

ABSTRACT

OGUNKOYA, DOLANIMI OLUGBENGA. Investigation of the Effects of Emerging Alternative Fuels and Additives on Compression Ignition Engine Performance, Combustion and Emissions. (Under the direction of Dr. Tiegang Fang.)

Internal combustion engines play a significant role in present society. The use of internal combustion engines, however, has drawbacks mostly in the areas of fuel security and pollutant emissions. Renewable fuels are means by which both drawbacks may be resolved. As renewable fuels can be produced through different means and from different resources with quite different properties, there is a need to understand the effects on their applications in internal combustion engines. This dissertation focuses on contributing to the use of renewable fuels in internal combustion engines by testing and understanding the effects of emerging alternative fuels and renewable additives in compression-ignition engines.

The works discussed here were performed in a compression-ignition engine. In the first set of experiment, the performance, combustion and emissions from an engine running second generation biofuels, also called renewable diesel, were investigated. From this experiment, it was determined that diesel engine performance did not change much when run on renewable diesel. Renewable diesel had longer ignition delays and resulted in significantly lower engine emissions including soot with the exception of hydrocarbon emissions when compared to conventional diesel fuel.

Another emerging second generation biofuel, called biomass to liquid fuel (BTL), was compared to diesel fuel and a first generation biodiesel. It was determined from the result of this experiment that running a diesel engine on BTL improved fuel economy and thermal efficiency. The mechanical efficiency of the engine running on BTL was found to be similar to that of diesel and biodiesel as engine load increased. BTL was also observed to

have a shorter ignition delay when compared to conventional diesel but longer ignition delay when compared to biodiesel. Overall, diesel engine running on BTL had lower engine emissions with the exception of NO_x when compared to diesel.

The third experiment is a slight deviation from the concept of renewable fuels. In this experiment, fuel in water emulsion using a renewable surfactant (carboxymethylated Kraft Lignin) was used in the engine. Three different fuels, including diesel, biodiesel and jet fuel, were used in making the fuel emulsions. The fuel emulsions generally resulted in improved engine performance but poorer fuel consumption. Considering fuel content only in the emulsions, fuel economy became better than the base fuels with the exception of jet fuel. Fuel emulsions had longer ignition delays than their base fuel counter parts. Engine emissions of fuel emulsions depend on engine operating conditions and the type of base fuel.

The final study performed in this dissertation focused on the use of renewable fuel additives. These additives, catechol, vanillin, guaiacol, vanillin ester, catechol ester were obtained from the pyrolysis of lignin, a renewable compound. It was found from this study that when dissolved in a solvent and added in small quantities to diesel fuel as an additive, most of the compounds resulted in a better engine performance. With the exception of vanillin ester, the compounds mostly had little to no impact on the combustion profile of the engine but still resulted in much lower emissions when compared to diesel.

All these results have been positive especially with regards to emissions reduction with the additional bonus of been from renewable sources. It is clear then that fuels and fuel additives from renewable sources have the potential for improving the internal combustion engine with better combustion and lower emissions.

© Copyright 2014 by Dolanimi Olugbenga Ogunkoya

All Rights Reserved

Investigation on the Effects of Emerging Alternative Fuels and Additives on Compression
Ignition Engine Performance, Combustion and Emissions

by
Dolanimi Olugbenga Ogunkoya

A dissertation submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Doctor of Philosophy

Mechanical Engineering

Raleigh, North Carolina

2014

APPROVED BY:

Dr. Tiegang Fang
Chair of Advisory Committee

Dr. William Roberts

Dr. Stephen Terry

Dr. Alexi Saveliev

DEDICATION

Dedicated to my family for all their love, support and understanding.

BIOGRAPHY

Born in Lagos, Nigeria in 1985, Dolanimi had the opportunity to attend multiple high schools in different countries. He began his engineering education in 2003 at New Jersey Institute of Technology where he graduated with a B.S. degree in Mechanical Engineering. Feeling somewhat unaccomplished, he decided to pursue a Master's degree in Mechanical Engineering which he obtained from North Carolina State University in 2009 in the area of energy savings in industry. With a growing interest in renewable energy, Dolanimi decided to pursue a Ph.D degree which he began in 2010.

ACKNOWLEDGMENTS

I would like to express my gratitude to my advisor, Dr. Tiegang Fang, who gave me the opportunity and introduced me to internal combustion engines. Dr. Fang also helped me extensively through the program and did not give up on me even when I must have felt hopeless.

I would also like to thank members of my committee, Dr. Stephen Terry, who was the chair of my Master's committee and had to deal with all my shortcomings as a Master student. I would also like to thank Dr. Roberts who has also played an integral part in my research work. The renewable diesel discussed in this dissertation for instance was only made possible through his work on biofuel production. I would also like to thank Dr. Saveliev for his patience with me while attempting to explain some heat transfer theories. All of my interactions with members of the committee have been indispensable to me as a whole as well as my research. I would also like to use this opportunity to thank Dr. Wenqiao Yuan for taking time out of his busy schedule to act as the Graduate School Representative on my committee.

I am grateful to the invaluable help I received from Mr. Skip Richardson and Mr. Steve Cameron of the machine shop. I could not have gotten much done without their expertise.

I have worked with a lot of people in one way or another and do not think I can recall them all. Ji Zhang, Thomas Powell, Aaron McCullough, Wei Jing, Steven Bohon, Myles

Bohon, Brian McCann, Robert Natelson, Nirajan Thapaliya, Shanshan Yao, Pin-chia Chen, Zengyang Wu, Libing Wang, Priyesh Sharma, Shuai Li, Liang He, Dhana Savithri, Xiao Jiang amongst others have been invaluable in so many ways and I cannot thank them enough. I would also like to thank Ranjith Kumar specially for taking time off during his holiday to teach me how to operate the GC and for his continuous help with troubleshooting.

The research in this dissertation has been supported by, or in part by, Domtar Paper Company, LLC and the U.S. Department of Agriculture – National Institute of Food and Agriculture.

TABLE OF CONTENTS

LIST OF TABLES	xii
LIST OF FIGURES	xiii
CHAPTER 1	1
INTRODUCTION	1
1.2 OBJECTIVE	3
CHAPTER 2	4
LITERATURE REVIEW	4
2.1 Engine Performance Characteristics	5
2.2 COMBUSTION	7
2.3 Engine Emissions.....	9
2.3.1 Unburned Hydrocarbons	9
2.3.2 Carbon Monoxide	10
2.3.3 Oxides of Nitrogen (NO _x)	10
2.3.4 Particulates.....	12
2.4 Fuels and Additives Studied	12
2.4.1 Biodiesel.....	12
2.4.2 Green Diesel.....	15

2.4.3 Biomass to liquid	16
2.4.4 Fuel Emulsions	16
2.4.5 Lignin derived compounds as additives	18
CHAPTER 3	19
EXPERIMENTAL SETUP.....	19
CHAPTER 4.....	30
Investigation of the Effects of Renewable Diesel Fuels on Engine Performance, Combustion, and Emissions	30
4.1 Abstract.....	30
4.2. Introduction.....	31
4.3 Experimental Setup.....	34
4.4 Results and Discussion	35
4.4.1 Fuel Sample Characterization.....	36
4.4.2 Engine Testing	37
4.4.2.1 Performance	38
4.4.2.2 In-cylinder Combustion.....	41
4.4.2.3 Emissions	45
4.5 Conclusion	48

CHAPTER 5.....	63
Engine Performance, Combustion, and Emissions Study of Biomass to Liquid Fuel in a Compression Ignition Engine	63
5.1 Abstract.....	63
5.2. Introduction.....	64
5.3. Experimental Setup.....	67
5.4. Results and Discussion	68
5.4.1 Fuel Properties.....	68
5.4.2 Performance	69
5.4.3 Combustion.....	69
5.4.4 Emissions	73
5.5. Conclusion	75
CHAPTER 6.....	87
Performance, Combustion, and Emissions Study of a Compression Ignition Engine Running on Oil in Water Emulsions Made with Diesel, Jet fuel and Biodiesel with Carboxymethylated Kraft Lignin as a Surfactant.....	87
6.1 Abstract.....	87
6.2. Introduction.....	88
6.3. Experimental Setup.....	91

6.4. Results and Discussion	92
6.4.1 Fuel Properties	92
6.4.2 Performance	92
6.4.3 Combustion.....	94
6.4.4 Emissions	98
6.5. Conclusion	102
CHAPTER 7	113
Preliminary Testing of Lignin Derived Compounds as Viable Fuel Additives in Diesel Engines.....	113
7.1 Abstract.....	113
7.2 Introduction.....	114
7.3 Experimental Setup.....	117
7.4 Results and Discussion	118
7.4.1 Performance	118
7.4.2 Combustion.....	120
7.4.3 Emissions	122
7.5 Conclusion	124
CHAPTER 8	135
CONCLUSION	135

CHAPTER 9	138
FUTURE WORK.....	138
REFERENCES	139

LIST OF TABLES

TABLE 3.1: ENGINE SPECIFICATIONS	28
TABLE 3.2: FGA 4000 XDS GAS ANALYZER SPECIFICATIONS	28
TABLE 3.3: WAGER SMOKE METER SPECIFICATIONS.....	29
TABLE 4.1: FUEL NOMENCLATURE	50
TABLE 5.1: FUEL PROPERTIES ADAPTED FROM [67], [68], [52] AND [69]	77
TABLE 6.1: HIGHER HEATING VALUE (HHV) AND DYNAMIC VISCOSITY FOR THE TESTED FUELS AND FUEL EMULSIONS.....	104
TABLE 7.1: FUEL NOMENCLATURE	127

LIST OF FIGURES

FIGURE 1.0: CUMMINS AFTERTREATMENT SYSTEM [3].	2
FIGURE 3.1: ENGINE SETUP.	21
FIGURE 3.2 WATER BRAKE DYNAMOMETER.	22
FIGURE 3.3: KISTLER 6052A SENSOR PLACEMENT	22
FIGURE 3.4 GEAR BOX.	23
FIGURE 3.5 SIGNAL CALIBRATION	23
FIGURE 3.6 GEAR BOX AND OTHER SENSORS	24
FIGURE 3.7: EXHAUST GAS ANALYZER	24
FIGURE 3.8: WAGER 6500 SMOKE METER	25
FIGURE 3.9: SMOKE METER SETUP	25
FIGURE 3.10: SCHEMATIC OF THE SMOKE METER SETUP	26
FIGURE 3.11: SCHEMATIC OF THE ENGINE SETUP	26
FIGURE 3.12: FRONT PANEL OF LABVIEW PROGRAM	27
FIGURE 4.1: GC-MS CHROMATOGRAM OF (A) DIESEL (B) JET FUEL (C) BIODIESEL	51
FIGURE 4.2: GC-MS CHROMATOGRAM OF (A) DCFA (B) DCFAH (C) CDCFA	52
FIGURE 4.3: GC-MS CHROMATOGRAM OF (A) DLA (B) IPCF	53
FIGURE 4.4: INDICATED WORK FOR ALL FUELS AT DIFFERENT BRAKE MEAN EFFECTIVE PRESSURES	54

FIGURE 4.5: (A) BRAKE WORK (B) MECHANICAL EFFICIENCY (C) BSFC (D) BRAKE THERMAL EFFICIENCY FOR ALL FUELS AT DIFFERENT BRAKE MEAN EFFECTIVE PRESSURES. NOTE BSFC AT 0 BAR HAS NOT BEEN REPRESENTED AS IT TENDS TO INFINITY.....	55
FIGURE 4.6: IN-CYLINDER PRESSURE COMPARISON AT (A) 0 BAR (B) 1.26 BAR (C) 3.77 BAR....	56
FIGURE 4.7: $DP/D\theta$ AT (A) 0 BAR (B) 1.26 BAR (C) 3.77 BAR.....	57
FIGURE 4.8: HEAT RELEASE RATE COMPARISON AT (A) 0 BAR (B) 1.26 BAR (C) 3.77 BAR	58
FIGURE 4.9: (A) PEAK IN-CYLINDER PRESSURE (B) PEAK $DP/D\theta$ (C) IGNITION DELAY (D) PEAK HEAT RELEASE RATE FOR ALL FUELS AT THE DIFFERENT BRAKE MEAN EFFECTIVE PRESSURES.	59
FIGURE 4.10: CUMULATIVE HEAT RELEASE COMPARISON AT (A) 0BAR (B) 1.26 BAR (C) 3.77 BAR	60
FIGURE 4.11: (A) HYDROCARBON (B) CARBON MONOXIDE (C) CARBON DIOXIDE (D) NOX EMISSIONS FOR ALL FUELS AT THE DIFFERENT BRAKE MEAN EFFECTIVE PRESSURES RESPECTIVELY	61
FIGURE 4.12: (A) SMOKE OPACITY (B) SOOT DENSITY FOR ALL FUELS AT THE THREE DIFFERENT BRAKE MEAN EFFECTIVE PRESSURES	62
FIGURE 4.13: EXHAUST GAS TEMPERATURE (CELSIUS) FOR ALL FUELS AT THE DIFFERENT BRAKE MEAN EFFECTIVE PRESSURES	62
FIGURE 5.1: GC/MS RESULTS FOR (A) DIESEL (B) BIODIESEL (C) BTL.....	78

FIGURE 5.2: (A) INDICATED WORK (B) MECHANICAL EFFICICENCY (C) BRAKE SPECIFIC FUEL CONSUMPTION (D) BRAKE THEMAL EFFICICENCY AT 0 BAR, 1.26 BAR AND 3.77 BAR BMEP	79
FIGURE 5.3: IN-CYLINDER PRESSURE AT (A) 0 BAR, (B) 1.26 BAR AND (C) 3.77 BAR BMEP.....	80
FIGURE 5.4: HEAT RELEASE RATE AT (A) 0 BAR, (B) 1.26 BAR AND (C) 3.77 BAR BMEP.....	81
FIGURE 5.5: CUMULATIVE HEAT RELEASE AT (A) 0 BAR, (B) 1.26 BAR AND (C) 3.77 BAR BMEP.	82
FIGURE 5.6: (A) PEAK CYLINDER PRESSURE (B) PEAK HEAT RELEASE RATE (C) PEAK CUMULATIVE HEAT RELEASE RATE (D) IGNITION DELAY AT 0 BAR, 1.26 BAR AND 3.77 BAR BMEP	83
FIGURE 5.7: ACTUAL AIR-FUEL RATIO UNDER DIFFERENT ENGINE LOADS	83
FIGURE 5.8: (A) HYDROCARBON EMISSIONS (B) CARBON MONOXIDE EMISSIONS (C) CARBON DIOXIDE EMISSIONS (D) NO _x EMISSIONS AT 0 BAR, 1.26 BAR AND 3.77 BAR BMEP.....	84
FIGURE 5.9: RELATIONSHIP OF PEAK HEAT RELEASE RATE TO NO _x EMISSIONS FOR ALL THE CONDITIONS	85
FIGURE 5.10: (A) SMOKE OPACITY AT 0 BAR, 1.26 BAR AND 3.77 BAR BMEP.....	85
FIGURE 5.11: EXHAUST GAS TEMPERATURE AT 0 BAR, 1.26 BAR AND 3.77 BAR BMEP	86
FIGURE 6.1: SCHEMATIC OF EXPERIMENTAL SETUP.....	105
FIGURE 6.2: FROM LEFT TO RIGHT, DIESEL, BIODIESEL, JET FUEL, DIESEL EMULSION, BIODIESEL EMULSION, JET FUEL EMULSION	105

FIGURE 6.3: (A) INDICATED WORK (B) MECHANICAL EFFICENCY (C) BRAKE SPECIFIC FUEL CONSUMPTION (D) ADJUSTED BRAKE SPECIFIC FUEL CONSUMPTION AT 0 BAR, 1.26 BAR AND 3.26 BAR BMEP.....	106
FIGURE 6.4: (A) BRAKE THERMAL EFFICIENCY (B) ADJUSTED BRAKE THERMAL EFFICENCY AT 0 BAR, 1.26 BAR AND 3.26 BAR BMEP	106
FIGURE 6.5: IN-CYLINDER PRESSURE AT (A) 0 BAR, (B) 1.26 BAR AND (C) 3.26 BAR BMEP... ..	107
FIGURE 6.6: HEAT RELEASE RATE AT (A) 0 BAR, (B) 1.26 BAR AND (C) 3.26 BAR BMEP.....	108
FIGURE 6.7: CUMULATIVE HEAT RELEASE AT (A) 0 BAR, (B) 1.26 BAR AND (C) 3.26 BAR BMEP.	109
FIGURE 6.8: (A) PEAK CYLINDER PRESSURE (B) PEAK HEAT RELEASE RATE (C) PEAK CUMULATIVE HEAT RELEASSE RATE (D) IGNITION DELAY AT 0 BAR, 1.26 BAR AND 3.26 BAR BMEP	110
FIGURE 6.9: (A) HYDROCARBON EMISSIONS (B) CARBON MONOXIDE EMISSIONS (C) CARBON DIOXIDE EMISSIONS (D) NO _x EMISSIONS AT 0 BAR, 1.26 BAR AND 3.26 BAR BMEP.....	111
FIGURE 6.10: RELATIONSHIP OF NO _x WITH PEAK HEAT RELEASE RATE FOR DIESEL, BIODIESEL AND THEIR EMULSIONS AT 0 BAR, 1.26 BAR AND 3.26 BAR BMEP.....	111
FIGURE 6.11: SMOKE OPACITY AT 0 BAR, 1.26 BAR AND 3.26 BAR BMEP.....	112
FIGURE 6.12: EXHAUST GAS TEMPERATURE AT 0 BAR, 1.26 BAR AND 3.26 BAR BMEP.....	112
FIGURE 7.1: LIGNIN [99] AND TESTED COMPOUNDS	128
FIGURE 7.2: BRAKE WORK PER CYCLE UNDER THE GIVEN ENGINE SPEED AND LOAD.....	129

FIGURE 7.3: (A) INDICATED WORK (B) MECHANICAL EFFICIENCY (C) BSFC (D) BRAKE THERMAL EFFICIENCY AT 2000 RPM AND 1.26 BAR BMEP	129
FIGURE 7.4: IN-CYLINDER PRESSURE AT 2000 RPM AND 1.26 BAR BMEP	130
FIGURE 7.5: HEAT RELEASE RATE AT 2000 RPM AND 1.26 BAR BMEP	131
FIGURE 7.6: CUMULATIVE HEAT RELEASE AT 2000 RPM AND 1.26 BAR BMEP	132
FIGURE 7.7: (A) PEAK IN-CYLINDER PRESSURE (B) PEAK HEAT RELEASE RATE (C) PEAK CUMULATIVE HEAT RELEASE (D) IGNITION DELAY AT 2000 RPM AND 1.26 BAR BMEP ..	133
FIGURE 7.8: (A) HYDROCARBON (B) CARBON MONOXIDE (C) CARBON DIOXIDE (D) NOX EMISSIONS AT 2000 RPM AND 25% LOAD	134
FIGURE 7.9: (A) SMOKE OPACITY (B) EXHAUST GAS TEMPERATURE AT 2000 RPM AND 25% LOAD	134

CHAPTER 1

INTRODUCTION

Modern Internal combustion engines are a form of heat engines which convert chemical energy in a fuel into useful work. Their uses vary but their presence is more readily felt in both the energy generation sector and in the transportation sector. As of 2012, roughly 254 million vehicles were registered in the United States alone [1] with transportation accounting for 28% of total energy consumption [2] in the US. Most internal combustion engines today are powered by fossil fuels which are fast depleting and prone to price variations based on the will of a few oil producing nations like the Organization of Petroleum Exporting Countries (OPEC).

The vast majority of internal combustion engines in use today as suggested by the above US statistics tell two tales. The first of which is the need for a high volume of fuel to power internal combustion engines on a daily basis and the second suggests a significant pollution problem. To tackle the issue of emissions, the governments of most developed countries have set stringent emissions standards which get stricter every year. Engine manufacturers have sought to improve the performance by making more efficient engines and by tackling the emissions directly through various after-treatment systems. An example of which is the Cummins after-treatment system shown in Fig.1 which makes use of several emissions reduction systems to target specific engine emissions.

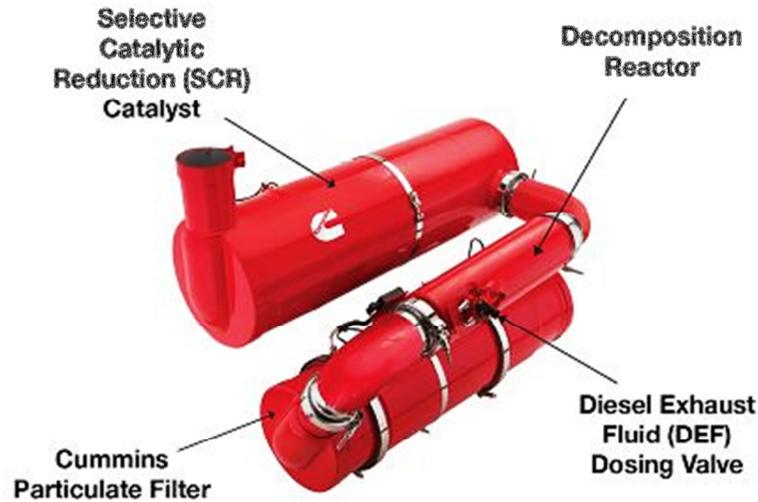


Figure 1.0: Cummins Aftertreatment System [3].

In order to solve the fuel issue, a lot of work has been done to find alternative fuel sources and replacements to the internal combustion engine. The most commonly used fuel alternatives are renewable fuels which are more or less carbon dioxide (CO_2) neutral [4]. This means that during the combustion process, the amount of CO_2 set free is simply the same amount that was used up in growing the biomass used for producing the renewable fuel. Apart from the obvious benefits of having a CO_2 neutral source, there is also no concern that the fuel would run out. Renewable fuels in the form of second generation biofuels like biomass to liquid fuels and green diesel are been engineered for specific purposes.

Unfortunately, the replacement of internal combustion engines for automobile use has yet to be very successful. The most common replacement for the internal combustion engine

is the electric vehicle of which less than 100 thousand were sold [2] compared to the 15.6 million cars sold in the United States in 2013[5, 6]. It would seem then that internal combustion engines are not likely going to be phased out anytime soon.

1.2 OBJECTIVE

The works presented in this dissertation are attempts to better understand the feasibility of various emerging renewable fuels and additives and their effects when used in a compression-ignition engine. These works will study the effect of different renewable fuels and additives made from a renewable source on diesel engine performance, combustion and emissions. The overall objective is to determine a practical fuel alternative with similar or better performance characteristics to standard fossil fuels (diesel) while also offering, more importantly, a reduction in engine emissions.

The fuels that were studied in this work include two sets of second generation biofuels (green diesel fuels and biomass to liquid fuels) and oil in water fuel emulsions. The additives studied are lignin derived compounds. In most of the cases studied, the fuel or additive blend is compared with diesel fuel which is typically used as the benchmark as well as conventional biodiesel and jet-fuel in some instances.

CHAPTER 2

LITERATURE REVIEW

There are two types of internal combustion engines typically in use today, the spark ignition engine and the compression ignition engine (diesel engine) based on the mode of ignition. In an SI engine, combustion per cycle starts with the use of a spark plug which produces an electric discharge that ignites the fuel-air mixture inside the engine combustion chamber. In a compression ignition engine, combustion is initiated when fuel-air mixture auto ignites as a result of high temperature and pressure in the combustion chamber from the compression of air.

Compression ignition (CI) engines are more efficient and have much higher torque capacities than spark ignition engines [7]. The efficiency of CI engines comes as a result of been able to vary engine speed by changing the fuel flow to the engine unlike SI engine which require the throttling of air into the engine in order to adjust engine speed. Other advantages compression ignition engines have is their high compression ratios 12-24 compared to 8-11 for SI engines. Compression ratio is the ratio of the total cylinder volume (sum of the clearance volume and the displacement volume) to the clearance volume. The higher compression ratio of CI engines means a higher efficiency since more power can be generated from combustion of the fuel air mixture in the combustion chamber. The downside to using compression ignition engines lies in their higher exhaust emissions when compared to spark ignition engines.

The search for and optimization of renewable fuels and additives, requires that not only do these fuels have to solve the problems associated with internal combustion engines (ICE), they should also not have major detrimental effects on the engine. As such there is a need to better understand their effects in ICEs particularly on engine performance and emissions. Furthermore, to better understand the transition from chemical energy to mechanical energy for these fuels; it is desirable to also understand their combustion in internal combustion engines.

2.1 Engine Performance Characteristics

The engine performance parameters of interest are work, power, torque and specific fuel consumption. Engine performance is most often determined with the use of a dynamometer coupled to an engine output shaft. Also of importance are the various efficiencies associated with ICEs.

Work is the output of the engine. In an ICE, when fuel-air combustion takes place the force generated drives the piston. The effect of the force acting on the piston is the indicated work. The actual work out from the engine at the shaft is the Brake work and is less than the indicated work as a result of mechanical and parasitic losses on the engine [8]. Indicated work is determined as shown in equations 2.0 and 2.1.

$$W_i = \int P A_p dx$$

(2.0)

Where P is the pressure acting on the piston, A_p is the area of the piston surface where

combusting gases act on and dx is the distance travelled by the piston.

$$W_i = \int P dv$$

(2.1)

dv in equation 2.1 is given by $A_p dx$. Brake work can be determined from the indicated work by subtracting work loss due to friction and parasitic loads as shown in equation 2.2. Where W_b and W_i are the brake work and the work loss due to mechanical and parasitic losses respectively.

$$W_b = W_i - W_l$$

(2.2)

Mean Effective Pressure (MEP) is the average pressure per cycle in the engine. It is the ratio of the work per cycle to the displacement volume. Depending on the type of work used, MEP can be indicated or brake mean effective pressure.

Torque is force multiplied by the perpendicular distance. For a four stroke engine, the torque is given in equation 2.3.

$$T = \frac{bmepVd}{4\pi}$$

(2.3)

Where $bmep$ is the brake mean effective pressure.

Power (\dot{W}) is the rate of work done by the engine.

$$\dot{W} = \frac{WN}{n}$$

(2.4)

Where, W is the work done by the engine, N is the engine speed and n is the number of revolutions per cycle. Depending on the type of work used, power can be indicated or brake power.

Specific fuel consumption (SFC) is a measure of how effectively the fuel consumed is used to provide power. As it is a factor that is determined based on the type of power used, SFC can be either indicated or brake. The equation for determining SFC is given in equation 2.5.

$$Sfc = \frac{m_f}{W} \quad (2.5)$$

Three primary efficiencies are of importance in internal combustion engines they are mechanical efficiency, thermal efficiency and volumetric efficiency. Engine combustion efficiency can be as high as 95-98% and it accounts for the fraction of fuel that is used up during combustion [8].

For an engine, the mechanical efficiency is the ratio of the power output to the power input.

$$\eta_m = \frac{\text{brake power}}{\text{Indicated power}} \quad (2.6)$$

Engine thermal efficiency is a measure of the amount of heat energy input that is made to do useful work in one cycle.

$$\eta_t = \frac{\text{work}}{Q_{in}} \quad (2.7)$$

Where, Q_{in} is the product of the mass flow rate of fuel, the heating value and the combustion efficiency of the fuel.

2.2 COMBUSTION

The combustion of fuel in an internal combustion engine is the most important aspect of the engine. It governs not only the performance of the engine but also the emissions out of the engine. As the studies in this dissertation were all carried out in a diesel engine, a brief

description of the combustion process and some parameters are described here.

Combustion in a diesel engine begins when fuel is injected into the engine combustion chamber containing hot compressed air under high pressure. Fuel is injected into the engine combustion chamber as a spray which allows for fuel atomization, the injected fuel is then vaporized rapidly as a result of the high temperature in the chamber. The mixing of air and vaporized fuel is non-homogenous in a diesel engine combustion chamber and as a result, combustion takes place at many different locations within the chamber.

Combustion in a diesel engine can be accounted for in four different steps; ignition delay, premixed combustion, mixing controlled combustion and the late combustion phase [9]. Ignition delay phase is the period between the start of fuel injection and the start of combustion in an engine's combustion chamber. The ignition delay phase is followed by a premixed combustion phase. In this phase, the combustion of fuel-air mixture occurs very rapidly in the engine combustion chamber over a few crank angle degrees. Following the premixed combustion phase is the mixing controlled phase in which the rate of heat release in the chamber is controlled by the rate at which fuel-air mixtures becomes available for combustion. The late combustion phase allows for the combustion of whatever unburned fuel is left at the end of the previous phases and is responsible for much lower heat release.

Combustion progress in an engine cylinder may be analyzed from in-cylinder pressure measurements. In particular heat release rate, cumulative heat release and fuel mass burning rate. Heat release rate may be calculated by using equation 2.8.

$$\frac{dQn}{dt} = \frac{\gamma}{\gamma-1} p \frac{dv}{dt} + \frac{1}{\gamma-1} V \frac{dp}{dt} \quad (2.8)$$

$\frac{dQn}{dt}$ is the apparent net heat release rate, P and V are pressure and volume respectively with γ been the ratio of specific heats ($\frac{c_p}{c_v}$) with a value of 1.35.

2.3 Engine Emissions

Unburned hydrocarbon, Carbon monoxide, oxides of Nitrogen (NO and NO₂) and particulate matter are the currently regulated emissions from internal combustion engines. These emissions pose several risks to both humans and the earth as a whole. As all of this work was done in a diesel engine, the four controlled emissions will be discussed from the perspective of the diesel engine.

2.3.1 Unburned Hydrocarbons

Engine hydrocarbon emissions are a result of incomplete combustion of hydrocarbon fuel. About 40% of exhaust hydrocarbon is made up of unburned fuel with the remaining 60% been smaller components of the original fuel usually as a result of thermal cracking [8]. The thermal cracking of hydrocarbon fuels means that the range of hydrocarbon in the exhaust can vary from small hydrocarbons such as methane to much large hydrocarbons depending on the constituents of the fuel. Hydrocarbon fuels can be reactive or non-reactive based on how well they can form oxidants in photochemical smog chemistry [8]. Fuels containing high aromatic and alkene contents produce higher concentration of hydrocarbons. Fuel-air combustion is the principal cause of hydrocarbon emissions in diesel engines. A very fuel

rich mixture, results in poor incomplete combustion which as a result leads to unburned fuel vapor remaining in the combustion chamber which may or may not be consumed by slow thermal oxidation during engine expansion phase. A very lean fuel-air mixture would not support auto ignition and flame propagation [9]. Diesel engine operating conditions significantly affect hydrocarbon emissions. Idle and light engine operating conditions produce higher hydrocarbon emissions than high load conditions. Other factors that may affect HC emissions are the amount of fuel injection and the combustion chamber wall quenching.

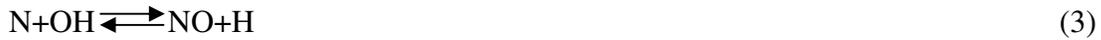
2.3.2 Carbon Monoxide

Carbon monoxide is a colorless, odorless oxide of carbon formed from the incomplete combustion of a hydrocarbon typically as a result of less air particularly oxygen. As diesel engines are generally air rich, carbon monoxide emissions are very small as most of the hydrocarbon fuel reacts to form CO₂.

2.3.3 Oxides of Nitrogen (NO_x)

NO_x from vehicle engine exhaust leads to acid rain, smog and may lead to severe respiratory problems and as such vehicle NO_x emissions are limited by various government agencies. Nitric oxide (NO) and Nitrogen dioxide (NO₂) are two important oxides of Nitrogen formed in internal combustion engines. There are several mechanisms associated with NO_x formation and they include the zel'dovich (Thermal) NO mechanism, Prompt NO mechanism, Fuel bound Nitrogen route, NO₂ route and N₂O route. Thermal NO_x mechanism is the primary NO mechanism from the combustion of hydrocarbon fuels without Nitrogen.

This mechanism consists of three principal reactions [10]



Reaction 1 is the rate determining step but because of the strong triple bond in N_2 , it has a high activation energy which makes the reaction fast only at high temperatures. NO formation through this mechanism occurs in the post flame gases with the reaction only occurring at temperatures above 1800k [10]. NO formation rate through the thermal mechanism is dependent on the concentration of N_2 and O.

The rapid reaction of hydrocarbon radicals with molecular Nitrogen from the combustion of hydrocarbon fuels leads to the formation of amines and hydrocyanic acids that react to form prompt NO. Reaction 4 below is responsible for prompt NO formation.



NO formation is determined by the peak temperature during combustion. At low temperatures (1000k), low pressures in a laminar flame and fuel-rich mixtures, the Fenmore mechanism dominates. On the other hand at a higher temperature (1800k) and high pressure, thermal NO mechanism dominates [10].

2.3.4 Particulates

Particulates from a diesel engine are made up of solid carbon compounds usually in the form of soot and are generated as a result of the incomplete combustion of hydrocarbon fuels as well some of the lubrication oil inside the combustion chamber. Temperatures in the engine exhaust and particulate treatment systems affect the composition of soot. Above 500°C, individual soot particles are made up primarily of small carbon spheres. At temperatures below 500°C however, these individual soot particles absorb organic compounds of high molecular weights such as hydrocarbons, esters and acids [9]. Diesel engine particulate emissions can be reduced with the diesel particulate filters (DPF). The three main technologies used in DPFs are wall flow filter, partial flow filter and diesel oxidation catalyst [11]. Most diesel particulate filters work by trapping soot particles from engine exhaust in channels made of ceramic and other materials. These filters allow exhaust gases to flow through but trap soot particles and as such filters have to undergo a regeneration cycle to oxidize accumulated soot.

2.4 Fuels and Additives Studied

2.4.1 Biodiesel

Biodiesel is a type of biofuel made from the trans-esterification process and involves reaction of a feed stock, usually oil or fatty acids from oil, with an alcohol in the presence of a catalyst [7]. The end product of the trans-esterification process is a fatty acid methyl ester (FAME), also called biodiesel. Biodiesel has several benefits over conventional fossil diesel; it is renewable, non-toxic, has a greater lubricity, generally lower emissions and most of all

has similar properties as convention fossil diesel [12]. Various experiments have been conducted to determine the performance of biodiesel on engine performance.

Work done by the authors [13] on methyl soyate blends with diesel ranging from 10 - 75% by volume of biodiesel suggest significant interaction between the effect of fuel blend and engine speed on power. The use of B10 (10% by volume methyl soyate) resulted in an engine power output increase of 4.06% when compared to diesel and decreases to 1.79% when B20 was used. Increase in the concentration of methyl soyate to 30% by volume resulted in a further decrease in power output 1.69% lower than the diesel power output. This trend continued till a decrease in power output of about 30% was observed when 100% Methyl soyate concentration was used. The results from [13] are in agreement with results in [14] in which a blend of biodiesel (B8) had a slightly higher brake power than diesel while the other biodiesel blends had lower brake power than diesel. The decrease in power can be attributed to the low heating value of the methyl soyate biodiesel fuel.

The general consensus is that specific fuel consumption for biodiesel is higher than for diesel and that it increases with increasing biodiesel concentration in the biodiesel-diesel blend [14, 15, 16]. The effect of diesel and biodiesel fuels on the brake thermal efficiency of an engine are regarded to be somewhat the same [15] at the same loads and engine speeds with diesel having a slightly higher brake thermal efficiency [14]. This results is further corroborated by [14], results obtained showed that the brake thermal efficiency for Jatropha biodiesel was lower than that of diesel at any given injection timing, load and speed.

Biodiesel- diesel fuel blends with low biodiesel concentrations of 10-20% have injector spray characteristics that are very similar to 100% diesel under the same engine conditions [15]. The high compressibility value of biodiesel results in an earlier injection of fuel into the engine cylinder and the higher cetane number of biodiesel results in a shorter ignition delay when compared with diesel fuel [12, 14, 15]. Biodiesel has a larger mean droplet size and higher distillation curve than diesel, as such its evaporation in the engine cylinder is slower than diesel [15] thus resulting in lower heat release. The peak in-cylinder pressure for biodiesel is lower than for diesel with a few exceptions. At low engine speeds, the peak pressure of biodiesel blends is initially higher than that of diesel, but as load increases, the peak pressure is observed to be lower than that of diesel.

