types: pre-combustion and post-combustion as shown in **Figure 2.2**.

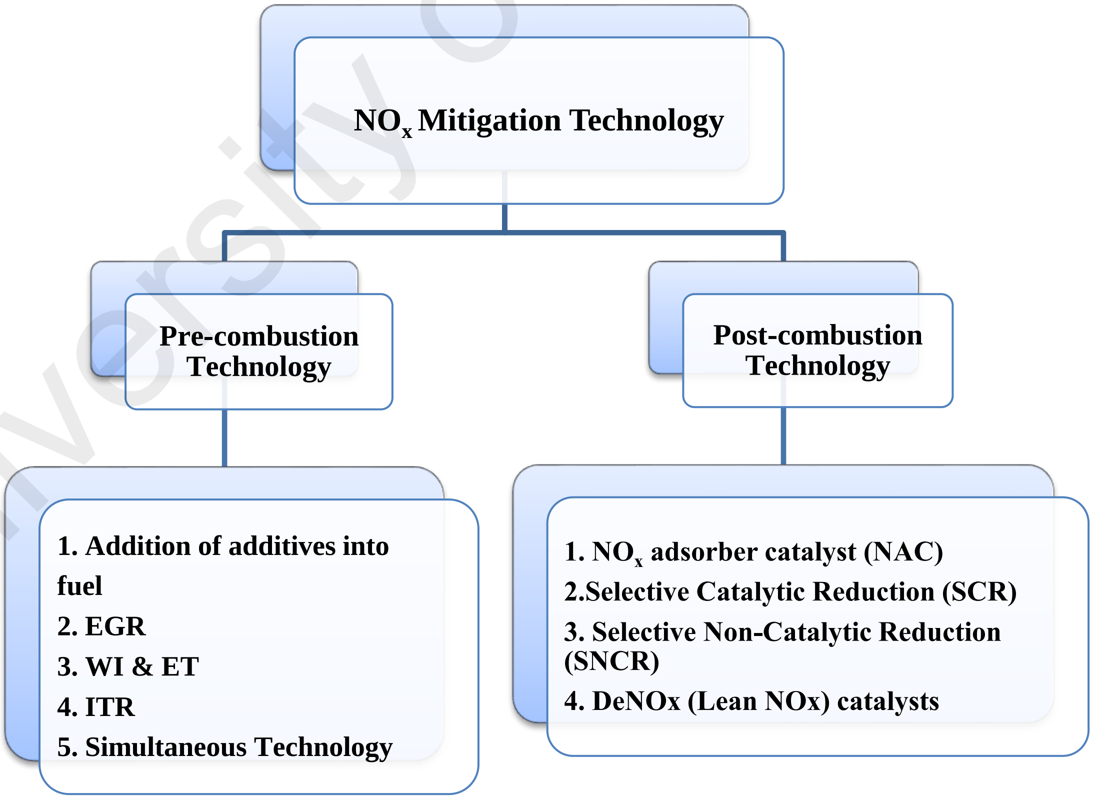


**Figure 2.2:** Classification of $NO_x$ mitigation technology

### 2.6.1. Pre-combustion techniques

#### 2.6.1.1. Use of different additives

Researchers have used different types of additives with biodiesel, such as metal-based additives, oxygenated additives, depressants and wax dispersants, lubricity, stability and ignition promoters, antioxidants, cetane number improvers and so on according to requirements (Ribeiro et al., 2007; K. Varatharajan & Cheralathan, 2012a). Among these, antioxidants (Kalam & Masjuki, 2008; Ryu, 2010), cetane number improvers (H. Kim & B. Choi, 2010; Xing-cai et al., 2004), metal based additives (Guru et al., 2010; Keskin et al., 2008) and oxygenated additives (dimethyl ether, ethanol, methanol) (Bhale et al., 2009; Cheung et al., 2009; Kwanchareon et al., 2007) were used to reduce the $NO_x$ emissions. The properties of some antioxidant and oxygenated additives are shown in **Table 2.5**. The rate of $NO_x$ formation can be determined by the formation rate of free radicals during combustion. Reduction of free radicals in turn reduces prompt $NO_x$ formation. Generally, antioxidants delay or inhibit oxidative processes by donating an electron or hydrogen atom to a radical derivative. The formation of free radical can be reduced by using antioxidants in four ways: chelating the transition metal catalysts, chain breaking reactions, reducing the concentration of reactive radicals and scavenging the initiating radicals (K. Varatharajan, 2012). Kalam and Masjuki (2008) carried out an experiment on a palm biodiesel-fueled engine using antioxidant 4-Nonyl phenoxy acetic acid (NPAA) additives and reported reduced $NO_x$ emissions as a result of reducing the combustion temperature because of the decreasing higher oxidation level and density, as well as viscosity, compared to the biodiesel without additives. The cetane number measures the readiness of the fuel to auto ignite when injected into the engine and is one of the most significant properties in specifying the ignition quality of any fuel in CI engines (Ribeiro et al., 2007). This cetane number also impacts on $NO_x$ and PM emissions from diesel engines fueled with biodiesel and its blends (Robert L. McCormick et al., 2001). Hess et al. (2005) studied the impacts of EHN as an additive to 20% biodiesel and concluded that it increases the cetane number of the fuel which leads to a shorter ignition time and thus decreases $NO_x$ emissions. Manganese, iron, copper, barium, cerium, calcium and platinum-based additives are also used normally to reduce $NO_x$ emissions (G. R. Kannan et al., 2011; Keskin et al., 2010; Keskin et al., 2007). Metal-based additives improve the oxidation of hydrocarbons by catalyzing the combustion, which in turn reduces emissions (G. R. Kannan et al., 2011; Nam, 2007). Oxygenated additives reduce $NO_x$ emissions by reducing the combustion temperature because of their lower calorific value (shown in **Table 2.5**) and higher latent heat of vaporization (Bhale et al., 2009; Cheung et al., 2009).

The drawbacks of using this technology are:

- Additives are not effective enough to reduce $NO_x$ emissions; they are expensive and produce higher CO, HC and PM emissions as well.
- It can promote autoxidation in biodiesel which greatly hampers on the combustion chamber.

**Table 2.5**
Properties of some antioxidant and oxygenated additives
(H. Aydin & IlkIlIē, 2010; Kalam & Masjuki, 2008; HH Masjuki et al., 2006; Rakopoulos, 2012; Randazzo & Sodré, 2011; K. Varatharajan, 2012; K. Varatharajan & Cheralathan, 2012a)

| **Properties**<br>**Additives** | **Densit-y (kg/m$^3$)** | **Melting point (K)** | **C.V. (MJ/ kg)** | **Flash point (K)** | **CAS number** | **Molecular Formula** | **M.W.** |
|---|---|---|---|---|---|---|---|
| NPAA | 1030 | 273 | - | 403 | 3115-49-9 | $C_{17}H_{26}O_3$ | 278.39 |
| DPPD | 1200 | 416-418 | - | 493-498 | 74-31-7 | $C_{18}H_{16}N_2$ | 260.33 |
| ODA | 980[b] | - | - | 458 | - | $C_{20}H_{27}N$ | 281.44 |
| NPPD | - | 342-348 | | - | 101-54-2 | $C_{12}H_{12}N_2$ | 184.24 |
| PPD | - | 414 | - | - | 106-50-3 | $C_6H_4(NH_2)_2$ | 108.14 |
| α-Tocopherol acetate | 960[b] | 245 | - | 383 | 7695-91-2 | $C_{31}H_{52}O_3$ | 472.75 |
| BHT | - | 343 | - | - | 128-37-0 | $C_{15}H_{24}O$ | 220.34 |
| L- ascorbic acid Vit C) | 1650 | 465 | - | - | 50-81-7 | $C_6H_8O_6$ | 176.13 |
| EDA | - | 414 | - | - | 107-15-3 | $C_2H_8N_2$ | 108.14 |
| DEE | 713[b] | - | 33.9 | - | | $C_4H_{10}O$ | 74.12 |
| Ethanol | 790[b] | - | 27.0 | 287 | - | $C_2H_6O$ | 46.06844 |

[a] At 313 K, [b] At 293K

### 2.6.1.2. Exhaust gas recirculation (EGR)

So far, EGR has been the most frequently mentioned $NO_x$ mitigation technology for diesel engines fueled with both diesel and biodiesel (Choi et al., 2011; Gomaa et al., 2011; Kiplimo et al., 2012; Kumaraswamy & Prasad, 2012; Labecki & Ganippa, 2012). Diesel engines are lean burn systems when overall air–fuel ratios are considered. However, in a microscopic sense, diffusion controlled diesel combustion is predominately a stoichiometric burn. The flames are prone to localize at stoichiometric regions within the overall fuel lean but with a heterogeneous mixture. Considering this phenomenon, it would be more effective to increase the specific heat capacity of the working fluid in order to produce a low flame temperature. Introducing $CO_2$ by recycling a fraction of exhaust gas into the engine is the most effective way to increase the specific heat capacity of the working fluid. At the same time, the EGR dilutes the $O_2$ concentration of the working fluid. Thus, formation of $NO_x$ can be reduced drastically (Ming Zheng et al., 2004), which is the main application of EGR technology. The other two suggested mechanisms are dilution (due to increased non-combustible mass), and chemical (due to increased molecular complexity leading to increased dissociation during reaction) (Ladommatos et al., 2000; H. Song et al., 2012). The accomplishment of EGR is straight forward for naturally aspirated engines because the exhaust tailpipe back pressure is generally higher compared to the intake pressure. A flow passage is established between the exhaust and the intake manifolds and is regulated by a throttling valve, as shown in **Figure 2.3**. The pressure differences are normally sufficient to drive the EGR flow of a desired amount, except during idling while a partial throttling in the tailpipe itself can be activated to achieve the desired differential pressure. If the exhaust gas is recycled to the intake manifold directly, the operation is called hot EGR. If an EGR cooler is applied to cool the recycled exhaust gas to the required temperature before entering into intake manifold, it is called cooled EGR (D. S. Kim & Lee, 2006). The $NO_x$ emissions reduced the chronological trends by raising the EGR rate (Jiménez-Espadafor et al., 2012; Donghui Qi et al., 2011). The expected EGR can be calculated as in Equation (1) which has been used by several researchers (D. Agarwal et al., 2006; Pradeep & Sharma, 2007; Saleh, 2009).

$$EGR(\%mass) = \frac{\dot{m}_{EGR}}{\dot{m}_{EGR} + \dot{m}_{AIR}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Here, $EGR(\%mass)$ is the mass percent of the recirculated exhaust gas ($\dot{m}_{EGR}$) in total intake mixture and $\dot{m}_{AIR}$ is the mass of intake air in total intake mixture.

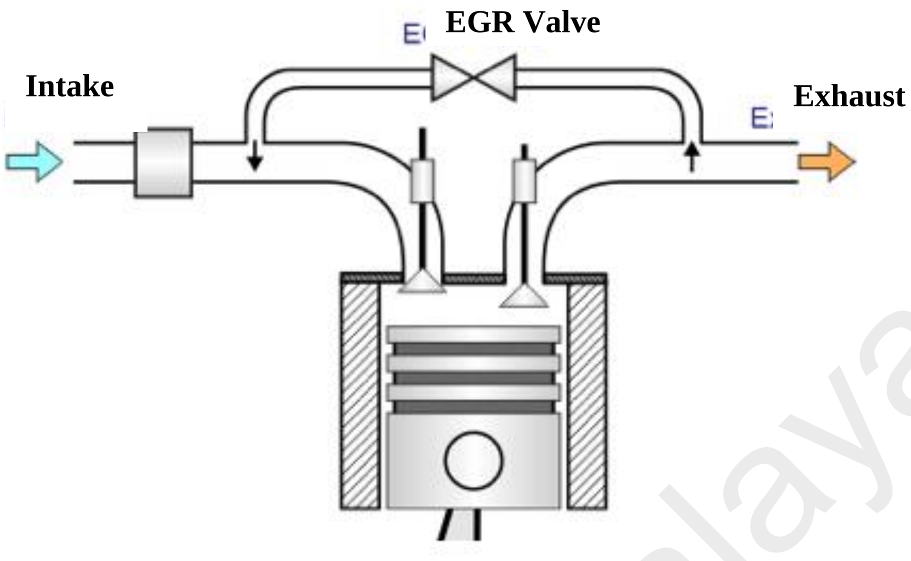


**Figure 2.3:** EGR technology

The disadvantages of using EGR as $NO_x$ mitigation technology are given below:

- Though EGR technology drastically reduces $NO_x$ emissions by about 30-60% by increasing the heat capacity of the working fluid, but it increases PM emission at high- temperature diesel combustion (Tauzia et al., 2010; Tesfa et al., 2012).
- At medium and high load conditions, EGR technology needs to enhance the boost pressure to manage the suitable air-fuel ratio (Alain Maiboom & Tauzia, 2011; Ming Zheng et al., 2009).
- At the high load condition, EGR could not reduce the $NO_x$ emissions, largely because of failing to reduce the air flow rate without hugely increasing the PM emission (Tauzia et al., 2010).
- In most cases, this technology increases the fuel consumption and smoke emission as the thermal efficiency is decreased if not perfectly optimized.
- In a cooled EGR system, there are some disadvantage viz. corrosion of the gas cooler, the cooling capacity at the higher load, it is expensive, it is difficult to

maintain and has extra weight, and so forth. On the other hand, a hot EGR is a low-cost technique effectively used to meet the standard level of $NO_x$ (Pradeep & Sharma, 2007).

### 2.6.1.3. Water injection (WI)

Water injection into the combustion chamber, directly or through the intake manifold, is another important strategy to control the $NO_x$ emissions from a CI engine. One important advantage using WI as an $NO_x$ mitigation technology is the enhanced possibility of reducing the $NO_x$ over the entire engine load range with a lesser negative effect on the PM emission (Tauzia et al., 2010). Although water is inert in the combustion environment, it promotes decreased local adiabatic flame temperature by absorbing its heat of evaporation (Park et al., 2000). Hence the $NO_x$ emissions that mostly depend on the peak flame temperature are decreased. WI can be achieved in two ways: Inlet water injection (IWI) or water fumigation and direct water injection (DWI) into the combustion chamber (Bedford et al., 2000; Tauzia et al., 2010). Fumigation is the technique of injecting liquid water into the intake manifold upstream of the intake valve. This technique is broadly used in large marine diesel engines (Tesfa et al., 2012). This is probably the easiest way to supply water to the engine. Various ways are described in the literature to achieve this. These approaches are multi-point WI into the air in the intake manifold close to the inlet valve (Brusca & Lanzafame, 2001; B. Kegl & Pehan, 2001), mono-point WI before the turbocharger (B. Kegl & Pehan, 2001) and mono-point water injection after the turbocharger (B. Kegl & Pehan, 2001; Tesfa et al., 2012). The advantages of the IWI are versatile; uniform on-line variation of water quantity, increase in volumetric efficiency due to the cooling effect, nearly or homogeneous water distribution in the combustion chamber, and so on (Şahin et al., 2012). In DWI technology, the water is supplied directly into the combustion chamber by applying a separate injector (Chadwell & Dingle, 2008; D. Hountalas et al., 2007; D. T. Hountalas et al., 2006; Psota et al., 1997) or with a separate injection system (Nishijima et al., 2002; Tanner et al., 2001). Chadwell and Dingle (2008) worked under the Southwest Research Institute and Delphi Diesel Systems respectively. They developed a real time WI system to apply in heavy-duty diesel engines. This system was integrated with ECU for precise metering of the water charge and for an instant response. ECU controls both the unit injector and the water metering system which enable it to inject fuel-only, or a fuel/water mixture in any proportion up to the limit of the system. The advantages of DWI technology over fumigation and emulsion techniques are having the capacity to reach water close to the flame rather than the cylinder wall and allowing changes to the fuel-water percentage for cold starts and different operating ranges (Bedford et al., 2000; Raheman & Ghadge, 2007).

The disadvantages of using WI as a $NO_x$ mitigation technology are given below:

- Though WI decreases the $NO_x$ and PM emissions due to the increased heat losses of the cylinder wall, it greatly hampers the engine's global efficiency (Kass et al., 2009; Tauzia et al., 2010).
- To gain 50% $NO_x$ mitigation by IWI technology, it needs water mass of about 60–65% of the fuel (Alain Maiboom & Tauzia, 2011; Tauzia et al., 2010). In addition, due to the excessive weight of the added water storage tank of the engine, it is quite difficult to maintain engine balance.
- The reduction rate of $NO_x$ for direct WI is approximately double that of the inlet manifold WI but its implementation complexity of increases engine costs (Tauzia et al., 2010).

- At low load and low combustion temperature engine mode, WI technology can reduce the PM drastically with the increase in the rate of WI, but it significantly increases the CO and HC emissions as well as BSFC.

#### 2.6.1.4. Emulsion technology (ET)

Fuel emulsification is another technique used to introduce water into the combustion chamber. This can be used to enhance the fuel combustion efficiency and to reduce the emission of $NO_x$, PM, smoke, and other pollutants (Lif & Holmberg, 2006; C.-Y. Lin & Wang, 2003). An emulsion is defined as two immiscible liquids wherein droplets of one phase (the dispersed or internal phase) are encapsulated within sheets of another phase (the continuous or external phase) (Chen & Tao, 2005). Although oil and water are inherently immiscible with each other, they can be emulsified by mechanical, electronic, magnetic, or ultrasonic forces with the help of a suitable surfactant to produce a dispersed phase uniformly distributed in another continuous phase (C.-Y. Lin & Chen, 2006; C.-Y. Lin & Wang, 2003). The emulsifying agent or surfactant may be any surface-active substance which can form a thin interfacial film between the two liquids and maintain the emulsion by minimizing the contact, coalescence and aggregation of the internal dispersed phase (Chen & Tao, 2005; Friberg et al., 1995; Moilanen et al., 2009). They reduce the surface tension between oil and water, and maximize their superficial contacting area. Kizling and Kronberg (1990) pointed out that emulsion stability depends on the structure of the surfactant. Emulsions can be conveniently divided in to two types: two phase emulsion and three-phase emulsion. Two-phase emulsions are mainly of two types, that is water-in-Oil (W/O) emulsions and oil-in-water (O/W) emulsions. Among these, W/O emulsion uses oil as the continuous phase and water for the dispersed phase. On other hand, in O/W emulsion, water is used as the continuous phase and oil for the dispersed phase. In W/O emulsions, asphaltene, resins and paraffin waxes act as natural emulsifying agents stabilizing the W/O mixture (Zaki et al., 2000). The three-phase emulsions can be divided conveniently into two types: oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) emulsions (Mataumoto & Kang, 1989). The O/W/O emulsion uses oil as the element for both the continuous phase and the inner phase, and water for the dispersed phase.

Although water-in-diesel emulsion has been studied extensively for many years (Armas et al., 2005; D. Hountalas et al., 2007), many researchers are now testing three phase emulsions using biodiesel (C.-Y. Lin & H.-A. Lin, 2007; C.Y. Lin & S.A. Lin, 2007; Manjula et al., 2011). There are three commonly used techniques for preparing three-phase emulsions: phase inversion, mechanical agitation, and two-stage emulsification (C.-Y. Lin & Wang, 2003). The last technique, two-stage emulsification is the most frequently used method. During the preparation stage, a hydrophilic surfactant is added into the water in the first O/W/O emulsion. After that oil is added into the water-surfactant mixture. A homogenizing machine is used to stir the mixture in order to form a two-phase oil-in-water emulsion (denoted as O/W) type. The O/W emulsion is then added into an oil and lipophilic surfactant mixture, which is again stirred by a homogenizing machine so that an O/W/O three-phase emulsion is produced. Lin and Wang (2003) used a mechanical homogenizing machine to prepare three-phase O/W/O diesel emulsions.

In general, the addition of water results in a decrease in temperature inside the combustion chamber due to evaporation, dissociation of water during combustion and an increase in local specific heat capacity (D. Hountalas et al., 2007). The theoretical aspect behind this in the case of a fuel emulsion is micro-explosion phenomena (United States Environmental

Protection Agency, December 2002). Micro-explosions (also called "secondary evaporation") accelerate the evaporation of fuel droplets in emulsions and are strong enough to eject fragments of droplets several millimeters away from the limits of the spray jet at high speeds, which can help to improve the air-fuel mixing mechanism. Furthermore, due to the presence of water more momentum is added to the fuel jet that improves the air entrainment rate per unit mass of fuel. Water in the biodiesel emulsion increases the kinematic viscosity and reduces the heating value of the fuel (C.-Y. Lin & Lin, 2008a). This in turn enhances the concentration of hydroxyl radicals and reduces the combustion temperature. Thermal $NO_x$ formation is controlled by the reduced combustion temperature (Fernando et al., 2006b; J. F. Sun et al., 2010) as introduced water particles convert into steam by taking up some heat from the combustion chamber as latent heat of vaporization during the compression stroke (Badrana et al., 2011). On the other, hand hydroxyl radicals do not combine effectively with nitrogen molecules to form NO which is also a cause of reducing $NO_x$ emissions (K. Kannan & Udayakumar, 2009; Kass et al., 2009). Biodiesel emulsions also reduce PM soot fractions compared to B100 and diesel fuels (Kass et al., 2009).

The demerits of using this technology are as below:

- In the low load condition, this technology reduces PM emission but sometimes PM increases in the high load condition (Alain Maiboom & Tauzia, 2011).
- This technology is inherently unstable and prone to phase separation, which may damage the engine components and increase the corrosive properties of the metal surfaces (Rajasekar et al., 2010).
- Redesigning the high accuracy controlling fuel supply system and using additional components may increase the engine operating costs.

- The higher viscosity and density of water emulsified fuel can significantly affect on the performance of the fuel injection system (Tesfa et al., 2012).
- Lower temperatures too early in the combustion due to emulsification may lead to increased ignition delay and engine noise (Bedford et al., 2000).
- The percentage of water in the emulsion is constant and cannot be changed for cold starts or other transient operating conditions (Bedford et al., 2000).

#### 2.6.1.5. Injection timing retardation (ITR)

Generally, there are two types of fuel injection system for a diesel engine: mechanical and electronic. A mechanical injection system include single plunger (measuring the correct amount of fuel and determining the timing of each injection) high-pressure fuel pump which is operated by the engine crankshaft. An electronic injection system supplies fuel constantly at high pressure with a common rail to each injector having a solenoid operated by ECU. Both mechanical and electronic injection systems can be used in either direct or indirect injection forms. The injection timing can be retarded or advanced from the original setting. Tuan Nghia et al. (2012) used a common rail fuel system with open ECU by using INCA software to vary the injection timing. INCA is software published by the ETAS group which enables engineers to adapt the behavior of the control and diagnostic functions to a variety of vehicle models without requiring the calculation routines to be modified. Ganapathy et al. (2011) applied the spill method to vary the injection timing in a CI engine fueled with Jatropha biodiesel. An adaptive needle is used to determine the spill. A circular protractor with a resolution of 0.5° was placed on the front side of the engine to mark the crank angle degree. The fuel injection pump was fitted with a number of shims or leaves to advance and retard the injection timing. Shims with 0.3 mm thickness were added to retard the injection timing and a shim of 0.295 mm thickness was removed from the original setting toadvance the injection timing. The combustion process is retarded due to the retardation of the injection timing. The concentration level of thermal $NO_x$ mainly depends on the combustion peak temperature; the $NO_x$ level will be lowered when the peak temperature remains low. In general, retarding injection timing reduces $NO_x$ emissions from the diesel engine because it decreases the combustion temperature as well as the residence time of the high-temperature-burned gas inside the cylinder (Dec, 1997). On the other hand, advanced injection timing, an earlier crank angle achieves high pressure and, hence, higher combustion temperature results in high $NO_x$ emissions.

The disadvantages of using ITR as a $NO_x$ mitigation technology are presented below:

- The retardation of injection timing technology reduces the high rate of $NO_x$ emissions, but, on other hand, it decreases the BTE and increases smoke emission.
- Applying ITR technology tends to increase PM emission.
- This technology contributes to increased fuel consumption, reduced power, increased HC and increased smoke emission (Pradeep & Sharma, 2007).

### 2.6.1.6. Simultaneous technology (ST)

The emission levels of $NO_x$ from a biodiesel-fueled CI diesel engine can be reduced moderately by using ST. Several STs have been applied to biodiesel-fueled engines to achieve optimum results, such as emulsion with EGR (Kass et al., 2009), additives with EGR (Pandian et al., 2010; Swaminathan & Sarangan, 2012; Venkateswarlu et al., 2012), EGR with ITR (Labecki & Ganippa, 2012; Donghui Qi et al., 2011).

#### 2.6.1.7. Low-temperature combustion (LTC)

In recent years, several investigators (Q. Fang et al., 2013; H. Zhu et al., 2012) have undertaken in-depth investigations into a type of combustion process known as LTC. It is a promising new technique which covers a number of advanced combustion strategies, including HCCI and PCCI. The use of these combustion modes in diesel engines over the next few decades will be absolutely vital to meet ever increasing governmental emissions regulations (Breen, 2013). In HCCI or PCCI advanced combustion strategies, the entire fuel and air charge is premixed prior to the start of combustion. The use of high EGR rates (up to 50%), high injection pressures, multiple fuel injection pulses per cycle, and late main injection even after TDC are generally applied to achieve the LTC mode of combustion (S. Kent Hoekman & Curtis Robbins, 2012). **Figure 2.4** is a flow diagram showing the high temperature combustion and LTC strategies in a diesel engine. In the LTC mode, combustion is controlled to occur in pre-defined relative air-fuel ratio and temperature zones that limit the formation of $NO_x$, PM, and soot emissions simultaneously (Soloiu et al., 2013). However, higher HC and CO exhaust emissions are the main disadvantages of the LTC mode of combustion.

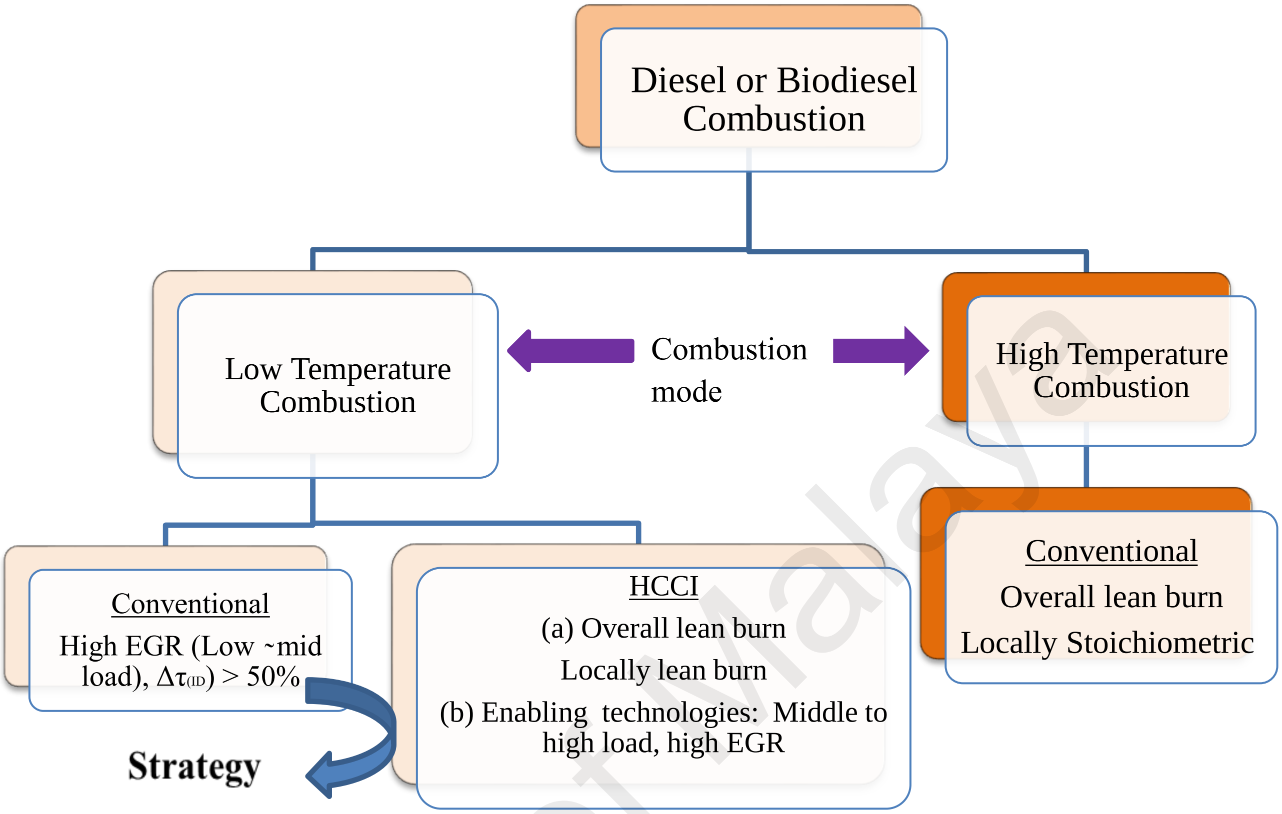


**Figure 2.4:** Generalized description of HTC and LTC strategies (adapted from (M. Zheng et al., 2008))

### 2.6.2. Post-combustion techniques

There are some important after-treatment approaches to reduce $NO_x$ emissions from diesel engines, such as $NO_x$ adsorber catalysts (NACs), selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) and $DeNO_x$ (Lean $NO_x$) catalysts. Among them SCR and SNCR are the most common post-combustion techniques.

#### 2.6.2.1. Selective catalytic reduction technique

SCR has been widely applied to stationary source, fossil fuel-fired, combustion units for emission control since the early 1970s (E.H. Pechan & Associates, 2006). The EAT as an

SCR is generally used when higher $NO_x$ reduction is required. SCR technology leads to a considerable reduction in particle formation and also fuel consumption by optimizing the engine conditions (López et al., 2009). However, the biodiesel combustion produces large amounts of $NO_x$ which can be eliminated by treating the exhaust gases (selective catalytic converter). A continuous supply of a urea solution is needed as a reducing agent to apply this technology. In the SCR catalytic converter, the $NO_x$ is converted into water and nitrogen by the presence of ammonia. $NH_3$ is obtained from the urea (AdBlue) by hydrolysis at high temperature. Using the SCR technique in a biodiesel combustion diesel engine is one of the solutions to meet the Tier 4 Final Emissions Regulations reported by McWilliam and Zimmermann (McWilliam & Zimmermann, 2010). They used a vanadium-based SCR system in an HD Caterpillar engine fueled with 20% and 100% biodiesel and observed a high reduction of $NO_x$ over the testing in a non-road transient cycle. However, the $NO_x$ conversion efficiency of the SCR system was reduced by 6% when operating on 100% biodiesel. A slight ammonia excess is helpful in maximizing the $NO_x$ reduction in the SCR catalyst, but this results in "ammonia slip" emissions. An additional oxidation catalyst may be used to treat this ammonia slip (S. Kent Hoekman & Curtis Robbins, 2012).

#### 2.6.2.2. Selective non-catalytic reduction technique

SNCR is another EAT technique to reduce $NO_x$ emissions in flue gas conversion to $N_2$ and water vapor. This technique is carried out using a nitrogen based reducing reagent, such as ammonia or urea. The reagent can react with a number of flue gas components but this reaction is favored for a specific temperature range and in the presence of oxygen. Using ammonia as the reagent is more profitable than urea. Krahl et al. (2010) used amine compounds at relatively high concentrations (2–4%) in both conventional diesel and biodiesel fuels and found $NO_x$ emissions could be reduced by about up to 22% and 47%, respectively through an SNCR under certain conditions. However, challenges with respect to amine solubility and costs are likely to restrict commercial application of this SNCR approach.

### 2.7. Effect of $NO_x$ Mitigation Technologies on Engine Performance and Emissions

In the preceding section, the reductions of $NO_x$ emissions were observed by using different technologies. However, all technologies impact on overall engine performance and other emissions. Hence, the aim of this section is to discuss the effect of different $NO_x$ mitigation technologies on exhaust emissions as well as engine performance to select a suitable technology to optimize engine performance with lower emissions.

#### 2.7.1. Use of different additives in fuel

In reducing $NO_x$ emissions, additives also impact on other emissions and engine performance. Keskin et al. (2008) studied the effect of Mn-Ni, and Mg-Mo metal-based fuel additives on the exhaust emissions of TOME and found that CO, smoke and $NO_x$ were reduced significantly due to improved fuel properties, such as the flash point, pour point and viscosity. Varatharajan et al. (2011) investigated mitigation of $NO_x$ emissions using different antioxidant additives in Jatropha biodiesel and observed that p-phenylenediamine is the more effective additive than other antioxidant additives such as ethylenedia-mine, a-tocopherol, butylated hydroxytoluene and ascorbic acid. It could reduce $NO_x$ emissions by about 43.55% compared to neat biodiesel. Varatharajan et al. (2012a) used DPPD antioxidant additives in soybean biodiesel and found a significant reduction in $NO_x$

emissions but other emissions, such as smoke, CO and HC, were found to have increased. However, antioxidant additives did not affect the variation of BTE. The main cause of the reduction in $NO_x$ emissions from antioxidant fuel mixtures is suppressed peroxyl free radical formations by reaction with aromatic amines. The p-phenylenediamine reacts with peroxyl radicals to form primary amine radicals where peroxyl radicals further react with amine radicals, because of the high reactivity of amine radicals, and produce benzoquinonediimine as well as nitroxyl radicals. The products of these reactions efficiently trap the free radicals (K. Varatharajan & Cheralathan, 2012a). Some metal-based additives such as Mn, Ni, Mg, Mo and Co, to tall oil biodiesel also reduce the $NO_x$ emissions while slightly decreasing CO, smoke and BSFC (A. Keskin et al., 2010; Keskin et al., 2007; Keskin et al., 2008). In contrast, some metal-based additives produced by synthesiz-ing resin acid (abietic acid) with $MnO_2$ or MgO lead to increased $NO_x$ emissions observed by Keskin et al. (2011). Recently, Basha and Raja Gopal (2011) analyzed the effect of additives and catalysts on the combustion, performance and emission characteristics of a biodiesel-fueled engine. As found from their valuable investigation, additives can improve the combustion characteristics. Based on the summary in Table 2.6, the following conclusions can be drawn:

- Using antioxidant additives in biodiesel reduces $NO_x$ emissions by about 4.06-43.55% but mostly increases the CO and HC emissions except for 1% of ODA and NPAA in a palm biodiesel-fueled engine. However, they reduce the BTE slightly and increase smoke emission.
- BTE and BSFC are improved by the addition of DEE in biodiesel which reduces the emissions of $NO_x$, smoke and CO, but not HC, with increasing percentages of DEE.

- At high speed, a 2-20% ethanol additive into biodiesel (soybean and sunflower) reduces the $NO_x$ emissions by up to 8% but increases at low speed. However, it increases the emissions of HC and CO, and, due to the lower cetane number of ethanol, results in longer ignition delay leading to incomplete combustion.
- The levels of $NO_x$, HC, CO and smoke emissions are reduced with improved BTE by using $Co_3O_4$ and Al-Mg additives in Jatropha biodiesel.

**Table 2.6** Review of emissions and performance analysis using different additives as a $NO_x$ mitigation technology for biodiesel fuel

| **Base fuel** | **Additives** | **Engine condition** | **Results compared to base fuel (increase or decrease)%** | | | **Sources** |
|---|---|---|---|---|---|---|
| | | | **$NO_x$** | **Other emissions** | **Performance** | |
| **CSB100** | 20% DEE or 20% n-butanol | 1C, 4S | ↓ compared to both diesel & BD | HC↑, CO↓, smoke↓ | BSFC↓ little, BTE↑ little | (Rakopoulos, 2012) |
| **SB20 & SB100** | N,N′-diphenyl-1,4-phenylenediamine | Kirloskar-1C, 4S, DI, WC,CR:17.5:1 75% load | ↓9.35 for SB20 & ↓28.36 for SB100 | HC↑10.52, CO↑9.09, smoke↑ 12.5 for SB20 & HC↑16.92,CO↑14.8, smoke↑ 6.6 for SB100 | BTE↓1.38 for SB20 & BTE Same but ↓0.88 at Full Load for SB100 | (K. Varatharajan & Cheralathan, 2012a) |
| **SB20 & SB100** | N-phenyl-1,4-phenylenediamine | Kirloskar-1C,4S,DI, WC, CR:17.5:1, , 75% load | ↓4.06 for SB20 & ↓20.96 for SB100 | HC↑, CO↑, smoke↑ for both SB20 & SB100 | - | (K. Varatharajan & Cheralathan, 2012a) |
| **KB30** | E10 | A Kirloskar, speed=C 1C, WC, DI, DE | ↑little | HC↓, CO↓, $CO_2$ nominal, smoke↓ | BSFC↑, BTE↑ | (Pushparaj et al., 2012) |
| **PB20** | 2% distilled water | Kirloskar 1C, 4S, AC, | ↓7 | HC↓, CO↑, $CO_2$↓ | BSFC ↑, BTE↑ | (Vedaraman et al., 2011) |
| **WCB** | Metal based additives ferric chloride ($FeCl_3$) | 1C, WC, DI, CS: 1500 rpm, IT= 25.5° BTDC | ↓compered to diesel, ↑ slight compared to BD | HC↓26.6,CO↓52.6/$CO_2$↑little, smoke ↓6.9 | BSFC↓8.6 , BTE ↑6.3 compared to diesel | (G. R. Kannan et al., 2011) |
| **SB30** | BE1 (5% DEE + SB25) & BE2 (5% E+SB25) | 1C, 4S, DI engine DE Speed: 2000 r/min | ↓ for BE1 but ↑ for BE2 | HC↑, CO↓ slightly, smoke↓ both for BE1 & BE2 | BSFC↓ for BE1 | (DH Qi et al., 2011) |
| **SB20** | E2 & E5 | TC, 16 valve, 4C, 4000 rpm. | ↓ 6.6 for E2 & ↓8.4 for E5 | HC↑42, CO↑ for E2 & HC↑↑ , CO↑ for E5 | - | (Randazzo & Sodré, 2011) |
| **JB100** | antioxidant p-phenylenediamine | 1C, 4S, WC, DE | ↓43.55 | HC↑, CO↑ | BSFC↓ slight | (K. Varatharajan et al., 2011) |
| **JB100** | $Co_3O_4$ & Al-Mg additives | 1C, 4S, AC, DI, DE, full load and 75% load | ↓45 for $Co_3O_4$<br>↓30 for Al-Mg additives | HC↓60, CO↓50, smoke↓22.94 for $Co_3O_4$ & HC↓70, CO↓41, smoke↓16.8 for Al-Mg additives | BTE↑ for both additives | (Ganesh & Gowrishankar, 2011) |
| **TPB** | 20% DEE | 1C, 4S, NA, WC, DI, DE | ↓24.56 | HC↑74,CO↑15.5, smoke↓23 | BTE↑4.3 | (T. Kannan & Marappan, 2011) |
| **SFB20** | E20 | Rainbow–186, 1C, 4S, DI, CR: 18:1, DE, 2500 rpm | ↓at HS, ↑ at LS | CO↓, but ↑$CO_2$ | BSFC↓20.13, BTE↑22.2 | (H. Aydin & IlkIlIē, 2010) |
| **TOME60** | Co | 1C, DI, DE at full load | ↓for (T60-8Co) | CO↓ 53.37, smoke↓29.47 | BSFC↓ slightly | (A. Keskin et al., 2010) |
| **TOME60** | Mg and Mo | 1C, DI, DE at full load | ↓(Mg›Mo) | CO↓ 56.42, smoke ↓30.43 | BSFC↓ slightly | (Keskin et al., 2008) |
| **PB20** | (NPAA)= 1% of B20 | WC, 4S, IDI, 4C, CS = 2250 rpm, CL=50 Nm | ↓22.69 | HC↓14.7,CO↓ | BSFC ↓, BTE↑4 | (Kalam & Masjuki, 2008) |
| **TOME60** | Mn and Ni | Unmodified DI, DE | ↓ (Ni›Mn) | CO↓64.3, smoke ↓30.91 | BSFC↓ slightly | (Keskin et al., 2007) |
| **MB20** | 5, 10, 15 & 20% DEE | Kirloskar ,4S, stationary, DI, CS:1500 rpm | ↓ compared to diesel and base fuel with ↑% DEE | (CO & smoke)↓ compared to diesel but ↑ with ↑ % of DEE | BTE↓than diesel, ↑than biodiesel but ↓ with ↑ % DEE | (Mallikarjun et al., 2013) |
| **PB20** | 1% of ODA | IDI,4C, 50 Nm load | ↓22.69 | HC↓, CO↓ | BSFC↓19.86, BTE↑ | (HH Masjuki et al., 2006) |

Note: ↓= decrease, ↑= increase, ↑↑= increase more than 100%, E= Ethanol

### 2.7.2. Exhaust gas recirculation

As reported by many researchers (Gill et al., 2012; Labecki & Ganippa, 2012; H. Song et al., 2012), EGR is a highly potential $NO_x$ mitigation technology. Although using EGR in a CI engine is an effective technology to reduce the $NO_x$ emissions, it is not totally free from disadvantages. It significantly increases smoke, fuel consumption and reduces thermal efficiency unless it is suitably optimized (Pradeep & Sharma, 2007). Qi et al. (2011) found that the BSFC and soot emission were slightly increased and $NO_x$ emissions were reduced with increasing EGR percentages. Tsolakis et al. (2007) investigated the effect of EGR on engine performance and emissions for a diesel engine operated with rapeseed biodiesel (RB) and ULSD blend fuel. They found that the use of 20% EGR was more effective and achieved a reduction of $NO_x$ emissions of about 10% and 30% at 4.5 bar IMEP for B50 and B100, respectively, with 3° CA retarding the injection timing. However, at 6.1 bar IMEP $NO_x$ mitigation was about 20% for both B50 and B100 without significant effect on fuel consumption and engine efficiency. Using EGR technology on a biodiesel-fueled engine, the BSFC increases may be because of altering the air-fuel ratio, reducing the oxygen content, the dilution effect, and the falling burn rate, hence making achieving stable combustion more difficult and so on (Donghui Qi et al., 2011; Saleh, 2009). Furthermore, this technology has a detrimental effect on volumetric efficiency at the high engine load because of reducing the cylinder-trapped mass due to the increase in temperature of the mixture of EGR and fresh inlet air (S.H. Yoon et al., 2009). Prasad et al. (2009) investigated a single cylinder diesel engine fueled with Mahua biodiesel using $NO_x$ mitigation technology with cooled EGR and reported that 5% EGR with neat biodiesel is highly recommended compared to neat diesel. In most cases biodiesel-fueled engines, the use of EGR results in increased smoke, HC, CO and reduced $NO_x$ emissions compared to cases without EGR application (Tsolakis et al., 2007). Dissociation of $CO_2$ to CO at peak loads can also contribute to higher CO emissions. The variation in HC emission was not significant with increasing EGR levels in the biodiesel-fueled engine observed by Pradeep et al. (2007). This is probably due to the oxygen content in bio-diesel compensating for oxygen deficiency and facilitating complete combustion. PM or soot emission increases with the increasing EGR rate because of the lower oxygen concentration (Donghui Qi et al., 2011; Ming Zheng et al., 2004). However, Gill et al. (2012) introduced a filter in the EGR loop for both diesel and RB fueled engine, and found a reduction of PM or soot emission of about 50% relative to engine without the filter, which improved the $NO_x$/PM trade-off. Kass et al. (2009) also reported that although using EGR in a diesel engine increases PM with reduced $NO_x$, it is the preferred approach among engine manufacturers due to its lower cost, lower required volume and its simplicity compared to the others. In **Table 2.7**, the emissions and performance data shows a considerable spread as there are variations in the EGR condition, different feedstock sources, and engine operating conditions. The following conclusions are reached:

- A reduction in $NO_x$ and an increase in PM or soot emissions with increasing EGR rates are observed both for diesel and biodiesel combustion.
- EGR technology increases the BSFC in most cases for biodiesel and its blend fueled engine.
- At 10-20% EGR, it decreases the $NO_x$ emissions by up to 49% with reducing engine efficiency of about 0.6-9.16% when fueled with RB100, RB50 and KB40 compared to biodiesel combustion without EGR.
- For SFB20 and RBB20 at 15% EGR, the engine efficiency reduces slightly compared to diesel combustion with the same EGR.

- In neat and blends of rapeseed, sunflower, jatropha, karanja, rice bran and jojoba biodiesel at 10-20% EGR, the emissions of smoke, HC, CO are observed to raise but remain below and the acceptable stage compared to diesel combustion.
- At high EGR rates, more than 25%, $NO_x$ reduces to a great extent but increases other emissions on a large scale compared to biodiesel and diesel combustion without EGR

**Table 2.7**

Review of emissions and performance analysis using EGR as a NO$_x$ mitigation technology for biodiesel fuel.

| Engine used | Fuel used | EGR condition | Results of EGR effect (%) | | | Reference |
|---|---|---|---|---|---|---|
| | | | NO$_x$ | Other emissions | Performance | |
| Kirloskar ,4S, stationary, DI, constant speed | MB20 | 10, 20 & 30% EGR, various load | ↓ with ↑ EGR(%) | HC↓$^{b}$, CO↓$^{b}$ & smoke↓$^{b}$ with ↑ EGR(10-20%) but ↑ at 30% EGR rate | BTE↓$^{b}$, BTE↑ with ↑EGR(10-20%) but ↓ at 30% EGR rate | (Mallikarjun et al., 2013) |
| 1S, DI, DE | RB100 | 10 & 20% EGR, CS: 1500 rpm | ↑$^{b, c}$ slight, but ↓$^{a}$ with ↑ % of EGR | (HC, CO & soot)↓$^{b, c}$ but (HC, CO & soot)↑$^{a}$ with ↑% of EGR | Overall efficiency ↓ for all condition | (Gill et al., 2012) |
| Kirloskar, 1C, 4S, DI, DE | PKB100 | 4, 7, 12 & 14% EGR with cooler | ↓$^{a}$ with ↑ % of EGR | (HC, CO & soot)↑$^{a}$ with ↑% of EGR | Not significant change | (Sekhar et al., 2012) |
| Comet diesel engine, 2C, Vertical, WC | JB100 | 5, 10 & 15% EGR | ↓$^{b}$ & ↓$^{a}$ with ↑ % of EGR | (HC & CO)↓$^{b}$, (HC↓$^{a}$ & CO↑$^{a}$ with ↑%EGR | BSFC↑$^{b}$, BSFC↓$^{a}$ with ↑ (% of EGR & BP), BTE↑ slight | (Panda, 2012) |
| 4C, WC, TC, IDI, DE | JB20 | 10-20% EGR | ↓(36-46)$^{b}$ | CO↓25$^{b}$, CO$_2$↑(10-21)$^{b}$, smoke ↓$^{b}$ | BTE↑(1.3-6.8)$^{b}$, BSFC↑(2.1-7.6)$^{b}$ | (Gomaa et al., 2011) |
| Ford Lion 6C, 4S, DI,WC, DE | SB100 | 38,43, 49 and 54% of EGR | ↓ | soot↑ slight$^{a}$ | BSFC ↑$^{a}$ | (Donghui Qi et al., 2011) |
| 2C, DI, CI, DE | KB40 | 15% EGR | ↓25.75$^{a}$ | (HC↑17.5,CO↑11.11, smoke↑16.92)$^{a}$ | BTE↓ 9.16$^{a}$ | (Pandian et al., 2010) |
| Lister-Petter, AC, 1C, DI, DE | RB100 & RB50 | C1: 10%EGR,<br>C2: 20%EGR, | ↓30.17$^{a}$,↑47.9$^{c}$ for C1& RB100; ↓51.76$^{a}$, ↑15.5$^{c}$ for C2 & RB100; ↓27.6$^{a}$, ↑34.8$^{c}$ for C1 & RB50; ↓49.2$^{a}$, ↑6.9$^{c}$ for C2 & RB50 | (Smoke↑,CO↑,HC↑6.2)$^{a}$, (Smoke↓,CO↓,HC↓57)$^{c}$ for C1& RB100; (Smoke↑↑,CO↑,HC↑15)$^{a}$, (Smoke↓,CO↓,HC↓56)$^{c}$ for C2 & RB100;(smoke↑51.9,CO↑↑,HC↑4.2), (Smoke↓,CO↑,HC↑28)$^{c}$ for C1 & RB50; (Smoke↑↑, CO↑↑, HC↑7.9)$^{a}$, (Smoke↓,CO↓,HC↑27)$^{c}$ for C2 & RB50 | (BSFC↑, η near same)$^{a}$, (BSFC↑14.05,η↑0.86)$^{c}$ for C1& RB100; (BSFC↑, η↓1.9)$^{a}$, (BSFC↑ 12.28,η↑2.5)$^{c}$ for C2 & RB100; (BSFC↑, η↓ 0.6)$^{a}$, (BSFC↑6.5,η near same)$^{c}$ for C1 & RB50; (BSFC↑, η↓ 2.5)$^{a}$, (BSFC↑4.8, η↑2.1)$^{c}$ for C2 & RB50 | (Tsolakis et al., 2007) |
| 4C, 16 valve Mercedes | SB100 | 27% EGR, Load:68 Nm | ↓87.7$^{a}$ ↓83.85$^{c}$ | (CO↑↑, CO$_2$↑5.5, PM↑↑)$^{a}$, (CO↑96, CO$_2$↑9.5, PM↑↑)$^{c}$ | BSFC↑ 4.25$^{a}$, BSFC↑ 17.92$^{c}$ | (Kass et al., 2009) |
| 2C, vertical DI, WC, DE | SFB20 | 15% EGR rate | ↓25$^{c}$ | (HC↓5,CO↓10, smoke↑ little)$^{c}$ | BTE↓ little$^{c}$ | (Rajan & Senthilkumar, 2009) |
| 2C,4S, WC, DI diesel engine | JOB100 | EGR 12% at full load, 1600 rpm | ↓36$^{a}$ | (CO↑, HC↑)$^{a}$ | BSFC↑9$^{a}$ | (Saleh, 2009) |
| 1C, DI, 4S, WC, DE. | JB100 | Hot EGR 15% at full load. | ↓74.8$^{a}$, ↓37.84$^{b}$ | (smoke↑, CO↑, HC↑)$^{a}$, (smoke↓ little, CO same, HC same)$^{b}$ | BTE↓ slightly$^{a}$, BTE↓4.4$^{b}$ | (Pradeep & Sharma, 2007) |
| Indec PH2 DE, 2C, DI, AC | RBB20 | 15% EGR, 1500 rpm, | ↑10.6$^{c}$ at 40% load ,↑29$^{c}$ @ML | (smoke↓, CO↓, HC↓ at 40% load)$^{c}$, (smoke↓, CO↓,HC↓ at ML)$^{c}$ | (BSFC↑4.3,η↓at 40% load)$^{c}$, (BSFC↑ little, η near same at ML)$^{c}$ | (D. Agarwal et al., 2006) |
| Kirloskar engine 1C, DI | PB40 | Hot EGR (15%) | ↓ | | Performance↓ | (Kumar & Vijayaraj, 2005) |

Note: $^{a}$ results compared to biodiesel without EGR, $^{b}$ results compared to diesel without EGR condition, $^{c}$ Results compared to diesel with the same EGR condition, ↑↑= about more than 100%

### 2.7.3. Water injection

The majority of works on WI in the combustion chamber are related to diesel or other hydrocarbon fuels. However, little other research is available dealing with the combustion characteristics and emissions from biodiesel based fueled CI engines. Tesfa et al. (2012) carried out an experiment into the effect of WI on engine performance and emission characteristics of a 4-cylinder, 4-stroke, turbocharged direct injection CI engine fueled with RB. They found that the WI at 3 kg/h rate resulted in $NO_x$ mitigation by 50% without a significant drop in engine performance, with increased CO emission of about 40% compared to base-fuel combustion. They also found that WI through the intake manifold did not show any significant variations in peak flame temperature or heat release rate during combustion when testing conditions such as speed and load. However, it affected the pre-mixed combustion flame temperature at which high concentrations of nitrogen and oxygen react to form nitrogen oxides (M. Gumus, 2010). Tauzia et al. (2010) investigated the effects of WI on ignition delay, rate of heat release and emissions of an automotive direct injection diesel engine. They described that higher water flow rate contributes to longer ignition delay, higher peak heat release, and lower $NO_x$ emissions but higher the production of CO and HC emissions.