Heat release rate is another important factor in the combustion that takes place in diesel engines. According to experiments performed by [17], the maximum heat release rate for biodiesel was higher than that of diesel up to a certain load after which it becomes lower than that of diesel. A look at the overall cumulative heat release for biodiesel shows a slightly lower heat release when compared to diesel.

There is no general consensus on the issue of hydrocarbon emissions (HC). Some experiments have reached conclusions that HC emissions increases when compared to diesel and it further increases with increasing biodiesel concentration in a fuel blend [15]. Some experiments however prove otherwise as in the case of [13, 14, and 17] with the latter agreeing that an increase in HC emissions would not occur because of the additional oxygen content present in biodiesel.

Carbon monoxide (CO) emission is generally agreed to be lower than that of diesel with CO emissions reducing with increasing concentration of biodiesel in the biodiesel-diesel blend. All the experiments attributed to NO_x emission measurements reach the same conclusion that NO_x emissions are higher with biodiesel and its blends than with diesel, with the amount of NO_x emitted increasing with increasing biodiesel concentration in a fuel blend. Smoke density is a typical indicator of how much soot is generated in an engine, the general conclusion from all experiments is that smoke density and consequently the mass of soot obtained from biodiesel exhaust emissions is lower than diesel. Based on the above information on emissions, we may conclude that biodiesel generally has lower emissions than diesel, a result attributed mostly to the oxygen content of the fuel.

2.4.2 Green Diesel

Green diesel is made from the deoxygenation of triglycerides or fatty acids [18 - 22]. The production process typically occurs in a reactor under high temperature and pressure in the presence of a catalyst. Hydrolysis is the first step of the process and involves splitting the fatty acids in the oil from the glycerol backbone by heating the oil under high pressure in the presence of water [18]. Upon separation from the water, the fatty acids then undergo deoxygenation via a thermo-catalytic process by which oxygen is removed from fatty acids. There are several pathways involved in this process depending on how oxygen is removed. The decarboxylation pathway removes oxygen as carbon dioxide while the decarbonylation pathway involves the removal of oxygen as carbon monoxide. The preference is usually for the decarboxylation pathway as carbon dioxide is less harmful to man and to the catalyst

used. Depending upon the degree of saturation of the fatty acid, and the mole fraction of hydrogen in the gas phase, the final product from this deoxygenation process is a straight chain n-alkane, with one less carbon than the corresponding fatty acid.

2.4.3 Biomass to liquid

Biomass to liquid fuels (BTL) are classified as second generation biofuels. They may also be classified as synthetic fuels since the fuel produced in this manner can be engineered to meet specific requirements and do not use food based feedstock. The steps involved in BTL production from biomass are gasification, gas cleaning and synthesis. Gasification is the first step in BTL production and it involves the breakdown of the feedstock in a reactor at high temperature and pressure into synthetic gases usually oxides of carbon and hydrogen. Gas cleaning involves the removal of contaminants as a result of tar production in the reactor from the synthesized gas. Gas cleaning is necessary before synthesis due to the sensitivity of catalyst in the synthesis stage [23]. Fischer Tropsch synthesis the final stage involves the reaction of CO and H₂ in the presence of an iron or cobalt catalyst to form hydrocarbons which can be modified to meet specific fuel requirements (gasoline, jet fuel or diesel). Work done by [24] suggest the use of BTL in a CI engine results in an overall lower emissions of HC, CO, NO_x and particulate matter but higher soot. From their research, they also found that SUNDIESEL had a lower BSFC and a lower peak heat release rate.

2.4.4 Fuel Emulsions

An emulsion is the mixing of two or more normally immiscible liquids with one of the liquids existing as a continuous phase and the other as a dispersed phase. It is created by

the agitation of the two liquids in the presence of a surfactant which possess both polar and non-polar properties which helps weaken the surface tension of the liquid in which it is dissolved [25].

Fuel emulsions are produced when fuel and water are mixed together in the presence of a surfactant with either water as the continuous phase and the fuel as the dispersed phase or vice versa. In most experimental studies on the use of emulsion in diesel engines, the normally accepted maximum content of water in the emulsion is 30% with greater water contents significantly lowering the efficiency of the engine. Results from research on the use of emulsion in diesel engines are inconclusive. Experiments by [25] show that that the percentage of water content in the fuel increases power while research by [26] show that increasing water content reduces power output of the engine. Experiments conducted by [27, 28, 29] show that brake specific fuel consumption increases with water content. Brake thermal efficiency has been found to generally increase for water diesel emulsion as experiments from [27, 29, and 30] have shown.

The general consensus from research suggest a decrease in NO_x emissions for emulsion fuels with a reduction in hydrocarbon and particulate emissions [25] from fuel emulsions compared to pure diesel fuel. CO emissions have been found [31] to increase for engines running on emulsions while some other researchers [29] have noticed a decrease in CO emissions when compared to pure diesel fuel.

2.4.5 Lignin derived compounds as additives

Lignin is the second most abundant natural polymer in the world after cellulose. It is an insoluble polyphenolic compound associated with polysaccharides in the plant cell wall [32]. Its chemical composition varies depend on the plant source. Lignin is responsible for the rigidity of plant cell walls and as it is hydrophobic, it allows for the transportation of water in the plant. Lignin is typically obtained in large quantities as a by-product of paper production.

In the paper mills, lignin can be obtained from sulfite pulping or Kraft pulping. Lignin can be used as a biomass to make renewable fuels such as biomass to liquid fuels but for the purpose of this dissertation the use of it's by products in diesel internal combustion engines are of more concern. The pyrolysis of lignin results in the formation of several products ranging from solid char to gaseous oxides of carbon. Due to the high oxygen contents of some byproducts of lignin (phenolic compounds) their use as fuels or additives in diesel engines may be feasible. There has however been little research on the effects of these compounds on diesel engine performance, combustion and emissions.

CHAPTER 3

EXPERIMENTAL SETUP

The experiments conducted in this dissertation were carried out in a 6.0 kW single cylinder air cooled compression ignition engine with a bore of 86 mm, a stroke of 72 mm, a displacement of 418 cc, and a compression ratio of 19:1 as shown in Figures 3.1a and b. The engine is coupled to a Go-Power water brake dynamometer shown in Figure 3.2 to accurately determine the load on the engine, a calibrated M5100 series pressure transducer is connected to the hydraulic load cell of the dynamometer. The engine specifications are given in Table 3.1. In-cylinder pressure is measured with a Kistler 6052A pressure sensor mounted vertically in the engine cylinder head as shown in Figure 3.3.

The diesel engine is coupled to a gear box which allows for the accurate determination of the engines top dead center (TDC). The gear box in Figure 3.4 contains a Hengstler 0521097 shaft encoder which is used in combination with a Hall Effect sensor and an AND gate to accurately determine crank angle positions of the engine. Figure 3.5 is an example of the calibration process involved in matching the signal from the shaft encoder with that from the hall- effect sensor and the in-cylinder pressure. Air and intake temperature into the engine are measured with a Bosch air mass flow meter attached to the engine air intake just past the air filter The pressure of intake air into the engine is measured with a SSI Tech pressure transducer placed at the air inlet into the engine as shown in Fig 3.6.

The mass flow rate of fuel into the engine is measured with either an OHAUS GT2100 or a METTLER PM4800 Scale or both depending on the fuel been tested. Exhaust

gas temperature from the engine is measured with a K-type thermocouple placed just after the muffler. Gaseous emission from the engine is measured with an Infrared Industries FGA 4000XDS gas analyzer shown in Fig. 3.7 which can measure five different exhaust gases. The gas analyzer specification is given in Table 3.2. Smoke opacity of engine exhaust gas is measured using a wagner 6500 full flow smoke meter shown in Figure 3.8, the meter specifications are given in Table 3.3. To take smoke opacity measurements, the exhaust tail pipe was designed with a T junction in order to allow for an increase in the light path length of the smoke meter. This is done to allow for more accurate opacity measurements under low engine load conditions. To prevent soot deposit on the smoke meters transmitter and receiver, two glass panels are placed on either ends of the exhaust T. Smoke opacity data at any instance is only collected after these glass panels have been cleaned and the opacity meter zeroed. The setup is shown in Fig 3.9 and a schematic of the setup is shown in Fig 3.10. A representation of the overall engine setup is shown in Fig. 3.11

Data from each sensor is collected with the use of a custom program written in Labview. The program collects in-cylinder pressure, engine rpm, engine load, air mass flow rate and intake temperature and pressure. A front view of the program is shown in Figure 3.12. Collected data is further analyzed using Microsoft excel and a Matlab program.

During the course of experimentation, the diesel engine was replaced with a newer same capacity engine as a result of the breakdown of the engine. The water brake dynamometer was also replaced as a result of a bearing failure which wore out its shaft. For these reasons, it should be noted that experimental results for renewable diesel fuel and lignin

derived additives cannot be compared to those of BTL and emulsions as the engine and dyno used for these experiments are different.



(a)



(b)

Figure 3.1: Engine Setup

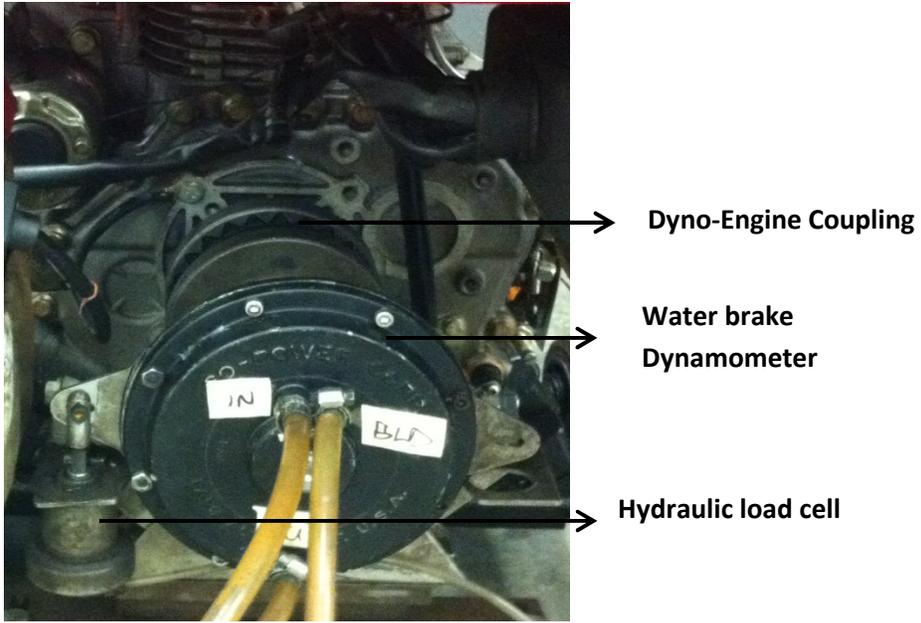


Figure 3.2 Water Brake Dynamometer

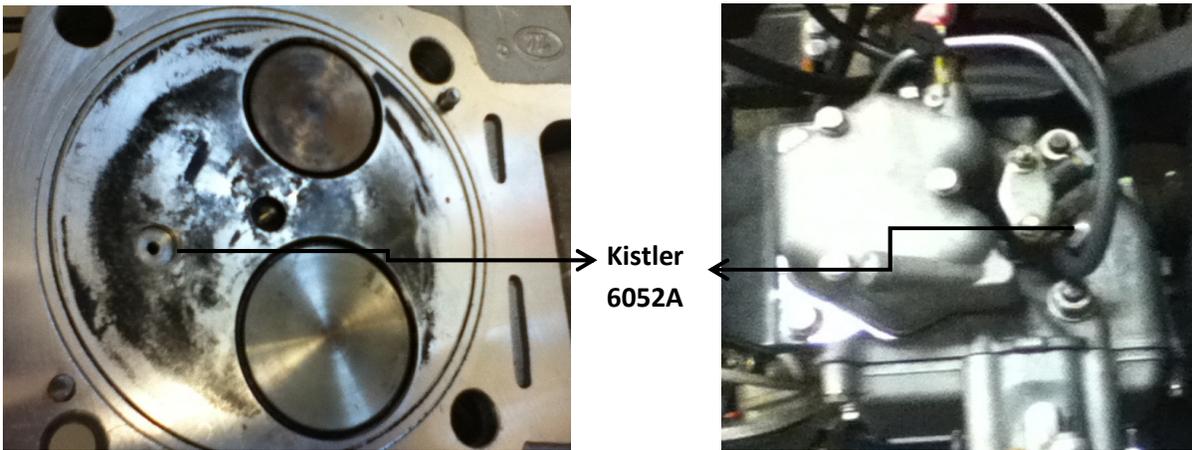


Figure 3.3: Kistler 6052A sensor placement

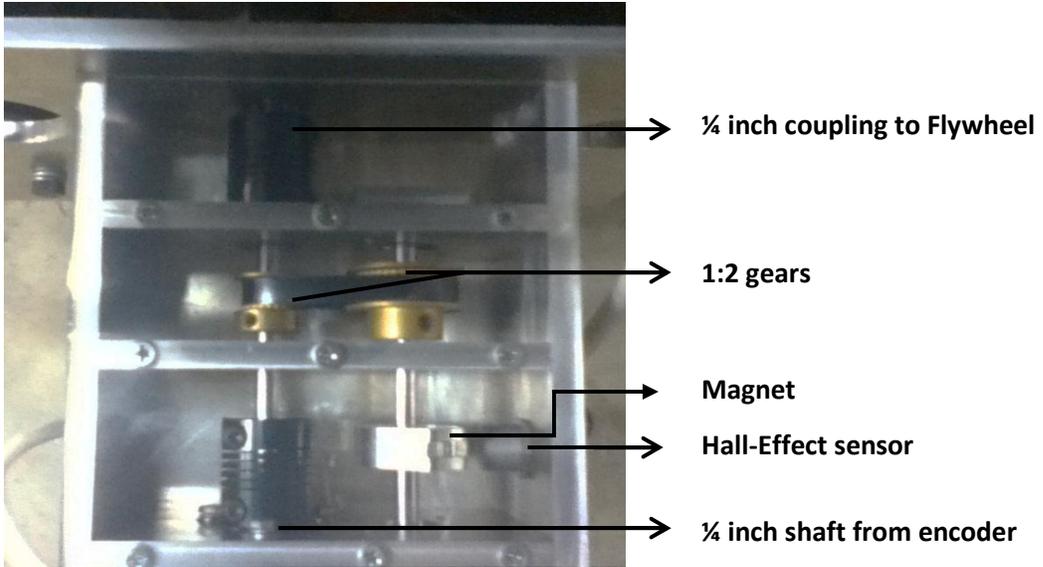


Figure 3.4 Gear Box

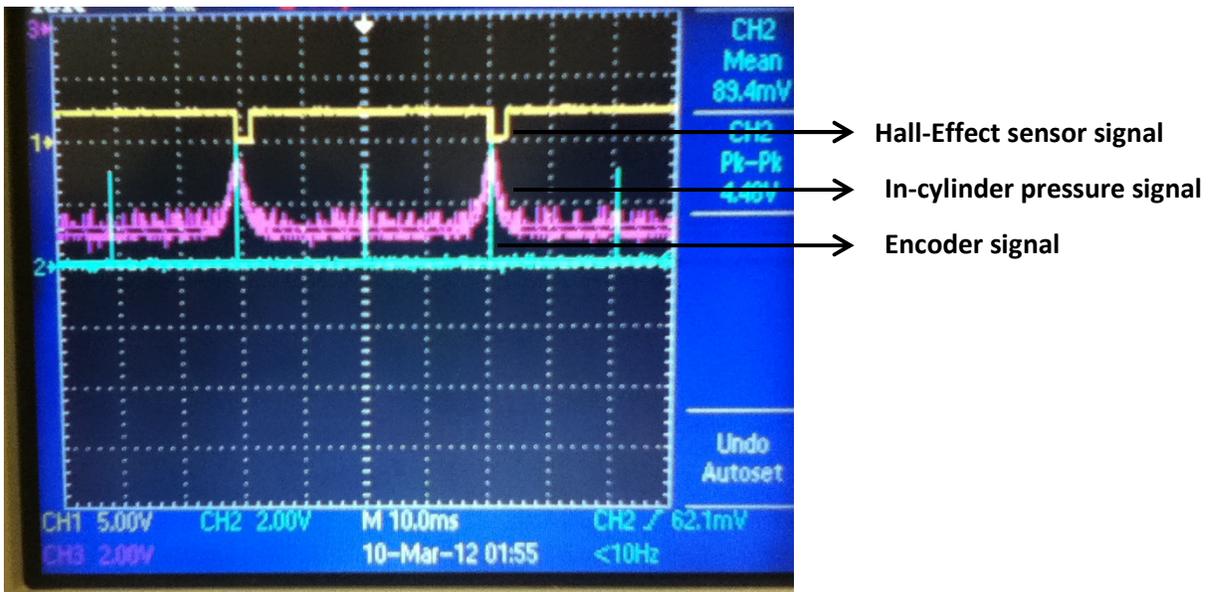


Figure 3.5 Signal Calibration

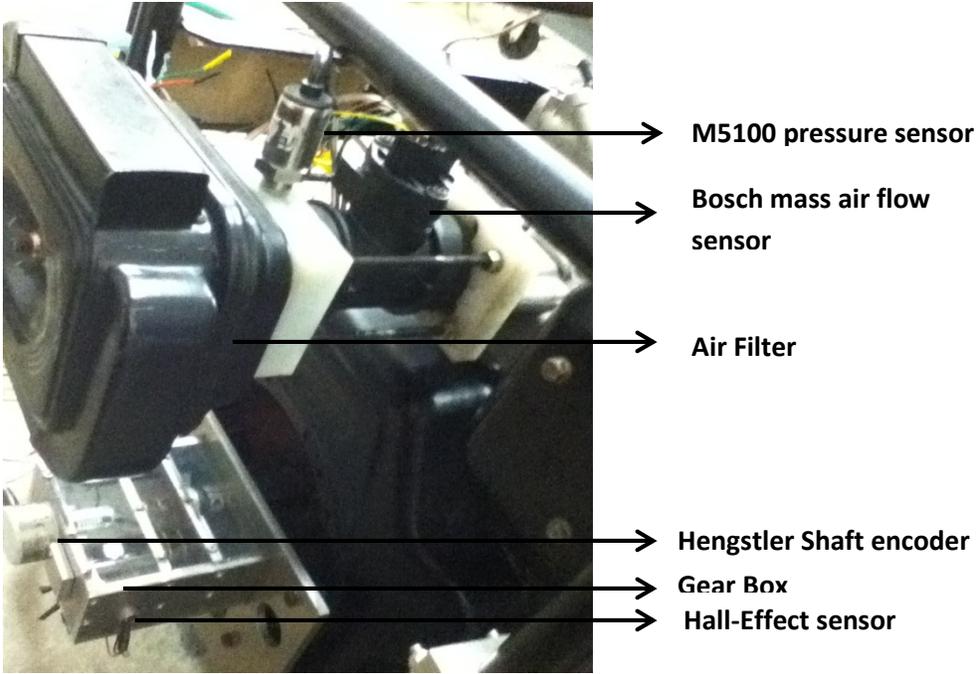


Figure 3.6 Gear Box and Other Sensors



Figure 3.7: Exhaust Gas Analyzer



Figure 3.8: Wager 6500 Smoke Meter



T junction

Engine Exhaust

Glass panels

Figure 3.9: Smoke Meter Setup

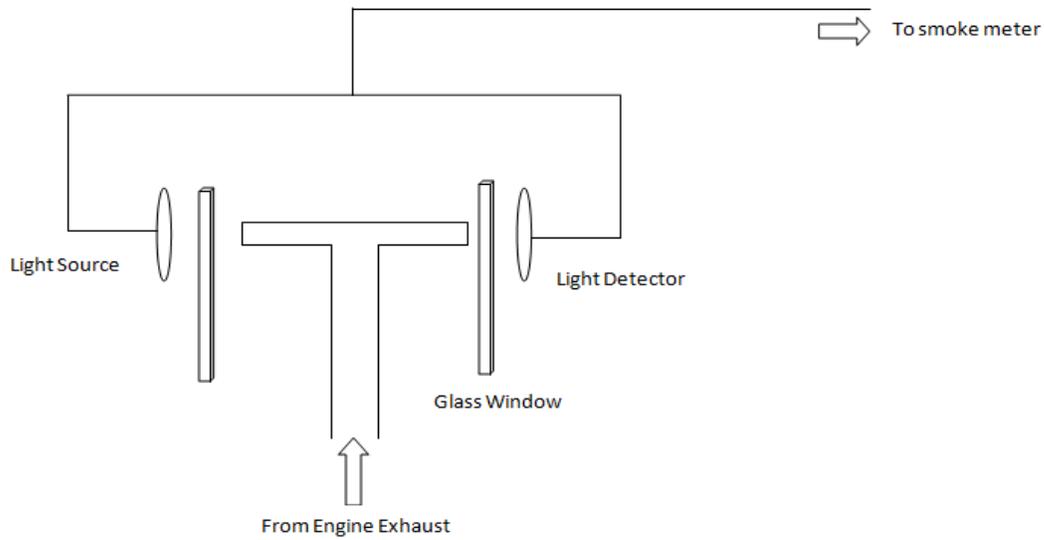


Figure 3.10: Schematic of the smoke meter setup

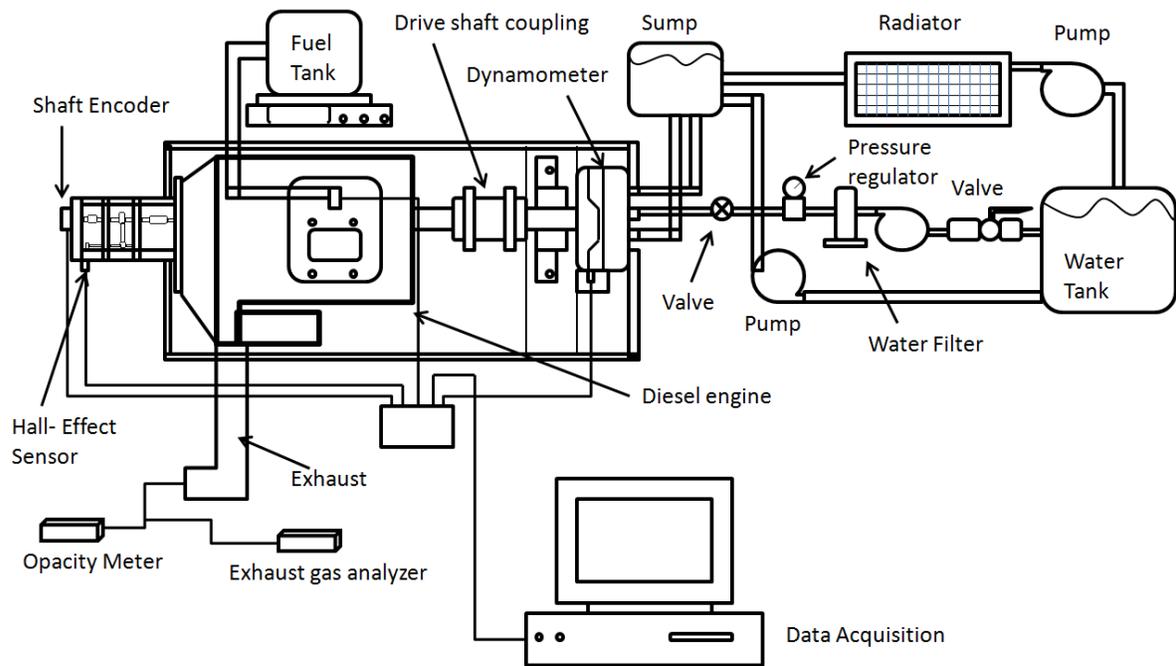


Figure 3.11: Schematic of the engine setup

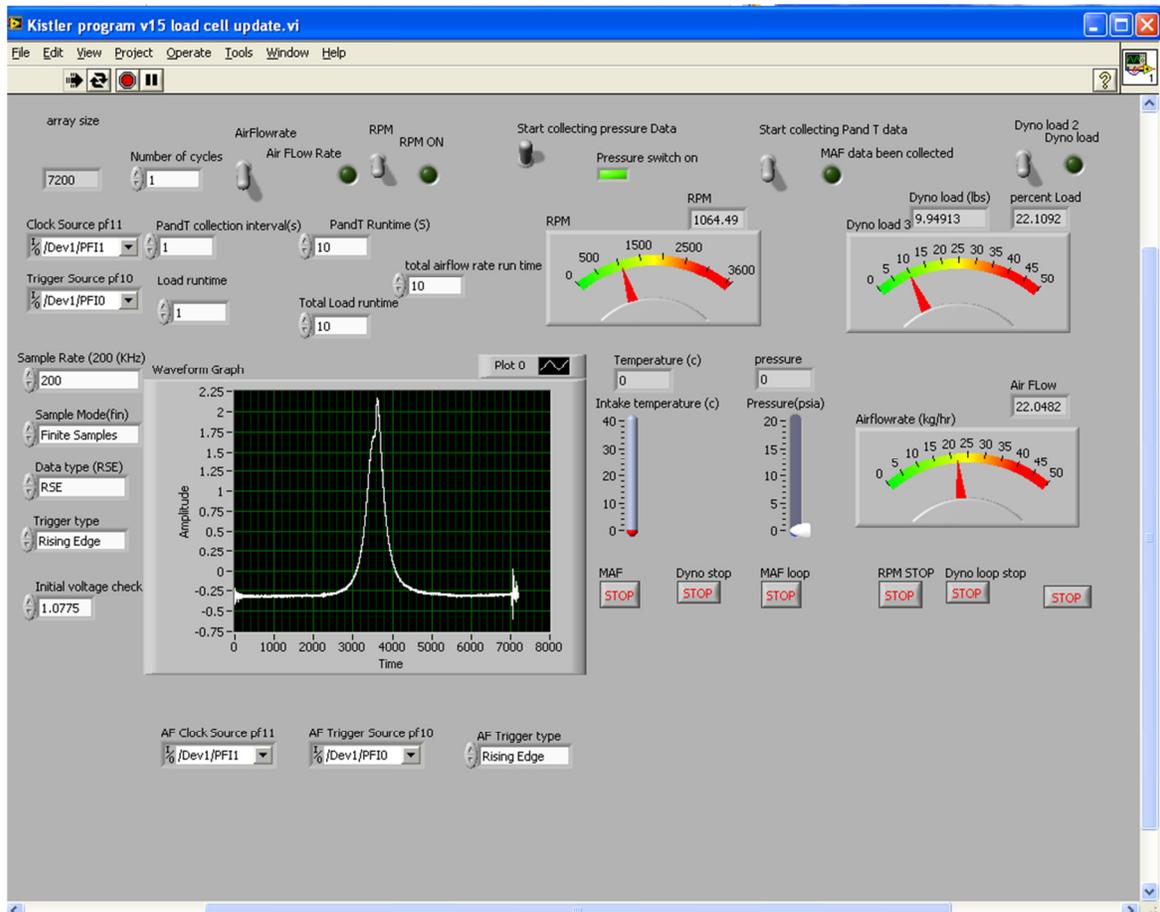


Figure 3.12: Front panel of labview program

Table 3.1: Engine Specifications

Engine	Single Cylinder, Vertical, Direct Injection 4 stroke
Compression Ratio	19:1
Bore × Stroke	86 mm × 72 mm
Method of Loading	Water brake dynamometer
Method of Starting	Electric Start
Method of Cooling	Air cooled
Type of Ignition	Compression Ignition
Rated Power	6.0 kW
Rated Speed	3600 rpm
Initial Injection	17.0 Crank Angle Degrees before TDC
Displacement	418 cc
Fuel Consumption at Rated Power	340 g/kW.hr

Table 3.2: FGA 4000 XDS Gas Analyzer Specifications

Measured Species	Measured Range/Techniques
HC,CO,CO ₂	Non-Dispersive Infrared (NDIR)
O ₂ and NO _x	Chemical Cell
CO	0 to 10.00%
HC	0 to 10,000 ppm
CO ₂	0 to 20%
O ₂	0 to 25%
NO _x	0 to 4,000 ppm

Table 3.3: Wager Smoke Meter Specifications

Light Source	LED – Green Gallium Phosphide 570 nm
Light Sensor	Si Photo Diode with IR Filter
Meter Accuracy	$\pm 1.0\%$ Nominal, $\pm 10^{\text{th}}$ digit
Range	0.0% - 100.0% opacity
Response Time	0.45 seconds for 0 - 90% opacity
Linearity	$\pm 1\%$ from 0 - 100% opacity

CHAPTER 4

Investigation of the Effects of Renewable Diesel Fuels on Engine Performance, Combustion, and Emissions

4.1 Abstract

A study was undertaken to investigate renewable fuels in a compression-ignition internal combustion engine. The focus of this study was the effect of newly developed renewable fuels on engine performance, combustion, and emissions. Eight fuels were investigated, and they include diesel, jet fuel, a traditional biodiesel (fatty acid methyl ester: FAME), and five next generation biofuels. These five fuels were derived using a two-step process: hydrolysis of the oil into fatty acids (if necessary) and then a thermo-catalytic process to remove the oxygen via a decarboxylation reaction. The fuels included a fed batch deoxygenation of canola derived fatty acids (DCFA), a fed batch deoxygenation of canola derived fatty acids with varying amounts of H₂ used during the deoxygenation process (DCFAH), a continuous deoxygenation of canola derived fatty acids (CDCFA), fed batch deoxygenation of lauric acid (DLA), and a third reaction to isomerize the products of the deoxygenated canola derived fatty acid alkanes (IPCF). Diesel, jet fuel, and biodiesel (FAME) have been used as benchmarks for comparing with the newer renewable fuels. The results of the experiments show slightly lower mechanical efficiency but better brake specific fuel consumption for the new renewable fuels. Results from combustion show shorter ignition delays for most of the renewable (deoxygenated) fuels with the exception of fed batch deoxygenation of lauric acid.

Combustion results also show lower peak in-cylinder pressures, reduced rate of increase in cylinder pressure, and lower heat release rates for the renewable fuels. Emission results show an increase in hydrocarbon emissions for renewable deoxygenated fuels, but a general decrease in all other emission including NO_x, greenhouse gases, and soot. Results also demonstrate that isomers of the alkanes resulting from the deoxygenation of the canola derived fatty acids are a viable and better replacement to conventional fossil diesel and biodiesel based on the experiments in this work.

4.2. Introduction

The rising cost as a result of depleting fossil reserves as well as problems relating to greenhouse gas emissions have been the most important drivers for seeking out new sources of energy [33]. Stringent emissions standards such as the newly proposed tier 3 standards by the Environmental Protection Agency (EPA) indicate that fuels that burn cleaner and have lower sulfur content will be favored [34]. A variety of alternative sources of energy, ranging from wind, solar, nuclear, etc., already exist but several challenges such as capital, portability, inefficiency, storage, and further environmental degradation make these sources of energy inadequate and in some cases non-viable.

For internal combustion (IC) engines, liquid biofuels have emerged as viable alternatives to fossil fuels. Biofuels are fuels typically made from renewable sources such as animal feedstock, plants, and biomass. Biofuels production and consumption has increased in recent years partly as a result of government support in the form of tax credits, mostly because they have been found to effectively supplement current fossil fuels [35].

Biodiesel is a type of biofuel made from the trans-esterification process and involves reaction of a feed stock, usually oil or fatty acids from oil, with an alcohol in the presence of a catalyst [7]. The end product of the trans-esterification process is a fatty acid methyl ester (FAME), also called biodiesel. Biodiesel has several benefits over conventional fossil diesel; it is renewable, non-toxic, greater lubricity, generally lower emissions and most of all has similar properties to convention fossil diesel [12].

Many studies have investigated the influence of biodiesel on engine performance, combustion and emissions [36-46]. From these studies, fuel physical and chemical properties play a significant role in the results obtained. Biodiesel has a high cetane number when compared to diesel and as such it has a shorter ignition delay [47-48]. Other properties such as fuel penetration, atomization and droplet size are also important for the combustion of the fuel and ultimately its emissions [49]. The general consensus is that biodiesel results in a slight increase in brake specific fuel consumption and higher brake thermal efficiency than diesel [36-37]. Biodiesel generally produces lower hydrocarbon and carbon monoxide emissions; however, NO_x emissions are typically higher than with diesel [36-37, 42, 43]. Biodiesel has some disadvantages such as higher production cost, restriction on feedstock use, lower energy density (due to oxygen content), higher viscosity, stability, and higher freezing point amongst others [7,12]. An attempt to resolve some of the disadvantages of biodiesel, with cost and chemical composition as the main focus, has led to the production of renewable diesel fuels.

Renewable diesel is a non-oxygenated fuel produced from a thermo-catalytic process that involves the conversion of feed stock or fatty acids into straight chain n-alkanes through deoxygenation [18]. These straight chain alkanes can then be further processed to meet specification standards of the desired fossil fuel. The production process of renewable diesel production is flexible enough to allow for the production of a wide variety of hydrocarbon fuels that can meet most fossil fuel standards.

In this work, renewable diesel is made from the deoxygenation of triglycerides or fatty acids [18-22, 50]. The production process typically occurs in a reactor under high temperature and pressure in the presence of a catalyst. Hydrolysis is the first step of the process and involves splitting the fatty acids in the oil from the glycerol backbone by heating the oil under high pressure in the presence of water [18]. Upon separation from the water, the fatty acids then undergo deoxygenation via a thermo-catalytic process by which oxygen is removed from fatty acids. There are several pathways involved in this process depending on how oxygen is removed. The decarboxylation pathway removes oxygen as carbon dioxide while the decarbonylation pathway involves the removal of oxygen as carbon monoxide. The preference is usually for the decarboxylation pathway as carbon dioxide is less harmful to man and to the catalyst used.

Depending upon the degree of saturation of the fatty acid, and the mole fraction of hydrogen in the gas phase, the final product from this deoxygenation process is a straight chain n-alkane, with one less carbon than the corresponding fatty acid. This alkane may then be reformed into an isomer via hydroreforming or an aromatic via dehydrocyclization

depending on the desired characteristics of the final fuel (e.g., cloud point, freeze point, flash point, octane or Cetane rating, etc.).

The absence of double bonds and oxygen are some of the advantages of renewable diesel over conventional biodiesel as it allows for an increase in the energy content of the fuel. Other advantages are lower viscosity, absence of sulfur (which reduces the efficiency of exhaust catalyst), and ease of customization, *i.e.*, renewable diesel can easily be tailored to meet other fuel requirements etc. Based on estimated cetane number values, it is expected that most of the renewable fuels may have higher cetane numbers than either diesel or biodiesel [51].

The objective of this work is to determine how these newly developed renewable fuels perform compared to fossil fuels (diesel and jet fuels) in a compression-ignition engine. The experiments focus on engine performance, combustion and emissions, and also serve to compare a first generation biofuels (biodiesel, *i.e.*, fatty acid methyl ester) with the second generation renewable fuels.

4.3 Experimental Setup

The setup for this experiment was discussed in chapter 3. Eight different fuels were used during the course of the experiments. Five of the fuels were renewable diesel fuels derived from thermo-catalytic deoxygenating either canola or lauric acid through a either fed batch or continuous processes. One of the fuels was further reformed via isomerization to alter its physical properties. These five renewable diesel fuels were: fed batch deoxygenation of

canola derived fatty acids (DCFA), fed batch deoxygenation of canola derived fatty acids with optimized H_2 mole fraction to promote decarboxylation and alkanes as products (DCFAH), continuous deoxygenation of canola derived fatty acids (CDCFA), fed batch deoxygenation of Lauric acid (DLA), and the isomerization (hydroreforming) of resulting n-alkanes from the deoxygenation of canola derived fatty acid (IPCF). The names given to the above mentioned renewable fuels are based on how they were produced. Commercially available biodiesel (ASTM D6751 FAME) from Piedmont Biofuels (North Carolina), Jet fuel (Jet-A), and diesel (DF No. 2) were the other three fuels used for these experiments. Due to the very high mole fractions of oleic and linoleic acids, resulting in heptadecane upon deoxygenation, the two renewable fuels produced via fed batch processes (e.g., DCFA and DCFAH) tended to solidify at room temperatures and thus during the course of the experiments they were kept at a temperature of 45 °C. CDCFA had a tendency to precipitate out and as such the fuel had to be stirred during the course of the experiment. Simplified names for the renewable fuels are given in Table 4.1.