### 2.7.4. Emulsion technology

ET has been applied to reduce nitrogen oxide emissions and to promote the combustion efficiency of fossil fuels. Emulsions based on water-in-diesel have been studied irregularly over the past 30 years (R. Crookes et al., 1980; R. J. Crookes et al., 1997; K. A. Subramanian, 2011). These emulsified fuels are of interest since they can dramatically reduce $NO_x$ and PM simultaneously, with or without penalty to fuel economy. However, the mass of the added water has been shown to increase the momentum of the fuel jet, thereby allowing improved atomization and air entrainment, which subsequently leads to premixed combustion and lower PM formation (Musculus et al., 2002; Nazha et al., 2001; K. Song et al., 2000). Improved atomization may also occur via micro-explosions of water droplets during combustion (Sheng et al., 1995). Additionally, OH radicals may also be formed by the dissociation of water to further lower $NO_x$ and PM emissions (D. T. Hountalas et al., 2006). Although water–biodiesel emulsion reduces smoke and $NO_x$ emissions significantly, it decreases the volumetric energy content resulting in higher BSFC (Namasivayam et al., 2010). On the other hand, this technology increases HC and CO emissions with increasing water content in emulsified fuel (Şahin et al., 2012). The important probable reasons for less $NO_x$ emissions for biodiesel emulsion combustion are the higher cetane number and the lower residence time compared to diesel fuel (Manjula et al., 2011). Once again, the oxygen content of the fuel enhances the ignition quality, thereby reducing the delay period of biodiesel emulsion. This may be another reason for the low $NO_x$ in the case of biodiesel emulsion. Kannan and Gounder (2011) investigated the effect of Thevetia peruviana emulsified biodiesel on exhaust emissions in diesel engines. They concluded that 15% water emulsified fuel showed better performance and lower emissions than that of the other percentages of blends. Kannan and Gounder (T. Kannan & Marappan, 2011) also compared water-biodiesel emulsion and DEE additives to fuel for reducing $NO_x$ and concluded that water-biodiesel is more efficient than DEE blended biodiesel because of the better performance and higher reduction in exhaust emissions. Some researchers (Abu-Zaid, 2004; Alahmer et al., 2010) found increased engine power; others (Davis et al., 2012; Kass et al., 2009) observed a reduction in performance by using ET. Another point of view is that, during converting water into vapor in the combustion chamber, it absorbs energy which reduces the force acting on the piston resulting in decreased engine power. On the other hand, during the phase change from liquid to gas, the expanding water content results in high pressure steam increasing the force acting on the piston and results in increased engine power (Davis et al., 2012). The following conclusions are drawn from **Table 2.8**:

- ET can reduce $NO_x$ emissions by about up to 38% in various engine conditions. Compared to diesel combustion it reduces by up to 33.6%.
- In most cases, 10-20% $H_2O$ in biodiesel fuel ET shows the penalties for BSFC and engine efficiency. However, emulsified JB and TPB show better results with regard to performance.
- Emulsified biodiesel mostly increases CO and HC emissions but remains at the same or a lower level when compared to diesel combustion without emulsion.
- ET reduces smoke and PM emissions as well.

**Table 2.8**

Review of emissions and performance analysis using Emulsion Technology as a $NO_x$ mitigation technology for biodiesel fuel.

| Emulsion | Test condition | Results of exhaust emission increase or decrease (%) | | Engine Performance | Sources |
|---|---|---|---|---|---|
| | | $NO_x$ | Other emissions | | |
| 5.6% and 10% $H_2O$ with neat biodiesel | Low and medium load conditions | ↓9[b] | HC↑[a & b], CO↑[a & b], smoke↓90[b] | NA | (Wu et al., 2013) |
| B100 (83% TOME+17% COB) + 10% $H_2O$ | Rated engine speed (2800±50) and peak torque conditions | ↓[a] & ↓[b] slight @ rated speed, (same)[b] & ↓14.5[a] @ peak torque | NA | BSFC↓[b] & $\eta_t$ (same)[b] @ rated speed; BSFC (same)[a] ,BSFC↑[b] $\eta_t$↑[a & b] @ peak torque | (Hunt, Johnson, & Edgar, 2013) |
| B20 (83% TOME+17% COB)+ 10% H2O | Speed (rpm) = 2400, 2900, 3300 & 3600 | ↓10.5[a], ↓(14.9-19.9)[b] | NA | (BSFC↑15, $\eta_t$↓14.2)[a],(BSFC↑17.6, $\eta_t$↓11.4-27.9)[b] | (Davis et al., 2012) |
| WCB70+ D10E20 M micro-emulsion | CS= 1500 rpm | ↓[b] | ($CO_2$↓, CO↓, HC↓, smoke↓)[b] | (BSFC↑17.85, BTE not varies)[b] | (G. Kannan & Anand, 2011) |
| 10% SB+4v% water containing $C_2H_5OH$ + 1v% butanol + 85% diesel | Engine load =1.6 Kw, 3.2 Kw | ↓5.2[b] @1.6Kw, ↓5.9[b] @3.2 Kw | (CO↑11.4,PM↓18.5 @1.6Kw)[b],(CO↓4.3,PM↓23.7 @3.2Kw)[b] | BSFC↑(0-0.27)[b] | (Lee et al., 2011) |
| 83% JB+ 15% $H_2O$+ 2% surfactant | Full load | ↓22.9[a] | (CO↑ little, HC↑45.8, smoke↓14.9)[a] | (BTE↑2.4, BSFC↓2.7)[a] | (J. S. Basha & Ananda, 2011) |
| X= TPB (85%) + 15% $H_2O$<br>Y= TPB (80%) + 20% $H_2O$ | Full load | ↓(38 for X; 41 for Y)[a], ↓(31.7 for X;35 for Y)[b] | (HC↓1.94, smoke↓7.22 for X; HC↓3.05, smoke↓9.63 for Y)[a], (HC↓27.2, smoke same for X; HC↓37, smoke↓2.4 for Y)[b] | (BTE↑6.87 for X; BTE↓ 3.78 for Y)[a], (BTE↑3.76 for X; BTE↓7.6 for Y)[b] | (T. K. Kannan & Gounder, 2011) |
| COME(82.8%), $H_2O$(15%), 2% $C_2H_5OH$, and 0.2% surfactant | Injection pressure ↑(5-10)% | ↓5.7[b] | (CO↓44, HC↓41, smoke ↓42)[b] | - | (Y.-S. Lin & Lin, 2011) |
| SB(80ml)+C2H5OH(20ml)+ H2O(1/0.5ml)+ surfactant (4gm) | CS= 1500 rpm | ↓[a] | CO↑(LL & ML)[a], HC↑ (LL & ML)[a], smoke↓(HL)[a] | BSFC ↑[a] | (D. H. Qi et al., 2010) |
| (10 wt% H2O+3.5% surfactant+ 86.5% SB) | Load= 68 Nm | ↓21.8[a], ↑2.7[b] | (HC↑94.8, CO↑56, CO2↓ 6.16, PM↑16.56)[a], (HC↓ 29.5,CO↑34, CO2↓2.6, PM↓1.5)[b] | BSFC↓1.65[a], BSFC↑11.25[b] | (Kass et al., 2009) |
| 10% CH3OH + WCB | CS= 1800 rpm, variable load | ↓6.2[b] | ($CO_2$↓2.5, CO & HC remain nearly same)[b] | Efficiency ↑ at LL but ↓ at HL[b] | (Cheng et al., 2008) |
| SB (90%) +$H_2O$ (10%) + aqueous $NH_3$ (5%) | Speed varied 1000-2200 rpm | ↓[a] | ($CO_2$↑,CO↑,$CO_2$↓(without aqueous $NH_3$) with increasing speed)[a] | BSFC ↑[a] | (C.-Y. Lin & H.-A. Lin, 2007) |
| RB80+10% H2O+0.5% surfactant+10% algae | With and without load | ↓(22.3-34.2)[a], ↓(15.3-33.6)[b] | CO2 ↓(6.7-7.3)[a], CO↑ (19.5-32.8)[a]: $CO_2$ ↓(1.6-9.6)[b], CO↑↑[b] | SFC↑4.95[a], SFC↑35.89[b] | (Scragg et al., 2003) |
| 10% $H_2O$+PB90 | 39 kw rating, variable speed (1000-4000) rpm | ↓15.6[a] , ↓9.9[b] | (CO↓8.7,HC↓9.3,Smoke↓13.9)[a] , (CO↓3.8,HC↓22, Smoke↓66.6)[b] | Power ↓[a & b] | (H. Masjuki, Abdulmuin, & Sii, 1997) |

Note: [a] Results compared to biodiesel without emulsion, [b] Results compared to diesel without emulsion

### 2.7.5. Injection timing retardation

Injection timing plays a significant role in determining both engine performance and pollutant emissions (C. Sayin et al., 2010a). As pointed out by many scientists (Bari et al., 2004; Labecki & Ganippa, 2012), $NO_x$ emissions can also be controlled by retarding the injection timing. Buyukkaya and Cerit (2008) observed that by retarding the injection timing 18° and 16° crank angle BTDC from the original injection timing of the 20° BTDC reduced the value of BSFC and $NO_x$ emissions by about 2% and 11% respectively at equal speed and load conditions. The effects of advanced and retarded SOI on exhaust emissions fueled with $C_nB$ blends were investigated by Sayin et al. (2010a). The authors concluded that advanced SOI presented the best result for smoke and CO emissions due to complete combustion. On the other hand, retarded SOI showed the minimum results for $NO_x$ and $CO_2$ emissions for both B0 and B100. Jaichandar et al. (2012) used a single cylinder DI diesel engine fueled with 20% Pongamia biodiesel to observe the effect of ITR of about 2°CA BTDC, from original injection timing of 23°CA BTDC, on engine performance and emissions. They noted that this technique reduce the engine performance due to the lower calorific value of B20. However, it reduced $NO_x$ emissions due to the shorter ignition delay. Shorter ignition delay reduces the air-fuel mixing time, which leads to the slowing of the burning rate in turn slowly raising the combustion temperature. Moreover, other emissions, for example HC, smoke and CO, increased marginally because of the poor initial phase of combustion. ITR increases soot or PM emission because of the slowing soot oxidation rates (M. Y. Kim et al., 2008; Kweon et al., 2002). Wang et al. (2012) investigated $NO_x$ formation for diesel and biodiesel in a light-duty CI engine by using CFD and concluded that, ITR is an efficient technology in reducing $NO_x$ emissions as a result of retarded combustion phasing (lower temperature). Based on the summary of **Table 2.9**, the following conclusions are drawn:

- Using ITR technology in a biodiesel-fueled engine reduces the $NO_x$ emissions by up to 37% compared to the original IT.
- Implementation of ITR technology in biodiesel-fueled diesel engines mostly lowers the performance characteristics.
- ITR technology increases the CO, HC and smoke emissions in most biodiesel fueled engines except KB and MB compared to the original IT.

**Table 2.9**
Review of emissions and performance analysis using ITR as a NO$_x$ mitigation technology for biodiesel fuel.

| Engine Specification | Retard the SOI timing | Fuel | Comparison results of exhaust emissions using biodiesel (%) | Performance | | Source |
|---|---|---|---|---|---|---|
| | | | | BSFC | BTE | |
| Lister-Petter TR1 NA, AC, 1C, DI | 3°CA from ORG 22° CA BTDC, | RB100, RB50 | (NO$_x$↓17.3, CO↑9.3, HC↑5.5 for RB100)$^a$, (NO$_x$↓25.9, CO↑6.3, HC↑4.2 for RB50)$^a$; (NO$_x$ ↑27.7, CO↓37.9, HC ↓53.4 for RB100)$^c$, (NO$_x$ ↑5.67, CO↓17.2, HC ↓27.3 for RB50)$^c$ | Same$^a$<br>↑(7.4-16.7)$^c$ | | (Tsolakis et al., 2007) |
| Lombardini 6 LD 400 1C,DI | 5°CA from ORG 20°CA BTDC | RB5, RB20, RB50 & RB100 | (NO$_x$↓30.1, CO↑11.39, HC↑9.1 for RB5)$^a$, (NO$_x$↓28, CO↑21.08, HC↑33.3 for RB20)$^a$, (NO$_x$↓15.59, CO↑31.25, HC↑27.03 for RB50)$^a$ , (NO$_x$↓9.77, CO↑35.11, HC↑44.68 for RB100)$^a$ | ↑(14.07-16.59)$^a$ | | (C. Sayin et al., 2010a) |
| MAN D 2566 MUM, 4S,6C, WC | 4°CA from ORG 23°CA BTDC | RB100 | (NO$_x$↓25, CO↓25, HC ↓30)$^c$ | - | - | (B. Kegl, 2008) |
| John Deere 4276T TC, DI, DE | 3°CA from standard IT | Oxidized (SB) | (NO$_x$↓21.2, smoke↑ exceedingly)$^a$, (NO$_x$↓11.2, smoke↓24.1)$^c$ | | | (Monyem & Van Gerpen, 2001) |
| Diesel engine | Retard | KB | (NO$_x$↓, CO↓, HC↓)$^a$ | - | - | (Suryawanshi & Deshpande, 2005b) |
| 4S, 1C, DI, WC, CI, engine | 4°CA from ORG 23° CA BTDC | KB | (NO$_x$↓37.89, CO↓10.9, HC↓7.75, smoke↓14)$^a$, (NO$_x$↓25.31, CO↑7.5, HC↑3.65, smoke↑6.45)$^c$ | - | ↑2.64$^a$↓ 2.48$^c$ | (Banapurmath et al., 2009) |
| Small power DE | Retarded SOI | KB | NO$_x$↓8.2 | | | (Jindal, 2011) |
| 1C,4S,AC, vertical , Greaves Cotton GL 400 II A, DE | 5°CA from ORG 15°CA BTDC | JB | (NO$_x$↓24.79, CO same, HC↑47, smoke↑63)$^a$, (NO$_x$↑41.9, CO same , HC↓16.6, smoke↑1.8)$^b$, (NO$_x$↑39, CO↓31.25 , HC↓43.16, smoke↓25)$^c$ | ↑5.5$^a$<br>↑13.75$^b$<br>↑9.67$^c$ | ↓2.4$^a$<br>↓9.6$^b$<br>↓6.8$^c$ | (Ganapathy et al., 2011) |
| Kirloskar,4S,TV,1C, DI, WC, DE | 3°CA from ORG 23° CA BTDC | MB25 | (NO$_x$↓24.89, CO$_2$↑28.31, HC↓10, Smoke ↓26.70)$^a$ | ↓4.10 | - | (Solaimuthu et al., 2012) |
| | | MB50 | (NO$_x$↓23.73, CO$_2$↑26.80, HC↓8.11, Smoke ↓18.52)$^a$ | ↓3.79 | - | |
| | | MB75 | (NO$_x$↓24.74, CO$_2$↑27.53, HC↓8.33, Smoke ↓14.29)$^a$ | ↓3.41 | - | |
| | | MB100 | (NO$_x$↓24.89, CO$_2$↑21.92, HC↓3.26, Smoke ↓16.51)$^a$ | ↓2.92 | - | |
| 1C, 4S, DI,WC, DE | 3°CA from ORG 23° CA BTDC | JB20 | (NO$_x$ ↓36.84, UHC↑15.26, Smoke↑40.95)$^a$, (NO$_x$↓37.13, UHC same, Smoke↑51.25)$^b$, (NO$_x$↑2.3, UHC↓6.88, Smoke↓2.14)$^c$ | - | ↓4.1$^a$<br>↓2$^b$<br>↑1$^c$ | (Dhananjaya et al., 2009) |
| | | JB100 | (NO$_x$↓28.25, UHC↑19.17, Smoke↑38.3)$^a$, (NO$_x$↓21.19, UHC↑30.31, Smoke↑67.35)$^b$, (NO$_x$↑22.47, UHC↑19.17, Smoke↑8.27)$^c$ | - | ↓2.4$^a$<br>↓5.6$^b$<br>↓2.7$^c$ | |

Note: $^a$Results compared to biodiesel with original IT; $^b$Results compared to diesel with original IT, $^c$Results compared to diesel with retardation of IT.

### 2.7.6. Simultaneous technology

Some researchers have undertaken experimental work based on simultaneous $NO_x$ mitigation technology. As an example, Qi et al. (2011) investigated the combined effect of EGR and ITR technologies on the combustion and emission characteristics of a split injection strategy DI-diesel engine fueled with soybean biodiesel. After elaborate analysis, the authors concluded that a higher EGR rate with ITR is an effective technology to reduce $NO_x$ emissions without the penalties of soot emission and BSFC. In the experiment carried out by Saravanan et al. (2012) fueled with RBB, 10% EGR with 220–230 bar injection pressure showed the most effective result for the reduction of $NO_x$ emissions with small penalties for smoke density and BTE at no load and partial load while injection timing is a more influential factor at full load. The combined effect of 15% emulsified Thevetia peruviana biodiesel fuel and blends, along with 5-20% diethyl ether (DEE) showed better performance and less emissions in comparison to the biodiesel-water-emulsion system in the experiment carried out by Kannan et al. (2012). Based on the summary in **Table 2.10**, the following conclusions are reached:

- 2% DEE, and 10% DME and EHN additives in FOB, KB and JB with 15-20% EGR at no load, maximum load and 80% load respectively can reduce $NO_x$ emissions by up to 95%. However, this combined technology adversely impacts on other emissions.
- Applying ET and EGR together on an SB fueled engine reduces $NO_x$ emissions by about 50% but largely increases the PM emission.
- The engine performance deteriorates slightly by applying more than one $NO_x$ mitigation technology.

**Table 2.10**

Review of emissions and performance analysis using Simultaneous Technology as NO$_x$ mitigation technology for biodiesel fuel.

| Fuel | Condition of NO$_x$ mitigation technology | Percentage of results deviation | | Performance | Reference |
|---|---|---|---|---|---|
| | | NO$_x$ | Other emissions | | |
| FOB | 2% DEE (A)+15% EGR at no load condition | ↓75.5[a]<br>↓69.5[b] | (HC↓68.8, CO↓25,CO$_2$↓29)[a], (HC↓ 24, CO↓ 70, CO$_2$↓ 57)[b] | (BSFC↑, BTE not vary)[a,b] | (Swaminathan & Sarangan, 2012) |
| | 2% DEE (A)+15% EGR at maximum load condition | ↓94.8[a]<br>↓ 92.3[b] | (HC↓ 90.2, CO↓52, CO$_2$↓37.5)[a], (HC↓ 52, CO↓ 91, CO$_2$↓ 61.5)[b] | (BSFC↑, BTE nearly same)[a,b] | |
| KB40 | 10% DMC + 15% EGR at 80% load | ↓22.01[a] | (HC↑2.5,CO↑0.69, smoke↑1.54)[a] | (BSFC↑0.35, BTE↓1.43)[a] | (Pandian et al., 2010) |
| SB | (10 wt% H$_2$O+3.5% surfactant+ 86.5% SB) +27% EGR, 68 Nm load | ↓91[a]<br>↓88.2[b] | (HC↑↑, CO↑69.9, PM↑↑)[a]<br>(HC↑ little, CO↑44.96, PM↑↑)[b] | BSFC↑3[a],<br>BSFC↑16.5[b] | (Kass et al., 2009) |
| SB | Increasing the EGR rate from 38 to 43% + retardation of injection at 4° CA from original IT | ↓50[a] | (soot↓ slightly at LL)[a] | BSFC↑ max$^{m}$2[a] | (Donghui Qi et al., 2011) |
| JB | 20% EGR+ EHN (cetane improver) | ↓33[b] | (CO, HC, smoke)[b]↑ with ↑EGR% | (BTE↑ with ↑EGR%, BSFC↓)[b] | (Venkateswarlu et al., 2012) |

Note: A= additives, [a] results compared to biodiesel without NO$_x$ mitigation technology, [b] results compared to diesel without NO$_x$ mitigation technology

## 2.7.7. Low temperature combustion

Generally, applying the LTC mode of combustion reduces NO$_x$ and PM emissions simultaneously, without using EAT devices, while maintaining or improving engine performance both for neat diesel and biodiesel blend fueled diesel engines (Soloiu et al., 2013; Tompkins et al., 2012; Valentino et al., 2012; Yang et al., 2013; J. Zheng & Caton, 2012). However, it is not appropriate for all operating conditions and also produces higher CO and HC emissions in most situations compared to conventional combustion modes. Yet, it appears to be an attractive strategy since it reduces both NO$_x$ and PM emissions simultaneously, which can overcome the barrier of biodiesel supply in the market. It was also reported that the HC and CO emissions come from lean, over-mixed regions with low temperatures just as $NO_x$ and soot come from rich, non-homogeneous areas with high temperatures (Breen, 2013). With the LTC mode, ignition delay increases, thus increasing the premixed combustion phase and decreasing the diffusion flame combustion phase. The overall in-cylinder temperature is reduced substantially, thereby reducing $NO_x$ formation. At the same time, PM is reduced due to the dominance of lean, pre-mixed combustion. Soloiu et al.'s (2013) study used port fuel injection with n-butanol in a 100% peanut biodiesel-fueled engine to attain an LTC/PCCI mode at idling speeds and loads with 1-3 bar IMEP. They found reduced soot/PM and $NO_x$, of about 98% and 74% respectively, at 3 bar IMEP compared to diesel without LTC mode, by controlling the combustion phases and modifying the classical $NO_x$-soot trade-off. However, HC and CO emissions increased greatly due to incomplete combustion during the premixed burn phase. Other factors may explain the enhancement of HC and CO emissions, such as lack of intake manifold heating, crude manifold injection strategy consequently produced fuel pooling in the intake and allowing the passage of some butanol directly from the intake into the exhaust manifold. They suggested that heating the intake manifold and improvement in the manifold injection strategy correlated with the valve's timing may be applied to eliminate these problems. Moreover, Northrop et al. (2009) reported that partially combusted fuel escaping the pre-mixed burn process from over-lean pockets in the combustion chamber is the main cause for higher HC and CO emissions using the LTC mode. Using a high EGR rate as an LTC technology, it has been established that $NO_x$ emissions are reduced by reducing the combustion temperature due to the high heat and energy absorption capacity of the introduced diluted exhaust gas (Han, Ickes, Bohac, Huang, & Assanis, 2011). However, Karra et al. (2008) reported that PM emission increases at first with increasing EGR rate and then reduces at high levels of EGR rate. Furthermore, Northrop et al. (2011) reported that the condensation of unburned biodiesel leads to the production of large scale PM emission under both late and early injection of the LTC strategy, an important concern in neat biodiesel combustion using the LTC mode. Espadafor et al. (Jiménez-Espadafor et al., 2012) also tested a diesel engine fueled with Colza biodiesel and its blends, applying the LTC mode of combustion as HCCI gained by high swirl ratio, EGR as well as late injection. They found that $NO_x$ and PM emissions decrease with increasing EGR rates and biodiesel blends; however, increased HC and CO emissions resulted for all tested fuels. They reported that exhaust gas temperature reduces with increasing percentages of EGR resulting in a reduction in the oxidation rate for HC and CO. Fuel properties can also have an effect on the emissions from LTC engines. The worse biodiesel mixture formation characteristics are higher surface tension, lower volatility and narrow boiling range, which increase fuel wall impingement. This fuel is not completely oxidized and therefore appears as large scale CO and HC emissions. However, the addition of oxygenated ethanol with biodiesel blends was not shown fully to be a better way to solve the problem of higher CO and HC emissions with LTC due to its incomplete combustion, because of having higher latent vaporization heat which leads to a lower combustion temperature (Q. Fang et al., 2013; Pidol et al., 2012). Applying EAT as an oxidation catalytic converter (OCC) reduced HC and CO by about 90-95% and 36-70% respectively from both diesel and biodiesel-fueled engines (Shi et al., 2012). Based on the summary in **Table 2.11**, the following conclusions are drawn:

- LTC reduces $NO_x$ emissions on average by about 66-93% compared to biodiesel and by 8.68-70% compared to diesel combustion, for different conditions reducing PM by up to 98%. However, it shows a little penalty on engine performance because of slight incomplete combustion.
- HCCI combustion ignites a homogeneous lean charge over the entire combustion chamber which produces very low PM emission due to part of the

fuel impinging on the cylinder and piston walls. With increasing injection pressure, the PM emission decreases due to improved atomization, and better vaporization and homogenization.

- Generally, all LTC technologies produce higher CO and HC emissions.

**Table 2.11**
Review of emissions and performance analysis using LTC as $NO_x$ mitigation technology for biodiesel fuel.

| **Fuel type** | **Test condition** | **Emission results deviations (%)** | | **Performance** | **Reference** |
|---|---|---|---|---|---|
| | | **$NO_x$** | **Other emissions** | | |
| Peanut biodiesel (PNB100) | PCCI/LTC (n-butanol injected into intake manifold & 3 bar IMEP, idling speed) | ↓ 75 | HC↑ large scale, CO↑ large scale, PM↓98 | SEC↑ but ↓with ↑ IMEP, $\eta_o$↓ but ↑ with ↑ IMEP | (Soloiu et al., 2013) |
| CB0, CB30, CB65, CB100 | HCCI (high swirl ratio, EGR & late injection) | ↓ (CB0 › CB100 & CB30 = CB65) with ↑ % of EGR rate | (HC& CO )↑(CB100› CB65 › CB30 › CB0 ), smoke↑(CB0 › CB30 › CB65 › CB100) with ↑% of EGR rate | NA | (Jiménez-Espadafor et al., 2012) |
| A= RB0, B= (RB40+20% E) | LTC for A (36% EGR, Pr. Rail: 860bar, $SOI_{main}$ -0.3°CA & $SOI_{pilot}$ 31.9°CA ) where for B (43.7% EGR, Pr. Rail: 600bar, $SOI_{main}$ 7°CA & $SOI_{pilot}$ NA ) at 1500 rpm & 3 bar of BMEP as optimized condition | ↓69.84 for fuel type B compared to A | HC↑43.77, CO↓3.19, smoke↓71.4 for fuel type B compared to A | BSFC↑13.28 for fuel type B compared to A | (Pidol et al., 2012) |
| PB0 PB20, PB100 | later-phased LTC (high EGR level + retard IT) | ↓ (PB0 › PB100& PB20› PB100) with retard IT | smoke↓ for all fuels, HC↑(PB0›PB20 & PB0›PB100), CO↓ (PB20), CO↓85 (PB100) | $\eta_c$ unchanged (PB100), $\eta_c$ ↓ for PB0 & PB20 with retard IT | (Tompkins et al., 2012) |
| RB100 | HCCI (variation of IP: a=400 bar, b=500 bar, c=600 bar, d=700 bar, 1500 rpm speed | ↓8.68 (a), ↓15.85 (b), ↓11.31 (c), same (d) compared to diesel | PM↓(0-13), CO↑(1.15-11.5), HC↓upto 41% compared to diesel | Little penalty on performance. | (Mancaruso & Vaglieco, 2010) |
| B0, B20, B100 | LTC (IP : 180 MPa, multiple injections & 30% EGR) | ↑(B20; B100) with ↑IP, $NO_x$ identical among B0 & B20 but ↑for B100 at LTC mode | (HC & CO)↑ at LTC mode but ↓ with retardation of IT, Soot↓ (B20; B100) at LTC mode | BSFC↑ at LTC mode | (Karra et al., 2008) |
| SB0, SB20, SB50, SB100 | CS:1500RPM, IP: 600 bar. Single injection, IMEP : 2.0 bar. a= -25, b= -10 and c = 3 CAD ATDC | ↓78.7(SB0);↓76(SB20);↓68.6(SB50);↓66.3(SB100) for b:a & ↓93.5(SB0); ↓92.7 (SB20);↓91.4(SB50); ↓91.3 (SB100) for c:a. | PM↓, (HC & CO)↑ | SFC↓ for (b) & (c) condition compared to (a) for all fuel samples | (T. Fang et al., 2008) |
| B100 | LTC (Speed: 1500 rpm, Pr. Rail: 950bar, Pr. Intake : 1.7bar (abs), IMEP: 8bar & 50-70% EGR | ↓ with increasing EGR rate, $NO_x$ formation rate was about constant but little at 60-70% EGR | (soot, CO and HC)↑ appreciably for early injection strategy, however improve CO and HC emissions at 340°CA SOI. | Improved indicated thermal efficiency at 340°CA SOI with LTC | (Ming Zheng et al., 2009) |
| SB0, SB20, SB50 & SB100 | late-injection premixed LTC mode (50% EGR and Injection Timing 5, 7 & 9° CA BTDC) | ↑ for IT advance and increasing biodiesel content, ↓ with ↑ (% of EGR & retardation of IT) | HC↑ for retardation of IT but ↓ with ↑ biodiesel blends, CO↑ for all cases, PM very low specially for SB100 | BSFC↑ with retardation of IT | (W. Northrop et al., 2009) |

Note: $\eta_c$ & $\eta_o$ = combustion & overall efficiency respectively, NA= Not Available

# CHAPTER 3: METHODOLOGY

## 3.1 Introduction

This chapter describes the research methodology and approaches for achieving objectives of current work. These include the production of biodiesel from crude non-edible oil, characterization of different physicochemical properties of biodiesel blends, fuel blending for engine run, and engine emission and performance analysis. Making fuel sample to run the engine by mixing $NO_x$ reducing antioxidant additive (DPPD) with Jatropha biodiesel blends are discussed. **Figure 3.1** gives a brief summary of the implemented works of this research.