4.4 Results and Discussion

The main fuels of interest are the renewable diesel fuels. While the chemical composition and chemical behavior is well understood, little is known on how effective they really are in a real world engine test. For the purpose of better understanding their characteristics, the performance, combustion, and emissions characteristics were measured.

4.4.1 Fuel Sample Characterization

GC-MS chromatograms of the fuels used for this experiment are shown in Figs. 4.1- 4.3. Figure 4.1a, 4.1b and 4.1c shows the GC-MS chromatograms for diesel, jet fuel and biodiesel, respectively. The fuel compositions of DCFA, DCFAH and CDCFA are shown in Figs. 4.2a-4.2c. Figures 4.3a and 4.3b show the chromatograms for DLA and IPCF. From the MS results, diesel fuel was composed of a wide range of hydrocarbons with varying chain lengths in the range of C-8 to C-21 and had a cetane number of 44 [53]. Similarly, jet fuel was made up of distribution hydrocarbons ranging from C-9 to C-16. The biodiesel used in this experiment is composed of C-15 to C-21 Fatty Acid Methyl Esters (FAMES) with Palmitic acid methyl ester and Octadecenoic acid methyl ester being the predominant components of the fuel. This biodiesel had a cetane number of 55.4 and a kinematic viscosity of $4.61\text{mm}^2/\text{s}$ [52]. CDCFA consisted primarily of C-11 to C-17 alkanes, further GC-FID analysis suggested heptadecane was the dominant species for this compound. CDCFA was estimated to have a cetane number of 80 [26]. DCFA and DCFAH also both had heptadecane as their predominant compound from GC-FID analysis. In addition, DCFAH also contained some methyl esters, indicating incomplete hydrolysis of the triglyceride, which are absent in DCFA.

DLA was almost entirely made up of undecane, the 11 carbon alkane. Dodecane was the primary solvent used in the deoxygenation process and appears in small quantities. During the isomerization process, hydrocarbon cracking also occurs and as such the components that make up IPCF include small and large hydrocarbons, ranging from C-4 to C-17

hydrocarbons. GC-FID analysis suggests that heptadecane is still the dominant species in IPCF, but may occur as an isomer due to the observed reduction of freeze point.

Based on hydrocarbon chain length, the energy content of the fuels may be estimated. An increase in hydrocarbon chain length typically results in an increase in energy density, an increase in boiling point and a decrease in volatility [53]. Normal alkanes have the highest ignition quality that increases with increasing chain length, and it may be inferred that the above renewable fuels will have very good ignition qualities. From gas chromatography results, CDCFA, DCFA and DCFAH and IPCF which were all made up predominantly of heptadecane, are expected to have the highest cetane ratings and possibly better combustion with the lowest volatility. Although IPCF contains isomers, if the branches of the isomer are concentrated at the ends of the chain length, there is less of a reduction in ignition quality because iso-alkanes tend to have slightly reduced ignition qualities [9]. DLA is expected to have poorer ignition properties, lower energy content, lower volatility and consequently a lower cetane number because of its short hydrocarbon length. As diesel fuel is composed of a range of hydrocarbons from C-8 to C-20, its properties are expected to be between IPCF and DLA.

4.4.2 Engine Testing

The experiments were carried out using the renewable fuels, biodiesel, jet fuel and diesel. For each experiment, engine throttle and water into the dynamometer were adjusted to meet the desired engine speed and load. For all of the experiments, the 10 hp engine speed was set at 2000 rpm for three different load settings (0 bar, 1.26 bar and 3.77 bar) corresponding to

output torques of 0 Nm, 4.18 Nm, and 12.53 Nm. Data was collected after the engine had sufficiently warmed up and had become stable. Fuel mass flow rate was collected over an interval of one minute for 10 minutes. Twenty five firing cycles of in-cylinder pressure data were collected and averaged for analysis. It should be noted that a constant γ of 1.35 [8, 9] was used in calculating heat release rate curves for all tested fuels. Smoke opacity and exhaust gas information were collected on a minute basis and averaged. At the end of each experiment, the new fuel to be used was allowed to run for twenty five minutes to ensure that all of the previous fuel in the fuel line had been completely consumed. Data from each experiment was collected with a Labview program and stored for further analysis using Matlab and Microsoft Excel.

4.4.2.1 Performance

Engine performance data was obtained either directly from the sensors or calculated based on outputs from the sensors. The indicated work calculated from combustion pressure is shown in Fig. 4.4. The indicated work increases with increasing engine load at the constant engine speed of 2000 rpm. This is expected as the engine would need to do more work in order to compensate for the increased load at a constant engine speed. From this figure, it is clear that biodiesel has the highest indicated work for all load conditions followed closely by DLA. The only exception to the trend is at the bmep of 3.77 bar where DLA is 0.5% greater than biodiesel. For all the load conditions, renewable diesel fuels have higher indicated work when compared to diesel. The higher indicated work for biodiesel and the green fuels may be

as a result of their shorter ignition delays as seen later in the in-cylinder process and the closeness of the peak in-cylinder pressure to TDC. A shorter ignition delay would result in combustion occurring just before TDC, and this would result in more positive work generation as a result of a more effective expansion stroke. A longer ignition delay on the other hand would result in combustion occurring when the piston has begun to move away from the TDC position, resulting in work loss.

The brake performance parameters are shown in Fig. 4.5. From Fig. 4.5a, we observe that the brake work was kept constant for each experiment by design. Mechanical efficiency is the ratio of the brake power delivered by the engine to the indicated power. As shown in Fig. 4.5b, mechanical efficiency increases with increasing load. At the bmep of 1.26 bar, diesel has the highest mechanical efficiency of about 62% followed by jet fuel with 3.2% less. At the bmep of 1.26 bar DCFAH has the highest mechanical efficiency within the renewable diesel fuels, with a decrease of about 8.9% from diesel. At bmep of 3.77 bar, jet fuel has a higher mechanical efficiency than diesel with a small increase of less than 0.1% over diesel. Of the renewable diesel fuels, CDCFA has the highest mechanical efficiency of about 86% which is roughly 0.1% less than jet fuel. Loss of mechanical efficiency is typically attributed to friction from the piston, bearings, pump loss, and other mechanical components of the engine [9].

Based on information from Fig. 4.5b, it can be inferred that as engine load increases, the power generated by the engine is higher than the power loss due to friction, hence the higher mechanical efficiency. As mechanical efficiency is a function of indicated power and brake

power which has been kept constant, the changes observed in the plot are a result of the varying indicated power which can again be linked to variation in ignition delay and the proximity of the peak in-cylinder pressure to TDC.

Brake specific fuel consumption (BSFC) is a measure of how efficiently the engine is using the fuel supplied to produce work. The lower the BSFC the better, as this means the engine is able to do work more efficiently. From Fig. 4.5c, BSFC decreases with increasing engine load. From this figure, it is clear that jet fuel has the lowest BSFC at 1.26 bar and 3.77 bar followed by DCFAH with an increase of 5.6% at 1.26 bar and IPCF an increase of 4.9% over jet fuel at 3.77 bar. The low BSFC value of jet fuel may be attributed to its lower viscosity which would allow for better fuel atomization coupled with the effect of its relatively high heating value. The trends observed for biodiesel and diesel are similar to those reported in previous results [36-37].

The brake thermal efficiency (BTE) is a measure of the engine's ability to convert the chemical energy stored in the fuel to shaft work. Figure 4.5d gives the BTE of the engine using the different fuels. From this figure, we note that BTE increases with increasing load for all the fuels. Biodiesel had the highest BTE at 1.26 bar followed closely by jet fuel with a decrease of about 2.6%. The renewable diesel fuel with the highest BTE was DCFAH with a value of 19.5% a drop of about 8% from biodiesel. An increase in engine load to 3.77 bar makes jet fuel have the highest BTE followed closely by biodiesel with a difference of about 4%. Of the renewable diesel fuels, IPCF has the highest BTE with an efficiency of 5% below jet fuel. Fuel is pumped into the engine on a volumetric basis. As such, the fuel with a higher

density and comparable heating values would have produced more torque and power resulting in a higher BTE. Biodiesel's relatively high brake thermal efficiency may be attributed to its high density, and its oxygen content which allows it to have more complete combustion. These two factors are believed to supersede the effect of its lower heating value and high viscosity. As was observed in Fig. 4.5b, jet fuel has a low BSFC attributed to its low viscosity and high energy content. As a result of this, jet fuel is able to maintain a high BTE value which, at 3.77 bar, surpasses that of biodiesel. From this figure, we also note that the longer hydrocarbon chain fuels have higher brake thermal efficiencies suggesting that the higher energy content of these fuels contributed to the increase in the thermal efficiency of the engine. The result observed here for biodiesel and diesel is consistent with previous results [36].

4.4.2.2 In-cylinder Combustion

Combustion information was obtained from the Kistler 6052A pressure sensor located in the engine cylinder head. Figure 4.6 shows in-cylinder pressure plots at different load settings. In-cylinder pressure increases with increasing load with maximum pressure occurring further away from TDC as engine load increases. Pressures from different fuels follow a similar pressure curve with their differences becoming more pronounced as engine load increases. From Fig. 4.6a, it is observed that the renewable diesel fuels seem to follow the same trend. The in-cylinder pressure plot suggests slightly earlier combustion and shorter ignition delay for the renewable diesel fuels when compared to diesel, jet fuel, and biodiesel.

The rate of pressure rise for the renewable diesel fuels is also noticeably smaller around TDC than for the three reference fuels.

As engine load increases, as shown in Figs. 4.6b and 4.6c, there is a noticeable increase in the rate of pressure rise for diesel, jet fuel, and biodiesel which is not as pronounced as the renewable diesel fuels. CDCFA has the highest cylinder pressure for the renewable diesel fuels at 0 bar and 1.26bar. At 3.77 bar DCFAH had the highest cylinder pressure among the renewable diesel fuels. In all of these cases, DLA has the lowest pressure. With the exception of the no load condition, where biodiesel has the highest peak pressure, jet fuel has the overall highest peak pressure. The high jet fuel pressure values may be as a result of the fuels low viscosity which allows for better atomization and relatively high heating value [54]. Another factor for jet fuels high peak pressure may be a lower cetane number of the fuel, leading to more premixed combustion. Biodiesel's high pressure at the no load condition may be attributed to its better combustion due to its oxygen content. The effect of fuel oxygen content, however, becomes insignificant as engine load is increased.

Figure 4.7 shows the in-cylinder pressure variation rate ($dp/d\theta$) at different crank angles for the three different load conditions. It is seen from these plots, similar to those in Refs [38-39], that the renewable fuels mostly have their peak $dp/d\theta$ just before TDC with a tendency to move towards the TDC as load increases. It is also noted that the cylinder pressure variation rate increases with increasing engine load thus confirming results shown in Fig. 4.6. The large change in pressure variation as load increases might be a result of the high temperature and pressure environment which would allow for faster combustion upon fuel

injection. This mainly depends on the fuel chemical and physical properties, which affect the mixing and ignition process. Higher in-cylinder pressure increasing rate generally leads to more combustion noise.

Figure 4.8 shows the plots of the heat release rate comparison for the different fuels under the three different load conditions. The heat release rate shapes for the different fuels follow a similar pattern. They all have a pre-mixed combustion phase and a diffusion combustion phase. As engine load increases, the peak heat release rate increases. As shown in Fig. 4.8c, jet fuel has a longer ignition delay than any of the fuels regardless of the engine load (further confirming the highest peak pressure).

DLA has the longest ignition delay of all the renewable diesel fuels. Furthermore, in general, with the exception of DLA, the renewable diesel fuels have shorter ignition delays and lower heat release rates when compared to diesel, jet fuel and biodiesel. Biodiesel has a shorter ignition delay for all loads when compared to diesel. The shorter ignition delays experienced by majority of the renewable diesel fuels may be due to thermal cracking which tends to break up longer chain hydrocarbons to form smaller hydrocarbons and gaseous compounds which are liable to ignite much faster than their longer chain hydrocarbon counterparts. The renewable fuels have a higher cetane number with the exception of DLA. From literature [28] the higher the cetane number, the shorter the ignition delay. Further investigation of the ignition characteristics for renewable diesel fuels is necessary.

The peak pressures for the different fuels are shown in Fig. 4.9a. It is noted that as engine load increases, the maximum cylinder pressure increases. From this figure, and as was shown

in Fig. 4.6, DLA has the lowest peak pressure for the different engine loads. It is expected that DLA has relatively poorer ignition qualities and a lower cetane rating when compared to the other fuels used based on its short C-11 hydrocarbon chain length. In addition DLA has a relatively low density which means that since fuel is pumped into the engine on a volumetric basis, the energy density of this fuel is not as high. As a result, combustion of DLA does not achieve as high enough pressure as other fuels do. Figure 4.9b is a comparison of the peak $dp/d\theta$ for the different fuels. From this figure, the rapid rate of pressure increase at 3.77 bar observed in Fig. 4.6c is clearer. This figure also shows the slight increase in peak $dp/d\theta$ as engine load increases.

Ignition delay was determined by calculating the crank angle difference between the engine's start of fuel supply at 17° before TDC and the crank angle at which the heat release rate crosses the zero mark. Figure 4.9c shows the ignition delays for the different fuels at the different load settings. It is observed that under different engine loads, jet fuel has the longest ignition delay with DLA having the longest ignition delay amongst the renewable diesel fuels. Figure 4.9d shows the comparison between peak heat release rates for the fuels at the different engine loads. A slight increase in heat release rates for renewable diesel fuels and a more distinct increase in heat release rates of diesel and jet fuel.

Figure 4.10 shows the comparison of the cumulative heat releases at different loads. From Figs. 4.10a and 4.10b, it is seen that at low loads, jet fuel has the lowest cumulative heat release while biodiesel has the highest. The low cumulative heat release of jet fuel at low loads may be attributed to its longer ignition delay and relatively poor combustion

process compared with other fuels. Biodiesel on the other hand has a slightly shorter ignition delay and the oxygen content of biodiesel also allows for more complete combustion of biodiesel. At 3.77 bar, it is noticed that the trends for all the fuels are somewhat similar with jet fuel still having the lowest cumulative heat release but with the renewable diesel fuels having slightly higher cumulative heat release. This may be attributed to soot processes in the cylinder with radiative heat losses. Again, further studies on the combustion are necessary in optically accessible experimental devices including optical engines [40] or constant volume combustion chambers [41].

4.4.2.3 Emissions

Gaseous emission information was obtained directly from the exhaust of the engine using a gas analyzer and a smoke opacity meter. Hydrocarbon (HC) emissions are shown in Fig. 4.11a. From this figure, DCFAH had the highest HC emissions for all load settings. High HC emission is typically attributed to poor air-fuel mixing and incomplete combustion. From this same figure, it is noted that biodiesel mostly has lower HC emissions when compared to all the fuels; this is believed to be as a result of its oxygen content which would allow for a more complete combustion. By looking at results from Fig.4.10, biodiesel has the highest cumulative heat release which suggests a more complete combustion. The high HC emissions of jet fuel and DLA may be attributed to their long ignition delays as seen in Fig. 4.10c with more incomplete combustion, which also contributes to their lower cumulative heat release. The longer ignition delay of these fuels would result in incomplete combustion as a result of heat loss and pressure drop in the cylinder.

Carbon monoxide (CO) is a by-product of the incomplete combustion of hydrocarbons in air. In Fig. 4.11b, it is noted that carbon monoxide emissions decreased significantly as engine load increased. This is expected since as engine load increases, engine becomes warmer with higher in-cylinder temperatures allowing for better fuel-air mixing. The increase in cylinder temperature and pressure as engine load increases also plays a part in the reduction of CO emissions as it allows for more complete combustion within the cylinder. Biodiesel has relatively high CO emissions, which might be due to its long combustion tail during the late stage as shown in the heat release rate curves. Of the renewable fuels, DLA had the lowest amount of CO emissions. The CO results of biodiesel are somehow different from the previous publications [12]. This might be due to the specific conditions for the current experimental setup. More experiments are necessary for other engine speeds and loads.

From Fig. 4.11c, Carbon dioxide (CO₂) emission increases with increasing load. This is not surprising based on results from Fig. 4.11b as it suggests that as engine load increases, more complete combustion becomes more feasible, possibly as result again of better fuel-air mixing and high in-cylinder temperature and pressure. DCFAH has the highest CO₂ emissions at the different engine loads. In general, the renewable diesel fuels have lower CO₂ emissions.

Oxides of Nitrogen (NO_x) emissions are usually formed at high temperatures when nitrogen reacts with oxygen. From Fig. 4.11d, as engine load increases, NO_x formation increases. This is as a result of the increased thermal NO_x formation mechanism due to high

in-cylinder temperature. In general, the renewable diesel fuels have lower NO_x emissions. By looking at Figs. 4.8d and 4.9 a trend between heat release rate and NO_x emissions is observed. From this figure, it is noted that the fuels with high heat release rate peaks have high NO_x emissions. This is as expected since a high heat release rate results from the premixed combustion stage and corresponds to a high temperature condition promoting thermal NO_x formation [44].

Figure 4.12a shows the result of the opacity measurement for each experiment. Smoke opacity increases with increasing engine load. For the same condition, it is observed that a general decrease in opacity compared to diesel. A decrease in opacity can be interpreted as a decrease in soot from the exhaust thus suggesting that the renewable fuels also have lower soot emissions. By using a soot density calculator [55], soot density information for the different fuels was obtained from the opacity measurements. Soot density information follows the same trend as smoke opacity measurements. It should be noted that based on the method used in collecting soot opacity data, the soot density measurements shown are a relative value and not necessarily the absolute values for the fuels used at the given conditions. The result of these calculations is shown in Fig. 4.12b. The lower soot emissions observed for the renewable fuels may be attributed to complete combustion of the fuel, probably as a result of their higher ignition qualities and heating values, lack of aromatics and relatively shorter ignition delays. Their slightly higher exhaust gas temperatures (Fig. 4.13) can be seen as proof of this. From Fig. 4.13, as engine load increases exhaust gas temperature increases. Renewable diesel fuels in general have higher exhaust gas

temperatures than the reference fuels, possibly as a result of their generally higher cetane ratings and their shorter ignition delays. Diesel also has higher exhaust gas temperatures when compared to biodiesel, thus supporting this result. Slower late stage combustion with a longer combustion duration lasting into late crank angles would in turn lead to higher exhaust gas temperature.

It should be noted that the experiments in this work are limited to one engine speed under different loads in a single cylinder engine; it is possible that the trend is different for other engine speeds and loads in multi-cylinder diesel engines. Further investigations are necessary in the future for better understanding of the operation and combustion characteristics of the newly developed renewable diesel fuels in practical diesel engines.

4.5 Conclusion

Experiments were conducted to study the effects of a number of different renewable diesel fuels in a compression-ignition engine. Engine performance, fuel combustion and emissions were measured. Based on the results obtained from these preliminary experiments, some important finding can be summarized in the following:

1. Renewable diesel fuels have slightly lower mechanical efficiencies when compared with diesel but their lower brake specific fuel consumption compensates for this as less fuel is needed to do the same amount of work. Fuel conversion efficiency is roughly the same for all the renewable fuels, with values higher than that of diesel. The renewable fuels also have comparable brake thermal efficiencies with that of diesel, with the exception of CDCFA at the lower load 1.26 bar;

2. Renewable diesel fuels with the exception of DLA have shorter ignition delays when compared with diesel. At low engine loads, jet fuel has the longest ignition delay, which remains unchanged as engine load increased. There is, however, a noticeable rise in the rate of pressure increase for jet fuel and diesel at 3.77 bar. Most of the renewable diesel fuels are also observed to have lower peak in-cylinder pressure and heat release rates;
3. Renewable diesel fuels have remarkably lower emissions with the exception of HC emissions. CO₂ and CO emissions are lower for the renewable fuels when compared to diesel, biodiesel and jet fuel. NO_x emissions are significantly lower for the renewable fuels. Soot emissions for the renewable fuels are also lower when compared to diesel, biodiesel and jet fuel;
4. From these experiments, DLA may be eliminated as a viable replacement for diesel because its ignition delay is relatively long and it has a tendency to decrease engine performance. DCFA and DCFAH are also not viable replacements for diesel as they have high freezing points and tend to solidify at room temperature. CDCFA is also not a viable alternative as it tends to precipitate out at room temperature. This precipitation also leads to the clogging of fuel lines when the engine cools down. A very attractive alternative to diesel, without the need for additional engine modifications, is the IPCF. Engine performance using this fuel is slightly better than diesel and all its emissions including hydrocarbons are lower than diesel;

Table 4.1: Fuel Nomenclature

Fuel Name	Acronym
Fed batch deoxygenation of canola derived fatty acids	DCFA
Fed batch deoxygenation of canola derived fatty acids optimized with H ₂	DCFAH
Fed batch deoxygenation of Lauric Acid	DLA
Continuous deoxygenation of canola derived fatty acids	CDCFA
Isomerization product of canola derived fatty acid alkanes	IPCF

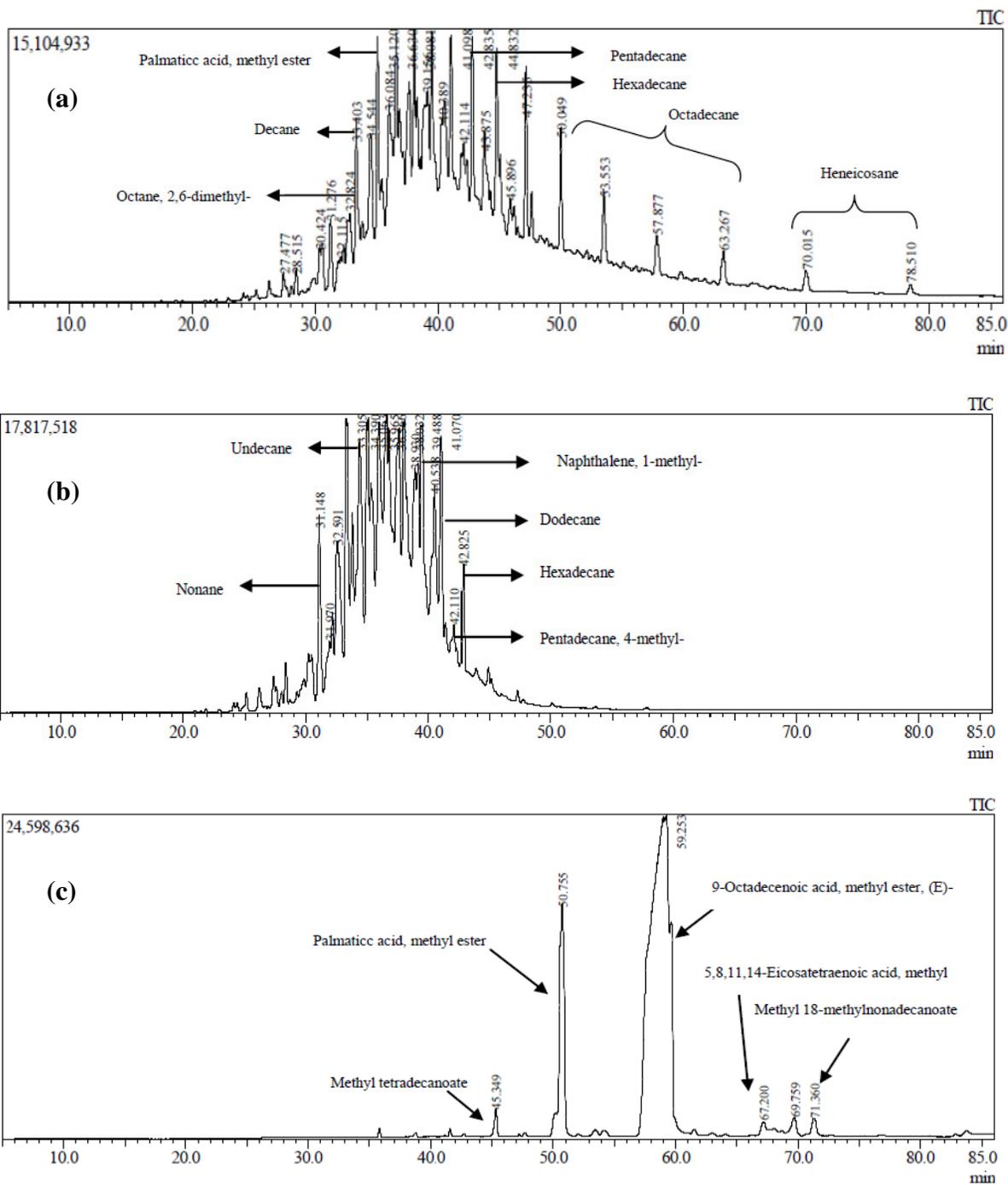


Figure 4.1: GC-MS chromatogram of (a) Diesel (b) Jet fuel (c) Biodiesel

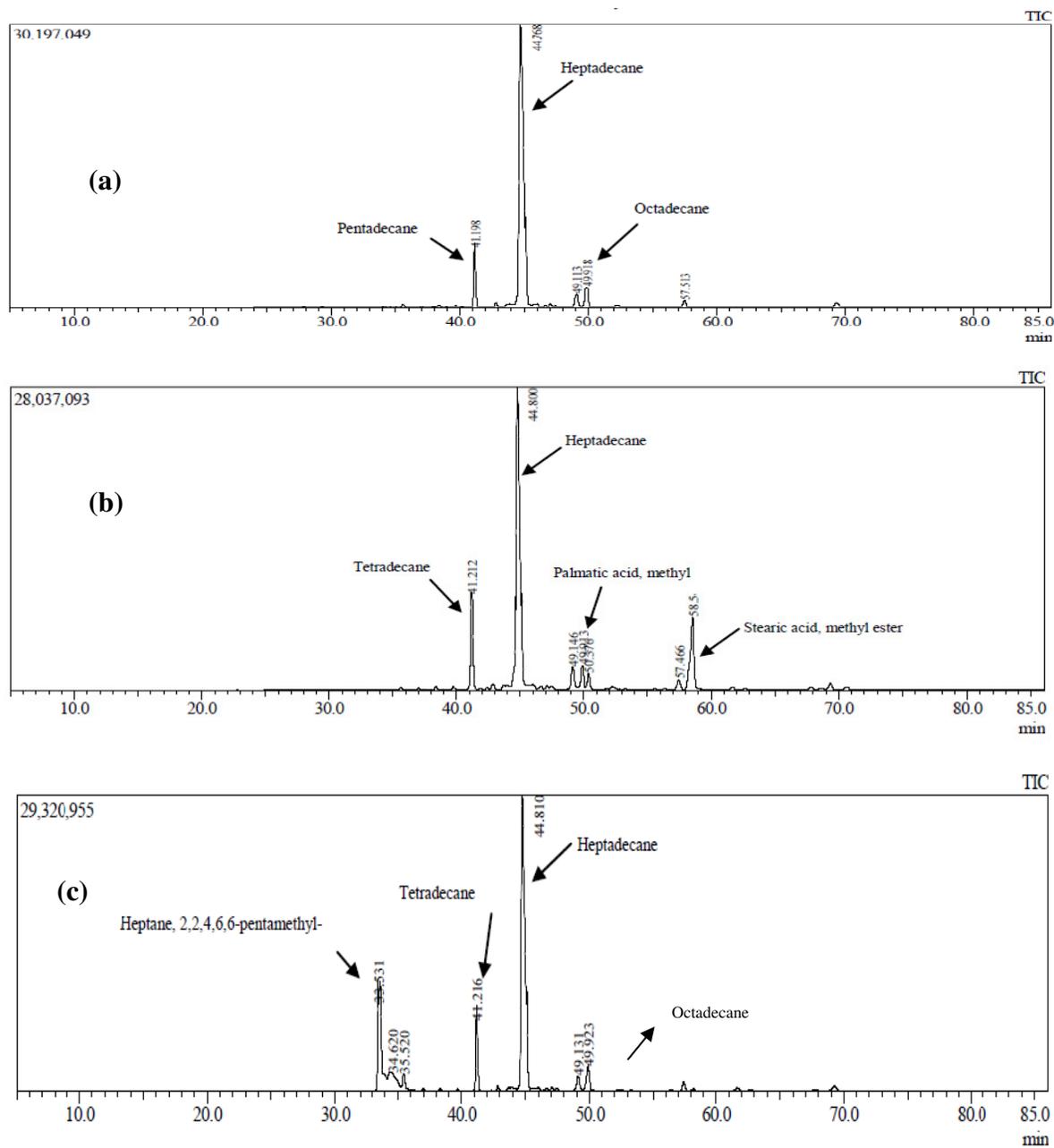


Figure 4.2: GC-MS chromatogram of (a) DCFA (b) DCFAH (c) CDCFA

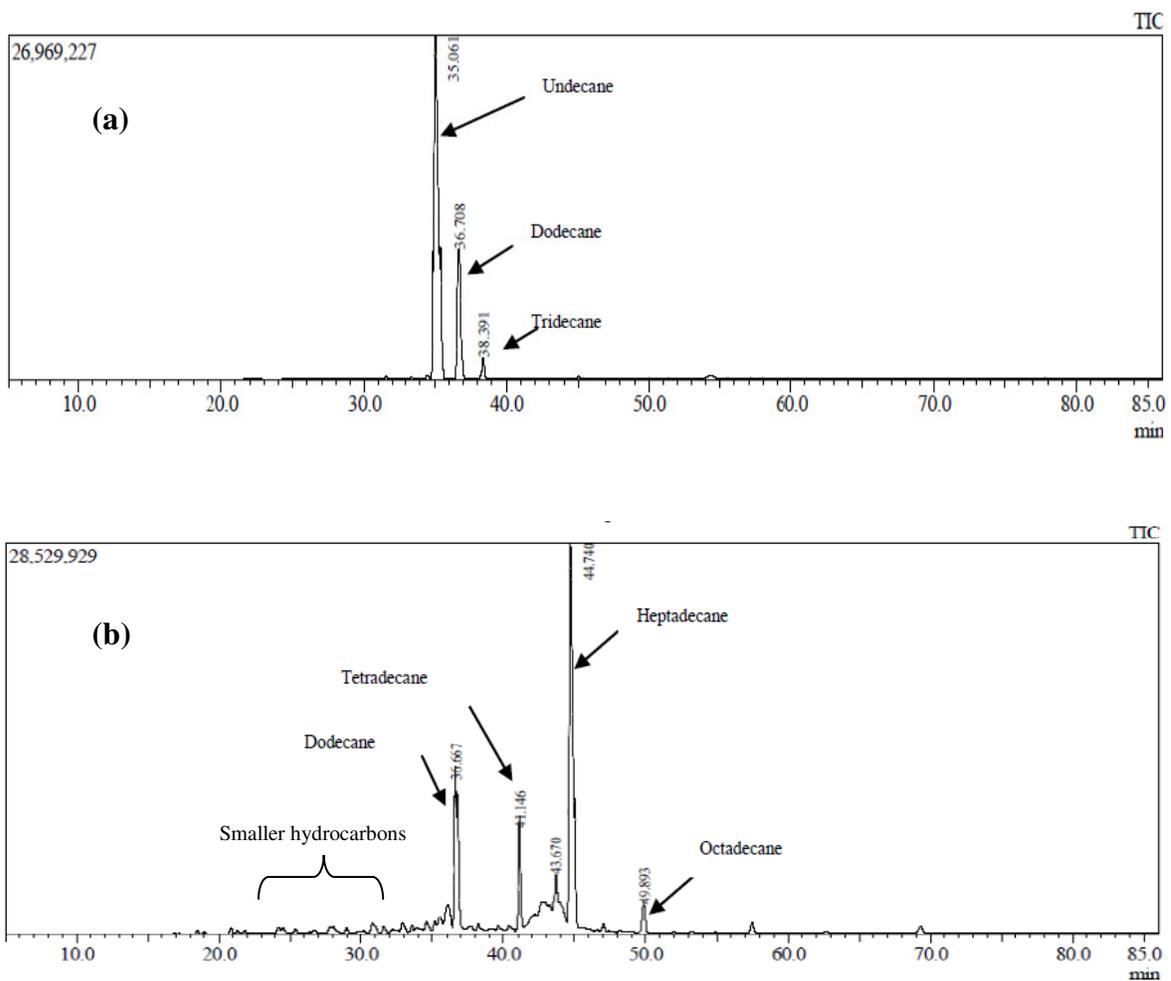


Figure 4.3: GC-MS chromatogram of (a) DLA (b) IPCF

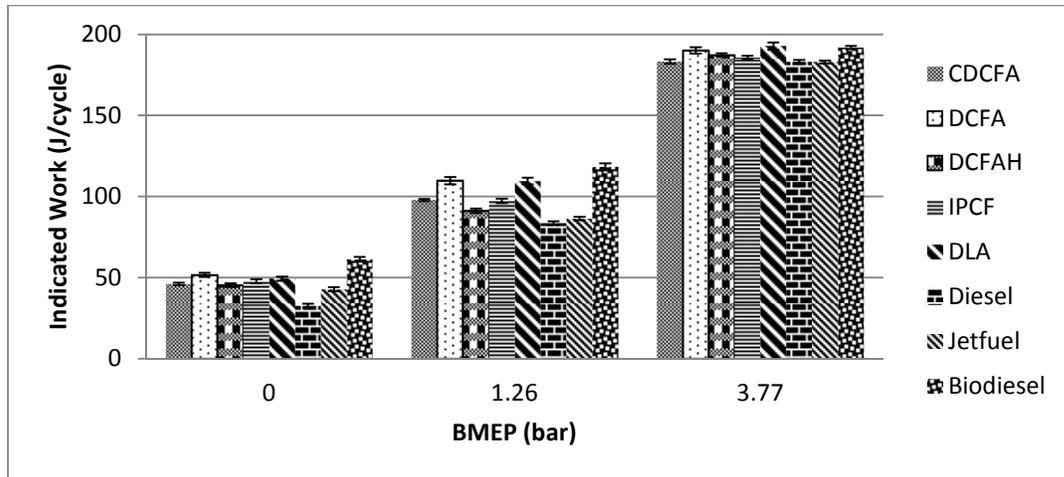


Figure 4.4: Indicated work for all fuels at different Brake Mean Effective Pressures

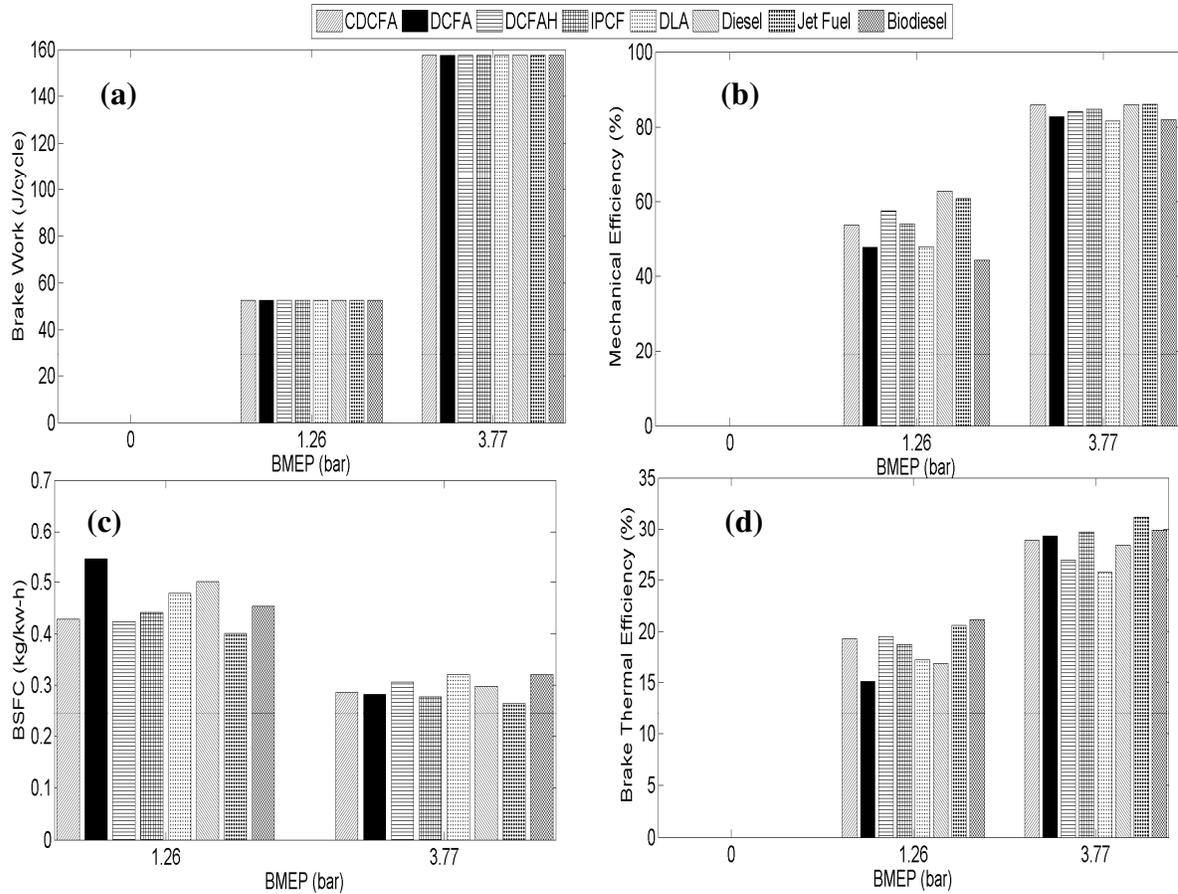


Figure 4.5: (a) Brake Work (b) Mechanical Efficiency (c) BSFC (d) Brake Thermal Efficiency for all fuels at different Brake Mean Effective Pressures. Note BSFC at 0 bar has not been represented as it tends to infinity.