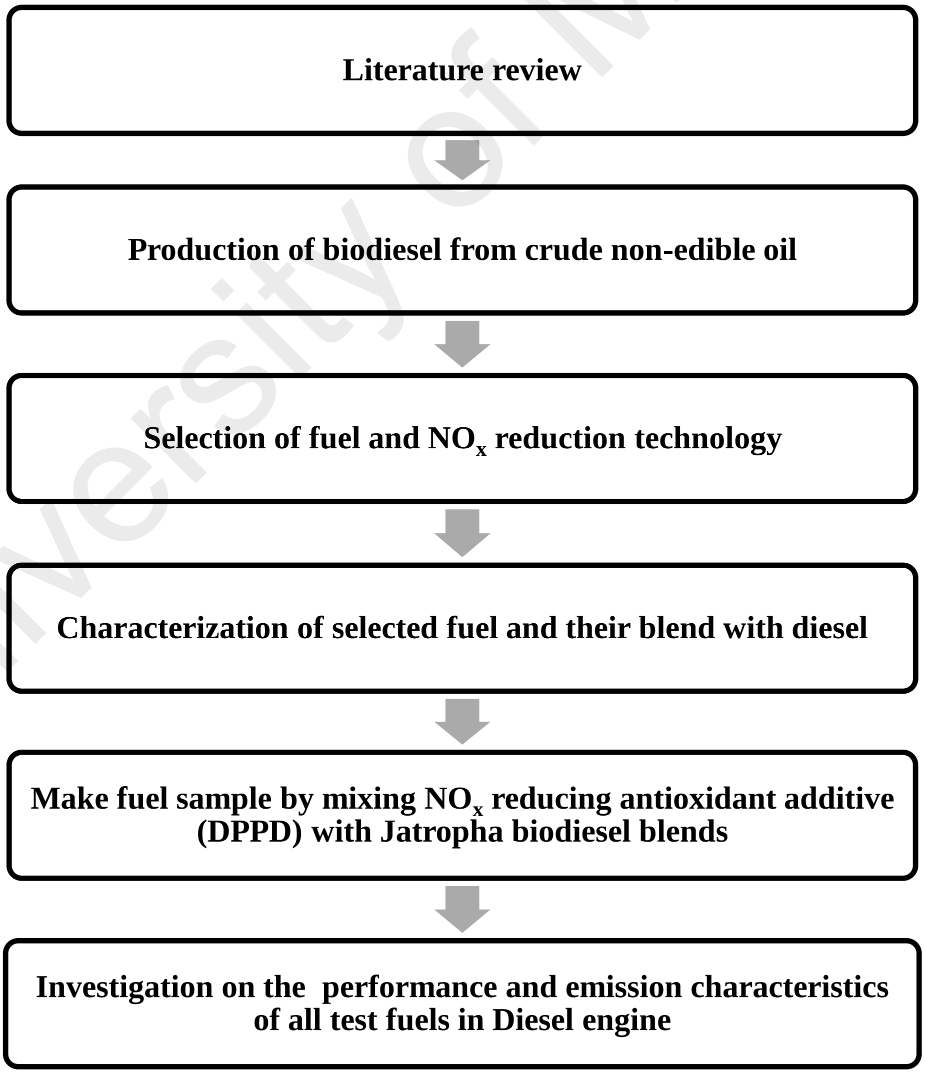


**Figure 3.1**: Flow chart of research methodology

## 3.2. Materials and methods

### 3.2.1. Materials and chemicals

The crude AP oil (CAPO) was purchased from Bangladesh. Crude Jatropha oil was collected from Forest Research Institute Malaysia (FRIM). Other chemicals such as methanol, potassium hydroxide (KOH) and anhydrous sodium sulfate ($Na_2SO_4$) were of Friendemann Schmidt Chemicals, USA. All purchased chemicals i.e. methanol, hydrochloric acid (HCl) etc. was of analytical grade and catalysts were of 99.5% purity. In this work, CAPO and CJCO were selected as feedstock because both are non-edible oil and not hampered on food chain. The main advantages of non- edible oil are their liquid nature portability, ready availability, renewability, higher heat content, lower sulphur content, lower aromatic content and biodegradability.

### 3.2.2. List of apparatus

The summary of the equipment used to measure the properties of CAPO, CJO, neat biodiesel, and its blends with diesel are shown in **Table 3.1**.

**Table 3.1.**

Summary of the apparatus used to measure the fuel properties

| Property | Equipment | Manufacturer | Test method |
|---|---|---|---|
| Kinematic & dynamic viscosityat 40 °C | SVM 3000 | Anton Paar, UK | ASTM D7042 |
| Density at 40 °C | SVM 3000 | Anton Paar, UK | ASTM D7042 |
| Density at 15 °C | DM 50 | Mettler Toledo, Switzerland | ASTM D1298 |
| Oxidation stability | 873 Rancimat | Metrohm, Switzerland | EN ISO 14112 |
| Flash Point | Pensky-martens NPM 440 | Norma lab, France | ASTM D93 |
| Cloud and Pour point | Cloud and Pour point tester NTE 450 | Norma lab, France | ASTM D2500, ASTM D97 |
| Cold filter plugging point | Cold filter plugging point tester NTL 450 | Norma lab, France | ASTM D6371 |
| Calorific value | C2000 basic calorimeter | IKA, UK | ASTM D240 |
| Viscosity index | SVM 3000 | Anton Paar, UK | N/A |
| Transmission and absorbance | Spekol 1500 | Analytical Jena, Germany | N/A |
| Refractive index | RM 40 Refractometer | Mettler Toledo, Switzerland | N/A |

### 3.2.3. Calculation of the cetane number, iodine value, and saponification number of biodiesel

The cetane number, iodine value, and saponification number of APME were determined empirically using the equations presented in the literature (Mohibbe Azam et al., 2005; Rizwanul Fattah et al., 2014).

$$\mathrm{SN}=\sum\left(\frac{560 * \mathrm{A_i}}{MW_i}\right)\text{.........................................}(1)$$

$$\mathrm{IV}=\sum\left(\frac{254 * \mathrm{D} * \mathrm{A_i}}{MW_i}\right)\text{.................................}(2)$$

$$\mathrm{CN}=\left(46.3+\left(\frac{5458}{\mathrm{SN}}\right)-(0.225*\mathrm{IV})\right)\text{..................}(3)$$

Where,

Ai ≡ the percentage of each component,

D ≡ the number of double bond and

MWi ≡ the molecular mass of each component.

### 3.2.4. Biodiesel production from Crude Oil

The high acid value of CAPO, 26.1 mg KOH/g of oil, prevents the use of a single-step alkaline-transesterification process. Therefore, a two-step process of acid-base catalysis was used to produce biodiesel. In the first stage, the esterification process was used to reduce the high acid value of the crude oil, while in the second stage; the transesterification process was used to convert the esterified oil to methyl ester or biodiesel (APME). Figure 3.2 shows a detailed flow chart of the production of biodiesel from CAPO.

Crude Jatropha oil was collected from Forest Research Institute Malaysia (FRIM). **Table 3.2** shows physical properties of crude Jatropha oil and also making comparison with existing literature. It was observed that viscosity of the crude oil is very high (52 $mm^2/s$) and it is about 11 times higher than that of diesel fuel. Free fatty acid (FFA) is the main identifier of biodiesel production process from crude oil. For higher FFA contains of Jatropha oil, it is required two steps process because of forming fatty acid salts during the conversion of FFA into FAME (Fatty acid methyl ester) using alkaline catalyst. The fatty acid salt prevents to separate FAME layer from glycerin (Berchmans & Hirata, 2008). Therefore two step (acid-base catalyst) processes were selected to convert crude Jatropha oil into Jatropha oil methyl ester/Jatropha biodiesel (JBD). The production of biodiesel was conducted in the laboratory scale using 1L batch reactor. After that the physical properties of the Jatropha biodiesel and their blends were evaluated as per the ASTM standards.

**Table 3.2**

Properties of crude *Aphanamixis Polystachya* and Jatropha oil

| Properties | Units | Standards | CAPO | Jatropha oil | Jatropha oil[a] |
|---|---|---|---|---|---|
| Kinematic Viscosity at 40°C | $mm^2/sec$ | ASTM D445 | 35.093 | 52 | 47-54.8 |
| Density at 15°C | $Kg/m^3$ | ASTM D4052 | 934 | 921 | - |
| Calorific Value | MJ/kg | ASTM D240 | 38.73 | 38.66 | 37.830-42.050 |
| Flash Point | °C | ASTM D93 | 228 | 220 | 210-240 |
| Cloud Point | °C | ASTM D2500 | 5 | 9 | 2 |
| Pour Point | °C | ASTM D97 | 4 | 4 | -3 |

[a] Data obtained from ref. (May Ying Koh & Tinia Idaty Mohd Ghazi, 2011)

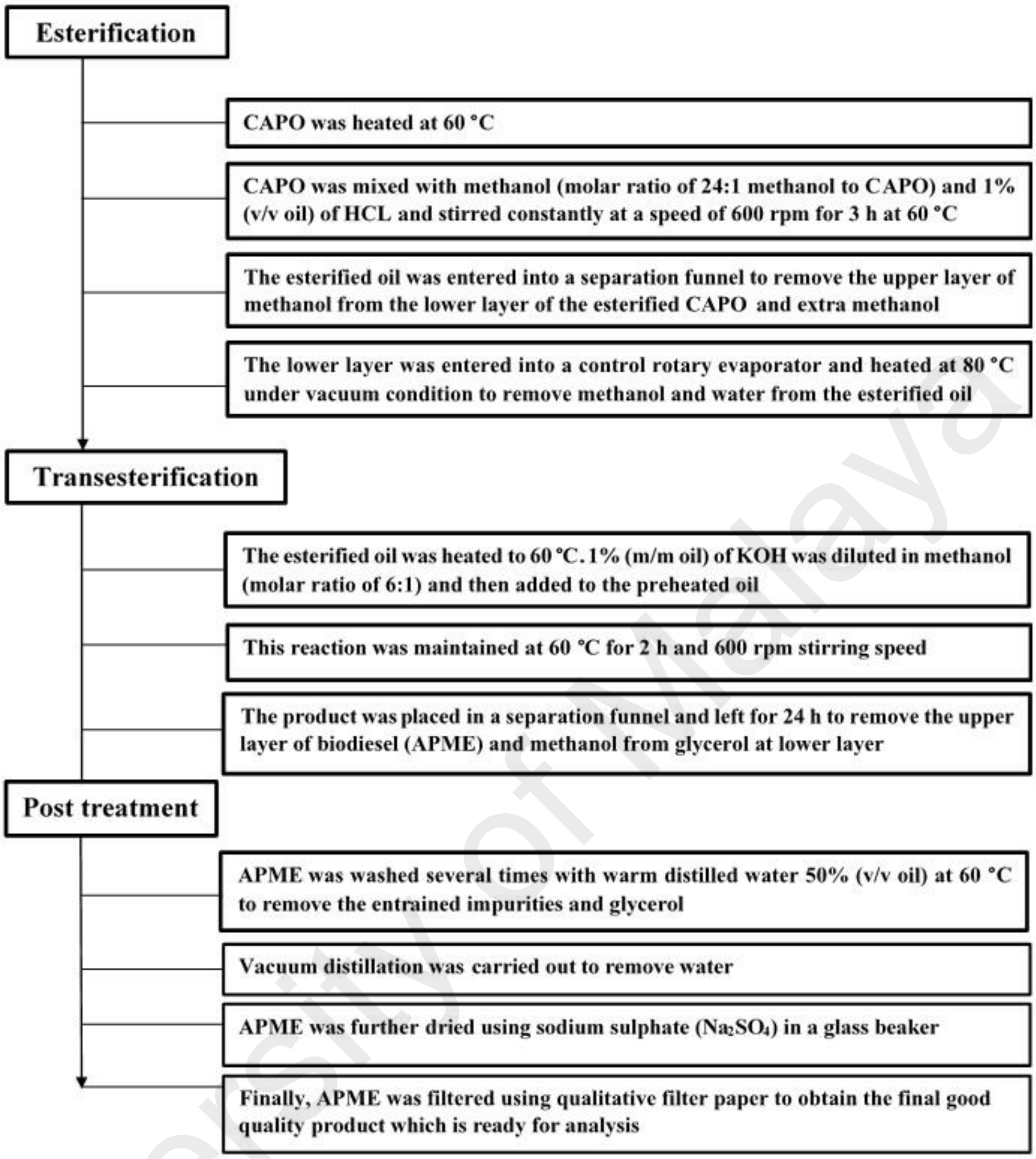
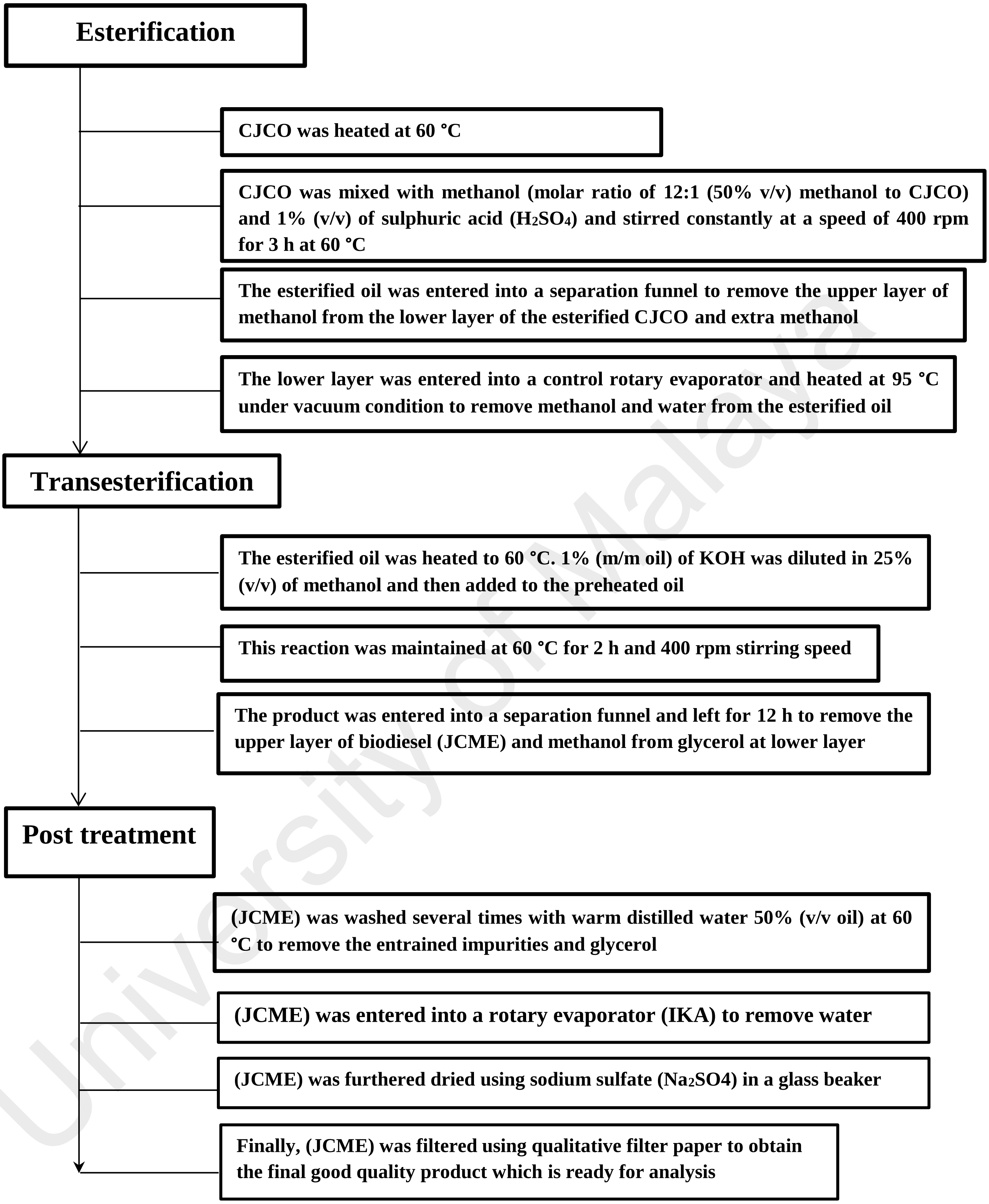


**Figure 3.2a:** Flow chart of biodiesel production from CAPO



**Esterification**

CJCO was heated at 60 °C

CJCO was mixed with methanol (molar ratio of 12:1 (50% v/v) methanol to CJCO) and 1% (v/v) of sulphuric acid ($H_2SO_4$) and stirred constantly at a speed of 400 rpm for 3 h at 60 °C

The esterified oil was entered into a separation funnel to remove the upper layer of methanol from the lower layer of the esterified CJCO and extra methanol

The lower layer was entered into a control rotary evaporator and heated at 95 °C under vacuum condition to remove methanol and water from the esterified oil

**Transesterification**

The esterified oil was heated to 60 °C. 1% (m/m oil) of KOH was diluted in 25% (v/v) of methanol and then added to the preheated oil

This reaction was maintained at 60 °C for 2 h and 400 rpm stirring speed

The product was entered into a separation funnel and left for 12 h to remove the upper layer of biodiesel (JCME) and methanol from glycerol at lower layer

**Post treatment**

(JCME) was washed several times with warm distilled water 50% (v/v oil) at 60 °C to remove the entrained impurities and glycerol

(JCME) was entered into a rotary evaporator (IKA) to remove water

(JCME) was furthered dried using sodium sulfate ($Na_2SO4$) in a glass beaker

Finally, (JCME) was filtered using qualitative filter paper to obtain the final good quality product which is ready for analysis

**Figure 3.2b:** Flow chart of biodiesel production from CJCO

### 3.2.5. Gas chromatography method

The fatty acid composition (FAC) of APME was determined using a GC setup. To determine the fatty acid composition of biodiesel sample (1µL) was injected into gas chromatography (Shidmadzu, GC-2010A series) equipped with a flame ionization detector and a BPX70 capillary column of 30 m x 0.25 µm x 0.32 mm. An initial temperature of 140 °C was held for 2 minutes, which was then increased at 8 °C per minute to 165 °C, 3 °C per minute to 192 °C and finally 8 °C per minute to 220 °C. The column was held at the final temperature for another 5 minutes. The oven, injector and the detector ports were set at 140, 240 and 260 °C, respectively. The carrier gas was helium with column flow rate at 1.10 mL min-1 at a 50:1 split ratio. Then, made comparison with other feedstocks such as JCME, CIME, PME, SME and CME. **Table 3.3** shows the GC operating conditions.

**Table 3.3.**

Gas chromatography (GC) operating conditions

| **Property** | **Specifications** |
|---|---|
| Carrier gas | Helium |
| Linear velocity | 24.4 cm/sec |
| Flow rate | 1.10 mL/min (column flow) |
| Detector temperature | 260.0 °C |
| Column head pressure | 56.9 kPa |
| Column dimension | BPX 70, 30.0 m x 0.25 µm x 0.32 mm ID |
| Injector | 240.0 °C |
| Column Oven | |
| Temperature ramp | 140.0 °C (hold for 2 minutes) |
| | 8°C/min 165.0 °C |
| | 3°C/min 192.0 °C |
| | 8°C/min 220.0 °C (hold for 5 minutes) |

### 3.2.6. Biodiesel-diesel blending

APME was blended with diesel at 5%, 10%, 20%, 30%, 40%, 60%, and 80% by volume, using a magnetic stirrer (IKA C-MAG HS 7) at 2000 rpm for 30 min and a shaker (IKAKS 130 basic) at 400 rpm for 30 min. JCME was blended 80%, 85%, 90%

and 95% by volume, using a magnetic stirrer (IKA C-MAG HS 7) at 2000 rpm for 30 min and a shaker (IKAKS 130 basic) at 400 rpm for 30 min.

### 3.2.7. Engine tests

The engine testing was carried out on a 2.5 L turbocharged four-cylinder indirect injection (IDI) diesel engine. The detail of the engine is described in Table 3.4. The test engine was directly coupled to Froude Hofman AG250 eddy current dynamometer. Engine oil, cooling water, exhaust gas and inlet air temperatures were measured using K type thermocouples. Fuel flow was measured using KOBOLD ZOD positive-displacement type flow meter. REO-dCA Data Acquisition System collects the data. A flow diagram of the engine test bed is shown in **Figure 3.3**. To allow rapid switching between fuels, the engine fuel system was modified by adding separate tanks with two way valve. The exhaust gas emissions CO, $CO_2$, HC, and NO emissions were measured by gas analyzer (BOSCH BEA350). The CO, $CO_2$ and HC measuring instrument uses the non-dispersive infrared (NDIR) detectors and the NO analyzer uses electrochemical detectors.

To carry out tests using biodiesel blends, steady operating condition was first attained by running engine with diesel. Then fuel was changed to a biodiesel blend. The engine was run for 10 minutes to ensure the removal of residual diesel in the fuel line. After that the data acquisition was started. After each test engine was again run with diesel to drain out all the blends in the fuel line. This procedure was followed for all the blends. The test fuels were diesel, 95% diesel and 5% biodiesel (B5), and 10% biodiesel and 90% diesel (B10) blends. Test fuels were blended using a homogenizer device at a speed of 3000 rpm for 10 minutes. The engine was operated between 1000 rpm to 4500 rpm with a step of 500 rpm at 100% load condition. The performance and emission measurements were repeated more than 10 times to carry out Student’s t-test. Statistical analysis was carried out by applying two-sided Student's t-test for independent variables to test for significant differences between samples set means using Microsoft Excel 2013. Differences between mean values at a level of p = 0.05 (95% confidence level) were considered statistically significant.

For Jatropha biodiesel, experiments were conducted with different biodiesel blends (JB5, JB10, JB15 and JB20) and also with addition of DPPD (0.15%m) antioxidant for each fuel sample. Moreover, all tests were taken with variation of engine speed from 1000 rpm to 4000 rpm (interval 500 rpm) at full throttle condition. All experimental data were collected through the REO-DCA controller data acquisition system. The BOSCH BEA-350 exhaust gas analyzer was used to record the data of all exhaust gas emissions. Details of gas analyzer are shown in **Table 3.5**. To get the average values, all tests were repeated three times.

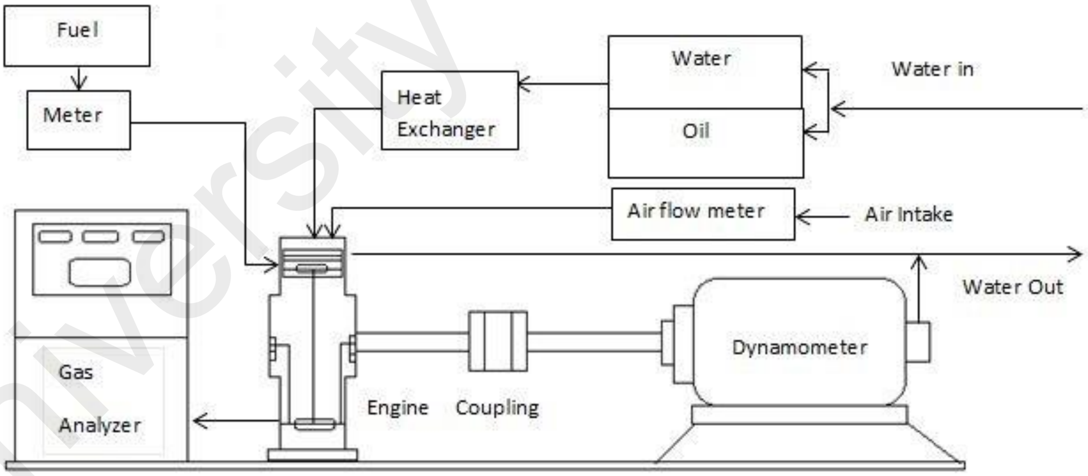


**Figure 3.3:** Flow diagram of engine test bed

**Table 3.4.**

Detailed technical specification of the tested engine

| Parameter | Specification |
|---|---|
| **Type** | Four cylinder IDI diesel engine |
| **Displacement (L)** | 2.5 |
| **Cylinder bore x stroke (mm)** | 92x96 |
| **Compression ratio** | 21:1 |
| **Maximum engine speed (rpm)** | 4200 |
| **Fuel system** | Distribution type jet pump |
| **Lubrication system** | Pressure feed |
| **Combustion chamber** | Swirl type |
| **Cooling system** | Radiator cooling |

**Table 3.5.**

Details of the exhaust gas analyzer

| **Equipment** | **Method** | **Measurement** | **Upper Limit** | **Accuracy** | **Percentage uncertainties** |
|---|---|---|---|---|---|
| BOSCH BEA350 gas analyzer | Non-dispersive infrared | CO | 10.00 Vol.% | ±0.001 vol.% | 0.002 vol.% |
| | Non-dispersive infrared | $CO_2$ | 18.00 Vol.% | ±0.001 vol.% | 0.150 vol.% |
| | Flame ionization detector (FID) | HC | 9999 ppm | ±1 ppm | 2 ppm |
| | Electro-chemical transmitter | NO | 5000 ppm | ±1 ppm | 21 ppm |

# CHAPTER 4: RESULT AND DISCUSSION

## 4.1 Introduction

The results of all analysis done throughout the research is presented and discussed in this chapter. In the first section, physicochemical properties of two biodiesel fuel (APME and JCME), diesel with their blends is shown. Then comparison the different sample fuels properties with diesel are discussed. $NO_x$ reducing antioxidant additive (DPPD) with Jatropha biodiesel blends are discussed. Finally, engine performance, emission and combustion characteristics of different blends are addressed and compared with diesel fuel.

## 4.2. Results and discussions

This study presents the prospect of biodiesel derived from *Aphanamixis polystachya* oil and Jatropha non edible oil in diesel engine. The study deals with the physicochemical properties of *Aphanamixis polystachya* methyl ester (APME), *Jatropha curcas* methyl ester (JCME) and their individually blends with diesel followed by evaluation of performance and emission characteristics in a multi-cylinder diesel engine. The impacts of aromatic antioxidant (DPPD) as $NO_x$ reduction technology on engine performance (Power & BSFC) and emissions such as NO, HC, and CO fuelled with Jatropha biodiesel blends (JB5, JB10, JB15 & JB20) in diesel engine were systematically investigated in this study also.

### 4.2.1. Characterization of CAPO and CJCO

**Table 4.1** shows the physicochemical properties of CAPO and CJCO. In this table, a comparison with other crude oils such as *Jatropha curcas* oil (CJCO), *Calophyllum inophyllum* oil (CCIO), palm oil (CPaO), canola oil (CCaO) and soybean oil (CSO) is presented. The main findings of crude oil properties show that the kinematic viscosity at 40 ◦C and 100 ◦C, dynamic viscosity at 40 ◦C for CAPO are lower than the other presented crude oil. However, CAPO possesses the highest density of 916 kg/m$^3$ at 40 °C. However, CSO has the best viscosity index of 223.2. Oxidation stability for CAPO is .09 hour which not so good. Acid value for CAPO is 26.7 mg KOH/g which higher than CJCO. CAPO possesses the highest refractive index of 1.4789 and calorific value of 38,729 kJ/kg. The properties of crude jatropha oil are presented in **Table 3.2**. Finally, the transmission value of CAPO and CJCO were found that 61.6% and 61.7% respectively. The next sections will discuss some of main the finding of this study beside a comparison with literature.

**Table 4.1.**

Properties of CAPO and CJCO

| Property | unit | CAPO | CJCO | CJCO[a] | CCIO[a] | CPaO[a] | CCaO[a] | CSO[a] |
|---|---|---|---|---|---|---|---|---|
| Kinematic viscosity at 40 °C | mm$^2$/s | 35.093 | 52.0 | 48.091 | 55.677 | 41.932 | 35.706 | 31.739 |
| Kinematic viscosity at 100 °C | mm$^2$/s | 7.2547 | 8.91 | 9.1039 | 9.5608 | 8.496 | 8.5180 | 7.6295 |
| Dynamic viscosity at 40 °C | mPa.s | 32.159 | 43.12 | 43.543 | 51.311 | 37.731 | 32.286 | 28.796 |
| Viscosity Index (VI) | - | 177.9 | 172.3 | 174.10 | 165.4 | 185.0 | 213.5 | 223.2 |
| Cloud Point (CP) | °C | 5 | 9 | - | - | - | - | - |
| Pour Point (PP) | °C | 4 | 4 | - | - | - | - | - |
| Density at 40 °C | kg/m$^3$ | 916.4 | - | - | - | 899.8 | 904.2 | 907.3 |
| Density at 15 °C | kg/m$^3$ | 934 | 921 | 915 | 951 | - | - | - |
| Calorific value | kJ/kg | 38,729 | 38,660 | 38,961 | 38,511 | 39,867 | 39,751 | 39,579 |
| Oxidation stability | h at 110 °C | 0.09 | 0.41 | 0.32 | 0.23 | 0.08 | 5.64 | 6.09 |
| Acid value | mg KOH/g | 26.7 | 18.32 | 17.63 | 41.74 | N/D | N/D | N/D |
| Refractive Index | - | 1.4789 | 1.464 | 1.4652 | 1.4784 | 1.4642 | 1.471 | 1.471 |
| Transmission | % | 61.6 | 61.7 | 61.8 | 34.7 | 63.2 | 62.9 | 65.2 |
| Absorbance | Abs | 0.209 | 0.21 | 0.209 | 0.46 | 0.199 | 0.202 | 0.186 |

[a] Data taken from Ref.(Atabani et al., 2013)

### 4.2.2. Fatty acid composition and characterization of APME and JCME

The FAC of APME, JCME and a comparison with the FAC of different methyl esters e.g. *Jatropha curcas* (JCME), *Calophyllum inophyllum* (CIME), palm (PaME), canola (CaME) and soybean (SME), is shown in **Table 4.2**. It is observed that APME is mainly comprised of oleic acid (18.3%), linoleic acid (26.7%) and linolenic acid (23.3%), while PaME mainly consists of Palmitic acid (42.8%) and Oleic acid (40.5%). CIME and JCME are dominated by oleic acid (34.09% and 44.6%, respectively) and linoleic acid (38.26% and 31.9%, respectively). The saturated fatty acid content of APME is 30.7%, while it is 48.4 % for PaME, 22.7% for JCME and 24.96% for CIME, respectively. In general, APME shows a trend comparable to that of CIME and JCME. Therefore, it can be understood that non-edible biodiesel feedstock’s exhibit similar fatty acid compositions. And for selected test fuel as JCME biodiesel, it is also dominated by oleic acid 44.5%, linoleic acid 35.4% and palmitic acid 13% like reference JCME biodiesel. Finally, it is found that the amount of polyunsaturated fatty acid for APME is higher than the others. It is also found that the amount of saturated fatty acid for JCME is lower than the others.

The significant physicochemical properties of APME and JCME were studied and compared with those of PaME, SME, CaME, JCME, CIME, and the ASTM D6751 standard specification. The detailed physicochemical properties are shown in **Table 4.3**. In this table, it is found that the viscosity index for APME (220.7) is higher than the others. However, the kinematic viscosity at 40 °C and 100 °C for APME is lower than JCME. From **Table 4.3**, it is found that the oxidation stability for APME is not fulfilling the ASTM standard. The oxidation stability of APME is less than the prescribed ASTM standard. This indicates that the use of antioxidants is necessary to meet standards specifications.

## Table 4.2.

FAC of APME, JCME and comparison with other methyl esters (wt.%)

| Fatty acid | Molecular weight | Structure | Systematic name | Formula | APME | JCME | JCME[a] | CIME[b] | PaME[c] |
|---|---|---|---|---|---|---|---|---|---|
| Caprylic | 144 | 8:0 | Octanoic | $C_8H_{16}O_2$ | N/D | N/D | N/D | N/D | N/D |
| Capric | 172 | 10:0 | Decanoic | $C_{10}H_{20}O_2$ | N/D | N/D | N/D | N/D | N/D |
| Lauric | 200 | 12:0 | Dodecanoic | $C_{12}H_{24}O_2$ | N/D | N/D | 0.1 | N/D | 0.1 |
| Myristic | 228 | 14:0 | Tetradecanoic | $C_{14}H_{28}O_2$ | N/D | 0.1 | 0.1 | N/D | 1.0 |
| Palmitic | 256 | 16:0 | Hexadecanoic | $C_{16}H_{32}O_2$ | 18.4 | 13 | 14.6 | 12.01 | 42.8 |
| Palmitoleic | 254 | 16.1 | hexadec-9-enoic | $C_{16}H_{30}O_2$ | 0.3 | 0.7 | 0.6 | N/D | N/D |
| Stearic | 284 | 18:0 | Octadecanoic | $C_{18}H_{36}O_2$ | 11.8 | 5.8 | 7.6 | 12.95 | 4.5 |
| Oleic | 282 | 18:1 | cis-9-Octadecenoic | $C_{18}H_{34}O_2$ | 18.3 | 44.5 | 44.6 | 34.09 | 40.5 |
| Linoleic | 280 | 18:2 | cis-9-cis-12 Octadecadienoic | $C_{18}H_{32}O_2$ | 26.7 | 35.4 | 31.9 | 38.26 | 10.1 |
| Linolenic | 278 | 18:3 | cis-9-cis-12 | $C_{18}H_{30}O_2$ | 23.2 | 0.3 | 0.3 | 0.3 | 0.2 |
| Arachidic | 312 | 20:0 | Eicosanoic | $C_{20}H_{40}O_2$ | 0.5 | 0.2 | 0.3 | N/D | N/D |
| Gondoic | 310 | 20:1 | 11- Eicosenoic | $C_{20}H_{38}O_2$ | 0.2 | N/D | N/D | N/D | N/D |
| Behenic | 340 | 22:0 | Docosanoic acid | $C_{22}H_{44}O_2$ | N/D | N/D | N/D | N/D | N/D |
| Erucic | 339 | 22:1 | (Z)-Docos-13-enoic acid | $C_{22}H_{42}O_2$ | 0.6 | N/D | N/D | N/D | N/D |
| Saturated | | | | | **30.7** | **19.1** | **22.7** | **24.96** | **48.4** |
| Monounsaturated | | | | | **19.4** | **45.2** | **45.2** | **34.09** | **40.5** |
| Polyunsaturated | | | | | **49.9** | **35.7** | **32.2** | **38.56** | **10.3** |
| Total | | | | | **100** | **100** | **100** | **97.61** | **99.2** |

[a] Data taken from Ref.(Mofijur, Masjuki, Kalam, & Atabani, 2013).

[c] Data taken from Ref.(Rizwanul Fattah et al., 2013a).

**Table 4.3.**

Physicochemical properties of APME and JCME

| **Property** | **unit** | **APME** | **JCME** | **JCME[a]** | **CIME[a]** | **PaME[a]** | **ASTM D6751** |
|---|---|---|---|---|---|---|---|
| Kinematic viscosity at 40 °C | $mm^2/s$ | 4.7177 | 4.7227 | 4.9476 | 5.5377 | 4.6889 | 1.9-6.0 |
| Kinematic viscosity at 100 °C | $mm^2/s$ | 1.8239 | 1.8337 | 1.8557 | 1.998 | 1.7921 | N/A |
| Dynamic viscosity at 40 °C | mPa.s | 4.1210 | 4.2651 | 4.2758 | 4.8599 | 4.0284 | N/A |
| Viscosity Index (VI) | - | 220.7 | 190.1 | 194.6 | 183.2 | 203.6 | N/A |
| Cloud Point (CP) | °C | 8 | 5 | 10 | 12 | 16 | Report |
| Pour Point (PP) | °C | 8 | 3 | 10 | 13 | 15 | Report |
| Cold filter plugging point(CFPP) | °C | 5 | 3 | 10 | 11 | 12 | Report |
| Density at 40 °C | $kg/m^3$ | 873.5 | 865 | 864.2 | 877.6 | 859.1 | - |
| Density at 15 °C | $kg/m^3$ | 893 | - | - | - | - | - |
| Specific gravity (f/t) at 15 °C | - | 0.8938 | - | - | - | 0.873 | 0.86 |
| Flash point | °C | 188.5 | 182.5 | 186.5 | - | 214.5 | 130 (min) |
| Acid value | mgKOH/goil | 0.448 | 0.4208 | - | - | 0.24 | 0.80 (max) |
| Calorific value | kJ/kg | 39,960 | 39,827 | 39,738 | 39,513 | 40,009 | N/A |
| Oxidation stability | h at 110 °C | 0.16 | 0.05 | 4.84 | 6.12 | 23.56 | 3h (min) |
| Cetane number | - | 44 | - | - | - | 54.6 | 47 (min) |
| Iodine value | g I/100 g | 129.4 | - | - | - | 54 | 120 (max) |
| Saponification number | - | 202.9 | - | - | - | - | - |
| Refractive Index (RI) at 25°C | N/A | 1.4583 | 1.443 | 1.4513 | 1.4574 | 1.4468 | - |
| Transmission at WL 656.1 | %T | 82.0 | 89.3 | 90.3 | 87.7 | 89.1 | - |
| Absorbance at WL 656.1 | Abs | 0.086 | 0.60 | 0.045 | 0.057 | 0.05 | - |

[a] Data taken from Ref.(Atabani et al., 2013)

### 4.2.3. Physicochemical properties of APME-diesel blends

In this paper, the properties of B5, B10, B20, B40, B60, and B80 blends were determined and compared with the ASTM D7467 standard. In addition **Table 4.4** shows the physicochemical properties of diesel, APME, and APME-diesel blends. The effect of blending of APME with diesel on physicochemical properties has been studied. Kinematic viscosity at 40 ◦C & 100◦C, dynamic viscosity at 40◦C, density at 40 ◦C & 15 ◦C, specific gravity 15 ◦C, viscosity index (VI), acid value and flash point are increased with increasing biodiesel percentage in diesel-biodiesel blends. However, the value of calorific value and oxidation stability are decreased with increasing biodiesel percentage in diesel-biodiesel blends. The physicochemical properties of JCME and JCME-diesel blends are shown in **Table 4.5**.

**Table 4.4.**

Physicochemical properties of diesel, APME and APME-diesel blends

| **Property** | **Unit** | **Diesel** | **B5** | **B10** | **B20** | **B40** | **B60** | **B80** | **B100** |
|---|---|---|---|---|---|---|---|---|---|
| Kinematic viscosity at 40 °C | mm²/s | 3.3920 | 3.4673 | 3.5357 | 3.656 | 3.9602 | 4.1599 | 4.413 | 4.717 |
| Kinematic viscosity at 100 °C | mm²/s | 1.3240 | 1.3479 | 1.368 | 1.4029 | 1.511 | 1.6066 | 1.712 | 1.8239 |
| Dynamic viscosity at 40 °C | mPa.s | 2.8148 | 2.8851 | 2.9501 | 3.0663 | 3.3577 | 3.5632 | 3.8185 | 4.121 |
| Density at 40 °C | kg/m³ | 829.8 | 832.1 | 834.4 | 838.7 | 847.9 | 856.6 | 865.1 | 873.5 |
| Density at 15 °C | kg/m³ | 847.1 | 849.4 | 852.1 | 856 | 865.3 | 874.2 | 883 | 893 |
| Specific gravity at 15 °C | N/A | 0.8479 | 0.8502 | 0.8529 | 0.8568 | 0.8661 | 0.875 | 0.8838 | 0.8938 |
| Viscosity Index (VI) | N/A | 116.9 | 122.8 | 132.2 | 138.4 | 150.4 | 184.8 | 208.7 | 220.7 |
| Cloud Point (CP) | °C | -4 | -4 | -3 | -3 | 0 | 2 | 5 | 8 |
| Pour Point (PP) | °C | -4 | -3 | -3 | -2 | 1 | 3 | 4 | 8 |
| Cold filter plugging point | °C | -7 | -4 | -3 | -3 | -3 | -1 | 2 | 5 |
| Flash point | °C | 84.5 | 84.5 | 85.5 | 86.5 | 91.5 | 98.5 | 118.5 | 188.5 |
| Calorific value | kJ/kg | 45,389 | 44,995 | 44,702 | 43,252 | 42,892 | 41,739 | 40,656 | 39,960 |
| Oxidation stability | h at 110 °C | N/D | N/D | N/D | 1.55 | 3.4 | 2.43 | 0.4 | 0.16 |
| Acid value | mgKOH/goil | 0.1120 | 0.1611 | 0.2242 | 0.2804 | 0.2804 | 0.3366 | 0.3916 | 0.448 |

N/D- Not Determined

### 4.2.4. Test fuel standardization (JCME)

The properties of Jatropha biodiesel and their blends with and without DPPD amine antioxidant have compared with ASTM biodiesel standards. The tested properties of methyl ester of Jatropha and their blends with and without addition of DPPD antioxidant have found to be reasonable agreement with ASTM 6751. **Table 4.5** represents the physical properties of Jatropha biodiesel and its blends as well as with addition of $NO_x$ reduction additive. It is observed from **Table 4.5** that no significant changed of density and pour point with addition of DPPD additive. However, calorific value and flash point for JB5, JB10 and JB20 biodiesel blends are improved with addition of antioxidant additive. Improvement of calorific value of fuel could be enhancing the engine performance. The calorific value of diesel fuel is higher than biodiesel and its blends. The presence of oxygen content into biodiesel helps to complete combustion of fuel in the engine. Moreover, higher flash point of biodiesel and their blends with and without DPPD additive is safer to store compared to diesel alone. Further using DPPD antioxidant additive into biodiesel has reduced the cloud point but enhance the oxidation stability significantly. The specifications of test amine DPPD antioxidant are shown in **Table 4.6**.

#### 4.2.4.1. Addition of DPPD additive into JCME biodiesel

For JB100DPPD0.15% sample, the volume of JB100 is 200 ml. The weight of 200ml JB100 (100% biodiesel) sample is 172.788 gm. So the amount of DPPD will be 0.15% of JB100 by weight is 0.259182 gm. For JB5DPPD0.15%, the volume of JB5 (5% biodiesel, 95% diesel) is 200 ml. The weight of 200ml JB5 (5% biodiesel, 95% diesel) sample is 165.532 gm. So the amount of DPPD will be 0.15% of JB5 by weight is 0.248298gm. Similarly, other sample has been prepared to test the engine.

**Table 4.5**

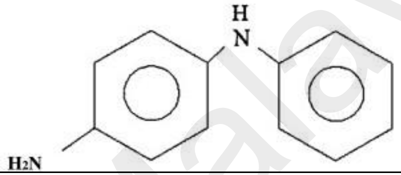
Properties of test fuels (for Jatropha biodiesel)

| Properties | Kinematic Viscosity at 40°C (mm$^2$/sec) | Density (kg/m$^3$) at 313 K | Calorific Value (MJ/kg) | Flash Point (°C) | Cloud Point (°C) | Pour Point (°C) | CFPP (°C) | Acid Value (mg KOH/g oil) | Oxidation Stability (h) |
|---|---|---|---|---|---|---|---|---|---|
| JB0 (Diesel) | 3.0699 | 828 | 45.265 | 72.5 | 8 | 6 | -7 | 0.1120 | N/D |
| JB100 | 4.7227 | 865 | 39.827 | 182.5 | 5 | 3 | 3 | 0.4208 | 0.05 |
| JB100DPPD0.15% | 4.7672 | 865.3 | 39.813 | 184.5 | 3 | 3 | 5 | 0.673 | 35.7 |
| ASTM D6751$^{a}$ | 1.9-6 | - | - | 403 (LL) | -1 | - | - | - | - |
| EN 14213$^{a}$ | 3.5-5.0 | 860-900$^{b}$ | 35 | 393 (LL) | - | 0 (UL) | - | 0.5 (UL) | 4.0$^{c}$ (LL) |
| EN 14214$^{a}$ | 3.5–5.0 | 860-900$^{b}$ | - | 374 (LL) | - | - | - | - | 6.0$^{c}$ (LL) |
| JB5 | 3.1382 | 829.2 | 45.023 | 82.5 | 6 | 0 | 5 | 0.3088 | 15.0 |
| JB5DPPD0.15% | 3.2041 | 829.7 | 45.253 | 87.5 | 6 | 0 | 6 | 0.3931 | 20.0 |
| JB10 | 3.1908 | 831.5 | 44.728 | 85.3 | 6 | 1 | 5 | 0.3088 | 45.4 |
| JB10DPPD0.15% | 3.2185 | 831.2 | 44.935 | 85.5 | 6 | 0 | 5 | 0.3928 | 35.71 |
| JB15 | 3.2288 | 832.7 | 44.709 | 83.5 | 6 | 0 | 5 | 0.2805 | 37.8 |
| JB15DPPD0.15% | 3.2693 | 833.7 | 44.583 | 94.5 | 6 | 0 | 5 | 0.3926 | 40.0 |
| JB20 | 3.2879 | 834.6 | 44.191 | 87.5 | 6 | 0 | 4 | 0.420 | 18.83 |
| JB20DPPD0.15% | 3.2757 | 833 | 44.466 | 88.5 | 5 | 0 | 5 | 0.3364 | 57.20 |

$^{a}$Data collected from ref. (Seta Biofuel Testing), $^{b}$at 288 K, $^{c}$at 383 K, LL= Lower limit, UL= Upper limit.

**Table 4.6**

Specifications of test amine antioxidant

| Specifications | N, N´-diphenyl-1, 4- phenylenediamine (DPPD) |
|---|---|
| CAS Registry Number (assigned by Chemical Abstracts Service) | 74-31-7 |
| Molecular weight | 260.34 |
| Chemical formula | $C_{18}H_{16}N_2$ |
| Melting Point | 144°C |
| Purity | 98% |
| Chemical Structure |  |

### 4.3. Engine performance for *Aphanamixis polystachya* Biodiesel

Biodiesel comprises of high molecular weight fatty acids of varying carbon chain length and number of double bonds along with substantial amounts of oxygen in their structure (Knothe, 2008). *Aphanamixis polystachya* oil contains mostly long chain unsaturated fatty acids, presence of which leads to a high density, kinematic viscosity and CN (Ramos et al., 2009). On the other hand, the oxygen content of biodiesel results in a reduced calorific value i.e. the energy content of the fuel. Thus, due to these inherent attributes, APME has a significant effect on engine performance as well as emissions. In this work, the purpose of APME blend up to 80% was intended to study the biodiesel blend properties. However, 5 and 10% blend were only allowed for engine test due to limitation of engine that can’t be run with high biodiesel percentage. Engine tests were carried out to enumerate the effects of APME blends on brake torque, BP, and BSFC etc.

### 4.3.1. Brake torque

**Figure 4.1** shows the variation of the engine torque at full load condition and different engine speeds when fuelled by diesel, APME5, and APME10. It has been observed that the torque for blends APME5 and APME10 was lower than that for diesel. These results are in agreement with the earlier literature (Buyukkaya et al., 2013a; Özener et al., 2014). It can be observed that, the trends for both biodiesel blends are almost similar to neat diesel fuel. Initially, engine torque increases as the engine speed increases until it reaches a maximum value and then starts decreasing with further increasing engine speed. At low speeds of the engine, because of lower vacuum of the cylinder and because of lower vaporization, the air-fuel ratio remain richer and resulting incomplete combustion which results in lower brake torque (Hueseyin Aydin & Bayindir, 2010). At higher speeds, the decrease can be attributed to two main factors; firstly, lower volumetric efficiency of the engine due to the increase in engine speed, and secondly, the augmentation in the mechanical losses (A. M. Liaquat et al., 2013). Over the whole speed range, the average torque values for diesel, APME5, and APME10 were found to be 146 Nm, 144.50 Nm, and 143 Nm, respectively. Thus, for the same amount of fuel injected, APME5 and APME10 gave an average reduction in torque of 0.9% and 1.81%, respectively, compared to pure diesel. These changes were significant at $p < 0.02$. This torque loss can be attributed to the lower heating value and higher density and kinematic viscosity compared to diesel fuel (İsmet Çelikten et al., 2012; H. Raheman & A. G. Phadatare, 2004).Higher kinematic viscosity and density of blends thereby lower volatility of blends and hence result in a poor mixture formation and lower brake torque output.

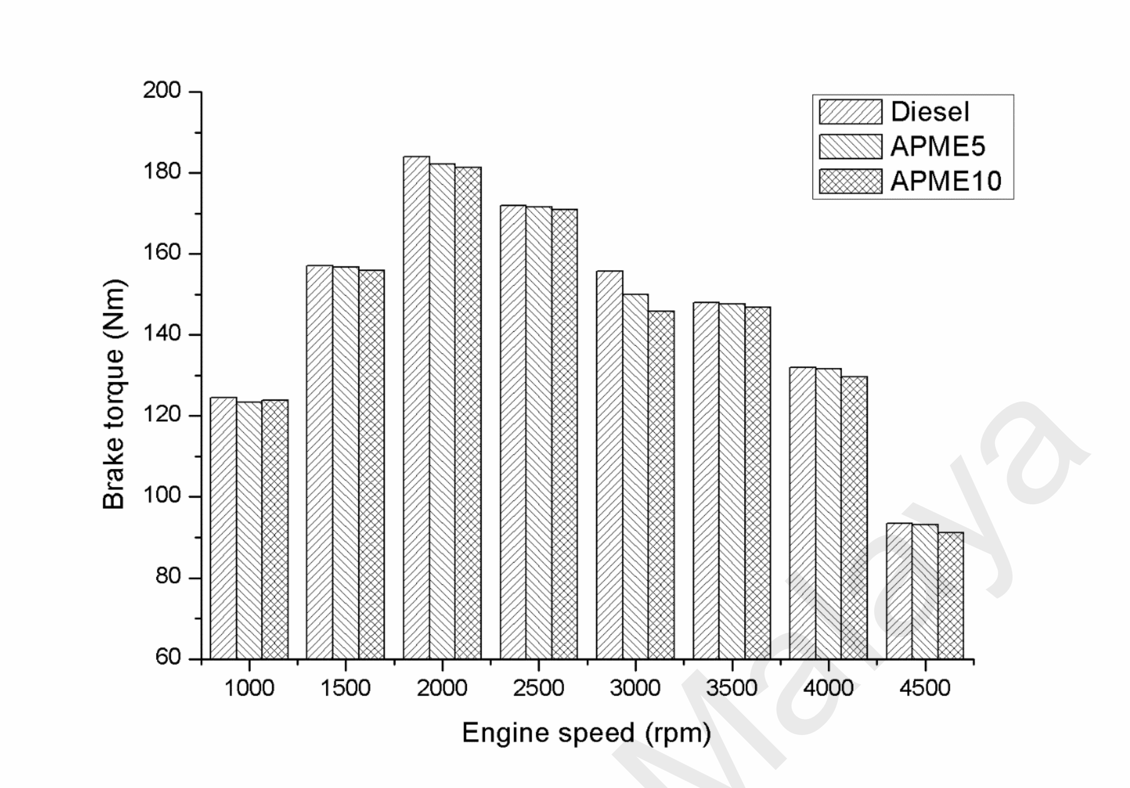


**Figure 4.1:** Variation of torque at different engine speeds and full load condition for APME.

### 4.3.2. Brake power

**Figure 4.2** shows the variation of BP of diesel, APME5, and APME10 at full load condition and different engine speeds. In general, biodiesel blends produce lower brake power compared to pure diesel fuel. Among the two biodiesel blends, it was found that APME5 had the highest and lowest BP values overall; a maximum BP value of 55.16 kW at 4000 rpm, and a minimum BP value of 12.91 kW at 1000 rpm. APME10 had a maximum BP value of 54.28 kW at 4000 rpm, and a minimum BP value of 12.97 kW at 1000 rpm. It was also observed that the BP gradually increased with increasing engine speed up to 4000 rpm and then decreased. In addition, the BP decreased with an increasing percentage of biodiesel in the blend. Over the entire speed range, the average BP for diesel, APME5, and APME10 were 40.5 kW, 40 kW, and 39.5 kW, respectively.