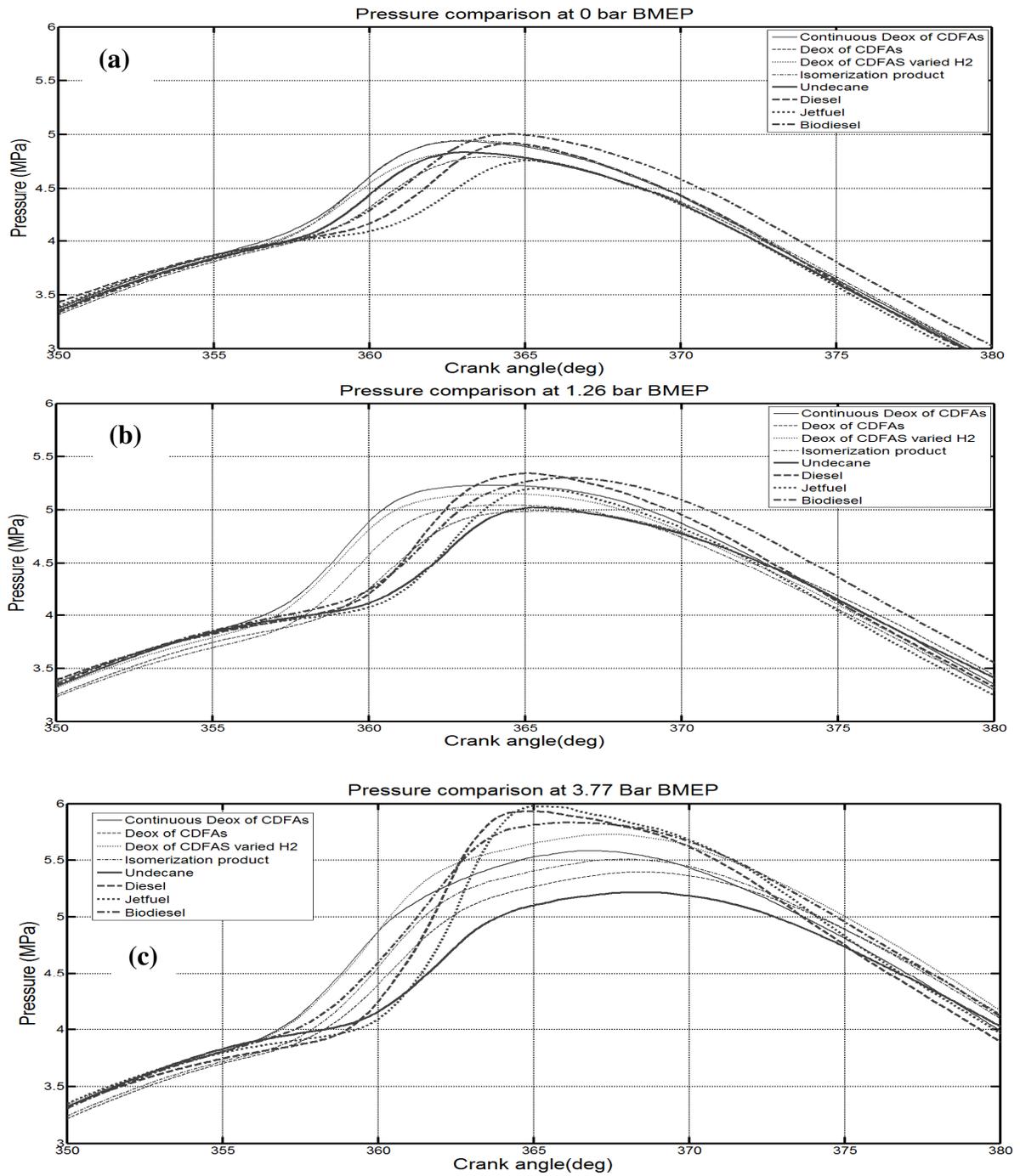


Figure 4.6: In-cylinder pressure comparison at (a) 0 bar (b) 1.26 bar (c) 3.77 bar

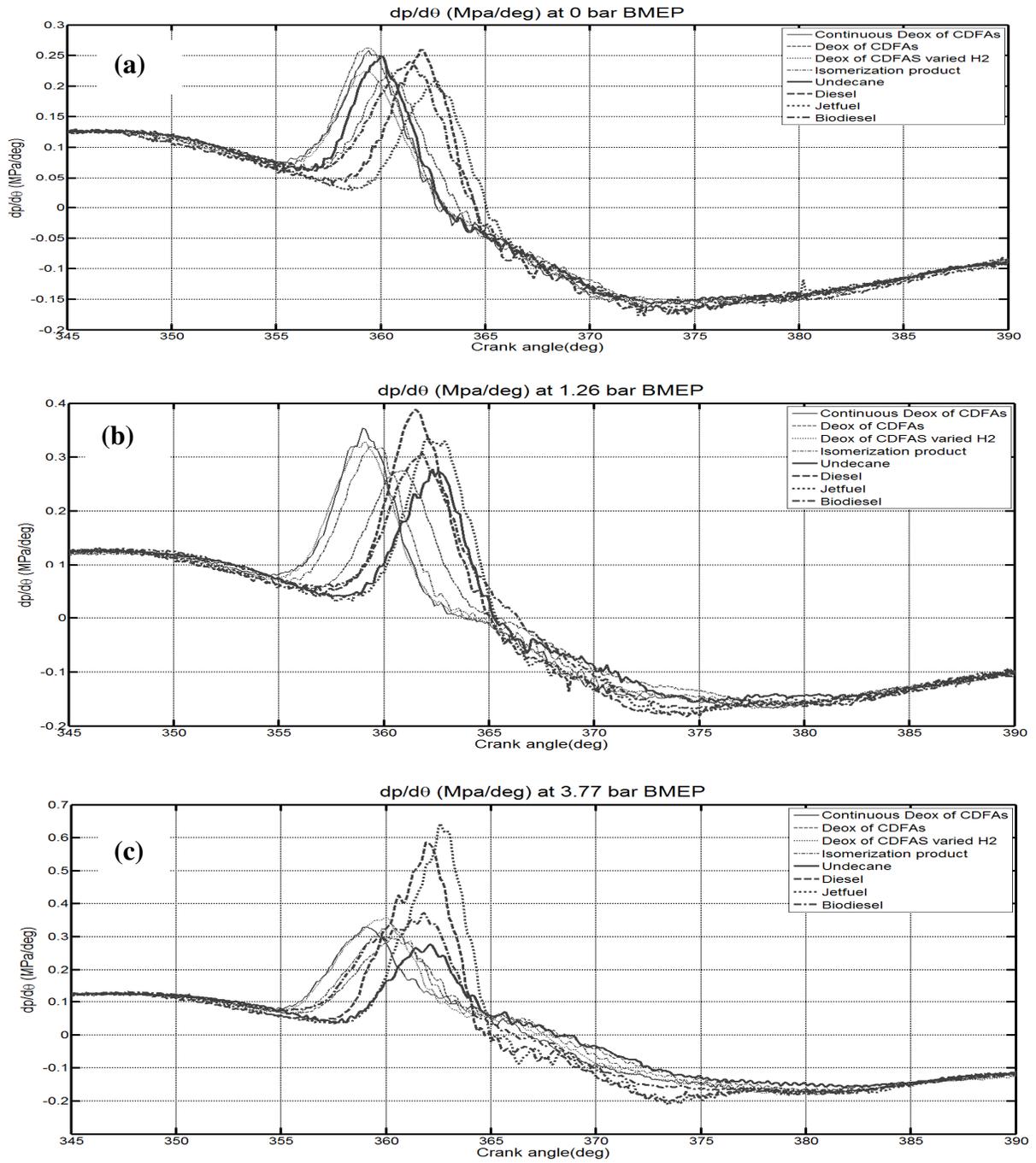


Figure 4.7: $dp/d\theta$ at (a) 0 bar (b) 1.26 bar (c) 3.77 bar

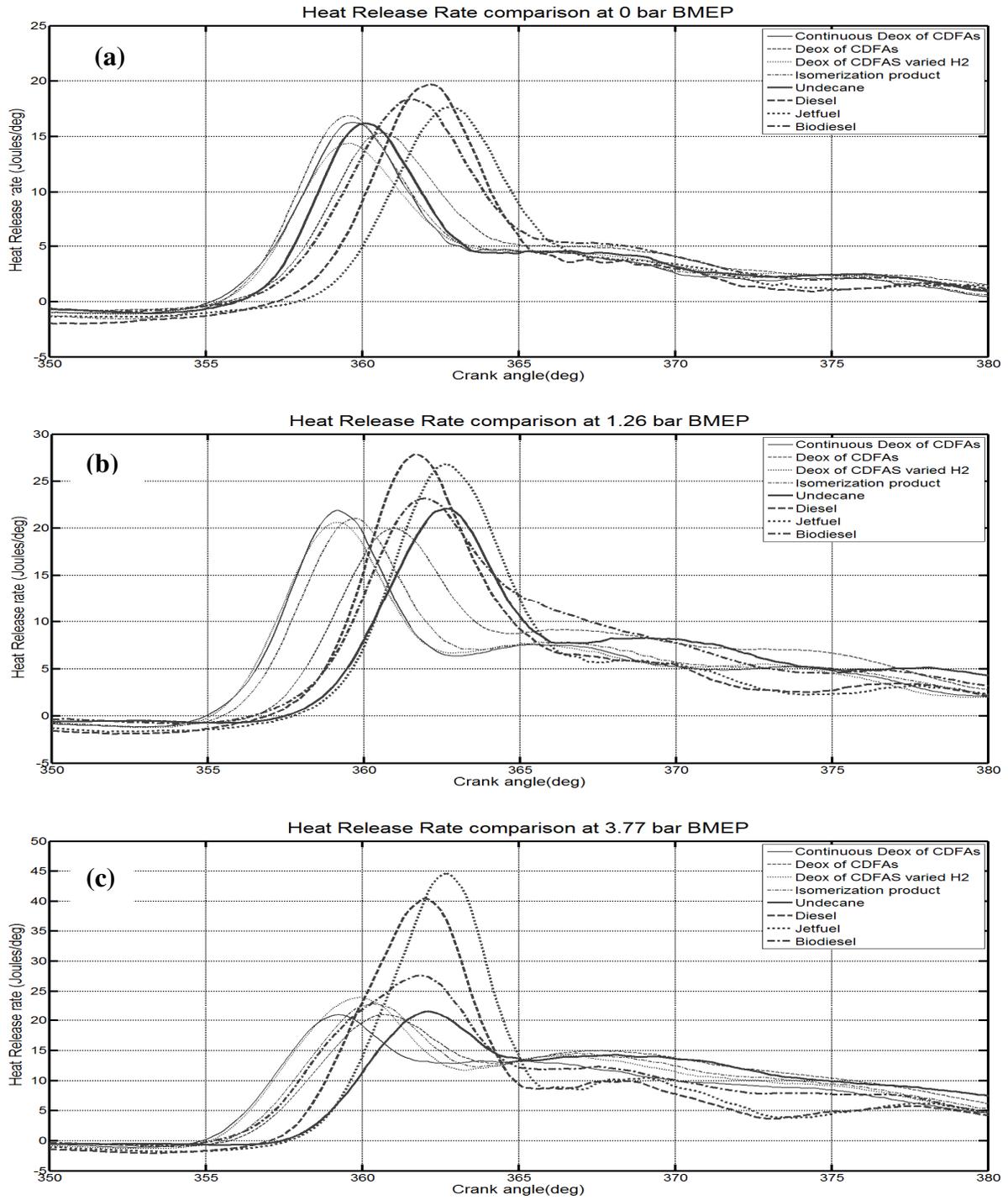


Figure 4.8: Heat release rate comparison at (a) 0 bar (b) 1.26 bar (c) 3.77 bar

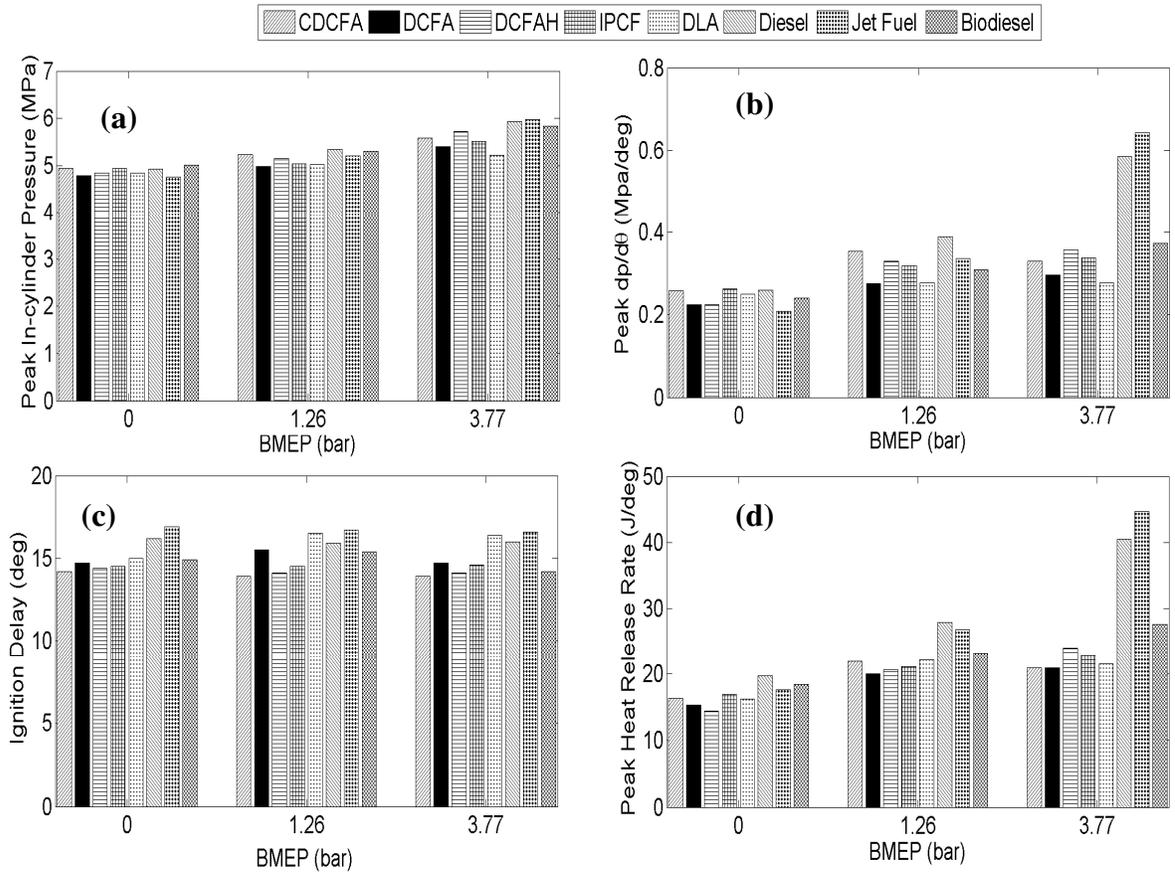


Figure 4.9: (a) Peak in-cylinder pressure (b) Peak $dp/d\theta$ (c) Ignition delay (d) Peak heat release rate for all fuels at the different Brake Mean Effective Pressures.

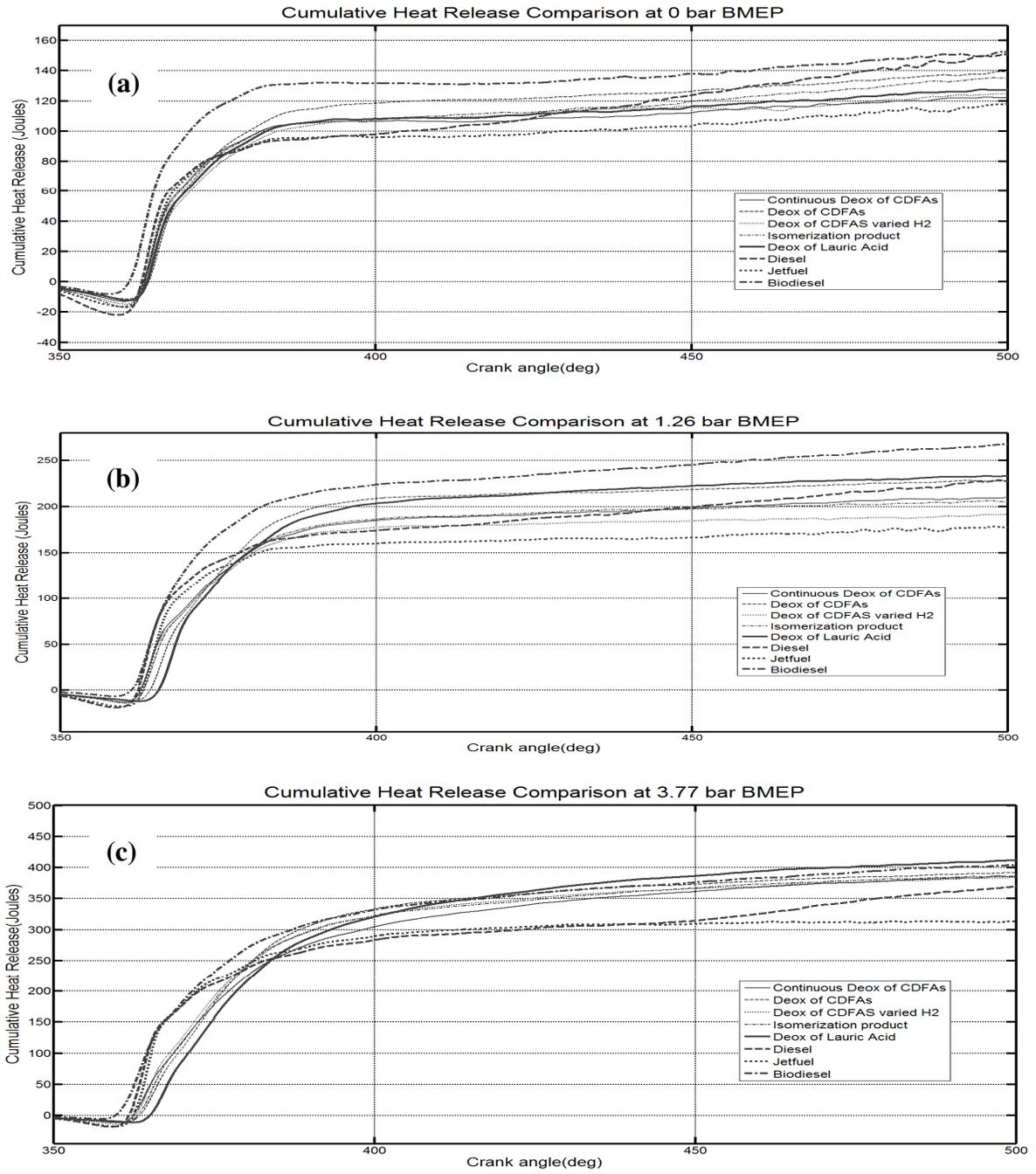


Figure 4.10: Cumulative heat release comparison at (a) 0bar (b) 1.26 bar (c) 3.77 bar

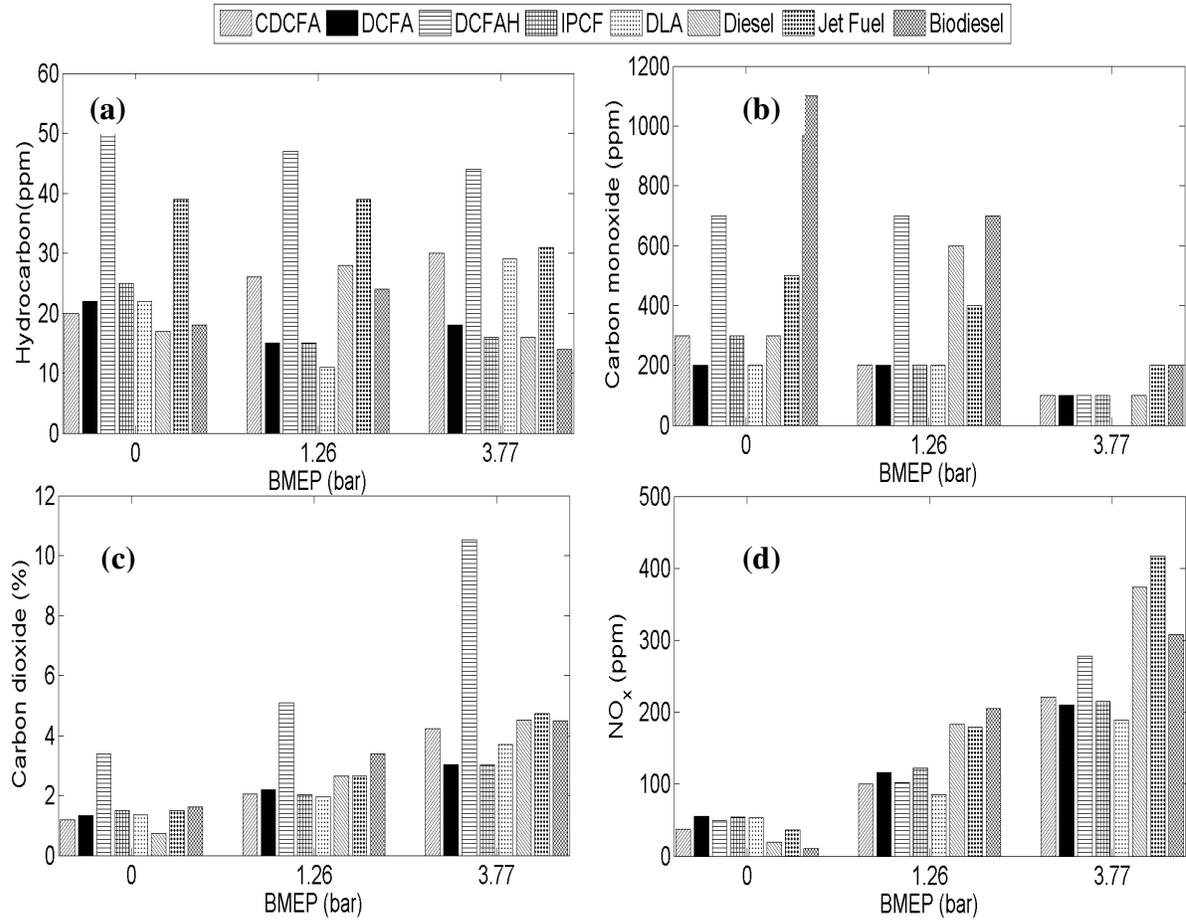


Figure 4.11: (a) Hydrocarbon (b) Carbon monoxide (c) Carbon dioxide (d) NOx emissions for all fuels at the different Brake Mean Effective Pressures respectively

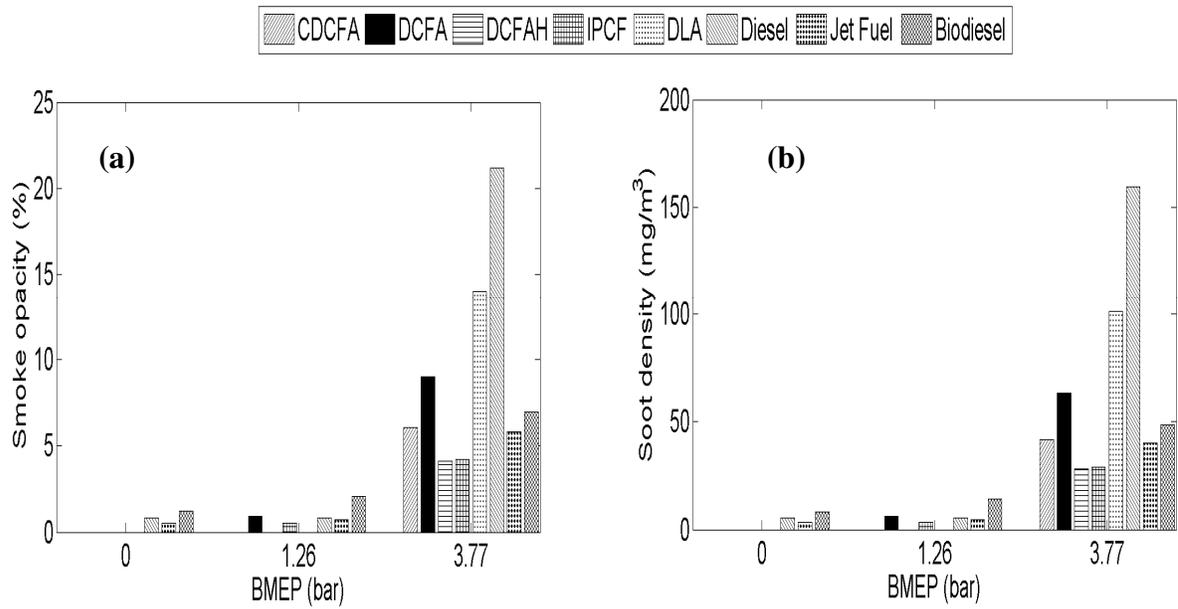


Figure 4.12: (a) Smoke opacity (b) Soot Density for all fuels at the three different Brake Mean Effective Pressures

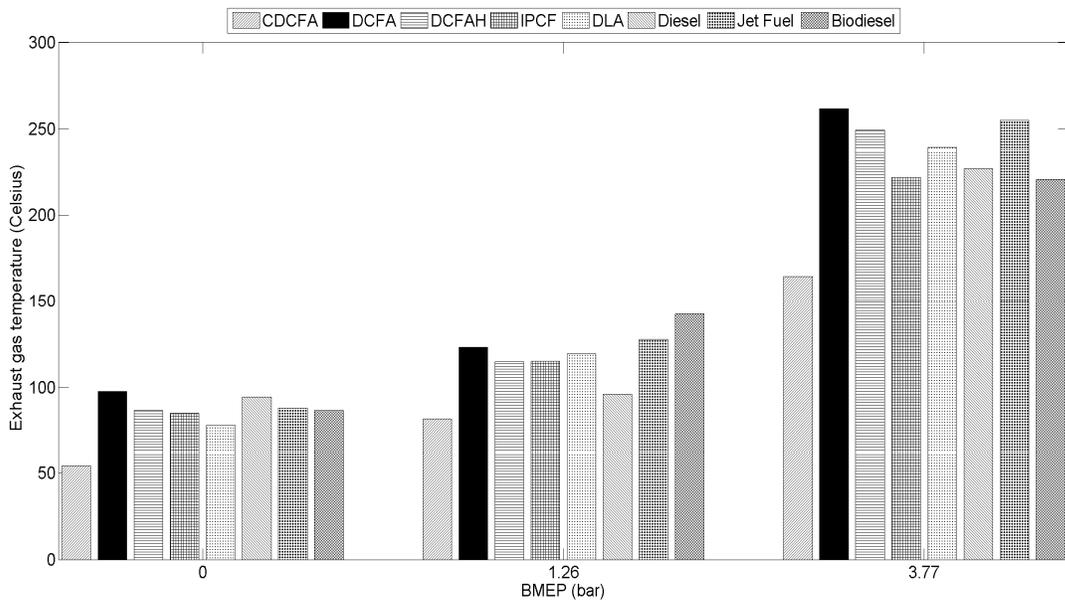


Figure 4.13: Exhaust gas temperature (Celsius) for all fuels at the different Brake Mean Effective Pressures

CHAPTER 5

Engine Performance, Combustion, and Emissions Study of Biomass to Liquid Fuel in a Compression Ignition Engine

5.1 Abstract

In this work, the effects of diesel, biodiesel and biomass to liquid (BTL) fuels are investigated in a single-cylinder diesel engine at a fixed speed (2000 rpm) and three engine loads corresponding to 0 bar, 1.26 bar and 3.77 bar brake mean effective pressure (BMEP). The engine performance, in-cylinder combustion, and exhaust emissions were measured. The results show an increase in indicated work for BTL and biodiesel at 1.26bar and 3.77bar BMEP when compared to diesel but a decrease at 0bar. Lower mechanical efficiency was observed for BTL and biodiesel at 1.26 bar BMEP but all three fuels had roughly the same mechanical efficiency at 3.77 bar BMEP. BTL was found to have the lowest brake specific fuel consumption (BSFC) and the highest brake thermal efficiency (BTE) among the three fuels tested. Combustion profiles for the three fuels were observed to vary depending on the engine load. Biodiesel was seen to have the shortest ignition delay among the three fuels regardless of engine loads. Diesel had the longest ignition delay at 0 bar and 3.77 bar BMEP but had the same ignition delay as BTL at 1.26 bar BMEP. At 1.26 bar and 3.77 bar BMEP, BTL had the lowest HC emissions but highest HC emissions at no load conditions when compared to biodiesel and diesel. When compared to diesel and biodiesel BTL had lower CO

and CO₂ emissions. At 0 bar and 1.26 bar BMEP, BTL had higher NO_x emissions than diesel fuel but lower NO_x than biodiesel at no load conditions. At the highest engine load tested, NO_x emissions were observed to be highest for diesel fuel but lowest for BTL. At 1.26 bar BMEP, diesel had a higher smoke opacity than BTL and biodiesel. At 3.77 bar BMEP, BTL had the highest smoke opacity with diesel fuel having the lowest opacity. This work also demonstrated the effectiveness of BTL as a renewable alternative fuel with characteristics comparable to regular diesel fuel.

5.2. Introduction

Rising cost as a result of depleting fossil fuel reserves as well as problems relating to greenhouse gas emissions have been the most important drivers for seeking out new sources of energy [33]. For internal combustion (IC) engines, liquid biofuels have emerged as viable alternatives to fossil fuels. Biofuels are typically made from renewable sources such as animal feedstock, plants, and biomass. Biofuel production and consumption has increased in recent years partly as a result of government support in the form of tax credits [56]. Biodiesel is a type of biofuel made from the trans-esterification process and involves reaction of oil or fatty acids from oil with an alcohol in the presence of a catalyst [7]. The end product of the trans-esterification process is a fatty acid methyl ester (FAME), also called biodiesel. Biodiesel has several benefits over conventional fossil diesel; it is renewable, non-toxic, greater lubricity, generally with lower emissions and most of all has similar properties to petro diesel [12].

Biomass to liquid (BTL) fuel is a second generation biofuel and a synthetic fuel. Unlike first generation biofuels which use specific parts of the biomass for biodiesel production, second generation biofuels can be made from any portion of the biomass. BTL is produced based on processes from the production of gas to liquid (GTL) and coal to liquid (CTL) using the Fischer Tropsch (FT) process [23, 57]. The steps involved in the BTL fuel production are gasification, gas cleaning and synthesis. Gasification is the first step in BTL production, which involves the breakdown of the feedstock in a reactor at high temperature and high pressure into synthetic gases, mainly carbon monoxide (CO) and hydrogen (H₂). Gasification can be divided into three parts: pyrolysis, char gasification, and partial char combustion [58]. Gas cleaning is the removal of contaminants as a result of tar production in the reactor, which is necessary due to the sensitivity of catalyst in the synthesis stage [23]. The final stage is the reaction of CO and H₂ in the presence of an iron or cobalt catalyst to form hydrocarbons. It is possible to adjust the final products to meet specific fuel requirements (gasoline, jet fuel or diesel).

The process of converting BTL fuels by the FT process has several benefits. Syngas produced in the gasification stage from the breakdown of biomass can lead to the production of a variety of products such as synthetic fuels, lubricating oils, synthetic waxes and chemical feedstocks [57]. BTL fuels have little to no sulfur or aromatic content, high fuel ignition quality and low fuel density [24]. As the fuel is produced from a renewable energy source, it can be CO₂ neutral with the additional benefit of reduced emissions from tailoring of the fuel to meet certain combustion requirements. Research carried out by Ng *et al* [24] showed that

oxides of Nitrogen (NO_x), CO and particulate matter emissions for sundiesel (a BTL fuel) they used were lower when compared to regular diesel fuel. Disadvantages from using BTL come from the cost of biomass which would normally be wood and the environmental impact of harvesting and re-growing the trees as feedstock. Sunde *et al* [59] estimated the cost of BTL production to be at about \$3.55 - \$5.67 per U.S gallon which puts the price range at about the same cost for fossil based diesel. Sundae and colleagues also estimated that BTL from sustainably managed forest biomass and woody waste may have lower overall environmental impact than fossil diesel.

BTL is a fuel made up of paraffins with very little to no sulfur and aromatic content and as an FT fuel, its end product is expected to be similar to GTL fuels which are generally FT fuels made from natural gas. Several works have been done on the use of GTL fuels in diesel engines with very positive results. Moon *et al.* [60] and Li *et al.* [61] investigated GTL fuels in turbo-charged diesel engines. In both of these cases, total hydrocarbon (THC) emissions and CO emissions were lower than regular diesel fuel. Moon *et al.* observed an increase in NO_x emissions [60]; however, Li *et al.* found a reduction in both NO_x and smoke emissions [61]. Abu-Jrai *et al.* conducted several experiments in a single-cylinder diesel engine under different engine operating conditions and observed improved engine efficiency as well as reduced NO_x and smoke for GTL fuel [62, 63]. They did, however, observe an increase in CO emissions. Clark *et al* [64] and Lapuerta *et al.* [65] carried out experiments using GTL in diesel engines. Their experiments both showed a reduction in particulate matter (PM). Clark *et al.* also observed reductions in NO_x from experiments carried out in several

buses and tractors. In addition to obtaining lower PM emissions, Lapuerta and colleagues also observed a decrease in smoke opacity and a reduction in THC. In an experiments carried out using a Euro III common rail heavy duty diesel engine fueled with GTL, Wang *et al.* observed reduced NO_x, CO and THC emissions as well as a decrease in max torque and power of the diesel engine when compared to regular diesel fuel [66].

There is an increasing demand for sustainable alternative fuel production and BTL fuel as a renewable fuel from biomass offers a sustainable solution. There are few studies in the literature on the effects of BTL on engine performance, in-cylinder combustion, and emissions. The main objective of this work is to better understand how BTL fuel perform in a diesel engine when compares with conventional diesel and biodiesel fuels, specifically in terms of engine performance, combustion, and gaseous exhaust emissions.

5.3. Experimental Setup

The setup for this experiment was discussed in chapter 3. In this work, diesel, biodiesel, and BTL were tested in the engine at a fixed engine speed of 2000 rpm for three different load settings at 0 bar, 1.26 bar and 3.77 bar brake mean effective pressure (BMEP) corresponding to engine torque outputs of 0, 4.18 and 12.53 N-m, respectively. The fuel of primary focus is BTL with the other two fuels used as references. Biodiesel is used as a reference because it is regarded as a first generation biofuel unlike BTL, which is considered as a second generation biofuel. To begin the experiment, the engine was allowed to run on the fuel to be tested continuously for 30 minutes till it is sufficiently warm then the desired

dynamometer load and rpm were set before data collection can commence. It should be noted that, the injection timing for the engine was kept the same regardless of the fuel to be tested.

5.4. Results and Discussion

5.4.1 Fuel Properties

Properties of the fuels tested are given in Table 5.1. Lower heating value (LHV) for BTL was obtained from [67] after unit conversion. The LHVs of diesel and biodiesel were taken from [68]. Flash point for diesel and biodiesel are derived from [52, 68]. Cetane number for biodiesel and diesel are from [52, 69]. All other fuel properties were measured in the laboratory. In order to characterize the fuel components, samples of the three fuels were measured in a gas chromatograph/mass spectrometer (GC/MS) system (Shimadzu). The GC/MS results for the three fuels are shown in Figs. 5.1a-c. From the GC/MS analysis, diesel is found to consist of $C_8 - C_{27}$ hydrocarbons. Biodiesel is made up of $C_{15} - C_{21}$ hydrocarbons and the BTL fuel used is made up of C_9 to C_{21} alkane hydrocarbons. The range of hydrocarbons for BTL indicates that it may have the lowest molecular weight. Due to its lower molecular weight, BTL is expected to have a lower boiling point and it can vaporize relatively easily. Furthermore, from the GC results, BTL has no aromatics and is made up entirely of alkanes. Considering its average hydrocarbon chain length, it is expected that BTL will have a reasonably high cetane number [9] which is supported by reported cetane values for BTL fuels from [24] and [67].

5.4.2 Performance

Figure 5.2 shows the engine performance parameters for the three different fuels. From Fig. 5.2a except at 0 bar BMEP, BTL has a higher indicated work than diesel fuel and about the same as biodiesel. Diesel results in a higher mechanical efficiency than both biodiesel and BTL at 1.26 bar (Fig. 5.2b). The engine's mechanical efficiency is, however, roughly the same for all three fuels at 3.77 bar. Figure 5.2c demonstrates the brake specific fuel consumption (BSFC) for all three fuels. BTL has the lowest BSFC of all three fuels followed by biodiesel. The lower BSFC value of BTL may be as a result of its slightly higher heating value. Brake thermal efficiency (BTE) is a ratio of the brake work per cycle to the chemical energy released in the combustion process. The chemical energy released in a cycle depends on the injected fuel mass per cycle and its heating value. From Fig. 5.2d, BTL is observed to have a much higher BTE than both diesel and biodiesel. Biodiesel is also noted to have a higher BTE than diesel fuel. Low BSFC coupled with a higher heating value is believed to be the primary reason for the higher BTE of BTL.

5.4.3 Combustion

Figures 5.3-5.6 show the combustion results with different combustion parameters of the three fuels in the engine. Figure 5.3 presents the in-cylinder pressure of the three fuels at the three different load settings. From Fig. 5.3a, biodiesel is observed to have the highest peak cylinder pressure followed by BTL and then diesel. The pressure rise after fuel injection is observed to be more rapid for biodiesel followed by BTL fuel when compared to diesel fuel. In Fig. 5.3b, the engine load is increased to 1.26 bar. A similar observation to Fig. 5.3a

is seen except in this case the BTL in-cylinder pressure is almost the same as diesel fuel. Biodiesel still has the highest peak pressure and rate of pressure rise followed by BTL and then diesel fuel. A further increase in engine load to 3.77 bar, shown in Fig. 5.3c, results in a decrease in the peak pressure and rate of pressure rise for BTL compared to diesel. This observation at 3.77 bar is quite similar to those reported in a previous publication [24].

Figure 5.4a shows the heat release rate results at 0 bar BMEP. Biodiesel has the highest peak heat release rate followed by diesel and then BTL. It should be noted that although BTL has a shorter ignition delay than diesel fuel, diesel has a higher peak heat release rate. This is because the longer ignition delay of diesel fuel allows for more air-fuel mixtures in the pre-mixed combustion phase which would ultimately result in a higher peak heat release rate upon ignition. In Fig. 5.4b at 1.26 bar BMEP engine load, a similar heat release profile is observed for BTL and diesel except that BTL has the highest peak heat release rate and more pre-mixed combustion when compared to both biodiesel and diesel fuel. An additional observation when comparing no load condition to 1.26 bar BMEP is that the ignition delay for the fuels is reduced as engine load is increased. For diesel and biodiesel, ignition delay decreases by 0.3 degrees from 0 bar to 1.26 bar while for BTL, it only decreased by 0.1 degrees. This shorter ignition delay for higher load is believed due to warmer engine conditions. From Fig. 5.4c at 3.77 bar BMEP, diesel is observed to have a significantly higher peak heat release rate with BTL having the lowest peak heat release rate. There is also an observable difference between the heat release profiles of the three fuels.

Although diesel and BTL appear to have similar ignition delays, the peak heat release rate for BTL was significantly lower than diesel at this engine load.

Figure 5.5 demonstrates the cumulative heat release results. As shown in Fig. 5.5a, diesel shows the highest peak cumulative heat release with BTL having the lowest at 0 bar BMEP. As the engine load is increased to 1.26 bar, diesel has the lowest cumulative heat release and BTL has the highest just barely above biodiesel, as shown in Fig. 5.5b. This same trend is observed in Fig. 5.5c. The higher cumulative heat release for BTL as engine load increases may be attributed to ignition delay effects coupled with high BTE and higher energy content, and in the case of 3.77 bar, later combustion in the mixing controlled phase.

Figure 5.6 shows the various peak values related to combustion results and the ignition delay. Figure 5.6a depicts the peak in-cylinder pressures at different engine loads. For all three load conditions, biodiesel has the highest peak in-cylinder pressure. At the two lower engine loads, BTL has higher peak in-cylinder pressure than diesel fuel. The higher in-cylinder pressure is believed to be as a result of BTL having a slightly shorter ignition delay than diesel as was shown in Figs. 5.4a and 5.4b. At 3.77 bar however, there is a noticeable spike in the in-cylinder pressure for diesel fuel with a more rapid rate of pressure change than BTL. Figure 5.6b shows the peak heat release rates for the three fuels at different engine loads. Biodiesel has a higher peak heat release rate at 0 bar. As engine load increases to 1.26 bar, BTL has the highest peak heat release rate followed by diesel with biodiesel having the lowest. The higher peak heat release rate for BTL may be attributed to the lighter molecular weight of BTL allowing it to vaporize much more quickly than diesel and biodiesel coupled

with its long ignition delay. Based on Fig. 5.4b, it can be assumed that ignition delay alone may not account for all the changes in the peak heat release rate observed at 1.26 bar since diesel and BTL have almost the same ignition delay of 11.3 deg. Figure 5.6c shows the peak cumulative heat release for the fuels. It is observed that while BTL has the lowest peak cumulative heat release at 0 bar, it has the highest value at 1.26 and 3.77 bar followed closely by biodiesel in both cases. Diesel has the lowest cumulative heat release rate at the two higher engine loads but has the highest peak cumulative heat release at 0 bar.

The ignition delay for the fuels is shown in Fig. 5.6d. Ignition delay was determined by calculating the crank angle difference between the engine's start of fuel supply at 17° before TDC and the crank angle at which the heat release rate crosses the zero mark. From Fig. 5.6d, biodiesel is observed to have the shortest ignition delay for all three load conditions. Diesel has the longest ignition delay except at 1.26 bar where diesel and BTL have similar ignition delay. The shorter ignition delay observed for biodiesel may be attributed to the higher bulk modulus of the fuel. Fuel injection system for this engine is a typical mechanical system including a pump, pipe, and injector. The fuel is injected on a volume basis. A larger bulk modulus of a fuel promotes faster pressure wave propagation in the pipe, which in turn opens the injector nozzle faster and leads to a shorter ignition delay [42]. The other reason for shorter ignition delay of biodiesel is expected to be from its relatively higher cetane number. The ignition delay for diesel and BTL fuel are rather close under all the conditions, it is expected that they have similar cetane numbers with BTL slightly higher.

Another parameter of considerable interest is the actual air to fuel ratio as shown in Fig. 5.7. The air-fuel ratio is calculated by dividing the mass of air (obtained from the mass air flow sensor) with the fuel flow rate into the engine. It is seen that air-fuel ratio decreases with increasing engine load due to more fuel injected per cycle. Diesel fuel is observed to have the lowest air-fuel ratio at all three load conditions. At 1.26 and 3.77 bar, BTL is observed to have the highest air-fuel ratio. These observations suggest that BTL and biodiesel combustion occur in a more fuel lean environment when compared to diesel fuel. There is a possibility of over-leaning in the case of BTL considering its lighter molecules. Over-leaning occurs when air-fuel mixture is beyond the lean limit of combustion. It may not auto-ignite and lead to a misfire, particularly under very low-load conditions [9].

5.4.4 Emissions

Gaseous fuel emissions were measured with an infrared industries FGA 4000 XDS exhaust gas analyzer. The emissions results are shown in Fig. 5.8. From Fig. 5.8a, it is observed that except at 0 bar, BTL has overall lower HC emissions than both diesel and biodiesel. These lower HC emissions may be attributed to better air-fuel mixing. From Fig. 5.7, since BTL has a high air-fuel ratio at 1.26 bar and 3.77 bar there is the possibility of more complete combustion which would result in lower HC emissions. The higher HC emission for BTL at 0 bar could be as a result of local over-lean air-fuel mixtures, which would result in local poor or incomplete combustion with un-burnt fuel going to the exhaust. Figures 5.8b and 5.8c show CO and CO₂ emissions, respectively. From these figures, BTL demonstrates a decrease in both CO and CO₂ emissions compared to diesel and biodiesel. It

is also remarkable to note that unlike biodiesel which has a lower CO emission but a higher CO₂ emission, BTL has lower emissions of both oxides of carbon. Biodiesel contains oxygen which would allow for the oxidation of CO to form additional CO₂ emissions. CO emissions at 3.77 bar for all three fuels is observed to be zero. This observation may be attributed to more complete combustion of the three fuels at the much higher engine load. Figure 5.8d is a comparison of the NO_x emissions. BTL has higher NO_x emissions than diesel except at 3.77 bar where it has lower NO_x emissions than the other two fuels. NO_x formation is typically a function of temperature. Thermal NO_x is formed at temperatures above 1800 K [70, 10] and is believed to be the principal NO_x forming mechanism for these fuels in diesel engine. The peak rate of heat release seems to have some correlations with the observed NO_x results as seen in Fig. 5.9 suggesting that the greater the peak heat release rate, the higher the amount of NO_x produced.

Smoke opacity from the engine exhaust was obtained with a wagner 6500 smoke meter. Smoke opacity is directly related to the amount of soot in the exhaust. Smoke opacity results are shown in Fig.5.10. It is observed that at 1.26 bar BMEP, BTL and biodiesel have little smoke emissions compared to diesel fuel. As engine load is increased to 3.77 bar, however, BTL and biodiesel have higher smoke opacity than diesel fuel. The increase in smoke opacity for these two fuels may be attributed to their reduced amount of premixed combustion phase due to their shorter ignition delay. The less amount of premixed combustion phase results in more diffusion fuel combustion occurring later with more soot generated [70]. It should also be noted that unlike diesel fuel with comparably high aromatic contents, biodiesel and BTL

have little to no aromatic content and as such the soot formation mechanism is expected to be quite different for these two fuels.

Exhaust gas temperature as shown in Fig. 5.11 was highest for biodiesel at all engine loads. BTL also had slightly higher exhaust gas temperature when compared to diesel fuel. There is a noticeable correlation between ignition delay at each load as shown in Fig.5.6d and exhaust gas temperature. Biodiesel with the shortest ignition delay has the highest exhaust gas temperature, while diesel fuel with the longest ignition delay has the lowest exhaust gas temperature. This is believed due to the longer late cycle combustion for biodiesel with more mixing controlled combustion period.

5.5. Conclusion

An experiment was conducted to study the characteristics of burning a biomass to liquid fuel in a compression-ignition diesel engine. Engine performance, in-cylinder combustion, and emissions were measured. Based on the results obtained from this experiment, some important findings can be summarized as follows:

1. The use of BTL in the diesel engine resulted in slightly lower indicated work and mechanical efficiency at low engine loads but increased mechanical efficiency at high engine loads. BTL also had lower BSFC and higher BTE when compared to both diesel and biodiesel.
2. BTL was observed to have a shorter ignition delay when compared to diesel fuel but a longer ignition delay than biodiesel. The effect of BTL on in-cylinder pressure, heat

release rate and cumulative heat release varied depending on engine operating conditions.

3. For all the tested exhaust gas samples, with the exception of NO_x and no load conditions, an improvement in emissions was observed. HC, CO and CO_2 emissions were lower for BTL when compared to both diesel and biodiesel except at 0 bar BMEP where HC emissions are higher. NO_x emissions were higher for BTL except at 3.77 bar. Smoke opacity was observed to be the same or lower for low engine loads for BTL and biodiesel but a significant increase in smoke opacity was observed for biodiesel and BTL at 3.77 bar BMEP.
4. As this experiment was carried out in a single-cylinder diesel engine at a fixed rpm, more work needs to be done to better understand the characteristics of BTL fuel in a diesel engine at varying engine speeds and loads. The results obtained from this experiment demonstrate promising potentials of using BTL in diesel engines.

Table 5.1: Fuel properties adapted from [67], [68], [52] and [69]

Properties	Diesel (No.2)	Biodiesel	BTL
Energy Content (lower Heating Value) (MJ/kg)	43.1 [68]	37.9 [68]	43.9 [67]
Flash point °C	74 [68]	>130 [52]	-
Auto ignition Temperature °C	~315 [68]	~149 [68]	-
Dynamic viscosity (Pa.s) at 25°C	1.99	4.12	2.0976
Density (kg/L)	0.832	0.875	0.762
Cetane number	46 [69]	55.4 [52]	-
Surface Tension (mN/m) at 25°C	27.4	29.3	24.96

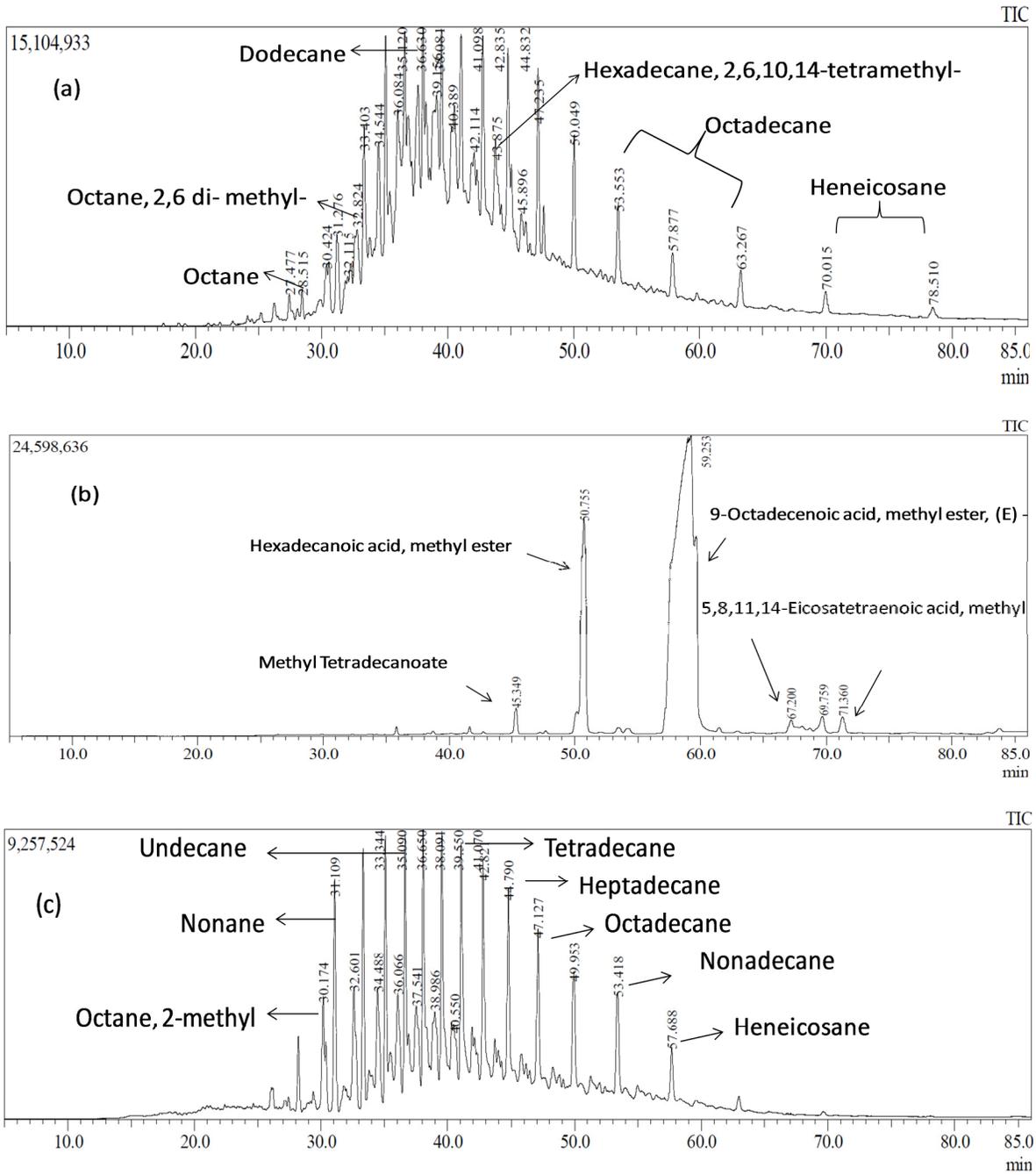


Figure 5.1: GC/MS results for (a) diesel (b) biodiesel (c) BTL

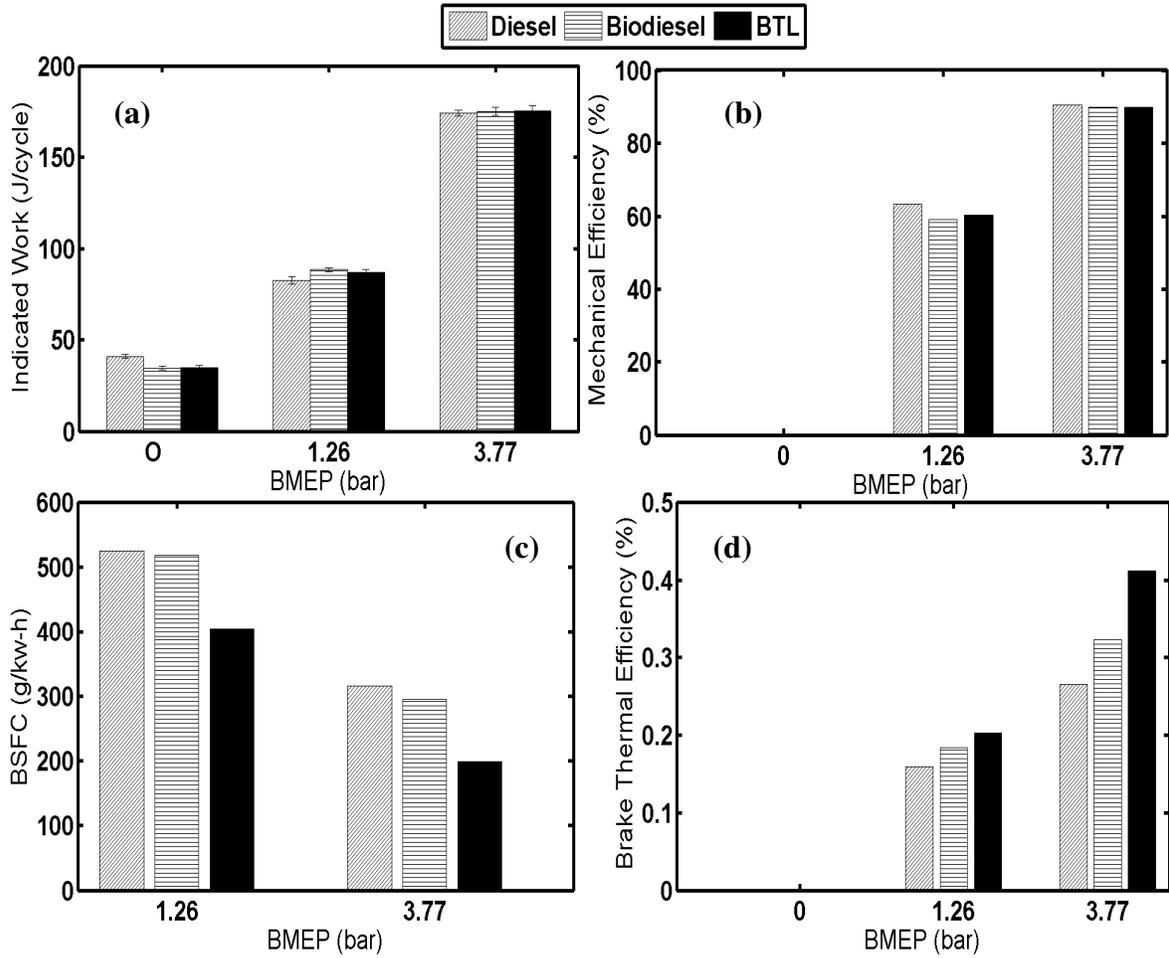


Figure 5.2: (a) Indicated work (b) Mechanical Efficiency (c) Brake Specific Fuel Consumption (d) Brake Thermal Efficiency at 0 bar, 1.26 bar and 3.77 bar BMEP

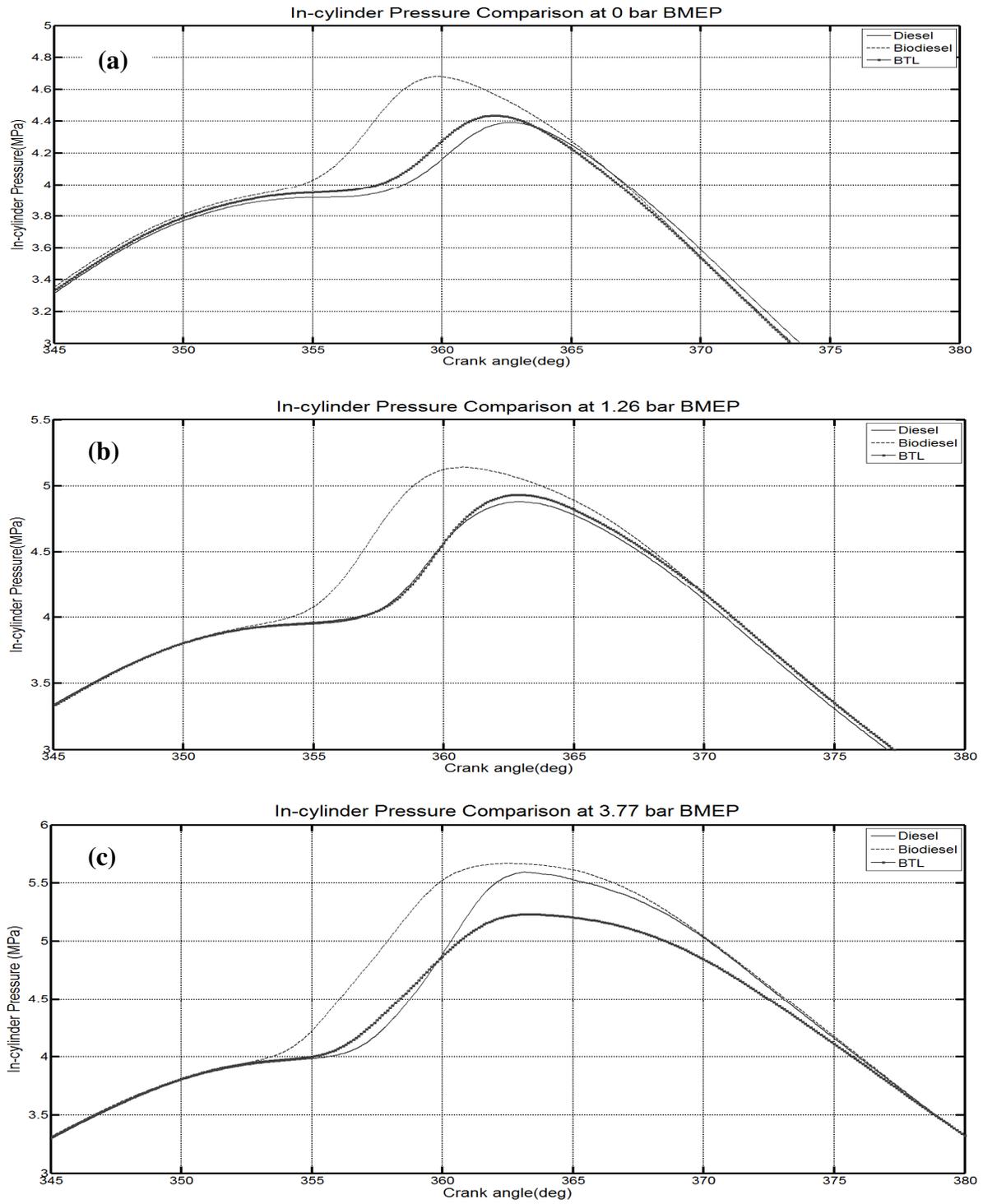


Figure 5.3: In-cylinder pressure at (a) 0 bar, (b) 1.26 bar and (c) 3.77 bar BMEP.

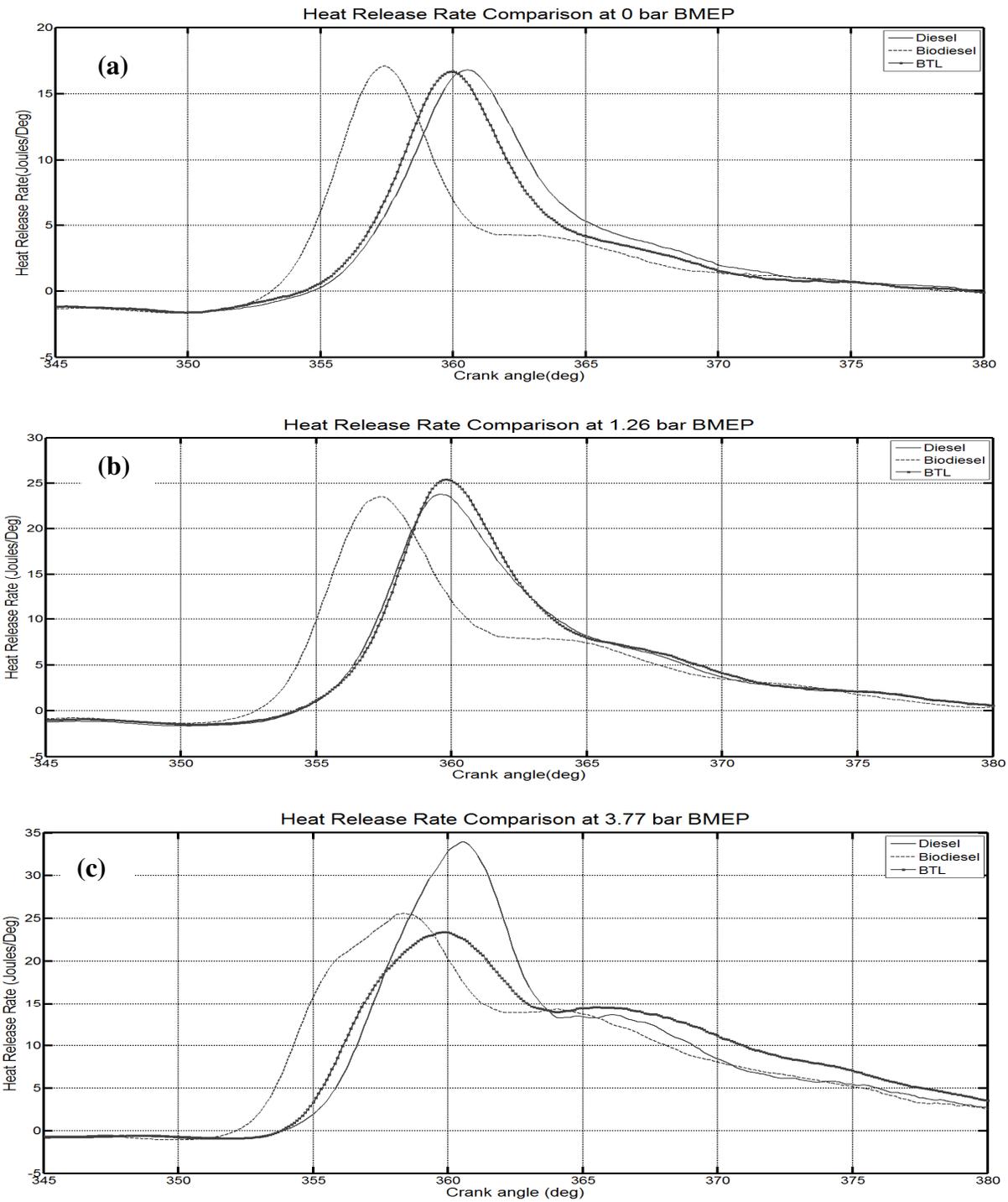


Figure 5.4: Heat Release Rate at (a) 0 bar, (b) 1.26 bar and (c) 3.77 bar BMEP.

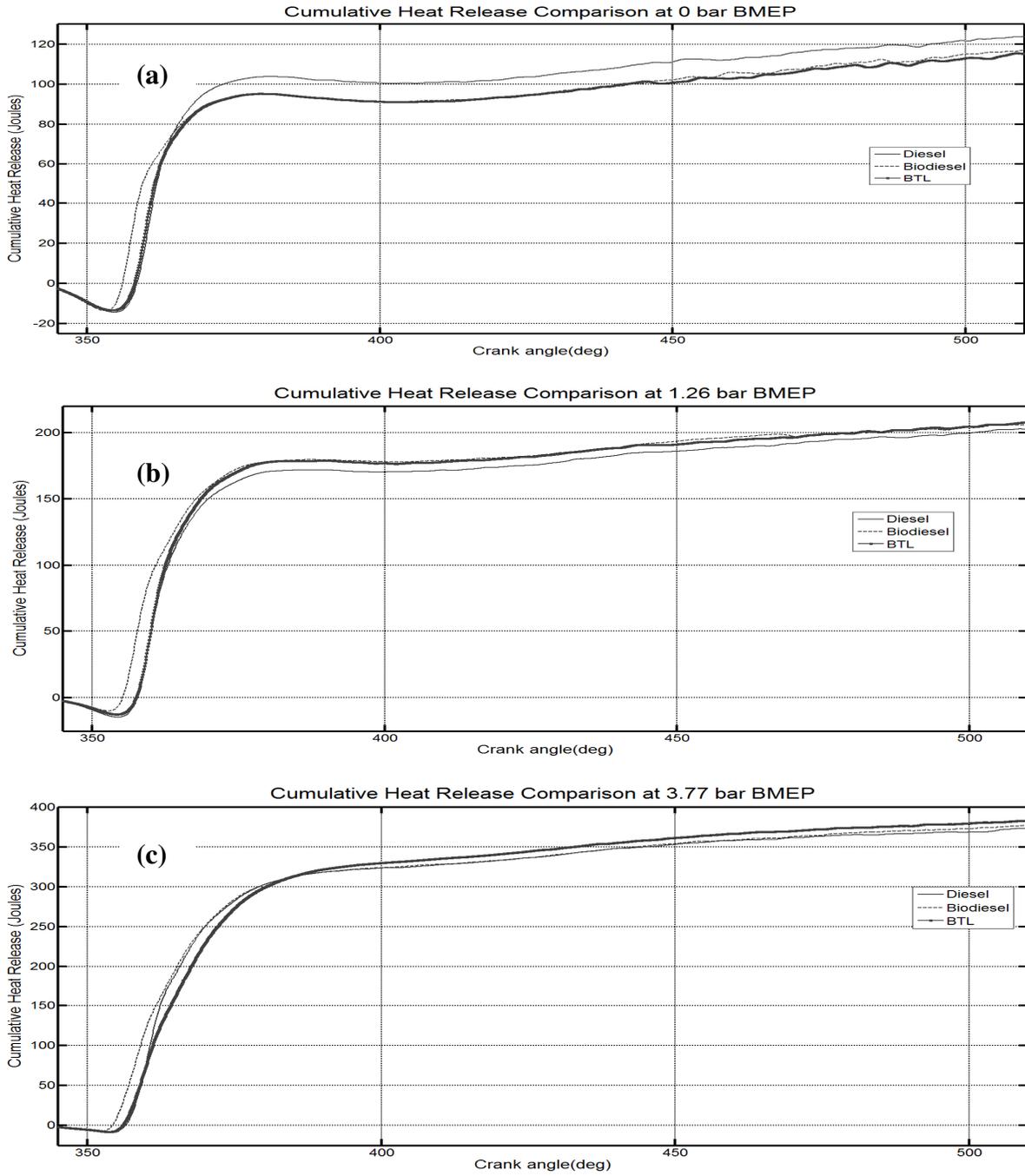


Figure 5.5: Cumulative Heat Release at (a) 0 bar, (b) 1.26 bar and (c) 3.77 bar BMEP.