The average reduction of BP compared to diesel for APME5 and APME10 was 0.9% and 2.1%, respectively. These changes were significant at $p < 0.04$. This reduction can be attributed to their lower calorific value and higher viscosity compared to diesel fuel (Hueseyin Aydin & Bayindir, 2010). Higher viscosity results in higher resistance in the fuel line for pump line nozzle system as in the tested engine, which results in a higher delay in start of injection. This also leads to poorer fuel atomization (Haşimoğlu et al., 2008).These together with higher volumetric fuel consumption results in lower power output compared to diesel.

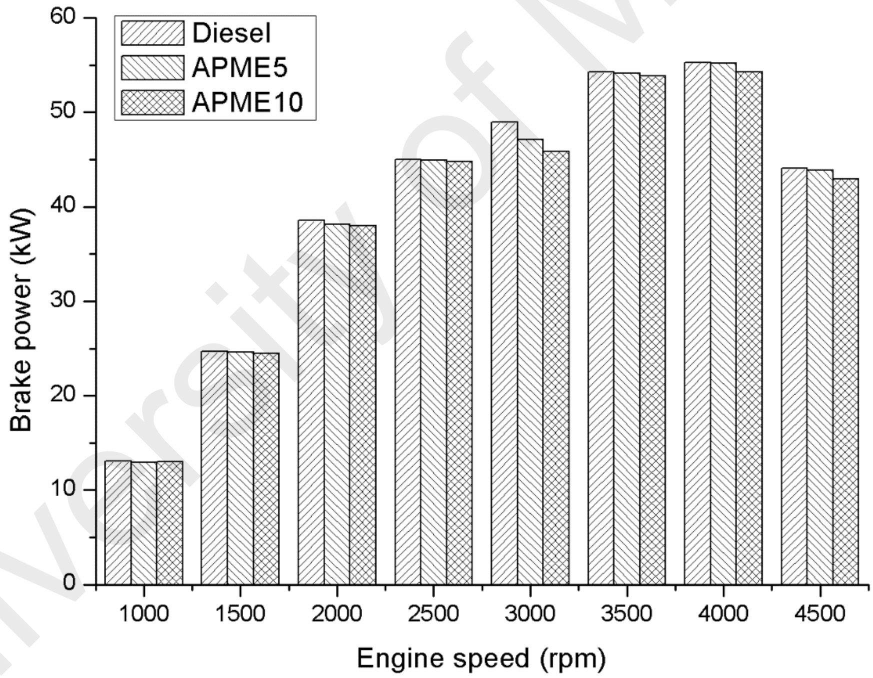


**Figure 4.2:** Variation of brake power at different engine speeds and full load condition for APME.

### 4.3.3. Brake specific fuel consumption (BSFC)

The BSFC of diesel engines mainly depends on the relationship between the volumetric fuel injection system, fuel density, viscosity, and energy contents (D. H. Qi et al., 2010b). Figure 4.3 shows the variation of BSFC for diesel, APME5, and APME10 at full load condition and different engine speeds. It was observed that BSFC values were higher when biodiesel blends were used at all engine speeds. These findings are supported in the literature (Bhupendra Singh Chauhan et al., 2012; X. Wang et al., 2013). Among the two blends, it was found that APME5 gave the lowest BSFC value, 328 g/kWh at 2000 rpm, while APME10 gave the highest BSFC value, 390 g/kWh at 4500 rpm. Over the entire speed range, the average BSFC values for diesel, APME5, and APME10were found to be 352.96 g/kWh, 356.05 g/kWh, and 359.29 g/kWh, respectively. The average increase in BSFC compared to diesel fuel for APME5 and APME10was around 0.87% and 1.78%, respectively. These changes were significant at $p < 0.03$. This phenomenon occurs primarily because of their lower calorific values and higher density (Jindal et al., 2010; Cenk Sayin, 2010). Higher density comes into action due to volumetric effect of constant fuel injection rate of the used engine.

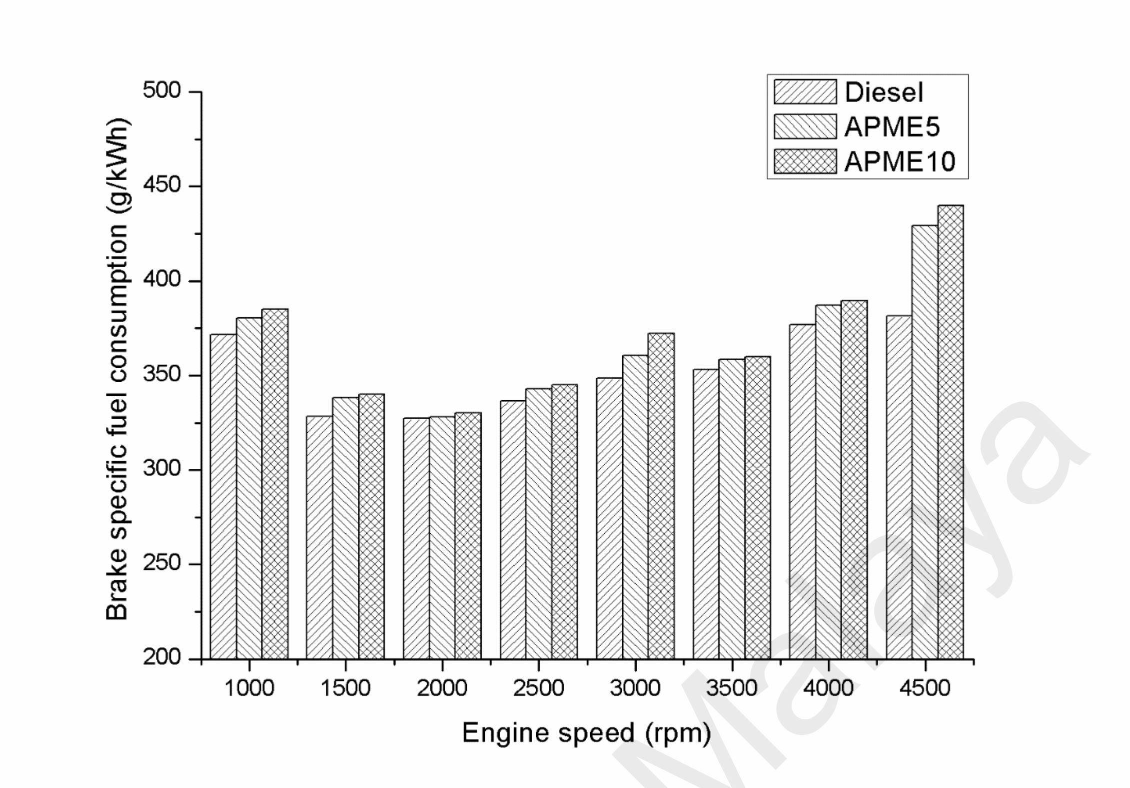


**Figure 4.3:** Variation of BSFC at different engine speeds and full load condition for APME.

## 4.4. Emission analysis for *Aphanamixis polystachya* Biodiesel

### 4.4.1. CO emission

CO is a toxic gas formed as a result of the incomplete combustion of any fuel. Generally, several factors have an effect on its emission, including engine speed, air-fuel ratio, injection pressure, injection timing, and the type of fuel used (Metin Gumus et al., 2012). Figure 4.4 shows the variation of the CO emission of diesel, APME5, and APME10 at full load condition and different engine speeds. For all samples, a reduction in CO emission was observed with engine speed increasing up to 2000 rpm, and then increased gradually up to 4500 rpm with some exceptions. For APME5, the change of CO emission compared to diesel was negligible. Over the entire speed range, APME10 gave an average reduction of CO as 4.69% compared to diesel. These results are also supported in the literature (Hirkude & Padalkar, 2012; Hwanam Kim & Byungchul Choi, 2010; Lapuerta et al., 2008a). This reduction is due to the combined effect of oxygen content and higher CN (Buyukkaya et al., 2013a; Puhan et al., 2007; Rizwanul Fattah et al., 2014). Higher CN exhibits shorter ignition delay and permits for better combustion. Then oxygen content of biodiesel comes into play which enhances the combustion process. In addition, as the percentage of biodiesel in the blend increases, the higher oxygen content of biodiesel allows more carbon molecules to burn, and therefore combustion becomes more complete.

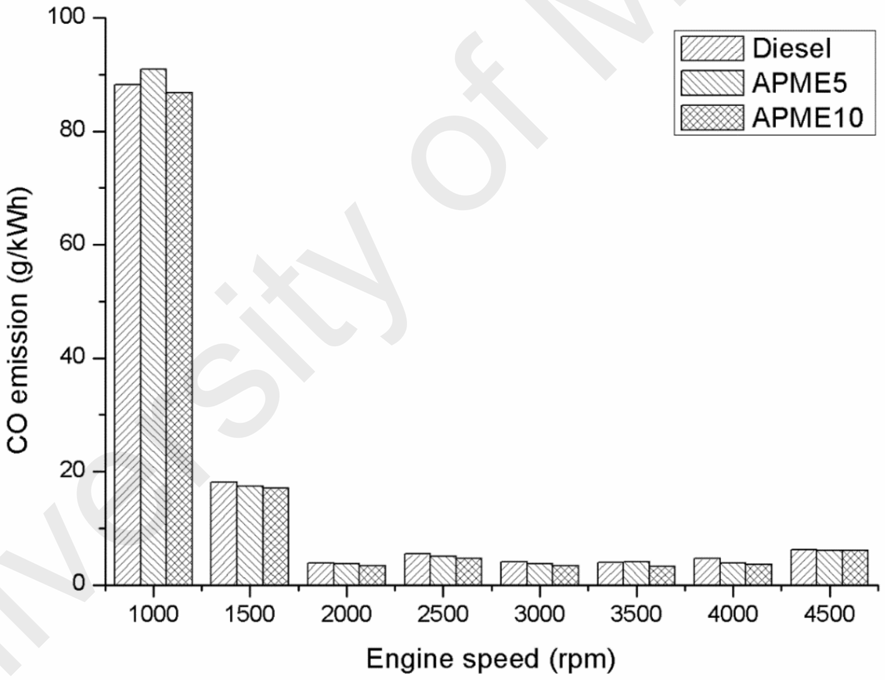


**Figure 4.4:** Variation of CO emissions at different engine speeds and full load condition for APME

### 4.4.2. HC emission

Unburned HCs are mainly emitted due to incomplete combustion of the fuel and the flame quenching in crevice regions and at cylinder walls. Figure 4.5 shows the variation of HC emission of diesel, APME5, and APME10 at full load condition and different engine speeds. It is evident that unburned hydrocarbon emissions for biodiesel-diesel blends are lower than that of diesel. Over the entire speed range, the average reduction of HC emission for APME5 and APME10 are of 9.86% and 22.32%, respectively compared to diesel fuel. It can be seen that HC emissions were reduced as the percentage of biodiesel in the blends increased. The oxygen content of biodiesel might have provided some advantageous conditions (post flame oxidation, higher flame speed, etc.) during air–fuel interactions, particularly in the fuel-rich regions, which enhanced the oxidation of unburned HC, thus reducing HC significantly (A. M. Liaquat et al., 2014; Ozsezen & Canakci, 2011a).

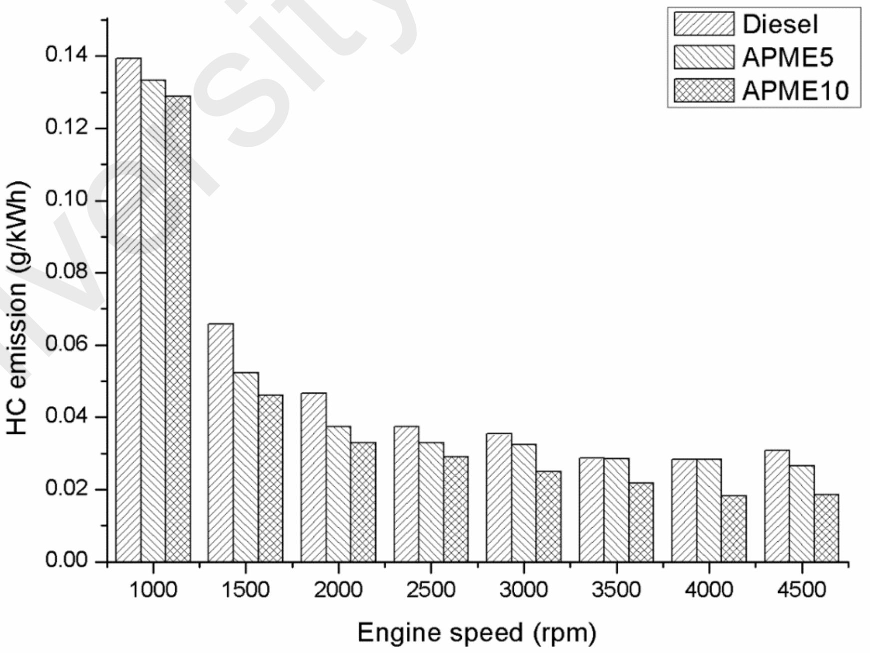


**Figure 4.5:** Variation of HC emissions with respect to engine speed at full load condition for APME

### 4.4.3. NO emission

**Figure 4.6** shows the variation of NO emission of diesel and biodiesel-diesel blends. It was observed that NO values were little higher when APME5 and APME10 blends were used. It was found that NO emission increased with increasing engine speed for all samples. A similar observation was made for other biodiesel blends in (Rizwanul Fattah et al., 2014). Over the entire speed range, the average NO emission for diesel, APME5, and APME10 was 4.39 g/kWh, 4.48 g/kWh, and 4.7 g/kWh, respectively. The average increase in NO emission for APME5 and APME10compared to diesel was 2.18% and 7.32%, respectively. These changes were significant at $p < 0.01$. Biodiesel is an oxygenated fuel and possesses a shorter ignition delay due to higher CN. High oxygen content of biodiesel creates high in-cylinder temperature under both premixed and diffusion combustion conditions (Adi et al., 2009; D. Kannan et al., 2012). Therefore, it is expected that biodiesel blends will combust earlier and hence form higher NO compared to diesel.

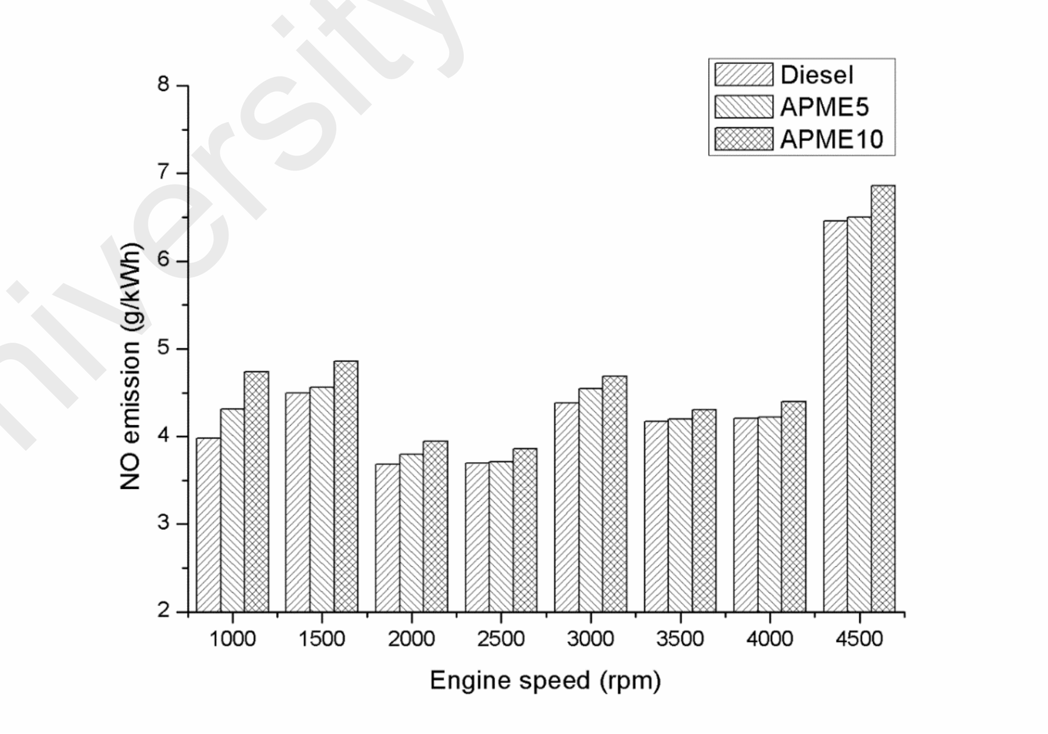


**Figure 4.6:** Variation of NO emissions at different engine speeds and full load condition for APME

### 4.4.4. $CO_2$ emission

The variation of $CO_2$ emission with engine speed for diesel, APME5, and APME10 is shown in **Figure 4.7**. $CO_2$ is the key parameter that indicates the combustion efficiency of a particular fuel. Higher $CO_2$ emission refers to better combustion (M. Gumus, 2010). The $CO_2$ emission of blends is always higher than that of diesel. This corroborates the earlier explanations provided. APME10 produces the highest $CO_2$ emission with a mean of 6.21% higher compared to diesel, due to presence of more fuel borne oxygen that results in better combustion (Roskilly et al., 2008). The average increase in $CO_2$ emission compared to diesel for APME5 was 4.41%.

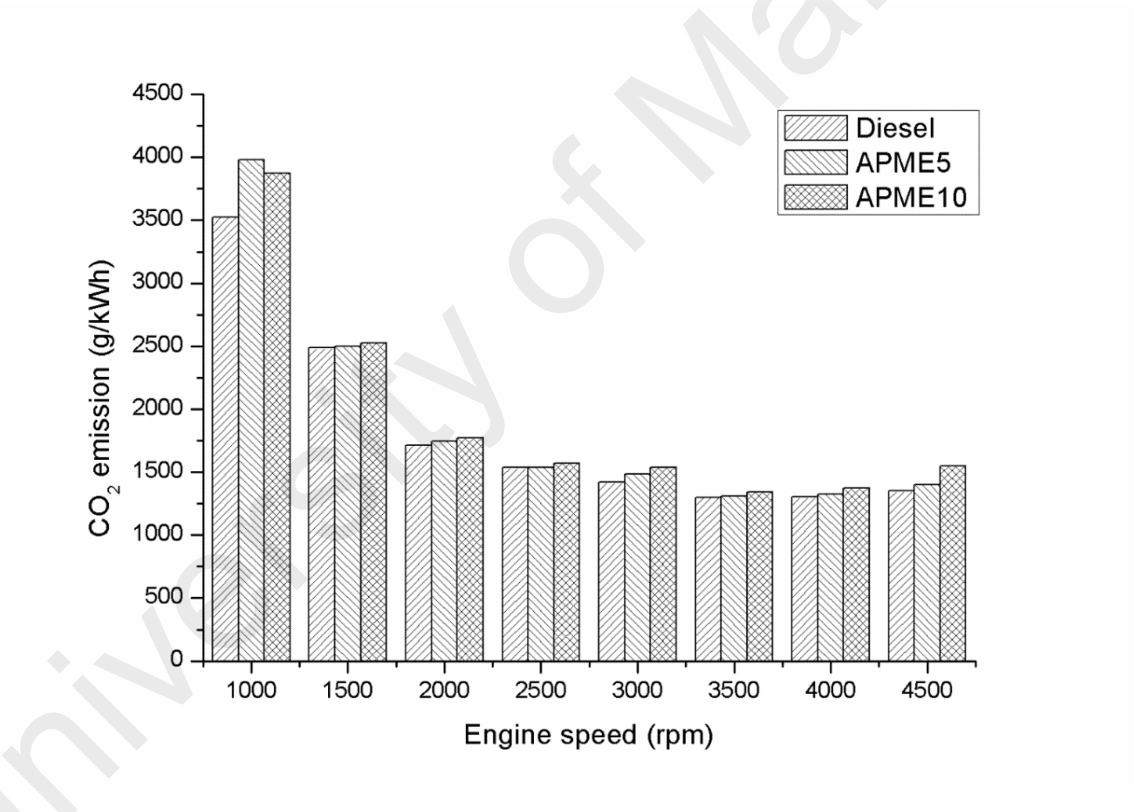


**Figure 4.7:** Variation of $CO_2$ emissions at different engine speeds and full load condition for APME

### 4.5. Engine performance for Jatropha Biodiesel

The results obtained in this study with neat diesel, different biodiesel blends (JB5, JB10, JB15 and JB20) have been discussed with respect to engine performance. Engine tests were carried out by varies the engine speed (1000 rpm to 4000 rpm). The effects of JCME blends on brake torque, brake power, and BSFC etc.; and are represented in the figures (**Figure 4.8** to **Figure 4.10**).

### 4.5.1. Brake torque

**Figure 4.8** shows the variation of the engine torque at full load condition and different engine speeds when fuelled by diesel, JB5, JB10, JB15 and JB20. It has been observed that the torque for blends JB5, JB10, JB15 and JB20 was lower than that for diesel. These results are in agreement with the earlier literature and also similarity with the results for APME blends. Initially, engine torque increases as the engine speed increases until it reaches a maximum value and then starts decreasing with further increasing engine speed. Over the whole speed range, the average torque values for diesel, JB5, JB10, JB15 and JB20 were found to be 115.8 Nm, 111.29 Nm, 110.71 Nm, 111.36 Nm and 110.14 Nm, respectively. Thus, for the same amount of fuel injected, JB5, JB10, JB15 and JB20 gave an average reduction in torque of 3.92%, 4.41%, 3.86% and 4.91%, respectively, compared to pure diesel. This torque loss can be attributed to the lower heating value and higher density and kinematic viscosity compared to diesel fuel. Higher kinematic viscosity and density of blends thereby lower volatility of blends and hence result in a poor mixture formation and lower brake torque output.

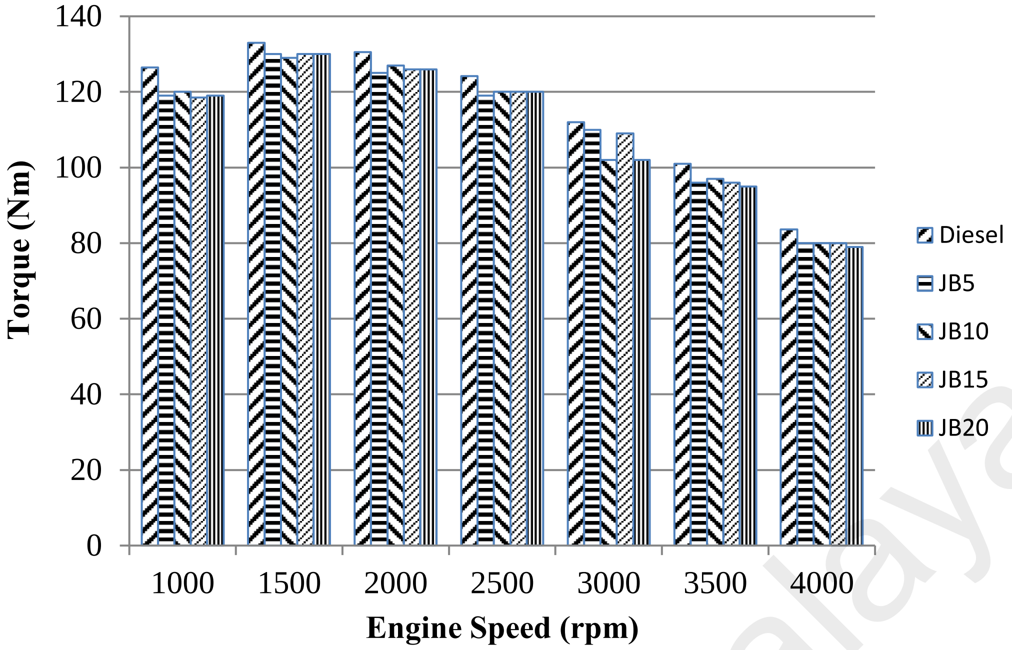


**Figure 4.8:** Variation of torque at different engine speeds and full load condition for JCME.

### 4.5.2. Brake power

**Figure 4.9** shows the variation of BP of diesel, JB5, JB10, JB15 and JB20 at full load condition and different engine speeds. In general, biodiesel blends produce lower brake power compared to pure diesel fuel. Among the four biodiesel blends, it was found that JB5 had the highest BP values overall; a maximum BP value of 37.7 kW at 3000 rpm, and a minimum BP value of 12.57 kW at 1000 rpm. JB10 had a maximum BP value of 36.44 kW at 3000 rpm, and a minimum BP value of 12.46 kW at 1000 rpm. JB15 had a maximum BP value of 35.19 kW at 3500 rpm, and a minimum BP value of 12.41 kW at 1000 rpm. JB20 had a maximum BP value of 34.82 kW at 3500 rpm, and a minimum BP value of 12.36 kW at 1000 rpm. It was also observed that the BP gradually increased with increasing engine speed up to 3000 rpm and then decreased. In addition, the BP decreased with an increasing percentage of biodiesel in the blend. Over the entire speed range, the average BP for diesel, JB5, JB10, JB15 and JB20 were 28.41 kW, 28.18kW, 27.93kW, 27.60kW and 27.37kW, respectively. The average reduction of BP compared to diesel for JB5, JB10, JB15 and JB20 were 0.8%, 1.68%, 2.84% and 3.68%, respectively.

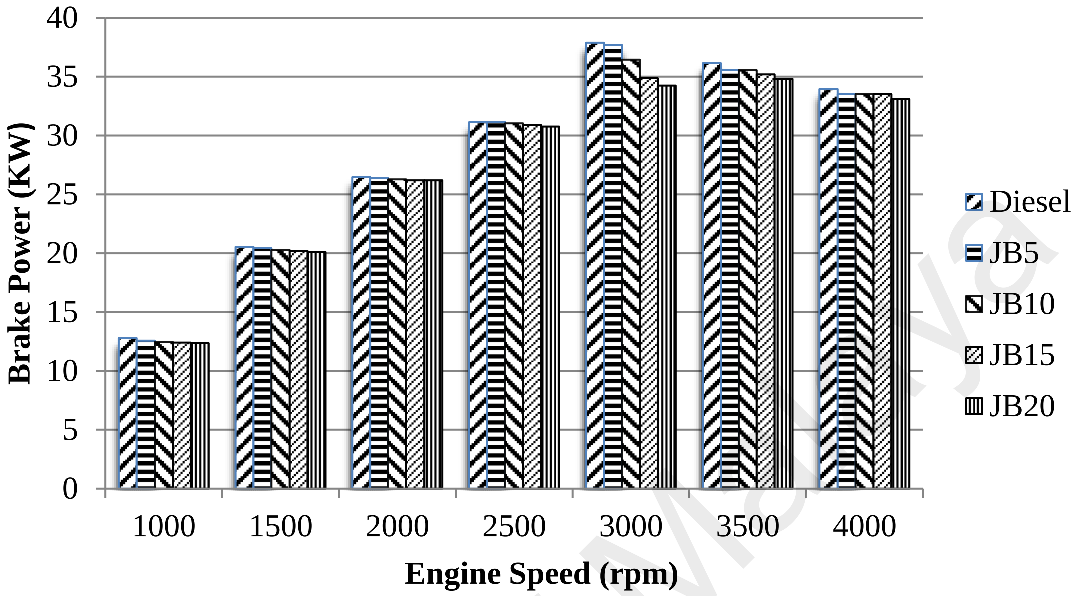


**Figure 4.9:** Variation of brake power at different engine speeds and full load condition for JCME.

### 4.5.3. Brake specific fuel consumption

The BSFC of diesel engines mainly depends on the relationship between the volumetric fuel injection system, fuel density, viscosity, and energy contents. Figure 4.10 shows the variation of BSFC for diesel, JB5, JB10, JB15 and JB20 at full load condition and different engine speeds. It was observed that BSFC values were higher when biodiesel blends were used at all engine speeds. Among the four blends, it was found that JB5 gave the lowest BSFC value, 350 g/kWh at 1500 rpm, while JB20 gave the highest BSFC value, 517 g/kWh at 4000 rpm. Over the entire speed range, the average BSFC values for diesel, JB5, JB10, JB15 and JB20 were found to be 380.43 g/kWh, 406.29 g/kWh, 412.14 g/kWh, 421.14 g/kWh, and 423.43 g/kWh, respectively. The average increase in BSFC compared to diesel fuel for JB5, JB10, JB15 and JB20 was around 6.80%, 8.33%, 10.70% and 11.30%, respectively.

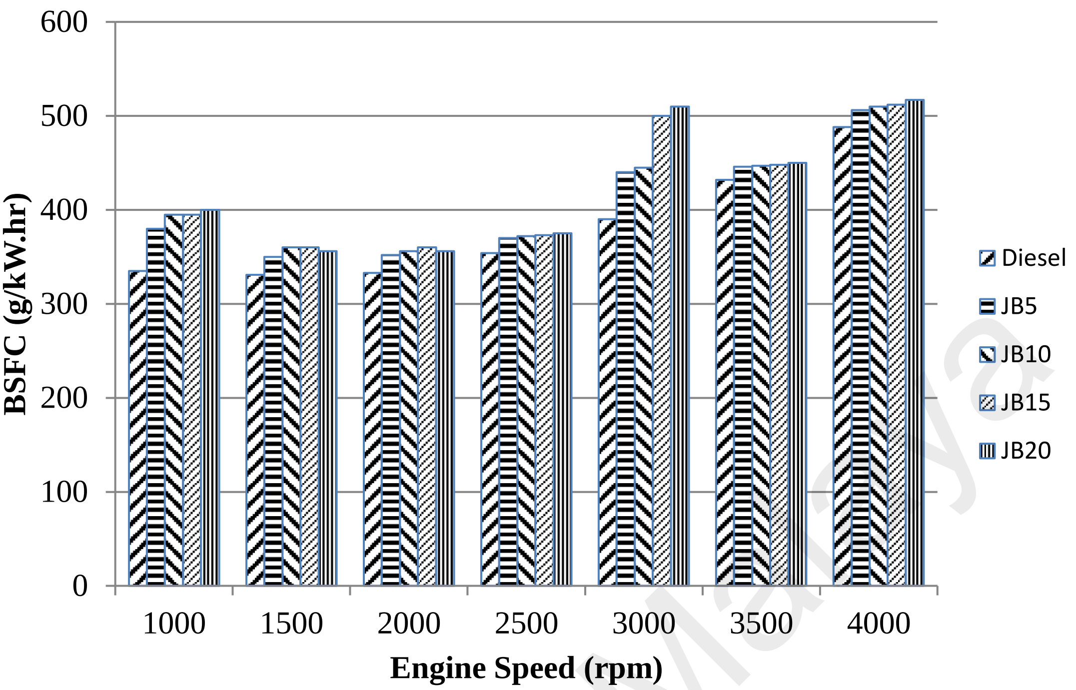


**Figure 4.10:** Variation of BSFC at different engine speeds and full load condition for JCME.

### 4.6. Emission analysis for Jatropha Biodiesel

#### 4.6.1. CO emission

Figure 4.11 shows the variation of the CO emission of diesel, JB5, JB10, JB15 and JB20 at full load condition and different engine speeds. For all samples, a reduction in CO emission was observed with engine speed increasing up to 2000 rpm, and then increased gradually up to 4000 rpm. Over the entire speed range, JB5, JB10, JB15 and JB20 the average reduction of CO were 9.74%, 11.60%, 39.87% and 53.05% compared to diesel. It was observed that CO decreased with increasing Jatropha biodiesel into blends. This reduction is due to the combined effect of oxygen content and higher CN. Higher CN exhibits shorter ignition delay and permits for better combustion. In addition, as the percentage of biodiesel in the blend increases, the higher oxygen content of biodiesel allows more carbon molecules to burn, and therefore combustion becomes more complete.

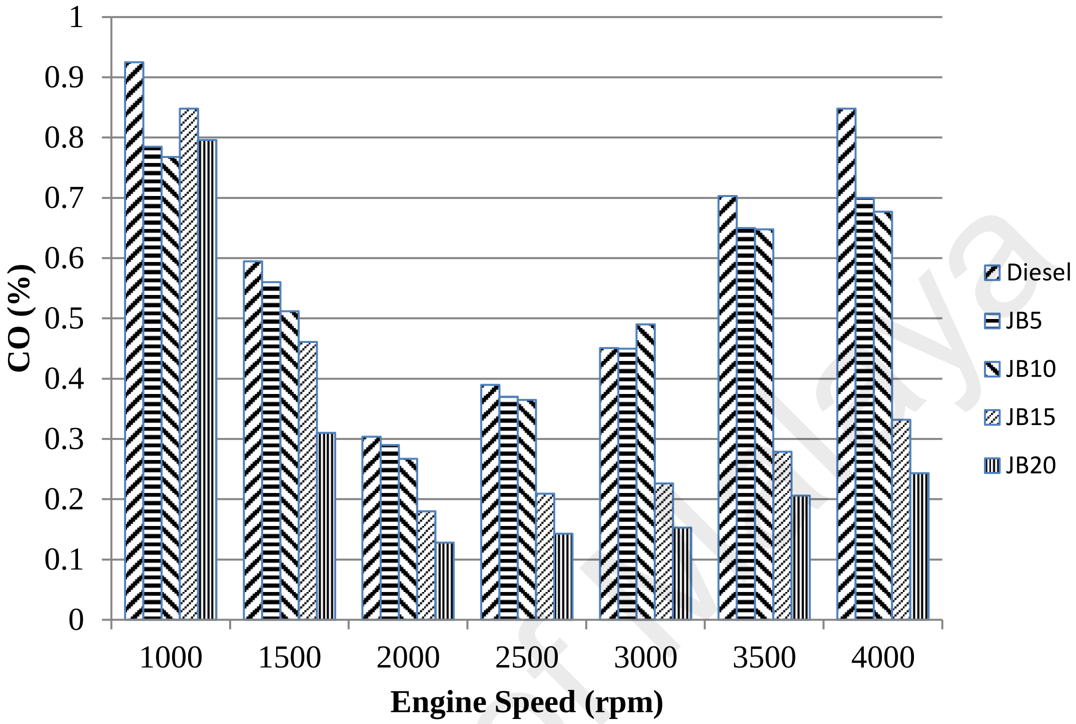


**Figure 4.11:** Variation of CO emissions at different engine speeds and full load condition for JCME.

### 4.6.2. HC emission

Unburned HCs are mainly emitted due to incomplete combustion of the fuel and the flame quenching in crevice regions and at cylinder walls. Figure 4.12 shows the variation of HC emission of diesel, JB5, JB10, JB15 and JB20 at full load condition and different engine speeds. It is evident that unburned hydrocarbon emissions for biodiesel-diesel blends are lower than that of diesel. For JB5, the change of HC emission compared to diesel was negligible. Over the entire speed range, the average reduction of HC emission for JB5, JB10, JB15 and JB20 are of 6.60%, 38.60%, 34.60% and 48.0%, respectively compared to diesel fuel. It can be seen that HC emissions were reduced as the percentage of biodiesel in the blends increased. The oxygen content of biodiesel might have provided some advantageous conditions (post flame oxidation, higher flame speed, etc.) during air–fuel interactions, particularly in the fuel-rich regions, which enhanced the oxidation of unburned HC, thus reducing HC significantly.

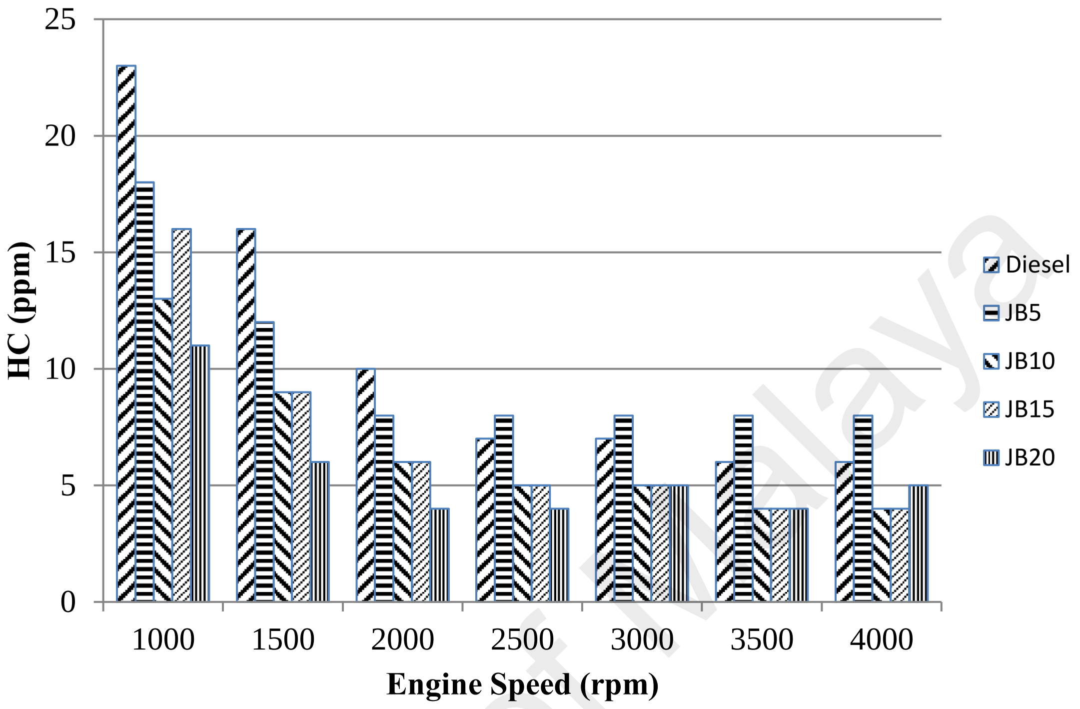


**Figure 4.12:** Variation of HC emissions with respect to engine speed at full load condition for JCME.

### 4.6.3. NO emission

**Figure 4.13** shows the variation of NO emission of diesel and biodiesel-diesel blends. It was observed that NO values were higher when JB5, JB10, JB15 and JB20 blends were used. It was found that NO emission increased with increasing engine speed for all samples. Over the entire speed range, the average NO emission for diesel, JB5, JB10, JB15 and JB20 was 199.43 ppm, 211.71 ppm, 216.14 ppm, 219.86 ppm and 222.0 ppm, respectively. The average increase in NO emission for JB5, JB10, JB15 and JB20 compared to diesel was 6.60%, 8.38%, 10.24% and 11.31%, respectively. Biodiesel is an oxygenated fuel and possesses a shorter ignition delay due to higher CN. High oxygen content of biodiesel creates high in-cylinder temperature under both premixed and diffusion combustion conditions. Therefore, it is expected that biodiesel blends will combust earlier and hence form higher NO compared to diesel.

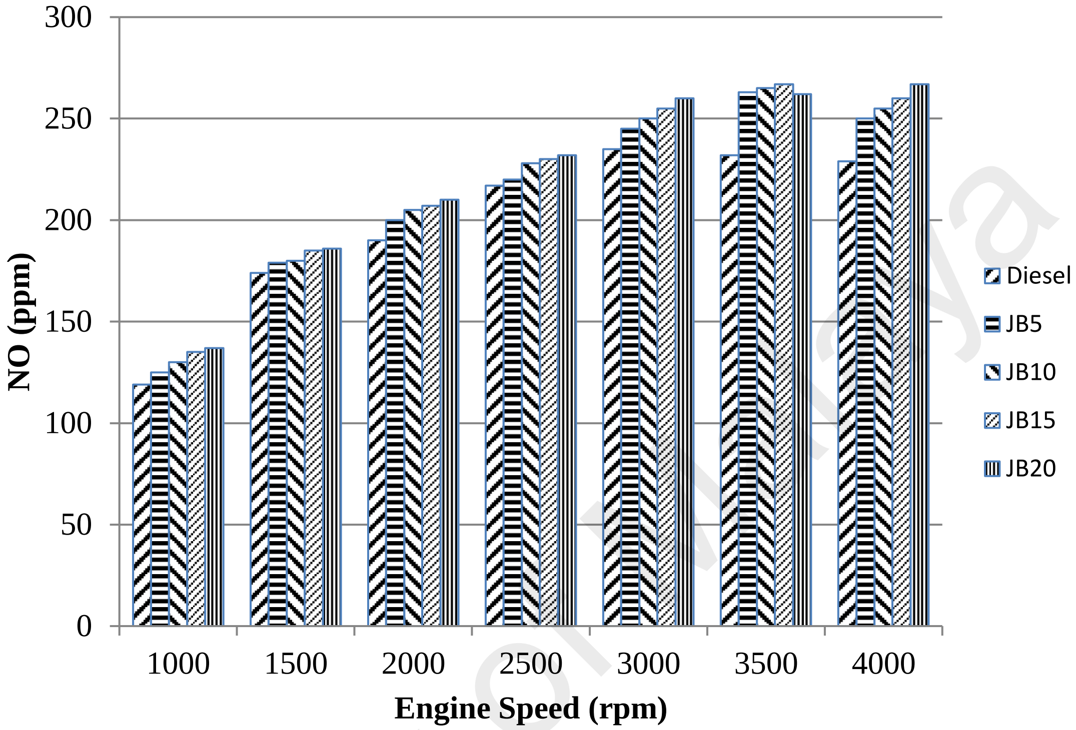


**Figure 4.13:** Variation of NO emissions at different engine speeds and full load condition for JCME.

### 4.6.4. $CO_2$ emission

The variation of $CO_2$ emission with engine speed for diesel, JB5, JB10, JB15 and JB20 is shown in **Figure 4.14**. $CO_2$ is the key parameter that indicates the combustion efficiency of a particular fuel. Higher $CO_2$ emission refers to better combustion (M. Gumus, 2010). The $CO_2$ emission for JB10 blends is higher than that of diesel. Over the entire speed range, the average $CO_2$ emission for diesel, JB5, JB10, JB15 and JB20 was 13.09 ppm, 12.92 ppm, 13.16 ppm, 12.98 ppm and 12.89 ppm, respectively. The change of $CO_2$ for Jatropha biodiesel blends with diesel is negligible.

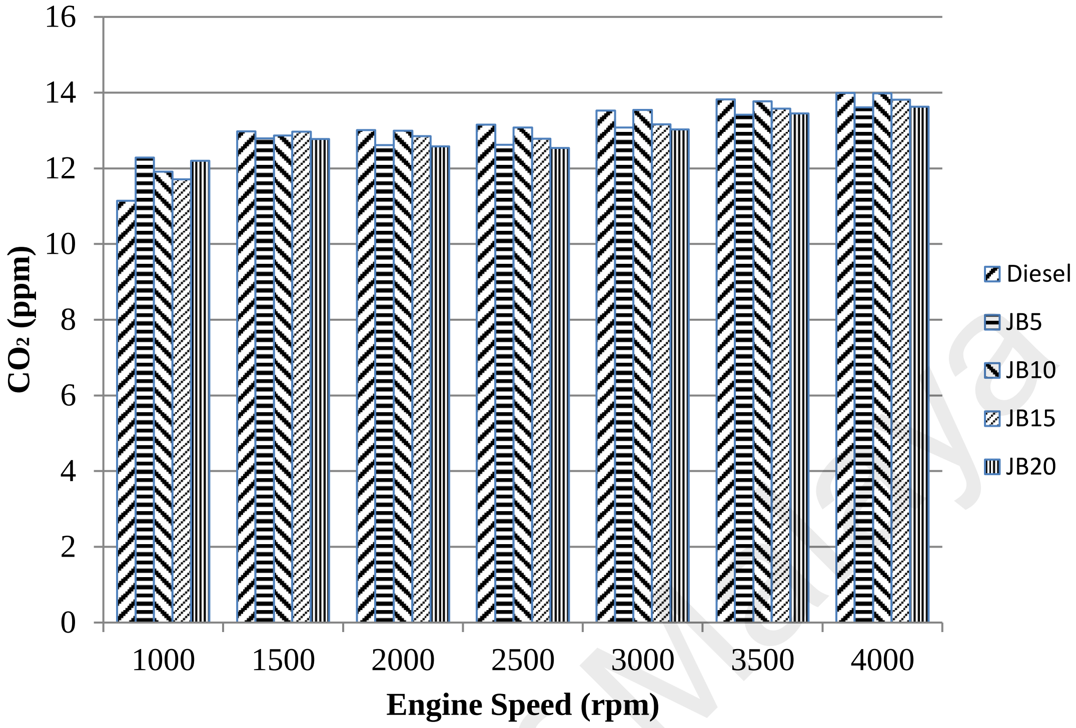


**Figure 4.14:** Variation of $CO_2$ emissions at different engine speeds and full load condition for JCME.

### 4.7. Engine performance for Jatropha Biodiesel with addition of DPPD into fuel

Performance parameters such as engine power and BSFC with respect to variable engine speed (1000~4000 rpm) have been evaluated for all test fuels and compared to diesel combustion under 100% throttle condition. The results obtained in this study with neat diesel, different biodiesel blends (JB5, JB10, JB15 and JB20) with DPPD antioxidant additive have been discussed with respect to engine performance; and are represented in the figures (**Figure 4.15** and **Figure 4.16**).

#### 4.7.1. Effect of speed, blending ratio and addition of DPPD additive on power

**Figure 4.15** represents the change in power for different biodiesel blends with and without DPPD additive compared to diesel combustion at 100% throttle position. The engine power for base diesel fuel at different engine speeds such as 1000, 1500, 2000, 2500, 3000, 3500 and 4000 rpm are 12.78, 20.53, 26.47, 31.15, 37.89, 36.14 and 33.93 kW respectively. The use of all biodiesel blends with and without DPPD additive, the reduction in power has been investigated as reasonable range +2.71% to -4.50% within 1000 to 2500 rpm engine speed. For higher engine speed operation (3000-4000 rpm), the reduction of engine power is higher for addition of DPPD antioxidant into biodiesel blends. The maximum reduction of power is observed for JB10DPPD.15 at 3000 rpm. The average reductions in engine power for JB5, JB5DPPD.15, JB10, JB10DPPD.15, JB15, JB15DPPD.15, JB20 and JB20DPPD.15 compared to JB0 are 0.80, 6.38, 1.68, 4.07, 2.84, 5.32, 3.69 and 8.24% respectively. The reason for the reduction of engine power with addition of antioxidant is possibly due to slight reduction of cylinder pressure, combustion temperature; which leads to incomplete combustion.

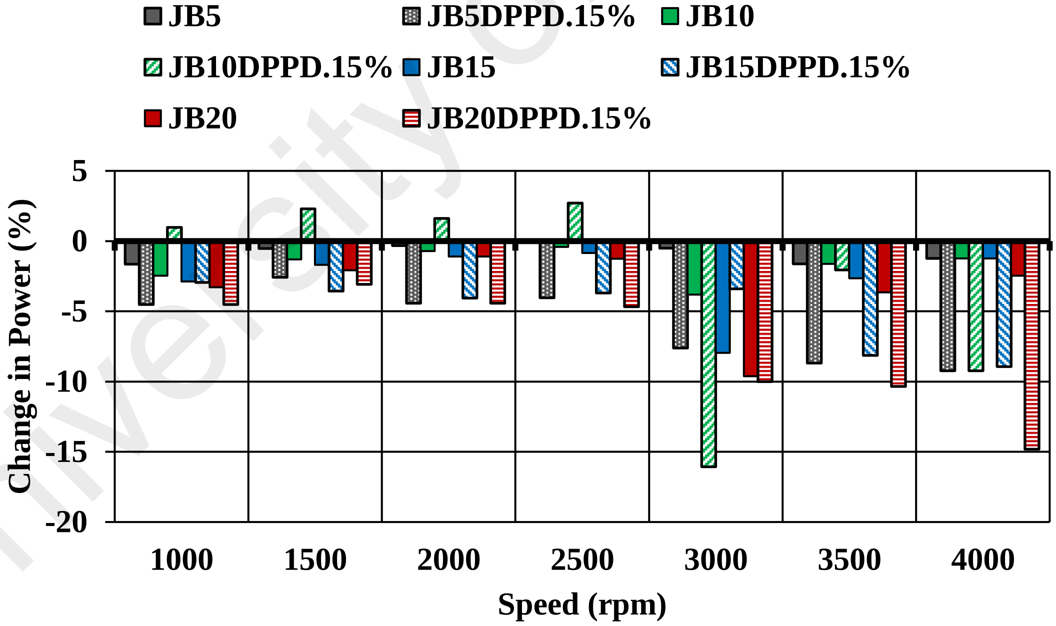


**Figure 4.15:** Change in Power (%) for different blends of Jatropha biodiesel with and without additive compared to diesel.

### 4.7.2. Effect of speed, blending ratio and addition of DPPD additive on BSFC

**Figure 4.16** presents the change in BSFC for all tested biodiesel blends with and without DPPD additive compared to diesel combustion. The value of BSFC for base diesel fuel at different engine speeds such as 1000, 1500, 2000, 2500, 3000, 3500 and 4000 rpm are 335.1, 331, 333, 354, 390, 432 and 488 g/kWh respectively. The increase in BSFC for all the biodiesel blends as well as addition of DPPD additive compared to diesel is found. It is also observed that BSFC increases with biodiesel blends. The maximum increase in BSFC (30.77% higher than that of diesel) is observed in case of JB20 at 3000 rpm. The remarkable increase in BSFC at 1000 and 3000 rpm both for with and without additive biodiesel blends JB15DPPD.15 at 3000 rpm as well as for JB20DPPD.15 at 1000 rpm is also found. However, at higher (3500-4000) engine speed, all biodiesel blends without additive are found less significant increase in BSFC compared to diesel combustion. The average increases in BSFC for JB5, JB5DPPD.15, JB10, JB10DPPD.15, JB15, JB15DPPD.15, JB20 and JB20DPPD.15 compared to JB0 are 6.79, 13.67, 8.33, 6.31, 10.7, 9.19, 11.97 and 5.99% respectively. The reason for increase in BSFC for all biodiesel blends due to lower heating value compared to diesel fuel. However, addition of DPPD antioxidant (0.15% of fuel) into JB10, JB15 and JB20 can reduce the BSFC about 1.86 1.36 and 5.35% respectively, compared to without additive into biodiesel blends. This reduction in specific fuel consumption might be due to friction reduction properties of the amines (K. Varatharajan et al., 2011).

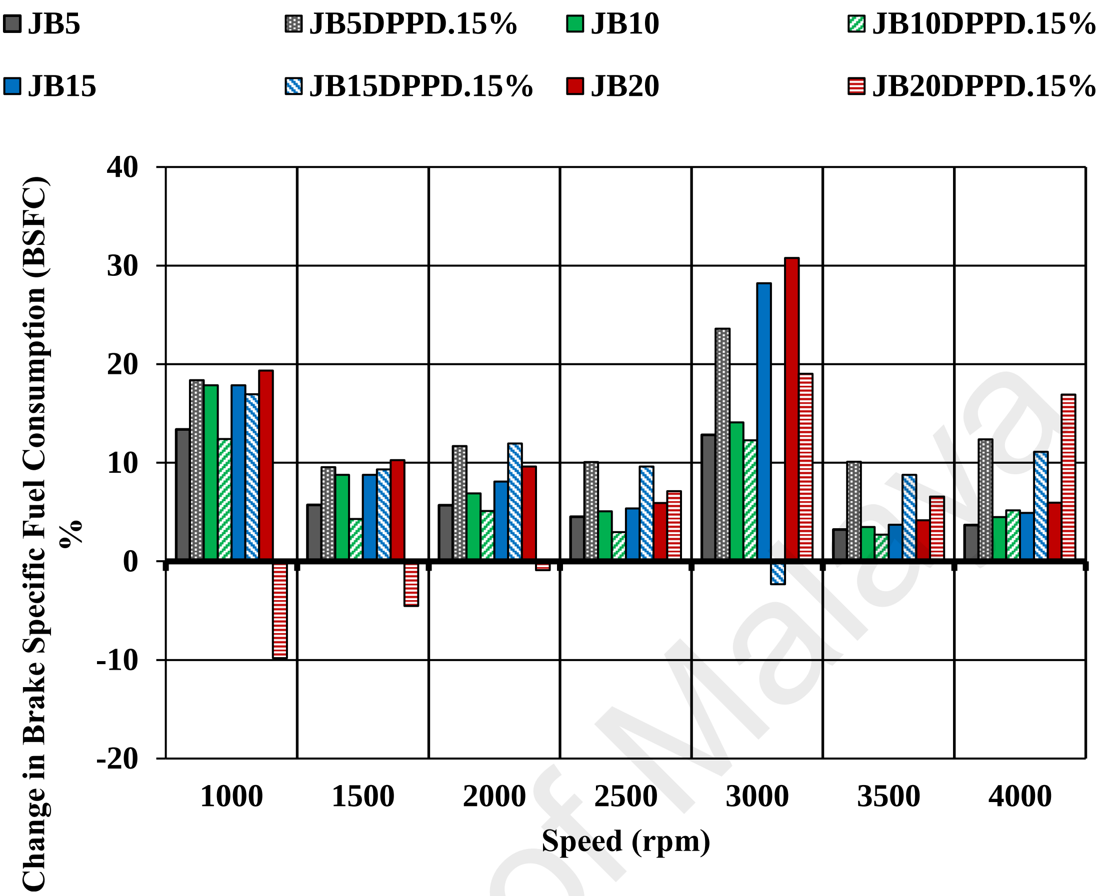


**Figure 4.16:** Change in BSFC (%) of different blends of Jatropha biodiesel with and without additive compared to diesel.