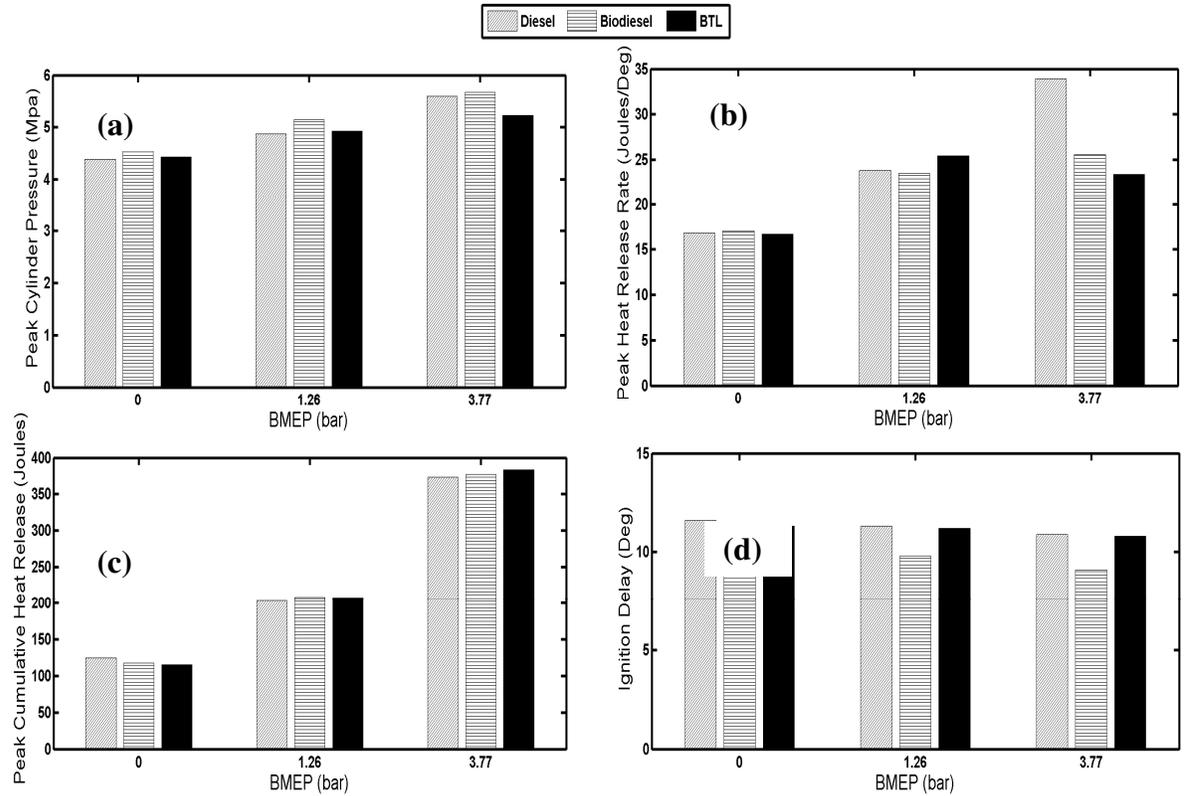


Figure 5.6: (a) Peak Cylinder Pressure (b) Peak Heat Release Rate (c) Peak Cumulative Heat Release Rate (d) Ignition Delay at 0 bar, 1.26 bar and 3.77 bar BMEP

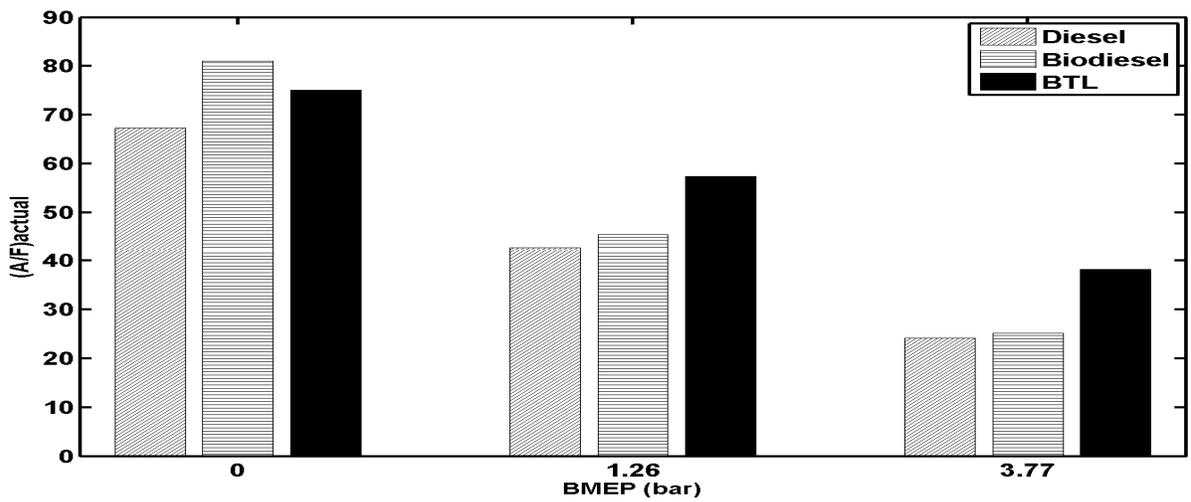


Figure 5.7: Actual air-fuel ratio under different engine loads

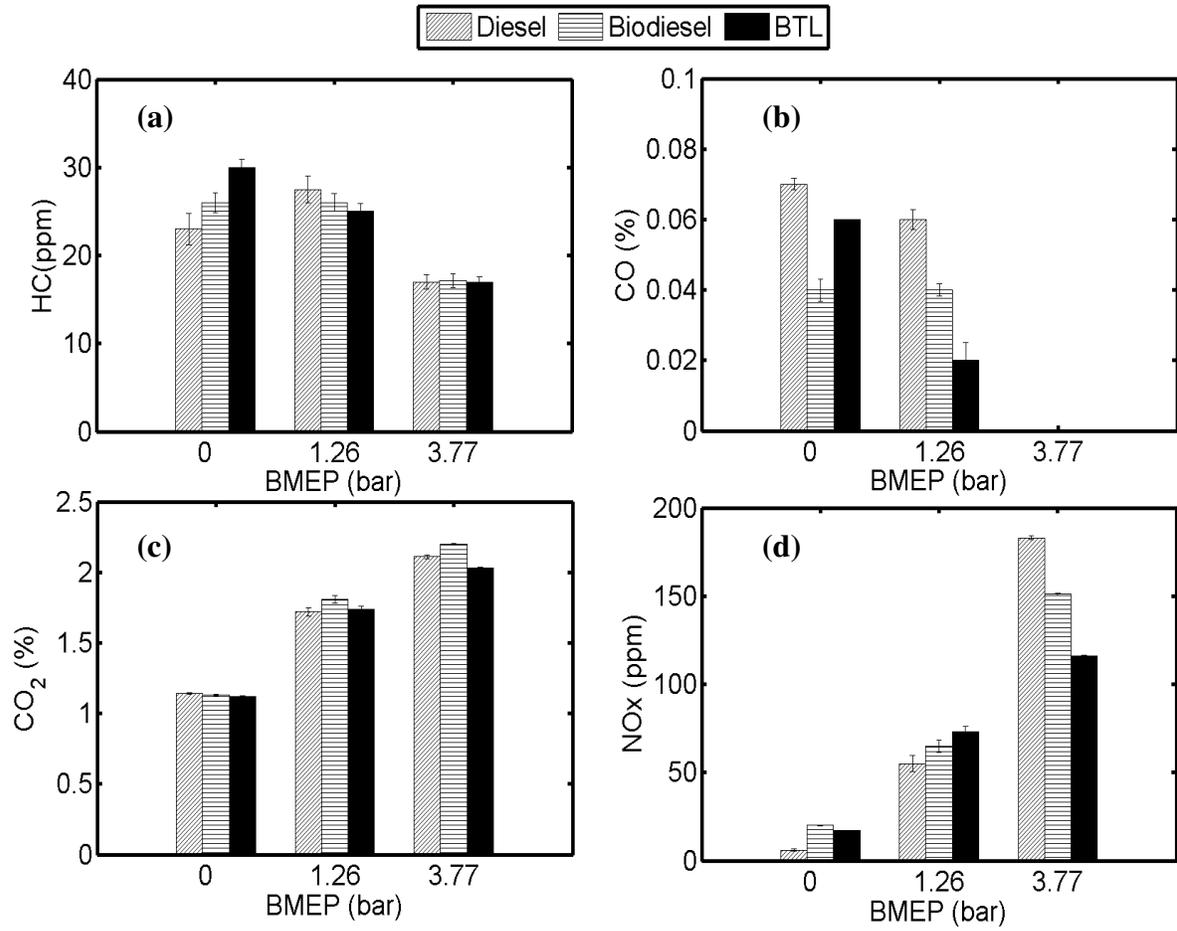


Figure 5.8: (a) Hydrocarbon emissions (b) Carbon Monoxide emissions (c) Carbon Dioxide emissions (d) NO_x emissions at 0 bar, 1.26 bar and 3.77 bar BMEP

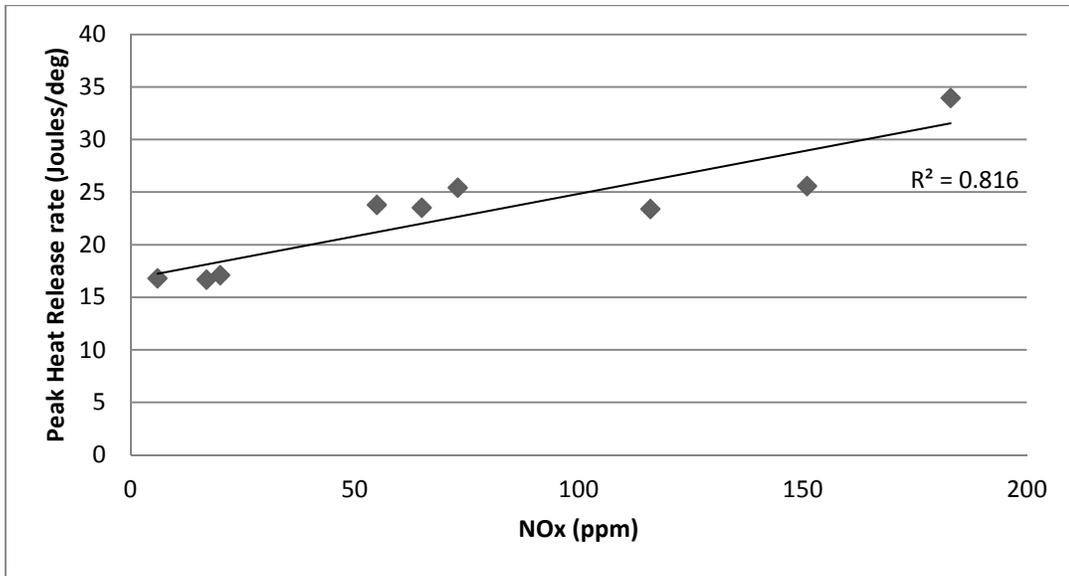


Figure 5.9: Relationship of peak heat release rate to NO_x emissions for all the conditions

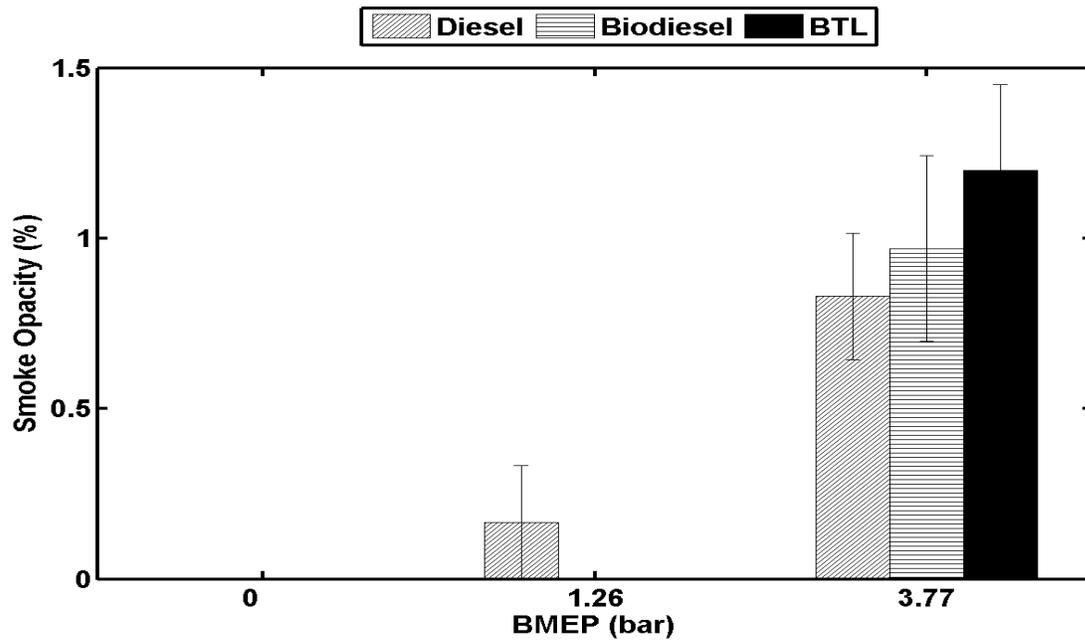


Figure 5.10: (a) Smoke Opacity at 0 bar, 1.26 bar and 3.77 bar BMEP

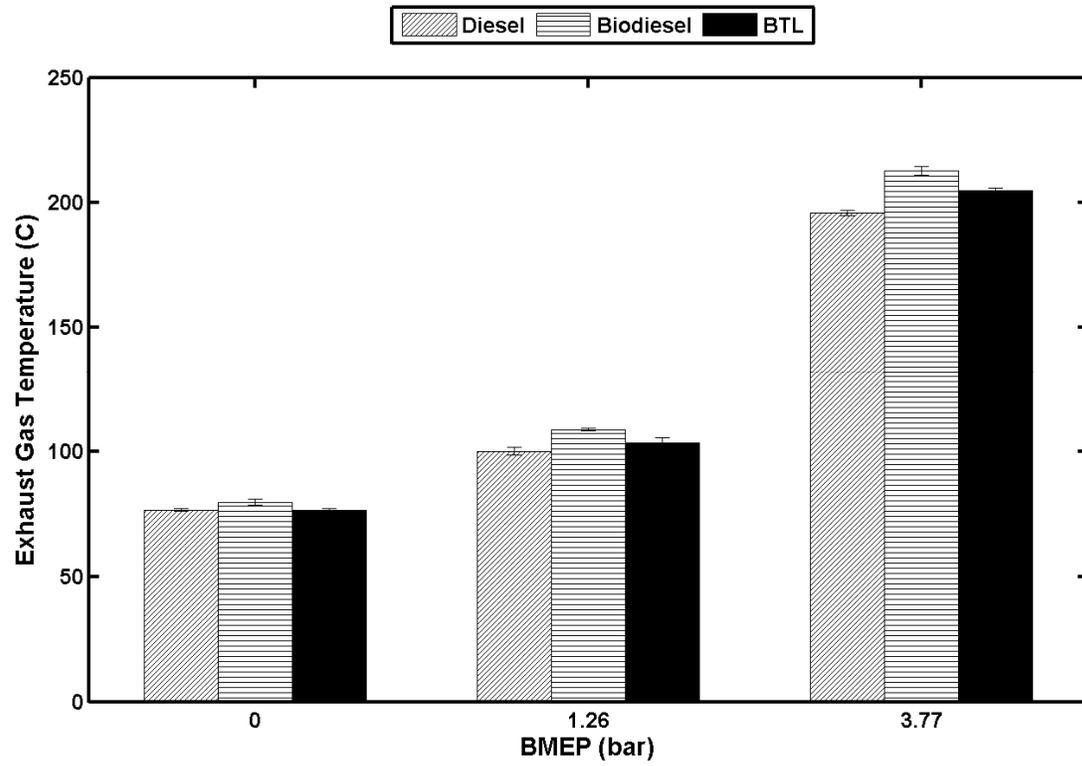


Figure 5.11: Exhaust gas temperature at 0 bar, 1.26 bar and 3.77 bar BMEP

CHAPTER 6

Performance, Combustion, and Emissions Study of a Compression Ignition Engine Running on Oil in Water Emulsions Made with Diesel, Jet fuel and Biodiesel with Carboxymethylated Kraft Lignin as a Surfactant

6.1 Abstract

In this work, three different fuels (diesel, biodiesel and jet fuel) and their emulsion counterparts were tested in a diesel engine. The emulsions were oil (fuel) in water emulsions at a ratio of 3:7 water/oil (W/O). The surfactant used for this experiment was carboxymethylated Kraft lignin. Testing was performed for fuel and emulsion at an engine speed of 2000 rpm under three engine loads corresponding to 0 bar, 1.26 bar and 3.26 bar brake mean effective pressure (BMEP). Engine performance, in-cylinder combustion, and exhaust emissions were measured. At no load condition, an increase in indicated work is observed for diesel emulsion and biodiesel emulsion when compared to pure diesel and biodiesel, respectively. Emulsions result in higher engine mechanical efficiency at 1.26 bar and 3.26 bar BMEP except in the case of jet fuel emulsion at 1.26 bar. When the total fuel mass for emulsions includes the water added, emulsions have higher brake specific fuel consumption (BSFC) than their base fuels. When only the fuel mass is considered, a lower adjusted BSFC is observed for emulsions. Fuel emulsions have higher brake thermal efficiency than their base fuels. Emulsions generally have lower peak in-cylinder pressure, lower heat release rates, and longer ignition delays at 1.26 bar and 3.26 bar BMEP when compared to pure fuel but have the opposite effect at no load conditions. There was also a

noticeable decrease in NO_x emissions for the emulsions, but an increase in carbon monoxide emissions at 1.26 bar and 3.26 bar. At 0 bar BMEP, emulsions produce less carbon monoxide emissions. The effect of emulsions on hydrocarbon emissions and smoke opacity depends on the fuel type and the engine load. This work demonstrates the effectiveness of W/O emulsions as viable fuels for diesel emissions reductions. It also shows that carboxymethylated Kraft lignin can be used as an effective surfactant for oil in water fuel emulsions.

6.2. Introduction

The US Environmental Protection Agency (EPA) is set to introduce Tier 3 motor vehicle emissions standard starting in 2017. The program will seek to lower vehicle emissions and reduce the sulfur content of gasoline. It is estimated that the program will reduce vehicle nitrogen oxides (NO_x) emissions by 25%, carbon monoxide (CO) emissions by 24% and direct particulate matter (PM) by 10% in 2030 [34]. Vehicle manufactures will need to find methodologies to meet the requirements of the new standard. Methods typically used to reduce emissions for diesel engines are the use of alternative fuels, introduction of water into the combustion chamber and mechanisms to tackle individual controlled emissions such as particulate filters and oxidation catalyst. Some of these methods are not cost effective, may require extensive modifications to the vehicle, and, in some cases, reduce some emissions at the expense of other regulated emissions.

Emulsions of water and fuel are a means by which regulated fuel emissions can be reduced effectively. The addition of water to fuel has the additional benefit of reducing the

overall volume of fuel consumed. An emulsion is a mixture of two or more liquids in which one is present as droplets, of microscopic or ultramicroscopic size, distributed throughout the other [71]. It is created by the agitation of two liquids in the presence of a surfactant which possess both polar and non-polar properties which helps weaken the surface tension of the liquid in which it is dissolved [25]. Fuel emulsions are produced when fuel and water are mixed together in the presence of a surfactant with either water as the continuous phase and the fuel as the dispersed phase or vice versa. Researchers have experimented with the use of waste cooking oil emulsions [72], animal fat emulsions [73], biofuel emulsions [74], diesel in water emulsions [26, 27, 29, 30, 75, 76], Three – phase emulsions [31, 28, 77] and diesel-ethanol emulsions in diesel engines [78]. Investigations were also performed on the use of heavy oil – water emulsions on a semi industrial scale [79].

Kumar *et al.* performed experiments in a diesel engine using waste cooking oil/water (WCO/W) emulsions and observed improvements in brake thermal efficiency (BTE) at high power outputs but low BTE at low power outputs when compared to neat diesel fuel [72]. Lower smoke opacity than WCO but higher smoke opacity than diesel fuel was also observed. Hydrocarbon (HC) emissions varied with power output. At high power output, WCO emulsion had lower HC emissions than diesel but at low power output it had higher HC emissions than diesel. Kumar *et al.* carried out additional experiments in a diesel engine using an emulsion of animal fat and water with ethanol [73]. They observed a decrease in smoke, NO_x, HC and CO when compared to pure animal fat and neat diesel at high power outputs. Animal fat emulsions were observed to have higher HC and CO emissions at light

engine loads. Kumar *et al.* [74] put together a comprehensive review on the use of biofuel emulsions in diesel engines. They came to the conclusion that biofuel emulsions improved the combustion efficiency and performance with reduced NO_x and PM emissions. Research work in Refs. [26, 27, 29, 30, 75, 76] shows a reduction in NO_x, soot, HC and PM emissions, and improved combustion efficiency for diesel-water emulsions. Alahmer *et al.* observed that as water content increased, BSFC increased at high engine speeds, BTE decreased, exhaust gas temperature (EGT) decreased, and NO_x also decreased [30]. In the case of Zaid's experiments, an increase in water content resulted in an increase in BTE, an increase in BSFC (diesel and water considered as total fuel) and a decrease in EGT [27]. Cherng-Yuan *et al.* [28, 31, 77] carried out a series of experiments to study three phase diesel emulsions in a diesel engine and the results showed an increase in BSFC and CO with a decrease in NO_x, CO₂ and smoke opacity. Ashok carried out experiments using varying concentration of diesel-ethanol emulsions in a diesel engine [78]. The results showed an increase in BTE, a decrease in specific fuel consumption and a decrease in NO_x as the volume of ethanol decreases. The general consensus from all the experiments carried out with water- oil emulsions in a diesel engine is that NO_x and smoke generally decrease.

Micro-explosion and puffing are the two most important phenomena attributed to emulsion combustion in a diesel engine. Micro-explosion is the quick break down of droplets which results in secondary atomization of droplets [80]. It occurs because water and oil have different boiling temperatures which results in water evaporating much faster than the oil in a hot combustion chamber. For water in oil emulsions, water droplets are typically

encapsulated by oil. In a hot combustion chamber, the water droplets will reach superheated phase much faster than the oil thus resulting in micro-explosion. In the case of puffing, water leaves the oil droplets as a fine mist [25, 80]. Not all researchers have, however, agreed on the occurrence of micro-explosions in diesel engines as was discussed by Weibiao *et al.* [75].

Most of the experiments carried out in diesel engine using fuel-water emulsions have typically used water as the dispersed phase with the oil (fuel) as the continuous phase. In this work, oil in water emulsions using diesel, jet fuel and biodiesel as base fuels are studied with carboxymethylated Kraft lignin as the surfactant. The objective of this work is to study the use of oil in water emulsions in a diesel engine and to determine the viability of carboxymethylated lignin as a suitable surfactant for diesel engine applications.

6.3. Experimental Setup

The experimental setup for this experiment has been discussed previously in Chapter 3. An additional fuel tank was used for emulsions in this experiment. A schematic of the setup is shown in Fig. 6.1. In this experiment, diesel, biodiesel, jet-fuel, and their corresponding emulsions are tested under given conditions. The diesel engine was set at 2000 rpm for three different torque outputs of 0, 4.18 and 10.86 Nm corresponding to 0 bar, 1.26 bar and 3.26 bar brake mean effective pressure (BMEP). Two fuel tanks containing a base fuel and an emulsified fuel were used. The two tanks each had a shut off valve and were connected with a T junction which fed into the engine's fuel pump. The testing of the emulsified fuels began by starting the engine with the base fuel while keeping the valve from

the tank containing the emulsion closed. The engine was left to run for 30 minutes to warm up the engine. With the engine sufficiently warmed up, the base fuel valve was shut and the emulsion valve was opened. The engine was further left to run on the emulsion fuel for an extended period of time in order to ascertain that no base fuel was present in the fuel line before data acquisition began. It should be noted that for this experiment, the fuel supply timing for all fuels tested was kept constant at 17 degree before TDC.

6.4. Results and Discussion

6.4.1 Fuel Properties

As mentioned before, the emulsions used for this experiment had water as the continuous phase and oil (fuel) as the dispersed phase, which is different from most of the emulsion experiments carried out by other researcher in diesel engines. The ratio of water to oil used in this experiment was 3:7 by mass. In order to make the emulsions, 0.5% of carboxymethylated Kraft lignin was dissolved in water before mixing with the fuel. The mixture was then mechanically agitated at room temperature with an Ultra Turrax at a speed of 20,000 rpm. The produced emulsion was subject to a vacuum pump for de-aeration. Fuel properties are given in Table 6.1. It is seen that oil-in-water fuel emulsions have much higher dynamic viscosities than the based fuel. Figure 6.2 shows samples of the tested fuels.

6.4.2 Performance

Engine performance parameters for each tested fuel are shown in Figure 6.3. Figure 6.3a shows the indicated work at the three different loads. As engine load is increased, indicated work increases for all the fuels. The fuel emulsions have lower indicated work than

the base fuels with the exception of the no load condition and jet fuel emulsion at 1.26 bar. Figure 6.3b depicts the engine's mechanical efficiency. Mechanical efficiency is observed to increase with increasing engine load for all tested fuels. Mechanical inefficiency is typically attributed to friction losses. Fuel emulsions result in higher mechanical efficiency. Jet fuel emulsion at 1.26 bar is the only exception with a lower mechanical efficiency than the base jet fuel. Figure 6.3c shows the brake specific fuel consumption (BSFC) for different engine loads. For this figure, both water and oil contribute to the total mass flow rate of fuel. BSFC determined in this manner decreases with increasing engine load and is higher for emulsion fuels when compared to their base fuels. The higher BSFC of emulsions is mainly due to their lower heating values due to the water contents. Figure 6.3d is a plot of BSFC determined by only considering the fuel in the emulsion. The percentage of fuel used in this experiment is seventy percent and as such only seventy percent of the total fuel emulsion flow rate is used in determining the BSFC. By determining the BSFC in this manner, a significant reduction in BSFC is observed for the fuel emulsions. The fuel emulsions are observed to have noticeably lower BSFC values when compared to the base fuels.

The brake thermal efficiency (BTE) is a ratio of the brake work per cycle to the chemical energy released in the combustion process [8]. From Figure 6.4a, BTE increases with increasing engine load for all fuels, it also increases for the fuel emulsions when compared to their base fuels, which is consistent with findings by other researchers [27, 30 and 76]. This difference in BTE becomes more significant when only the actual base fuel is

factored in as is shown in Figure 6.4b. In this figure, the brake thermal efficiency is adjusted to only consider the quantity of oil (base fuel) used.

6.4.3 Combustion

Combustion pressure was obtained from a Kistler 6052A pressure sensor installed in the cylinder head of the engine. Figure 6.5a shows the in-cylinder pressure at 0 bar BMEP. It is seen that the fuels and their emulsions have similar pressure profiles with the exception of jet fuel and its emulsion. This figure suggests a longer ignition delay and slower rate of pressure increase for jet fuel emulsion, diesel and diesel emulsion compared to biodiesel, biodiesel emulsion and jet fuel. In Fig. 6.5b, a major difference in pressure profile is observed for jet fuel and its emulsion compared to the other fuels. An initial decrease in cylinder pressure after fuel injection followed by a slight increase in cylinder pressure upon ignition can be seen from this figure for jet fuel and its emulsion with the observation been more pronounced for jet fuel emulsion. It is also observed that fuel emulsion have lower cylinder pressure than their corresponding base fuels with biodiesel and its emulsions still having a faster rate of pressure rise than diesel, jet fuel and their emulsions. The initial decrease in pressure after the start of fuel injection for jet fuel and its emulsion may be attributed to its higher volatility and longer ignition delay. A long ignition delay means fuel would accumulate in the combustion chamber for a longer period which would lead to significant cooling of the air-fuel mixture as a result of fuel evaporation.

At 3.26 bar, the effect of water evaporation are much more pronounced as shown in Fig. 6.5c. Emulsions have much lower peak cylinder pressures than their base fuel

counterparts and major differences between the pressure profiles of the fuels and their emulsions can be observed. Unlike the lower load conditions where biodiesel had the fastest rate of pressure increase, at 3.26 bar, diesel has the fastest rate of pressure increase after start of combustion. An additional observation is that while there is still a noticeable decrease in pressure for jet fuel and jet fuel emulsion, there is a significant increase in cylinder pressure shortly after possibly as a result of a hotter engine status which in turn reduces the cooling effect of water evaporation.

In Fig. 6.6a it is found that at no load condition there is no significant difference between the heat release rate profile of a pure fuel and its emulsion counterpart with the exception of jet fuel and its emulsion which are shown to have completely different profiles. The heat release rate differences observed for jet fuel and its emulsions may be attributed to spray development and ignition quality resulting in significant differences in their ignition delay. Diesel, its emulsion and jet fuel emulsion have a noticeably longer pre-mixed combustion phase when compared to the other fuels as a result of the longer ignition delay of these fuels. A longer ignition delay would result in more fuel present in the combustion chamber at the time when ignition finally takes place. The increased quantity of fuel would result in a significantly longer pre-mixed combustion phase and would also result in a higher peak heat release rate as was observed.

Figure 6.6b shows a marked difference in the heat release profiles of all the fuels tested at 1.26 bar BMEP. Biodiesel and its emulsion are observed to have different mixing –

controlled combustion phase when compared to the other fuels. The heat release rate between a fuel and its emulsion differs depending on the fuel type. While biodiesel and its emulsion have very similar heat release rate profiles, diesel, jet fuel and their emulsions have much larger differences in their heat release rate profiles. These observed differences may again be attributed to differences in heating values, spray development, and ignition quality. In Figure 6.6c, the engine load is increased to 3.26 bar BMEP. Jet fuel emulsion clearly stands out with a significantly longer ignition delay when compared to the other fuels. Biodiesel emulsion is noted to have a significantly longer pre-mixed combustion phase with a relatively lower heat release rate peak. Lower heating value, low ignition quality, and poor fuel atomization are believed to be the principal reasons behind the behavior of biodiesel emulsion in the pre-mixed combustion phase.

Figure 6.7a depicts the cumulative heat release of the fuels at no load condition. It shows the same fuel grouping observed from the pressure and heat release rate plots. The profiles of the fuels are similar. Jet fuel and its emulsion experience a dip in cumulative heat release just after combustion resulting in overall lower cumulative heat release when compared to the other fuels. Figure 6.7b shows cumulative heat release as engine load is increased to 1.26 bar. From this figure, we again notice a significant ‘scattering’ of the profiles. The high cumulative heat release associated with jet fuel and its emulsion can be attributed to their significantly longer ignition delay with more premixed combustion and less soot radiation heat loss. In Figure 6.7c, the cumulative heat releases of all tested fuels are similar regardless of the ignition delay. This is believed to be because as engine load increases, the effect of

heating value and ignition quality are no longer as pronounced in a warmer engine cylinder.

Figure 6.8a gives a quantitative representation of the peak in-cylinder pressure for all the tested fuels. It is seen that a general decrease in peak cylinder pressure at 1.26 bar and 3.26 bar for emulsions compared to their base fuels. At no load condition, however, emulsions have a higher peak cylinder pressure except for jet fuel emulsion. The increase in pressure is believed to be as a result of enhanced fuel atomization caused by micro-explosion. In the case of jet fuel emulsion, the ignition delay is significantly longer than neat jet fuel leading to a lower peak pressure. At higher engine loads, the effects of a lower ignition quality, longer ignition delay and lower heating values surpass the effects of micro-explosions hence the lower peak cylinder pressure for fuel emulsions. In Figure 6.8b, a similar trend as that shown in Fig. 6.8a is observed mostly for the peak heat release rate for the same reasons. The exceptions are jet fuel emulsion at no load condition and biodiesel emulsion at 1.26 bar. Jet fuel emulsion has a longer ignition delay. The long ignition delay results in more fuel in the chamber available for combustion, and as such upon ignition, there is a higher heat release rate than its corresponding base fuel. The slightly longer ignition delay of biodiesel emulsion is responsible for its slightly higher peak heat release rate. Figure 6.8c is a plot of the peak cumulative heat releases of the fuels. The figure shows that at no load condition, emulsions have higher cumulative heat release. This is different for diesel emulsions and biodiesel emulsions at 1.26 bar; at 3.26 bar the same trend as at no load condition is observed with the exception of jet fuel emulsion which has a lower cumulative heat release than pure jet fuel.

Ignition delay comparisons are shown in Figure 6.8d. From this figure, emulsions are observed to have longer ignition delays than their base fuels for the most part. Ignition delay is closely related to the ignition quality of the fuel, and for this reason, the emulsions which are expected to have lower cetane numbers (ignition quality) will have longer ignition delays [9]. The only exception observed is biodiesel emulsion at 1.26 bar which has a shorter ignition delay of 0.1 deg than pure biodiesel possibly as a result of its relatively high bulk modulus. Except the load conditions, biodiesel and its emulsion have shorter ignition delays than other fuels or emulsions. Although the heating values of biodiesel and its emulsion are lower than jet fuel and its emulsion, the higher bulk modulus of biodiesel and its emulsion would result in earlier fuel injection resulting in a shorter ignition delay.

6.4.4 Emissions

Figure 6.9a shows the HC emissions for the fuels. From this figure, the general trend observed for most of the tested fuels was an increase in HC emissions between no load condition and 1.26 bar followed by a decrease upon increasing engine load to 3.26 bar. The decrease in HC emissions of diesel emulsion and biodiesel emulsion when compared to their based fuel at no load conditions may be due to better atomization as a result of micro-explosion. According to Kadota and Yamasaki [83], oil in water emulsions also experience micro-explosion in the same manner as water in oil emulsions. This is believed to be caused by a phase inversion from O/W (oil in water) to W/O (water in oil) emulsions followed by a phase separation as a result of an increase in droplet temperature. In addition, these authors suggest that the base fuel vaporizes first for O/W emulsions because the micro-droplet

component in the emulsion always vaporizes first. The effect of a longer ignition delay would seem to outweigh the micro-explosion phenomena in the case of jet fuel, hence its higher HC emissions when compared to neat jet fuel.

In general, the effect of ignition delay as well as cylinder temperature seems to be the major factor affecting HC emissions. Fuel emulsions generally have lower combustion wall temperatures as a result of lower flame temperatures which in turn results in higher HC emissions. An increase in ignition delay results in an increase in HC emissions as a result of overmixing which results in a very lean mixture that won't support autoignition with misfire [9].

CO and carbon dioxide (CO₂) emissions are typically opposite sides to a coin. With more complete combustion, CO₂ emission is prominent and CO emissions limited; the reverse is true with incomplete combustion. Figures 6.9b and 6.9c are plots of CO and CO₂ respectively. For all the fuels tested, CO emissions decreased with increasing engine loads. The reasons for these are an increase in fuel consumption and a warmer cylinder which would support more complete combustion. At high loads 1.26 bar and 3.26 bar, CO emissions for emulsions increased when compared to pure fuel mostly because of the effect of water in the chamber which lowers the flame temperature [83] as a result of a significant increase in water vapor concentration which in turn lowers the cylinder temperature and hinders complete combustion. This is however not the case at no load condition where with the exception of diesel emulsion, less CO emissions is observed for the emulsions. The reason for this has been discussed previously and is attributed to micro-explosion which

allows for secondary atomization with better fuel- air mixing leading to more complete combustion. From Figure 6.9c, the general trend for all the fuels was an increase in CO₂ emissions as engine load increased. Emulsions also have a noticeable decrease in CO₂ emissions, as supported by Fig. 6.9b.

Nitrogen oxides (NO_x) in engine combustion chamber are typically formed either as prompt NO_x or thermal NO_x. Prompt NO_x formation pathway is dominant below 2000k while thermal NO_x mechanism is dominant for temperatures above 2500k. From Fig.6.9d, we observe an increase in NO_x for all fuels as engine load increased. Except at no load condition and biodiesel at 1.26 bar BMEP, we observe a decrease in NO_x emissions for emulsions when compared to their base fuels. The reduced in-cylinder temperature at 1.26 bar and 3.26 bar for emulsions helps the reduction of thermal NO_x, prompt NO_x formation is expected to be minimal seeing as the fuels and emulsions do not have nitrogen present in the fuel. According to Javier *et al* [79] NO_x formation is reduced as a result of a lower flame temperature as well as in increase in OH radicals which would react with excess oxygen thus reducing the amount of NO_x formed. The decrease in NO_x for emulsions is supported by previous results [25, 26, 28, 29, 31, 73, 74, 76, 77, 79]. There is a correlation between peak heat release rate and NO_x for diesel, biodiesel and their emulsions as shown in Figure 6.10. This correlation supports the observation that as in-cylinder temperature is increased, NO_x formation also increases.

Figure 6.11 depicts the effect of engine load on smoke opacity. At no load condition, a general decrease in smoke opacity is observed for fuel emulsions with the exception of

biodiesel emulsion. An increase in engine load to 1.26 bar results in the opposite effect as that observed at no load condition with biodiesel again the exception. As engine load is increased further to 3.26 bar, an increase in smoke opacity is observed for the emulsions compared to their base fuels with jet fuel been the exception in this case. The initial decrease in smoke opacity for the emulsions could be as a result of the overall decrease in hydrocarbon fuel quantity as compared to pure fuels. A decrease in hydrocarbon fuel quantity would imply lower carbon content and as such less smoke formation. As micro-explosion is a function of temperature, it is expected that as engine load increases and cylinder temperature increases, fuel emulsion should undergo significant secondary atomization which would facilitate better air- fuel mixing and more complete combustion. The improvement in combustion as a result of micro-explosion is outweighed by poor combustion due to a longer ignition delay for the emulsions with the exception of biodiesel emulsion and jet fuel emulsion at 1.26 bar at 3.26 bar respectively. Opacity results obtained from this experiment seem to be random. This randomness could be as a result of the accuracy of the smoke meter at very low smoke emissions.