## 4.8. Engine emission studies for Jatropha Biodiesel

### 4.8.1. Effect of speed, blending ratio and addition of DPPD additive on NO emission

**Figure 4.17** shows the variation of NO emission for all tested biodiesel blends with and without DPPD additive compared to diesel combustion. The values of NO emission for base diesel fuel at different engine speeds such as 1000, 1500, 2000, 2500, 3000, 3500 and 4000 rpm are 119, 174, 190, 217, 235, 232 and 229 ppm respectively. It is observed that using all biodiesel blends of Jatropha increase the NO emission compared to diesel combustion. The average increase in NO emission for JB5, JB10, JB15 and JB20 compared to JB0 are 6.16, 8.38, 10.24 and 11.32% respectively. Several researchers investigated and found that higher $NO_x$ emissions produced for biodiesel combustion is influenced by several factors such as physicochemical properties and molecular structure of biodiesel, adiabatic flame temperature, ignition delay time, injection timing etc. However, some studies have pointed out that higher biodiesel $NO_x$ emissions occur mainly due to increase in the formation of prompt $NO_x$ in biodiesel combustion in diesel engines. Fenimore (1971) suggested that the reactions of hydrocarbon radicals (CH, $CH_2$, $C_2$, C, and $C_2H$) with molecular nitrogen are the main contributors to produce prompt $NO_x$. The production rates of HCN, N and NO increases with increasing the concentration of free radicals. Garner et al. (S Garner & Brezinsky, 2011) investigated and found that the formation rate of CH radicals is high for biodiesel combustion in diesel engine. As a result it could be pointed that the higher formation rate of free radicals is the prime reason for higher $NO_x$ emissions of biodiesel fuel. From Figure 4 it is observed that using 0.15% DPPD antioxidant additive into biodiesel blends reduce the NO emission significantly. The average reduction of NO emission for JB5DPPD.15, JB10DPPD.15, JB15DPPD.15 and JB20DPPD.15 are 8.03, 3.503, 13.65 and 16.54% respectively compared to respective biodiesel blends without additive. Moreover, addition of DPPD antioxidant in Jatropha biodiesel blends causes the NO emission same or less compared to diesel combustion except JB10DPPD.15 sample. The maximum reduction of NO emission for JB20DPPD.15 is observed about by 12.76% compared to diesel combustion at 3000 rpm engine speed. The main cause of the reduction of $NO_x$ emissions for antioxidant fuel mixtures is suppressed peroxyl free radical formations by reaction with aromatic amines. The p-phenylenediamines reacts with peroxyl radical to form primary amine radical where peroxyl radical further reacts with amine radical because of the high reactivity of amine radical and produce benzoquinonediimine as well as nitroxyl radical. The products of these reactions efficiently trap the free radicals (K Varatharajan & Cheralathan, 2013).

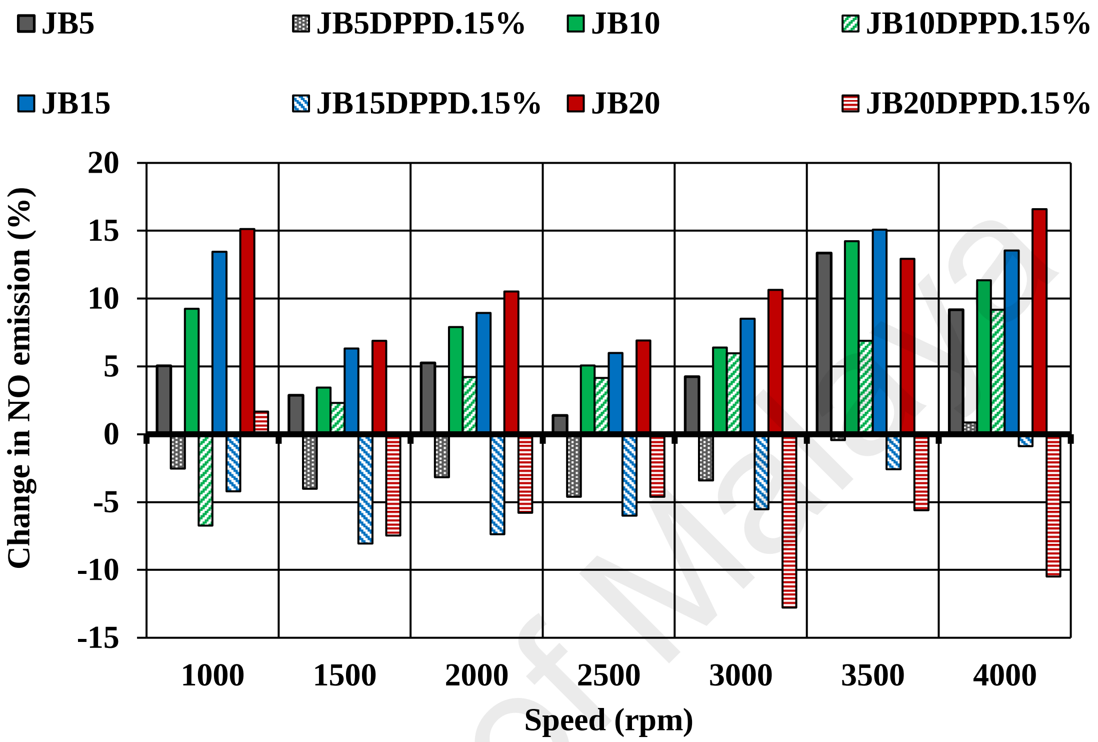


**Figure 4.17** Change in NO emission (%) of different blends of Jatropha biodiesel with and without additive compared to diesel.

### 4.8.2. Effect of speed, blending ratio and addition of DPPD additive on HC emission

Figure 4.18 shows the variation of HC emission for tested JB5, JB10, JB15 and JB20 Jatropha biodiesel blends with and without addition of DPPD antioxidant additive compared to diesel combustion at full throttle position. The values of HC emission for reference diesel fuel at different engine speeds such as 1000, 1500, 2000, 2500, 3000, 3500 and 4000 rpm are 23, 16, 10, 7, 7, 6 and 6 ppm. All biodiesel blends sample reduce HC emission significantly compared to diesel is observed from Figure 5. The average reductions of HC emission for JB5, JB10, JB15 and JB20 compared to JB0 are 12, 28 , 34.67 and 48% respectively. With addition of 0.15% DPPD antioxidant into

JB5, JB10, JB15 and JB20 biodiesel blends, the increase in HC emission compared to without additive into biodiesel blends are 3.03, 3.70, 10.20 and 7.69% respectively. Although with addition of DPPD antioxidant additive into biodiesel blends increase the HC emission due to reduce the oxidation capability of HC, these values are remain lower than that of diesel. The lower value of HC emission averagely for JB5DPPD.15, JB10DPPD.15, JB15DPPD.15 and JB20DPPD.15 compared to JB0 are 9.33, 25.33, 28 and 44% respectively. It is also observed from these results with or without additive that HC emission reduces continuously compared to diesel combustion with increasing biodiesel percentage into fuel. Having high oxygen content into biodiesel, it leads to prolong the complete combustion results lower HC emission.

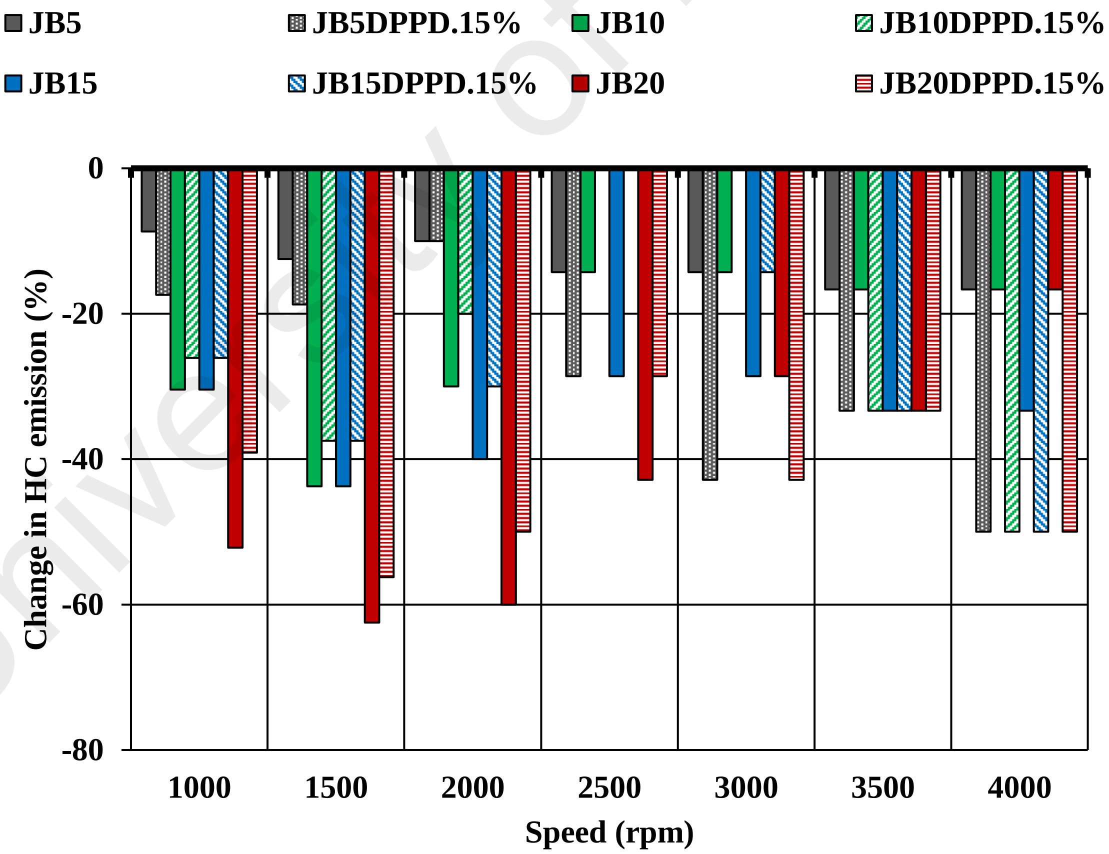


**Figure 4.18:** Change in HC emission (%) of different blends of Jatropha biodiesel with and without additive compared to diesel.

### 4.8.3. Effect of speed, blending ratio and addition of DPPD additive on CO emission

**Figure 4.19** shows the variation of CO emission for tested JB5, JB10, JB15 and JB20 Jatropha biodiesel blends with and without addition of DPPD antioxidant additive compared to diesel combustion at full throttle position. The values of CO emission for diesel combustion at different engine speeds such as 1000, 1500, 2000, 2500, 3000, 3500 and 4000 rpm are 0.925, 0.595, 0.304, 0.39, 0.451, 0.703 and 0.848 respectively. It is observed that biodiesel blends reduce the CO emission significantly compared to diesel. The average reduction of CO emission for JB5, JB10, JB15 and JB20 compared to JB0 are 9.75, 11.6, 39.88 and 53.06% respectively. The main reason of CO emission reduction with biodiesel combustion is that the high oxygen content of biodiesel which leads to complete combustion. However, the average change in CO emission with addition of DPPD antioxidant additive into tested biodiesel blends such as JB5DPPD.15, JB10DPPD.15, JB15DPPD.15 and JB20DPPD.15 compared to JB0 are +7.02, -47.89, +5.19 and -13.40% respectively. Moreover, with addition of additive into biodiesel blends increase the CO emission significantly. However, the level of CO emission with the addition of antioxidant is still lower than that of diesel. The reasons for the increase in CO emission with addition of antioxidant additive into biodiesel blends can be explained as additive reduce the oxidation capability of CO. However, during oxidation peroxyl ($HO_2$) and hydrogen peroxide ($H_2O_2$) radicals are produced successively. By absorbing heat inside the combustion chamber, these radicals are further converted into hydroxyl (OH) radicals. These OH radicals are mostly responsible for the conversion of CO into $CO_2$. As addition of DPPD antioxidant additive into Jatropha biodiesel blends reduce the peroxyl and hydrogen peroxide radicals, it has negative impact on the formation of OH radicals as well as oxidation of CO.

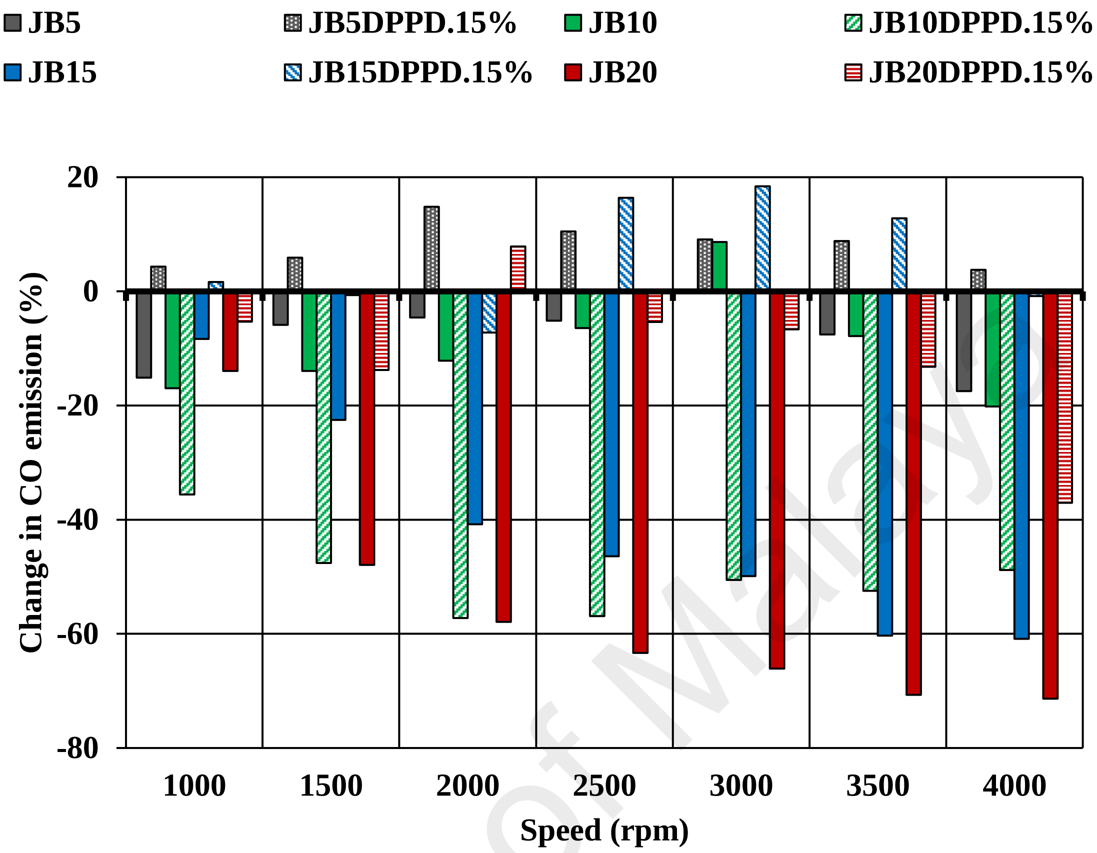


**Figure 4.19:** Change in CO emission (%) of different blends of Jatropha biodiesel with and without additive compared to diesel.

### 4.8.4. Effect of speed, blending ratio and addition of DPPD additive on Exhaust Gas Temperature (EGT)

Figure 4.20 shows the change in EGT for tested JB5, JB10, JB15 and JB20 biodiesel blends with and without addition of DPPD antioxidant additive compared to diesel combustion at full throttle condition. The values of EGT for diesel combustion at different speeds such as 1000, 1500, 2000, 2500, 3000, 3500 and 4000 rpm are 106.9, 136.7, 154, 185, 192.6, 211.5 and 230°C respectively. The results show that the exhaust gas temperature increased with increase in engine speed in all cases.  From Figure 4.13 it is observed that all biodiesel tested samples with or without addition of DPPD antioxidant increase the EGT compared to diesel combustion. The average increase in

EGT for JB5, JB5DPPD.15, JB10, JB10DPPD.15, JB15, JB15DPPD.15, JB20 and JB20DPPD.15 compared to JB0 are 9.89, 5.50, 6.44, 2.69, 2.41, 0.40, 7.75 and 6.21% respectively. This behavior may be related to the oxygenated nature of biodiesel which will lead more complete combustion compared to diesel combustion and so produce higher exhaust gas temperature. Moreover, the average reductions of EGT for JB5DPPD.15, JB10DPPD.15, JB15DPPD.15 and JB20DPPD.15 compared to respective Jatropha biodiesel blends are 3.99, 3.52, 1.95 and 1.43% respectively. This may happen due to reduction of the oxidation capability of HC and CO with the addition of DPPD antioxidant which leads to prolong the incomplete combustion compared to biodiesel blends and results lower the EGT.

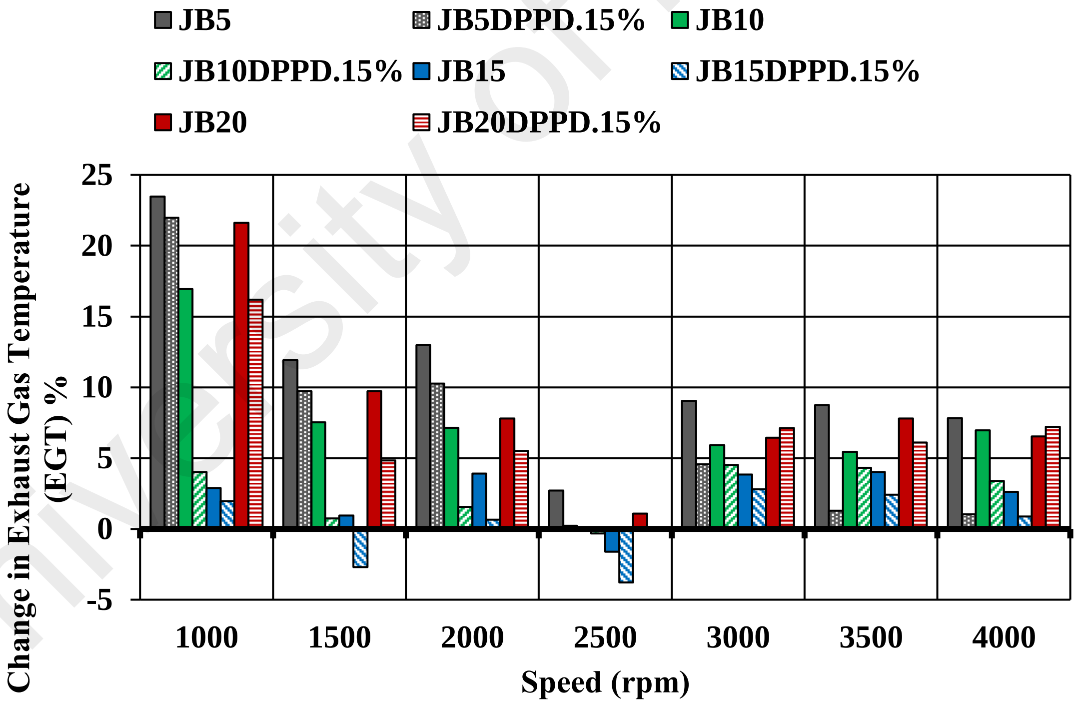


**Figure 4.20:** Change in EGT (%) of different blends of Jatropha biodiesel with and without additive compared to diesel.

# CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

As a renewable energy source, biodiesel has attracted a great attention among other transportation fuels. However, Biodiesel combustion produces high $NO_x$ emissions compared to diesel combustion. As such, this study presents the physicochemical properties of APME biodiesel and its blends 5% and 10% by volume blends of APME with diesel were evaluated in a multi-cylinder diesel engine. The aim of this experimental work was to investigate the impacts of DPPD antioxidant additive on $NO_x$ emissions from multi cylinder diesel engine fuelled with Jatropha biodiesel blends.
Based on the experimental results, the following conclusions can be drawn.

- Apart from oxidation stability and CN, the properties of *Aphanamixis polystachya* biodiesel, Jatropha biodiesel and their blends with diesel conform to ASTM D6751 and ASTM D7467standards, respectively.
- Over the entire speed range, the average reduction of brake power compared to diesel for APME5 and APME10 was 0.9% and 2.1%, respectively. APME5 and APME10 increased the BSFC by 0.87% and 1.78%, respectively, compared to that of diesel fuel. The average reduction of BP compared to diesel for JB5, JB10, JB15 and JB20 were 0.8%, 1.68%, 2.84% and 3.68%, respectively. The average increase in BSFC compared to diesel fuel for JB5, JB10, JB15 and JB20 was around 6.80%, 8.33%, 10.70% and 11.30%, respectively.
- APME10 gave an average reduction of CO emission by 4.69% compared to that of diesel. The average reductions in HC emission compared to diesel for APME5 and APME10 were 9.86% and 22.32%, respectively. Over the entire speed range, JB5, JB10, JB15 and JB20 the average reduction of CO were 9.74%, 11.60%, 39.87% and 53.05% compared to diesel.

- The average increase in NO emission for APME5 and APME10 compared to diesel were 2.18% and 7.32%, respectively. The average increase in NO emission for JB5, JB10, JB15 and JB20 compared to diesel was 6.60%, 8.38%, 10.24% and 11.31%, respectively.
- With addition of DPPD, the average reduction of NO emission for JB5DPPD.15, JB10DPPD.15, JB15DPPD.15 and JB20DPPD.15 are 8.03, 3.503, 13.65 and 16.54% respectively compared to respective biodiesel blends without additive. Moreover, addition of DPPD antioxidant in Jatropha biodiesel blends the value of NO emission remain same or lower compared to diesel.
- The addition of DPPD antioxidant additive addition in tested Jatropha biodiesel blends increase in HC emission slightly. However, compared to diesel, the average reduction of HC emission for JB5DPPD.15, JB10DPPD.15, JB15DPPD.15 and JB20DPPD.15 are 9.33, 25.33, 28 and 44% respectively.
- Increase in CO emission with addition of DPPD antioxidant in all Jatropha biodiesel blends significantly is observed. However, when compared to diesel these values remain lower.
- The engine performance was reduced with DPPD additive in Jatropha biodiesel blends. The reason for the reduction in engine power is possibly due to slight reduction of cylinder pressure as well as combustion temperature with addition of antioxidant.

The overall results showed that all biodiesel blends reduce the engine performance and HC, CO emissions. However they increase the $NO_x$ when compared to diesel combustion which is the main barrier for biodiesel market expansion. The addition of 0.15% (m) DPPD in all Jatropha biodiesel blends reduces the $NO_x$ emission averagely when compared to biodiesel combustion without addition of additive.

## 5.2 Recommendations

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

- Further research is required to study the investigation of $NO_x$ technology by in diesel engine. By modifying the engine test bed such as applying EGR, LTC are also better way to reduce $NO_x$ for biodiesel combustion in diesel engine.
- This research work only focusses for two types of non-edible based biodiesel on engine performance and emission for multi cylinder diesel engine. Other fuels can also be used.

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# APPENDIX A

## Journal Publications

1. **Palash, S.M.,** Kalam M.A., Masjuki H.H., Masum B.M., Rizwanul Fattah I.M. & Mofijur M., (2013), Impacts of biodiesel combustion on $NO_x$ emissions and their reduction approaches. *Renewable and Sustainable Energy Reviews*. Volume 23: p. 473-490. Doi: http://dx.doi.org/10.1016/j.rser.2013.03.003. [ISI indexed, Q1].

2. **Palash, S.M.,** Masjuki H.H., Kalam M.A., Masum B.M. Sanjid A & Abedin M.J. (2013), State of the art of $NO_x$ mitigation technologies and their effect on the performance and emission characteristics of biodiesel-fueled Compression Ignition engines. *Energy Conversion and Management*. Volume 76: p. 400-420. DOI: http://dx.doi.org/10.1016/j.enconman.2013.07.059. [ISI indexed, Q1].

3. **Palash S.M.,** Kalam M.A., Masjuki H.H., Arbab M.I., Masum B.M. & Sanjid A. (2014), Impacts of $NO_x$ reducing antioxidant additive on performance and emissions of a multi-cylinder diesel engine fueled with Jatropha biodiesel blends. *Energy Conversion and Management*. Volume 77, January 2014, Pages 577-585. DOI: http://dx.doi.org/10.1016/j.enconman.2013.10.016. [ISI indexed, Q1].

4. **Palash S.M.,** Masjuki H.H., Kalam M.A., Atabani A.E., Rizwanul Fattah I.M., & Sanjid, A. (2015), Biodiesel production, characterization, diesel engine performance, and emission characteristics of methyl esters from Aphanamixis polystachya oil of Bangladesh. *Energy Conversion and Management*. Volume 91, p. 149–157. DOI: http://dx.doi.org/10.1016/j.enconman.2014.12.009. [ISI indexed, Q1].

# Conference Publications

1. **Palash, S.M.,** Kalam M.A., Masjuki H.H., Masum B.M., & Sanjid A., (2013), Impacts of Jatropha biodiesel blends on engine performance and emission of a multi cylinder diesel engine. Proc. of the Intl. Conf. on Future Trends in Structural, Civil, Environmental and Mechanical Engineering -- FTSCEM 2013. ISBN: 978-981-07-7021-1 doi:10.3850/ 978-981-07-7021-1_58.

2. **Palash, S.M.,** Kalam M.A., Masjuki H.H. & Masum B.M., (2013) Impacts of N, N′-diphenyl-1, 4-phenylenediamine (DPPD) antioxidant additive in Jatropha biodiesel blends to reduce $NO_x$ emission of a multi cylinder vehicle type diesel engine. Advanced Materials Research Vols. 774-776 pp 784-790. doi:10.4028/www.scientific.net/AMR.774-776.784.

3. **Palash S.M.,** Masjuki H.H., Kalam M.A., Atabani A.E. & Masum B.M. (2014) Biodiesel Production from Aphanamixis Polystachya (Pitraj oil) and its Comparative Analysis of Fuel Properties with Diesel as an Alternative Fuel in Diesel Engine. Ref. No.: ICMERE-2013-PI-059.