In Figure 6.12, exhaust gas temperature (EGT) is shown. From this figure exhaust temperature difference between a fuel and its emulsion seemed to be dependent on the fuel type and engine load. At no load condition, emulsions had higher EGT than their base fuels. As engine load increased to 1.26 bar, emulsions had lower EGT except for diesel emulsion. At 3.26 bar, emulsions had lower EGT than their base fuels with the exception of jet fuel emulsion.

This experiment was a preliminary test of oil in water emulsions in a single cylinder diesel engine using carboxymethylated lignin as a surfactant, additional experiments would need to be carried out to verify the results obtained. It should also be noted that the experiment could not be carried out at much higher loads due to injection limitations from the use of fuel emulsions.

6.5. Conclusion

An experiment was conducted to study the effect of different fuel-water emulsions made with a carboxymethylated Kraft lignin surfactant in a compression-ignition diesel engine. Engine performance, fuel combustion and emissions were measured. Based on the results obtained from this preliminary experiment, some important finding can be summarized in the following:

1. For each of the fuel emulsions used in this experiment, there is a general decrease in indicated work but a general increase in mechanical efficiency when compared to the base fuels. There is also a noticeable increase in BSFC and BTE for the emulsions when compared to their base fuels
2. Peak cylinder pressure, peak heat release rate and peak cumulative heat release were observed to be higher for the fuel emulsions when compared to their pure counterparts. Fuel emulsions were observed to have longer ignition delays.
3. Emissions results are observed to vary based on fuel type and engine operating conditions. At high loads for instance, NO_x emissions were lower for all the emulsions but CO emissions were higher. At low engine loads, fuel emulsions were

observed to have higher NO_x but lower CO. For most of the fuel emulsions, HC emissions increased as engine load increased.

4. Based on the results obtained from this experiment, there would need to be a balance between what emission is to be reduced and engine operating conditions. The choice of fuel to use must also be factored in to maximize emission reductions.
5. The experiment in this work was preliminary and limited to three different loads and one engine speed in a single cylinder engine. It is possible that the results obtained could differ for other engine speeds and loads in multi-cylinder diesel engines. More experiments may need to be conducted before these fuels can become practical.

Table 6.1: Higher heating value (HHV) and dynamic viscosity for the tested fuels and fuel emulsions

	Diesel	Diesel Emulsion	Biodiesel	Biodiesel Emulsion	Jet Fuel	Jet Fuel Emulsion
HHV (MJ/kg)	45.3	29.12	38.27	26.69	44.73	29.43
Dynamic viscosity @ 25C (mPa-s)	2.00	29.30	4.10	10.00	1.10	41.10

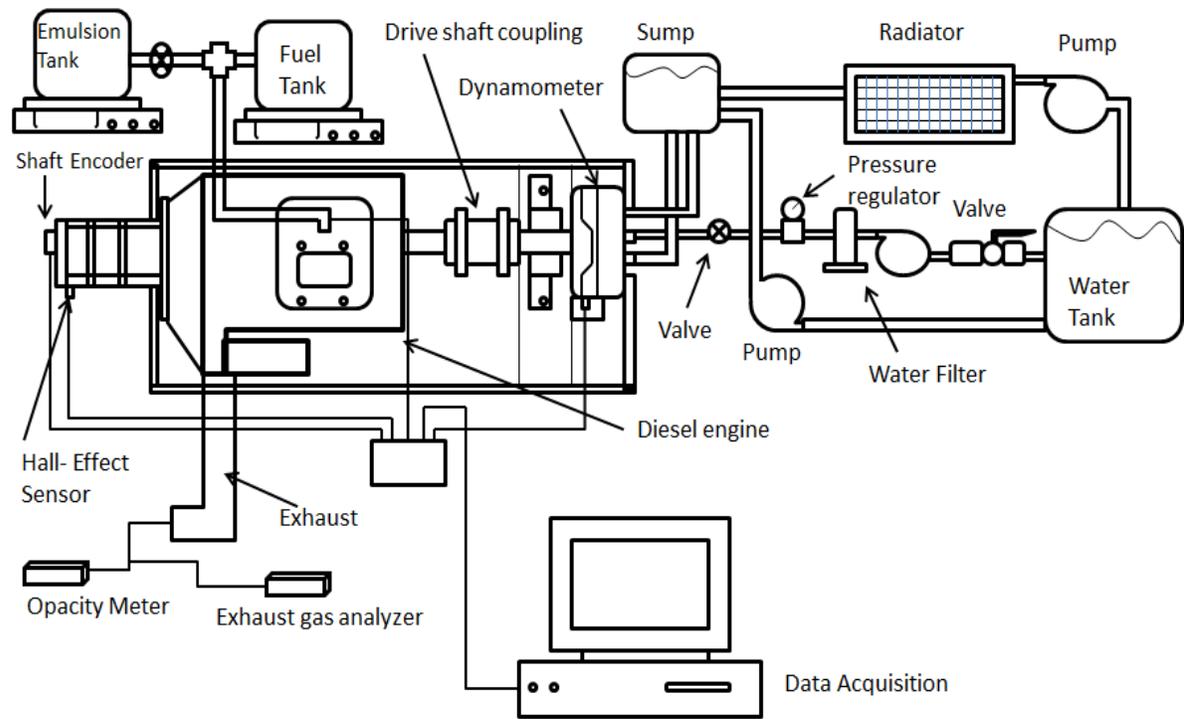


Figure 6.1: Schematic of experimental setup



Figure 6.2: From left to right, diesel, biodiesel, jet fuel, diesel emulsion, biodiesel emulsion, jet fuel emulsion

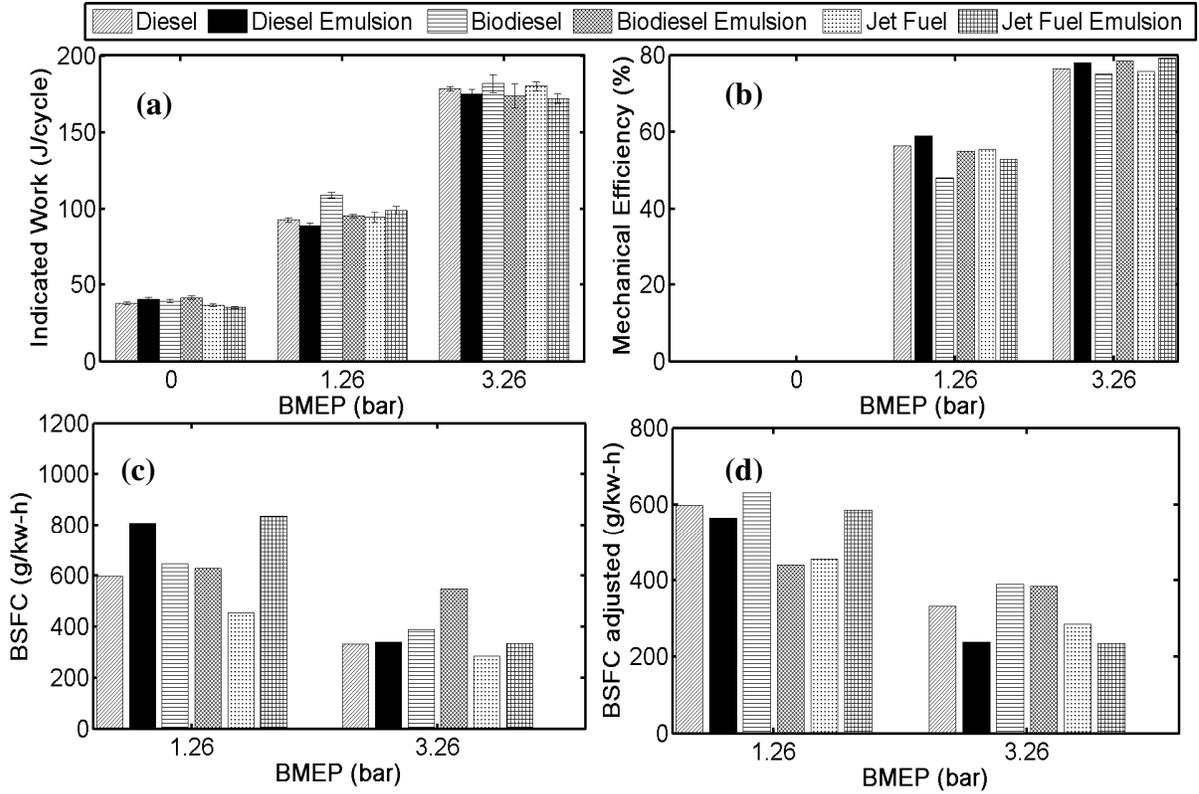


Figure 6.3: (a) Indicated work (b) Mechanical Efficiency (c) Brake Specific Fuel Consumption (d) Adjusted Brake Specific Fuel Consumption at 0 bar, 1.26 bar and 3.26 bar BMEP

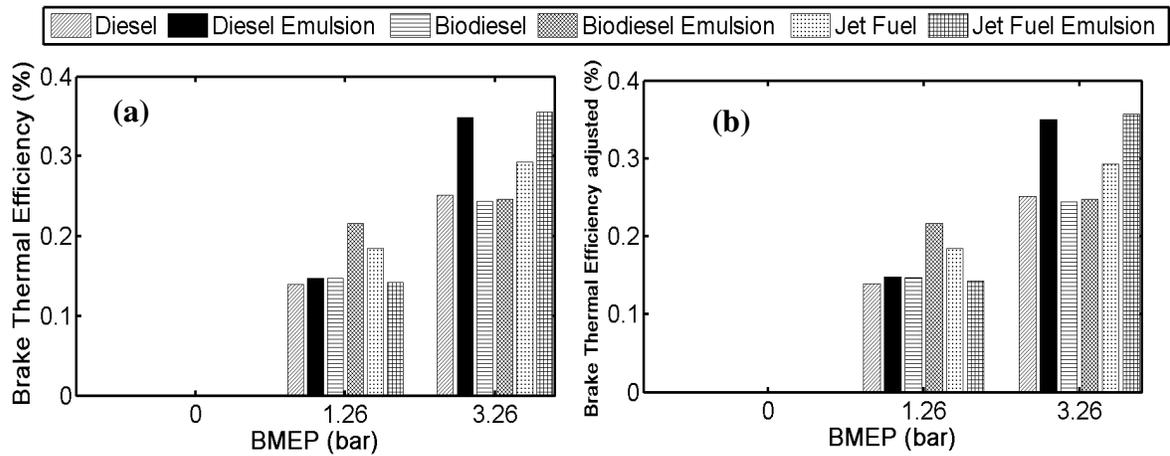


Figure 6.4: (a) Brake Thermal Efficiency (b) Adjusted Brake Thermal Efficiency at 0 bar, 1.26 bar and 3.26 bar BMEP

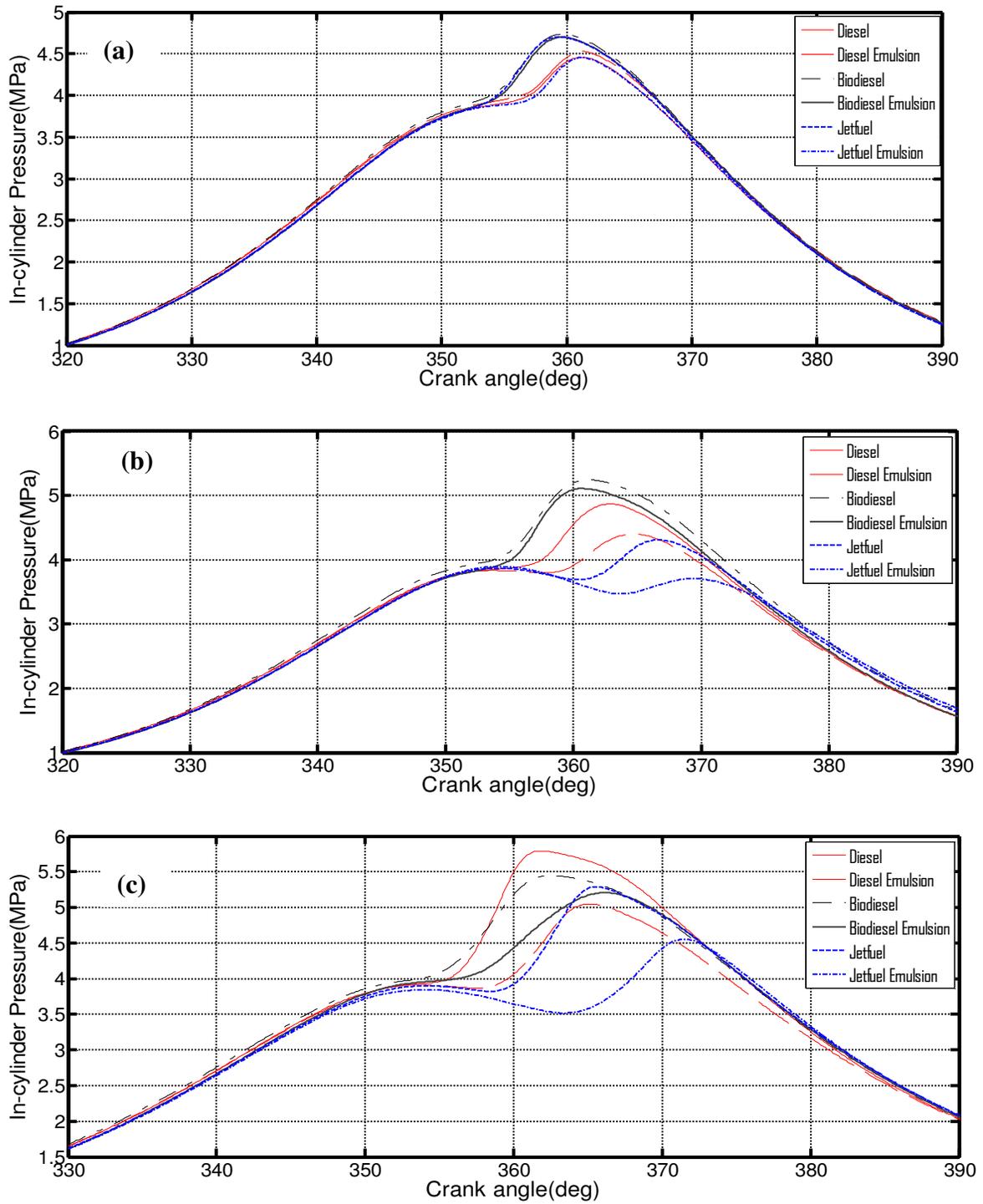


Figure 6.5: In-cylinder pressure at (a) 0 bar, (b) 1.26 bar and (c) 3.26 bar BMEP.

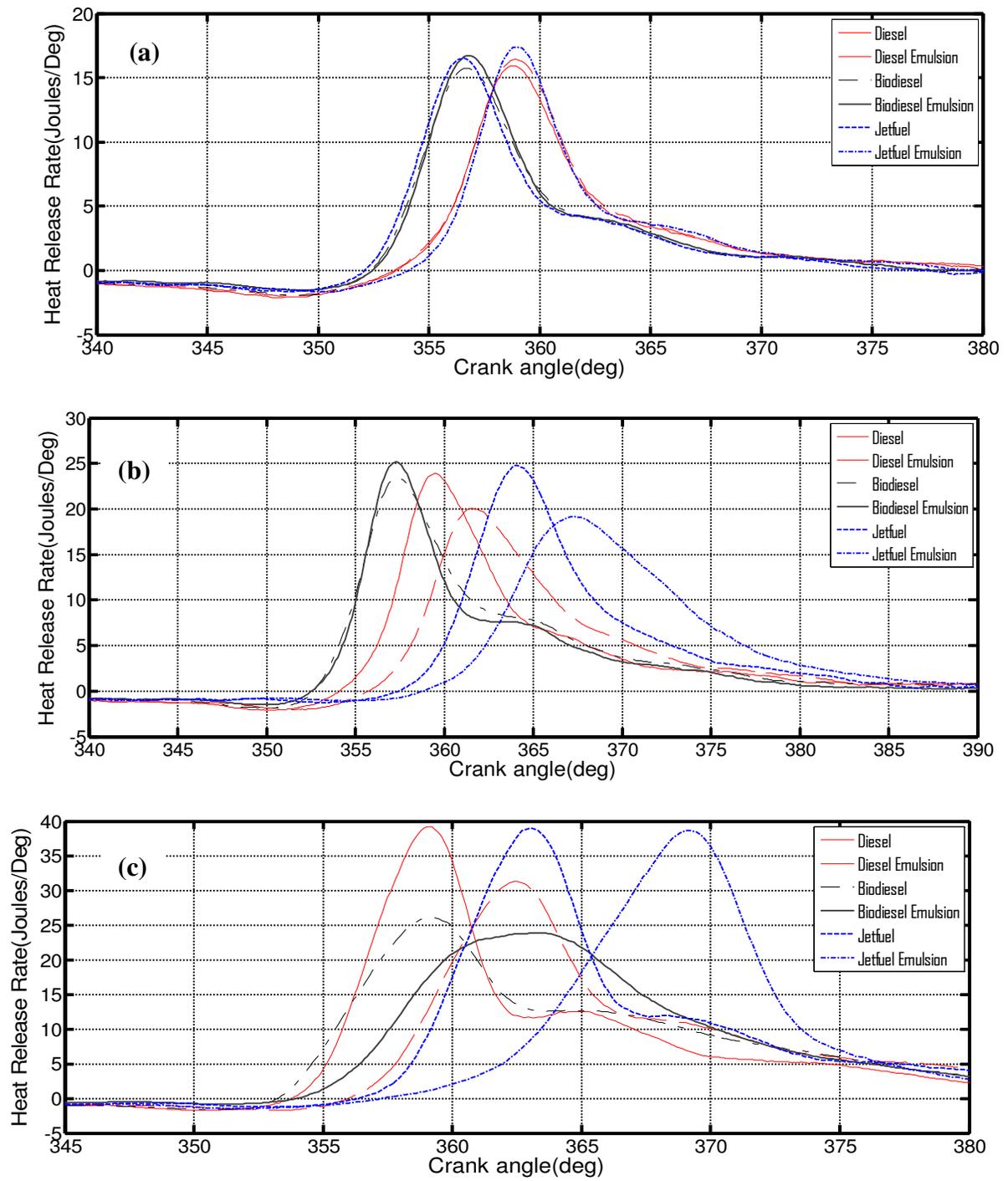


Figure 6.6: Heat Release Rate at (a) 0 bar, (b) 1.26 bar and (c) 3.26 bar BMEP.

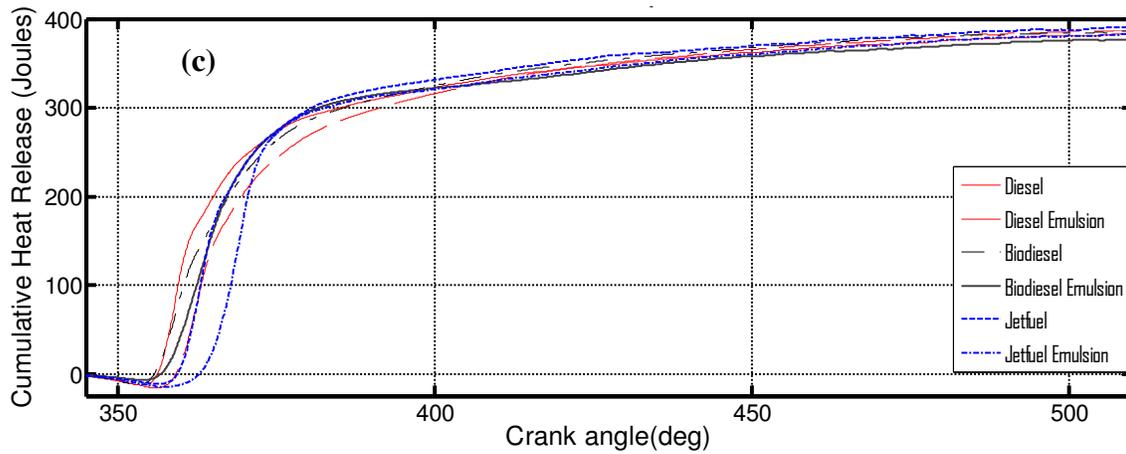
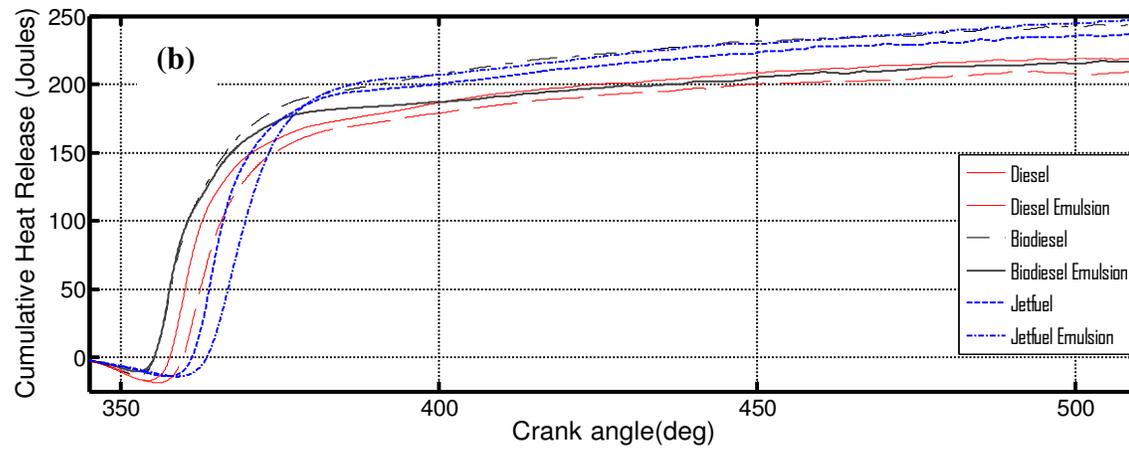
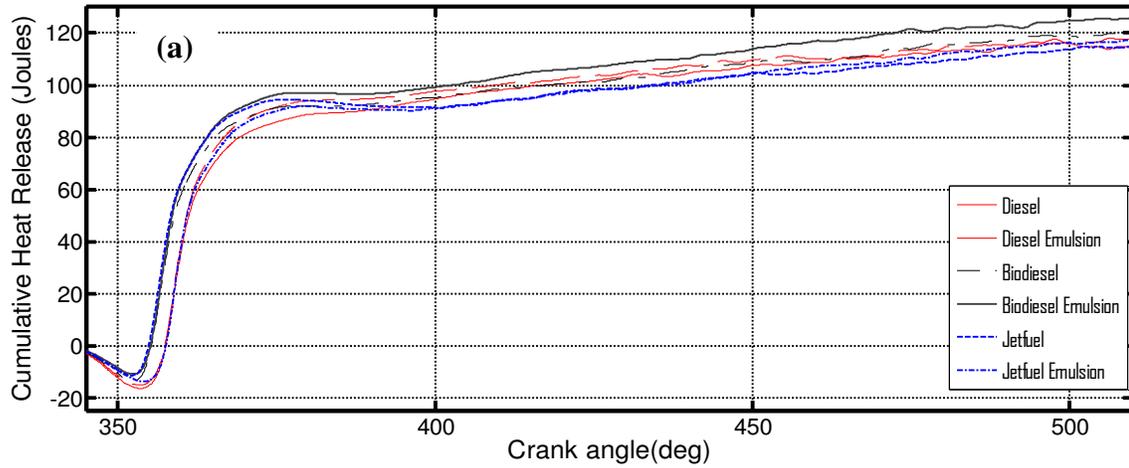


Figure 6.7: Cumulative Heat Release at (a) 0 bar, (b) 1.26 bar and (c) 3.26 bar BMEP.

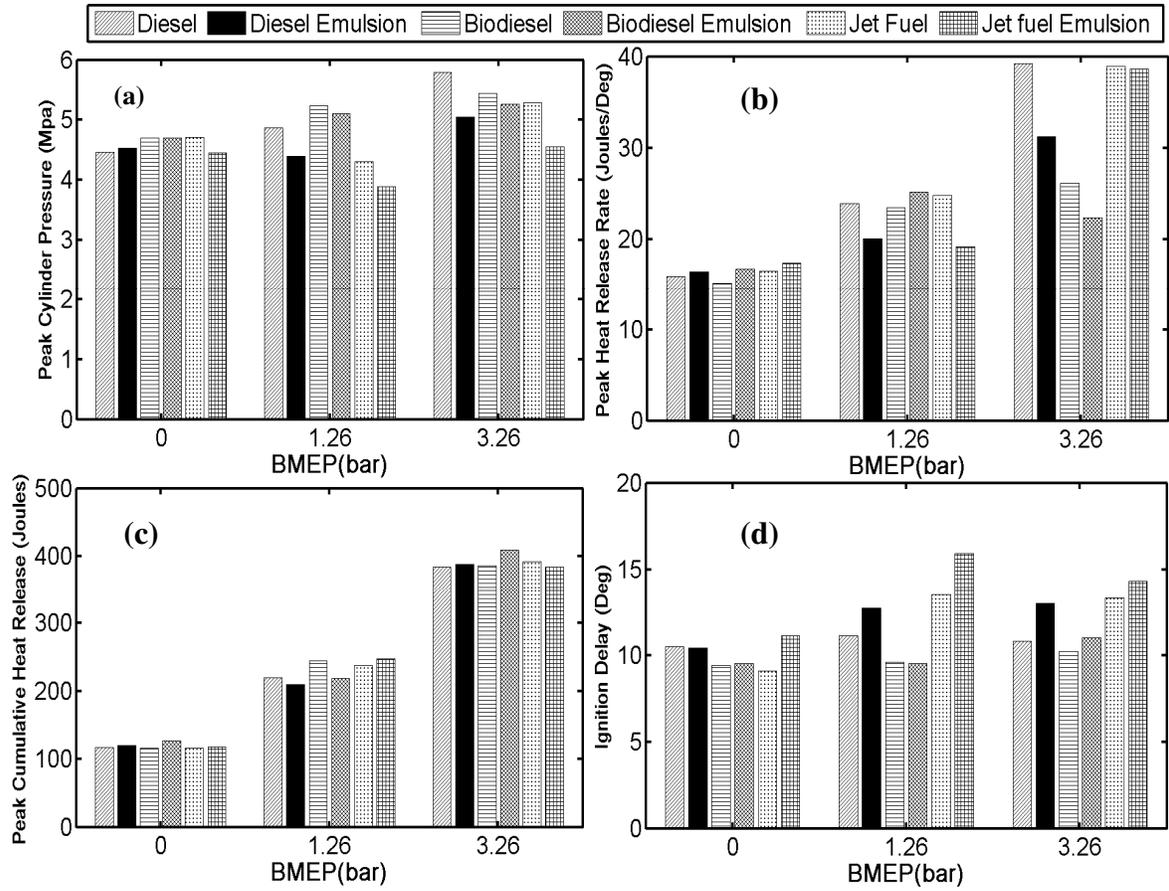


Figure 6.8: (a) Peak Cylinder Pressure (b) Peak Heat Release Rate (c) Peak Cumulative Heat Release Rate (d) Ignition Delay at 0 bar, 1.26 bar and 3.26 bar BMEP

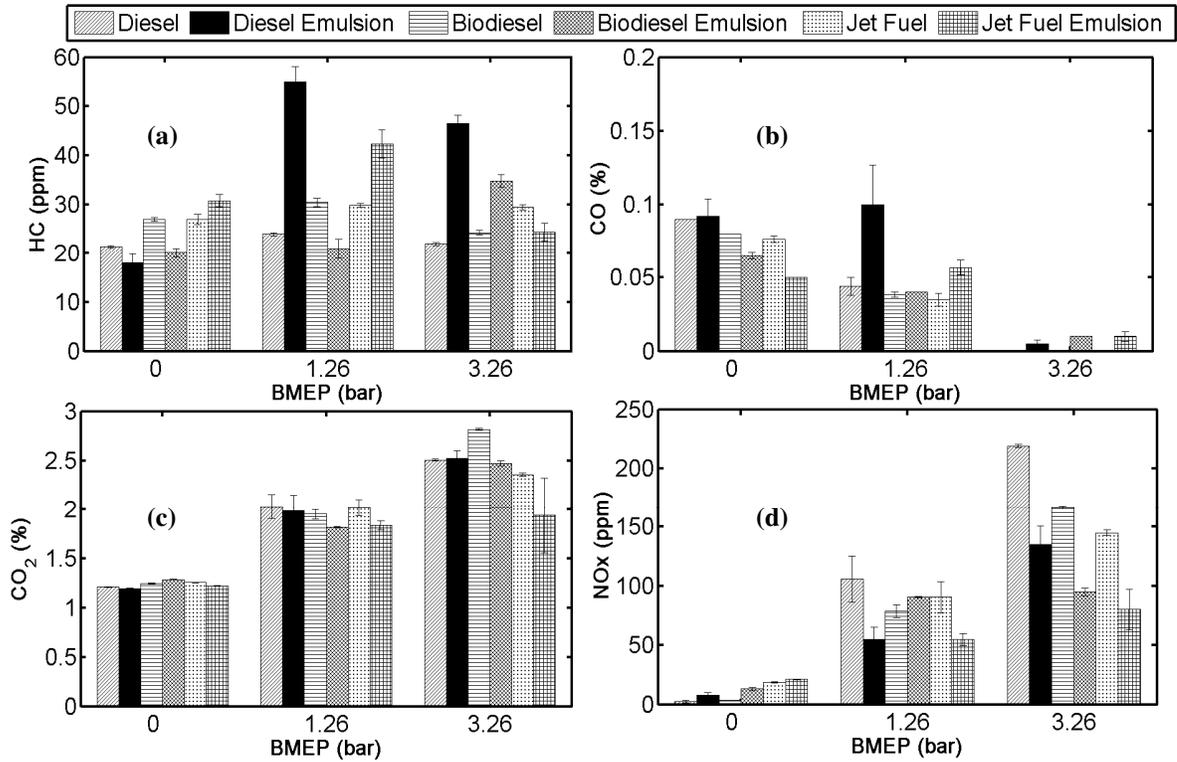


Figure 6.9: (a) Hydrocarbon emissions (b) Carbon Monoxide emissions (c) Carbon Dioxide emissions (d) NO_x emissions at 0 bar, 1.26 bar and 3.26 bar BMEP

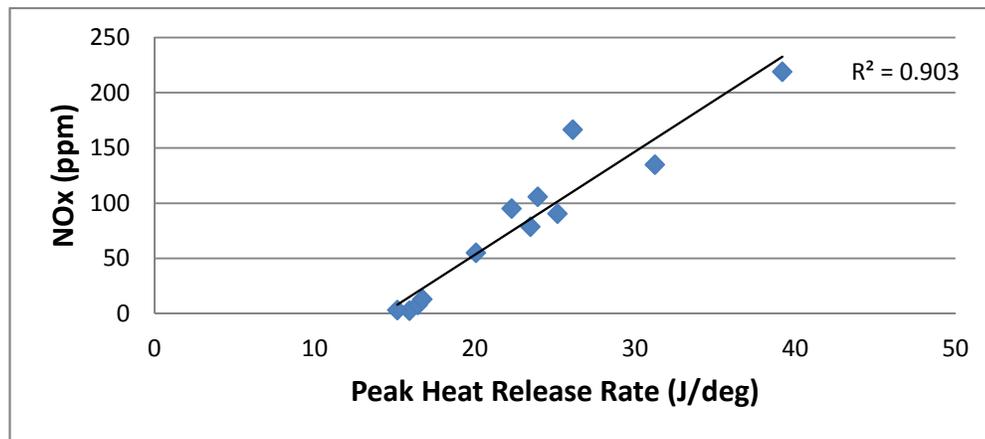


Figure 6.10: Relationship of NO_x with peak heat release rate for diesel, biodiesel and their emulsions at 0 bar, 1.26 bar and 3.26 bar BMEP

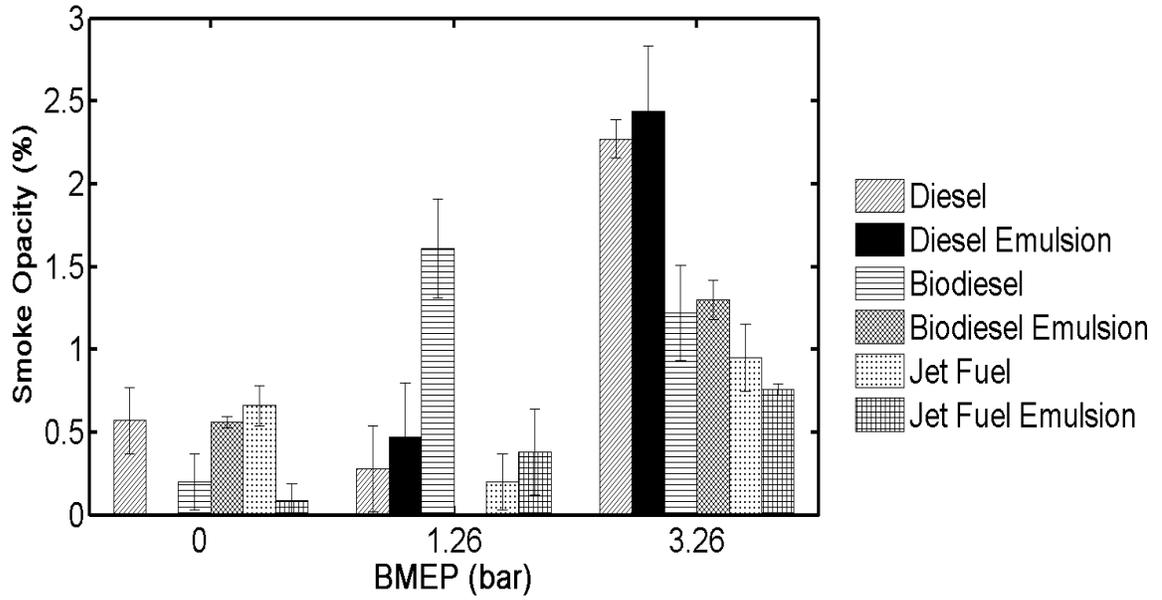


Figure 6.11: Smoke Opacity at 0 bar, 1.26 bar and 3.26 bar BMEP

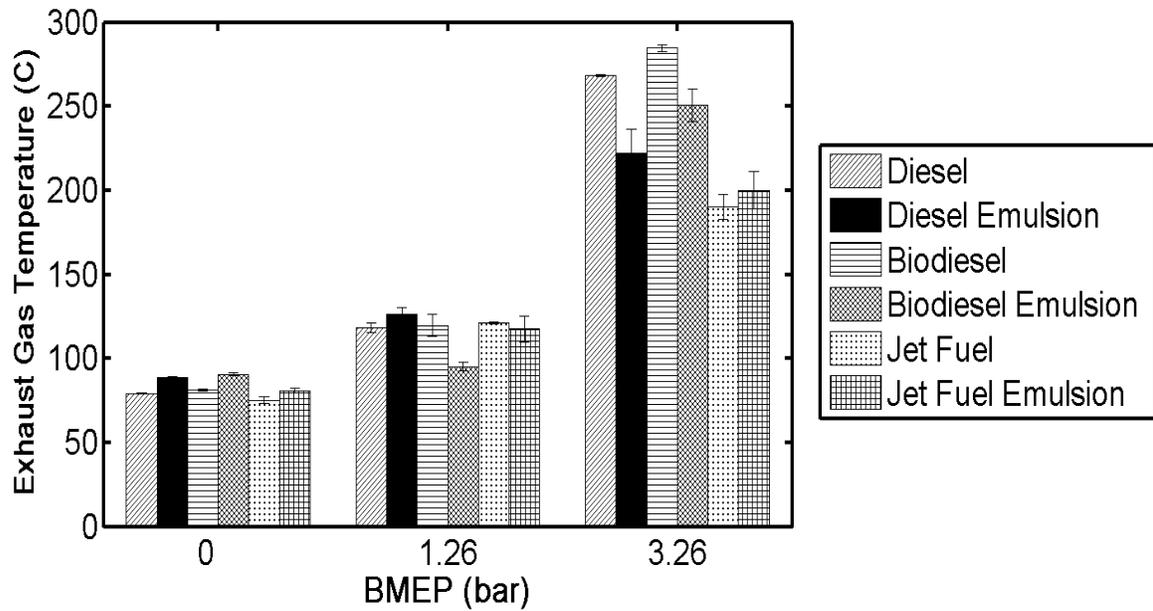


Figure 6.12: Exhaust gas temperature at 0 bar, 1.26 bar and 3.26 bar BMEP

CHAPTER 7

Preliminary Testing of Lignin Derived Compounds as Viable Fuel Additives in Diesel Engines

7.1 Abstract

In this work, preliminary testing of lignin derived compounds as additives in a diesel engine was conducted. Five chemical compounds were tested as fuel additives, including 2-methoxyphenol (guaiacol), catechol, catechol ester, vanillin, and vanillin ester. Four of these additives are solids with 2-methoxyphenol being the only liquid. In order to effectively test the solid additives, it was necessary to dissolve them in ethyl ether. Test was performed for each additive at an engine speed of 2000 rpm and an engine load of 25% corresponding to 1.26 bar brake mean effective pressure (BMEP). The parameters of engine performance, combustion process, and exhaust emissions were measured. No. 2 Diesel was used as a primary fuel and as a benchmark for comparing the effects of the different additives. In order to better monitor the changes observed from the solid additives, an additional run using pure ethyl ether was also performed. From the results obtained, engine performance remained close with relatively minor changes except fuel consumption where the additives lead to slightly higher fuel consumption rates and a corresponding increase in brake specific fuel consumption. There was hardly any noticeable difference among the combustion pressures and heat release rates of the different additives except vanillin ester which had a longer ignition delay with a lower peak in-cylinder pressure. Emissions from additive experiments

were also noticeably lower when compared with diesel except that vanillin and vanillin ester had slightly higher hydrocarbon and carbon monoxide emissions, respectively. All the tested fuels had lower NO_x emissions when compared to pure diesel. The smoke opacity, which is an important factor in determining the amount of soot present in the exhaust, was also noticeably lower for all the additives when compared with diesel.

7.2 Introduction

Fossil fuels have had major impacts in shaping today's world. The cost and difficulty associated with mining fossil fuels and their impact on today's climate have made it increasingly necessary to find alternative sources of energy. The use of fossil fuels for energy generation is not expected to cease any time soon in fact fossil fuel consumption is expected to increase for at least another two decades [83]. As a means of reducing the dependence on fossil fuels as a result of increasing cost of production and mining, depleting world reserves, and the negative impact on climate, drastic changes are being made. Some of the changes involve the use of the fossil fuels in combination with alternative sources of energy like electricity and bio – fuels thereby giving rise to hybrid system for power generation. Other changes involve improvements in fuel combustion systems and the use of fuel additives to improve fuel combustion and reduce emissions.

Fuel additives are chemicals added to fuel in very minute quantities to help improve engine performance, fuel properties or both with minimum undesirable effects [57]. Fuel

additives may be used to improve the lubricity of fuels, improve the combustion characteristics of the fuel (octane and cetane improver, anti-knock), clean the engine components such as valve and injectors by removing deposits and in the case of diesel fuel additives may be used to help cold weather startup by increasing the pour point of the fuel. Cheaper additives such as lead are no longer in use due to their effects on the environment and the damaging effects they have on engine exhaust after treatment systems. Other viable fuel additives such as amines are not necessarily safer nor are they cheap in comparison to having the fuels undergo additional refining [57]. The health issues, high cost and the large number of fuel additive use necessitates a cheaper and possibly safer source of fuel additives with the ability to meet one or more of the above stated uses.

Lignin is the second most abundant natural polymer in the world after cellulose. It is an insoluble polyphenolic compound associated with polysaccharides in the plant cell wall [32]. It provides rigidity in plant cell walls and is hydrophobic allowing for the transport of water in the plant. It makes up about 20-30% of trees (dry weight) with a slightly different chemical structure depending on the plant source. Lignin is typically obtained in large quantities as a by-product of paper production. In the paper mills, lignin can be obtained from sulfite pulping or Kraft pulping. The sulfite pulping process is recognized as the most important commercial source of lignin. The lignin from this process is in the form of lingsulfonates which because of the sulfonate group are generally soluble in water over a wide pH range. Kraft lignin is the most common pulping process used for paper production today. It involves the use of strong alkali with a sodium sulfide catalyst to separate lignin and

hemicellulose from cellulose fibers given rise to 'black liquor'. Black liquor contains dissolved lignin and hemicellulose. Lignin is extracted from black liquor by precipitation which involves the use of a suitable acid to lower the pH of the liquor [84-86]. Other sources of lignin production are the use of organic solvents and steam exploded lignin. Typical uses of lignin are as dispersants, binders, fuels, emulsifying agents and pesticides amongst others [87].

The abundance of lignin in nature, the additional cost for paper mills to process Kraft lignin and the increasing research to produce bio-fuels from cellulose (with lignin as a by-product) has led to the need for more economical uses of lignin. While lignin could be used to produce liquid fuels compatible with gasoline [88-89] and diesel combustion systems [90-91], the process is relatively expensive but given the high heating value, low cost (compared to fossil fuels) and rich oxygen contents from lignin pyrolysis, a more economical product for combustion application is needed. Lignin can be burnt directly, but it typically exists as a solid and depending on the process from which it is obtained, it can be high in sulfur content making it impossible to use as a direct fuel in internal combustion engines. The pyrolysis of lignin produces different oxygen rich phenolic compounds [90, 92] which can be used as the more economical fuel additive [93] with the possibility reducing emissions [94], fuel consumptions and possibly increasing the performance of combustion systems.

Pyrolysis is the thermochemical decomposition of organic materials at elevated temperatures in the absence of oxygen [92]. The pyrolysis of lignin results in the formation of many products. The most common gaseous products are carbon dioxide, carbon monoxide

and methane. Phenolic compounds are the most common liquid products with char and tar been the solid products from lignin pyrolysis [95]. Further decomposition of the liquid products vanillin, guaiacol and catechol result in the production of free radicals [96-68] which can help improve the cetane number of diesel fuel. Aromatics produced from the thermal decomposition of these liquid products can also help to greatly reduce engine knock in spark ignition engines [9].

This experiment has two purposes. The first objective of this experiment is find viable uses for lignin derived compounds as a means eliminating Kraft lignin as a waste for pulp and paper production. The second objective of this work is to reduce diesel engine emission without compromises in engine performance by using lignin derived compounds as fuel additives.

7.3 Experimental Setup

The setup for this experiment is discussed in chapter 3. In this experiment, the liquid products (phenolic compounds) and their esters formed from the pyrolysis of lignin are used. The phenolic compounds shown in Figure 7.1 are 2-methoxy phenol (guaiacol), catechol and its ester, vanillin and its ester. Guaiacol is a well-known substance attributed to adding flavor to other chemicals. It is a phenolic compound with an additional methoxy group. Guaiacol used in this experiment was a light pink liquid. Catechol has several uses which include pesticides, dyes, and polymerization inhibitor. Catechol is a phenolic compound with an additional hydroxyl group attached to it. Catechol and its ester used in this experiment were in the form of white crystals. Vanillin is a chemical typically used as a flavor, a fragrance and

an intermediate chemical for producing other chemicals. It is a phenolic compound with an aldehyde and a methoxy group. Vanillin ester used in this experiment has had the hydroxyl group of phenol replaced by an amide group. Vanillin and its ester used in this experiment were in the form of white powders. The chemical structures for these compounds are shown in Figure 7.1. As catechol, vanillin and their esters are solids; it is necessary to dissolve them in a solvent before mixing with diesel.

The solid compounds were dissolved in ethyl ether before further mixing with diesel. 2-methoxyphenol (guaiacol) was mixed directly with diesel for testing purposes. Pure diesel fuel was used as both the benchmark and the primary fuel. Since ethyl ether was used as a solvent for the solid compounds, it became essential to conduct a separate experiment for a diesel - ethyl ether blend in order to investigate any effect ethyl ether might have on the solid compounds. Table 7.1 provides the nomenclature used for the compound blends.

For every 500 milliliter of diesel 0.6 grams of compound was used. 0.6 grams of the solid compounds were first dissolved in 3.0 grams of ethyl ether before being mixed with diesel, for this reason, the diesel - ethyl ether blend experiment also had 3.0 grams of ethyl ether in 500 milliliter of diesel.

7.4 Results and Discussion

7.4.1 Performance

The effects of the five chemical compounds and the solvent on diesel engine performance are shown in Figures 7.2 and 7.3. Figure 7.2 shows that for each of the samples tested, the

brake work was kept the same. Figure 7.3a is a plot of the indicated work for each of the samples tested including the solvent (ethyl ether). From this figure, it can be observed that all the blends tested have lower indicated work when compared to pure diesel. A difference in indicated work of about 6% is also noted between diesel with the highest indicated work and vanillin ester- ethyl ether blend with the lowest. The lower indicated work observed for the vanillin ester-ethyl ether blend is believed to be as a result of its higher mechanical efficiency when compared to all the other samples tested. As a result of this, it has a lower peak in-cylinder pressure. Considering the similarity in the combustion profile of all the other fuels (Figures 7.4 - 7.6), we would expect to see a smaller percent difference between each sample. This is shown to be the case since the percent difference between pure diesel fuel and diesel-guaiacol blend is only 4.2%. Vanillin ester ethyl ether blend has the highest mechanical efficiency of about 52% as shown in Figure 7.3b. This is an increase of about 6.5% over pure diesel fuel; assuming the combustion results observed for vanillin ester ethyl ether blend play some roles in its higher mechanical efficiency, it should be noted that guaiacol still has a higher mechanical efficiency of about 4.4% over diesel.

Brake specific fuel consumption (BSFC) is a measure of how efficiently the engine uses the available fuel to do work [9]. From Figure 7.3c, the fuel blends are observed to have higher BSFC values when compared to pure diesel with the exception of vanillin ester ethyl ether blend which at this point will be considered an outlier. The vanillin ester ethyl ether blend has the lowest BSFC a difference of about 14% from diesel. Interestingly, guaiacol,

catechol and its ester all have approximately the same BSFC values. The lower BSFC of vanillin ester ethyl ether blend is believed to be as a result of an overall decrease in the heating value of the blend as a result of the introduction of the ester with oxygenates in the fuel.

Brake thermal efficiency is a measure of how efficiently the energy in the fuel is used to generate work. Vanillin ester ethyl ether blend has the highest brake thermal efficiency (BTE) as shown in Figure 7.3d. In general, however, all the tested sample blends have lower BTE when compared to pure diesel fuel. The higher brake thermal efficiency of vanillin ester ethyl ether blend may be attributed to the proximity of the peak in-cylinder pressure to TDC as seen in Figure 7.4. The closer the peak in-cylinder pressure is to TDC, the more positive work is generated. From Figures 7.4 and 7.5, we also observe that vanillin ester ethyl ether blend has a lower peak in-cylinder pressure as well as a lower peak heat release rate. Both of them help reduce the gas temperature with reduced heat loss to the wall. In addition, the lower soot emission (see in Section 7.4.3) for the condition also contributes to the lower radiative heat loss during the power stroke with increased thermal efficiency.

7.4.2 Combustion

The data of in-cylinder combustion pressure was obtained from the in-cylinder pressure sensor installed in the engine cylinder head. Figures 7.4 – 7.7 show an overview of the combustion process in this diesel engine. Figure 7.4 is a plot comparing the in-cylinder pressure for pure diesel and all the sample blends tested. From this figure, it is apparent that the vanillin ester ethyl ether blend behaves in a rather different manner compared to the other

tested fuels. It starts to split off from the rest at about 348°C and reaches a lower peak pressure of 5.0 MPa much later than all other fuels before rejoining the trend at about 375°C. This behavior is believed to be as a result of the much longer ignition delay for this blend. Considering that the vanillin ethyl ether blend did not behave in the same manner as vanillin ester ethyl ether blend, the amide group associated with this ester is believed to be the culprit responsible for the longer ignition delay observed. The carbon nitrogen bond in the amide group is a strong triple bond that is believed to reduce the ignition quality of the blend by reducing the cetane number hence resulting in a longer ignition delay.

Figure 7.5 shows the heat release rate of the different fuel blends. As is observed in earlier figures, the vanillin ester ethyl ether blend stands out again as a result of its much longer ignition delay compared to the other fuels. As vanillin ethyl ether blend does not exhibit this same property, it is believed that the amide group that replaced the hydrogen atom in vanillin is responsible for the much lower heat release rate observed. The introduction of a triple bond in place of a single bond tends to reduce the cetane number of a fuel. By reducing the cetane number of the vanillin ester ethyl ether blend, longer ignition delay is observed which in turn results in a lower peak heat release rate. Figure 7.6 shows the cumulative heat release comparison for the different samples. It is again noted that vanillin ester ethyl ether blend stands out. A more significant heat loss just after TDC for vanillin ester ethyl ether blend when compared to the other test blends is also noticed. This is again believed as a result of this blends poorer ignition quality as was observed in all the other pressure profiles discussed. Figures 7.7a and 7.7d are plots of the peak in-cylinder

pressure and ignition delay respectively. From these figures, we notice an inverse relation between the engines peak in-cylinder pressure and ignition delay. The longer the ignition delay, the lower the peak pressure, a result of combustion taking place just after TDC when the in-cylinder pressure is no longer at its maximum. This slight offset also leads to loss of power in the engine and consequently a lower peak heat release rate as can be seen in Figure 7.5. Figure 7.7b is a comparison of the peak heat release rates for the different blends. From this figure, catechol ethyl ether blend has the highest peak heat release rate followed closely by vanillin ethyl ether blend. The high peak heat release rate is as a result of less heat being needed for the overall dissociation of catechol bonds when compared to vanillin and the other compounds. From Figure 7.7c, which shows a comparison between the peak cumulative heat releases, pure diesel fuel has the highest cumulative heat release an increase of 0.4% over vanillin ethyl ether blend which has the highest cumulative heat release of the blends. The vanillin ester ethyl ether blend had the lowest cumulative heat release rate at about 216 joules which puts it at about 4.7% below pure diesel fuel.

7.4.3 Emissions

One of the more important reasons for carrying out this experiment was to study the effect of the lignin derived compounds on diesel engine emissions. The exhaust gases were collected and quantified by using a FGA 4000 XDS exhaust gas analyzer and a smoke opacity meter. Figure 7.8a shows the hydrocarbon emissions for the samples tested. It is seen from this figure that vanillin ethyl ether blend has the highest hydrocarbon emissions with vanillin ester ethyl ether blend having the lowest. With the exception of vanillin ethyl ether

blend, all the blends have lower or similar (catechol ester ethyl ether blend) hydrocarbon emissions than diesel. The higher hydrocarbon emission of vanillin ethyl ether blend could be as a result of it having a higher hydrocarbon content compared to the other compound blends. The high oxygen content of these blends could also be responsible for better and more complete combustion which would in turn result in lower hydrocarbon content in the exhaust.

In Figure 7.8b, carbon monoxide emissions for the different blends are compared. With the exception of vanillin ester ethyl ether blend, all the sample blends had lower carbon monoxide emissions than diesel. This could be attributed to the high oxygen content of the samples resulting in more complete combustion. In Figure 7.8c, carbon dioxide emissions are observed to be lower when compared to diesel. This could be as a result of the formation of poly cyclic aromatic hydrocarbons (PAH) and other radicals which react with excess oxygen and carbon atoms. At much higher temperatures, an abundance of Carbon monoxide and carbon dioxide could be expected as the PAHs further decompose to form mostly CO₂ and CO. Figure 7.8d shows a comparison of oxides of nitrogen in the exhaust for the different samples. It is observed that all the tested blend samples have lower NO_x emissions when compared to pure diesel. The absence of a higher NO_x content in the exhaust gas of vanillin ester ethyl ether blend suggest that the carbon nitrogen bond may not have dissociated successfully or as shown in the heat release figures the temperature inside the cylinder was not high enough to support the formation of oxides of nitrogen.

Smoke opacity comparison is shown in Figure 7.9a. In general, smoke opacity is an effective measure of measuring the soot content in the exhaust. The higher the opacity, the

more soot is present in the exhaust and vice versa. From this figure, all the tested sample blends have lower opacity and as such lower soot content than pure diesel fuel. This may be attributed to the high oxygen content of the sample blends resulting in more complete combustion and lower soot content. In Figure 7.9b, exhaust gas temperature for the tested blends is shown. Vanillin ester ethyl ether blend had the highest exhaust gas temperature with vanillin ethyl ether blend having the lowest. The high temperature observed for vanillin ester ethyl ether blend is due to its longer ignition delay which results in combustion occurring at a later time and thus higher exhaust gas temperatures when compared to the other test samples.

7.5 Conclusion

An experiment was conducted to study the effect on diesel fuel of five lignin derived compounds and a solvent in a compression-ignition diesel engine. Engine performance, fuel combustion and emissions were measured. Based on the results obtained from this preliminary experiment, some important finding can be summarized in the following:

1. The five compounds and solvent used as additives for this experiment have significant effects on the engine performance. The mechanical efficiency for the tested samples are higher than that of diesel mostly as a result of slightly higher fuel consumption with the exception of the vanillin ester ethyl ether blend which had both lower fuel consumption rates and higher mechanical efficiency. The compounds had lower brake thermal efficiency when compared to diesel with the exception of vanillin ester ethyl ether blend which had a higher brake thermal efficiency.

2. The maximum difference in ignition delay between the tested compounds and diesel fuel was 0.3° CA for all the tested samples with the exception of vanillin ester ethyl ether blend. As a result, the combustion profiles of the tested samples were all very similar. The outlier with the longer ignition delay had a lower peak in-cylinder pressure, lower heat release rate and a lower cumulative heat release rate.
3. The results of the lignin derived compounds on the engines emissions are outstanding. For all the tested exhaust gas samples, the compounds and solvent blend had overall lower emissions. Lower hydrocarbon, carbon monoxide, carbon dioxide, NO_x and soot were observed. The only deviation was observed for vanillin ethyl ether blend and vanillin ester ethyl ether blend which had higher hydrocarbon and carbon monoxide emissions respectively when compared to pure diesel.
4. Based on the results obtained from this experiment, the compound of choice would be vanillin ester dissolved in ethyl ether. From the results obtained, it improved engine performance and generally had lower emissions when compared to pure diesel. The only drawback is that it had a much longer ignition delay which resulted in some power loss. It also had a higher carbon monoxide emission when compared to pure diesel. Any of the other tested blends will also work as additives especially with regards to emissions considering their combustion profiles did not vary significantly from diesel.
5. The experiment in this work was limited to a fixed load and one engine speed in a single cylinder engine. The main fuel used was commercially available ultra-low

sulfur diesel (ULSD) which already had some fuel additives in it. It would be most interesting to perform this experiment again using un-altered diesel fuel, nevertheless, marked improvements were observed with ULSD. It is possible that the results obtained could differ for other engine speeds and loads in multi-cylinder diesel engines. Further investigation is necessary before application in practical engines.

Table 7.1: Fuel Nomenclature

Fuel Name	Acronym
Diesel guaiacol blend	D + O
Diesel ethyl ether blend	D + EE
Diesel ethyl ether catechol ester blend	D + EE + CE
Diesel ethyl ether catechol blend	D + EE + CA
Diesel ethyl ether vanillin blend	D + EE + VA
Diesel ethyl ether vanillin ester blend	D + EE + VE

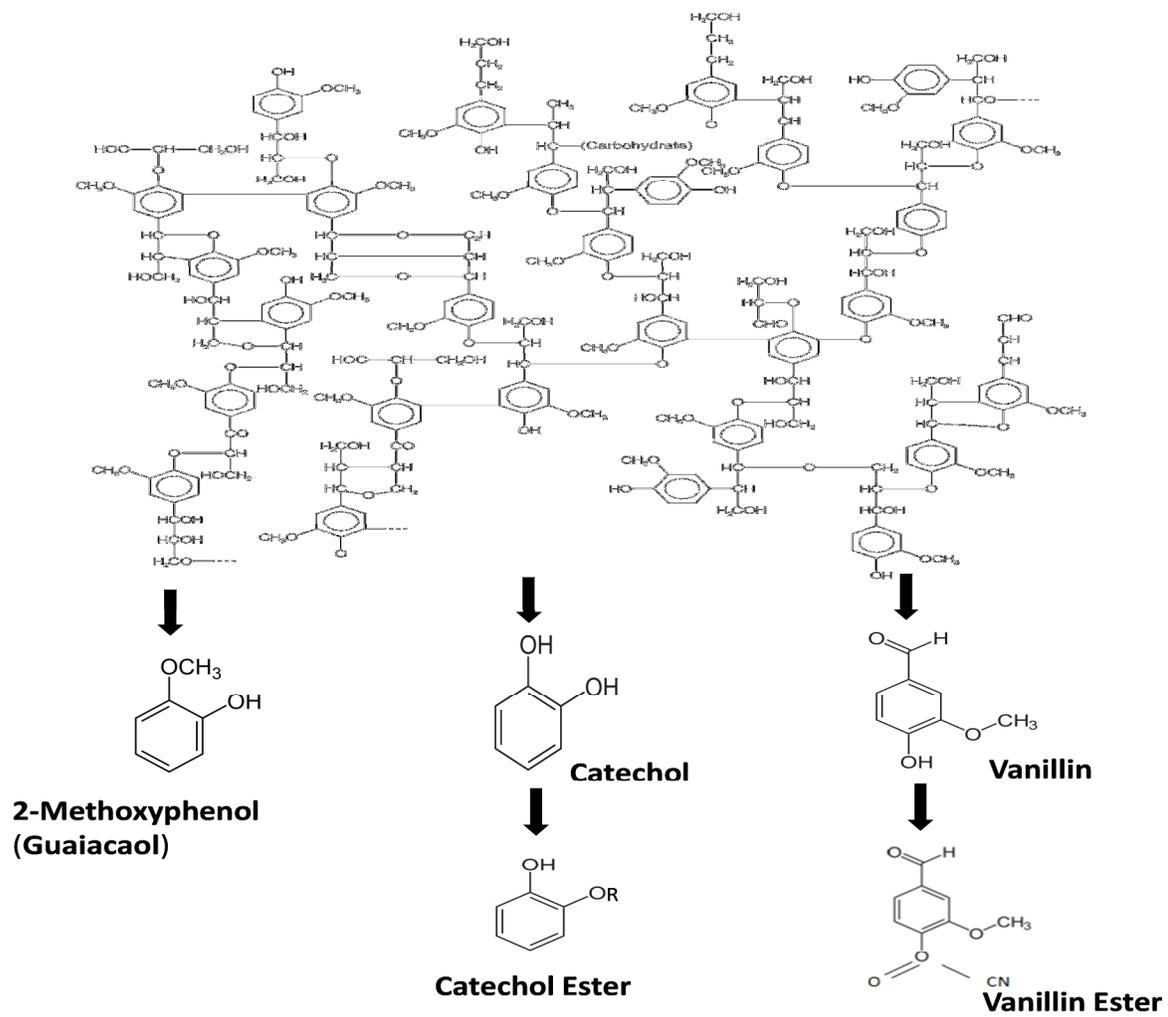


Figure 7.1: Lignin [99] and tested compounds

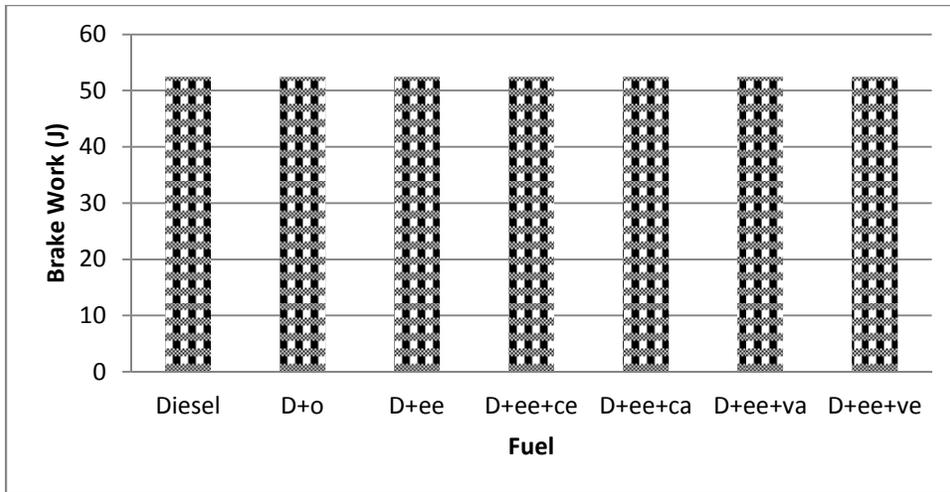


Figure 7.2: Brake work per cycle under the given engine speed and load

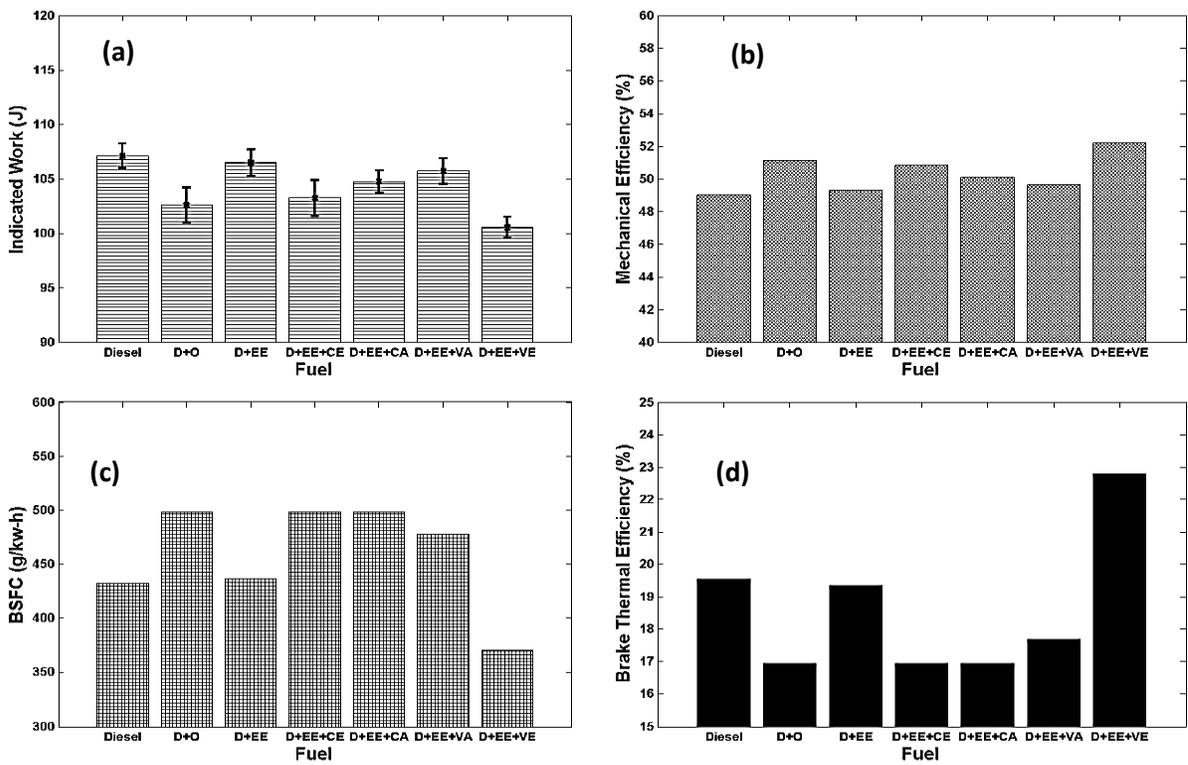


Figure 7.3: (a) Indicated Work (b) Mechanical Efficiency (c) BSFC (d) Brake Thermal Efficiency at 2000 rpm and 1.26 bar BMEP

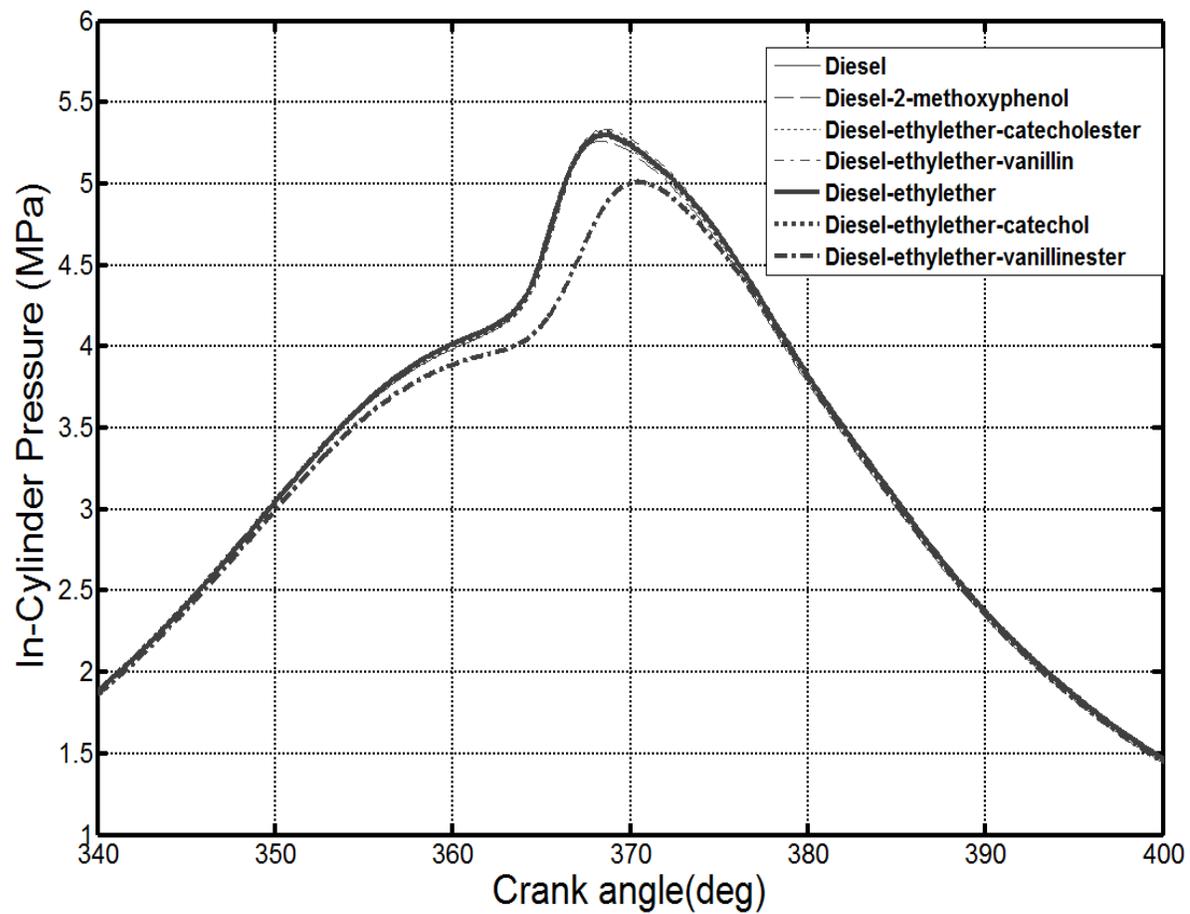


Figure 7.4: In-cylinder pressure at 2000 rpm and 1.26 bar BMEP

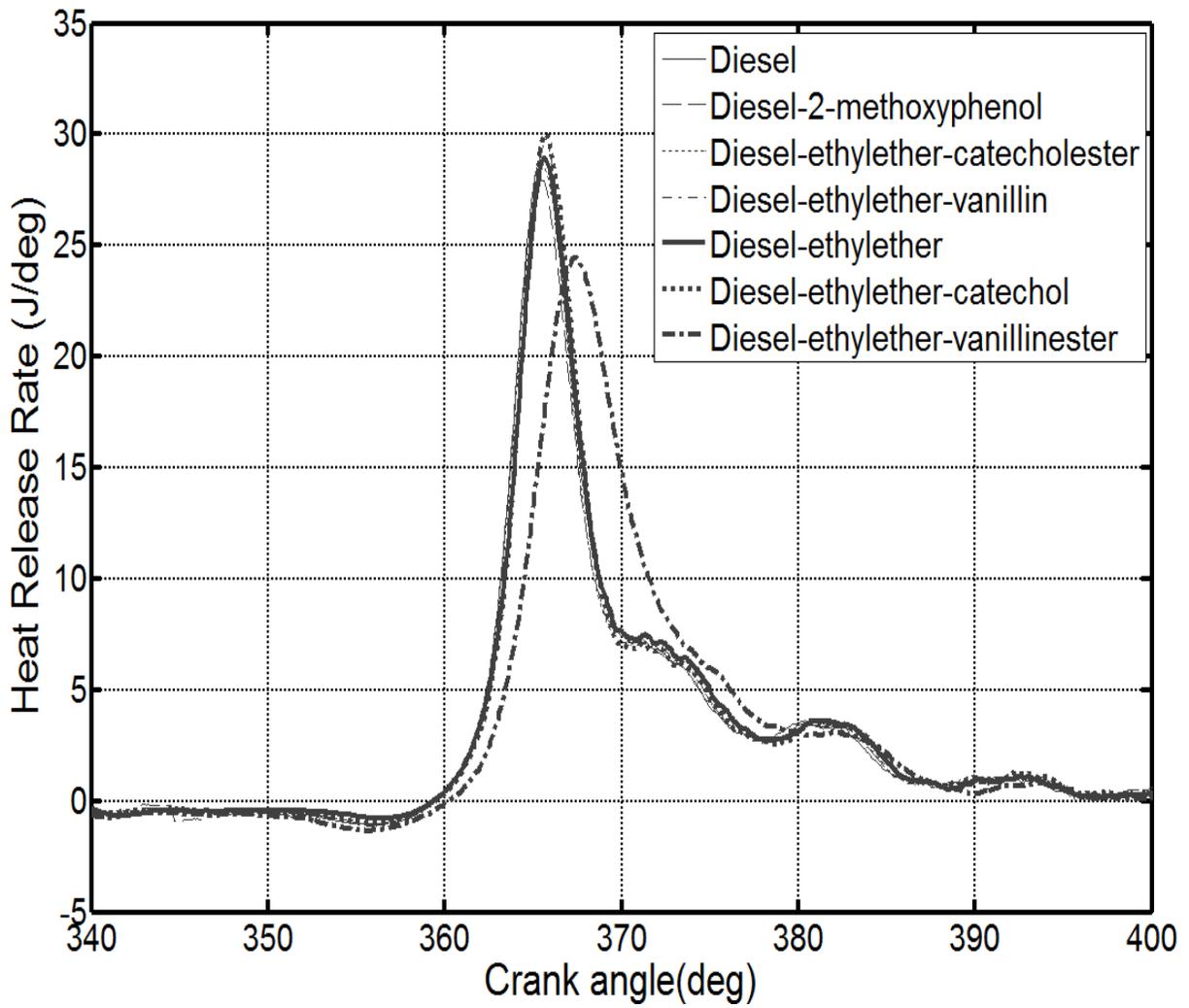


Figure 7.5: Heat release rate at 2000 rpm and 1.26 bar BMEP

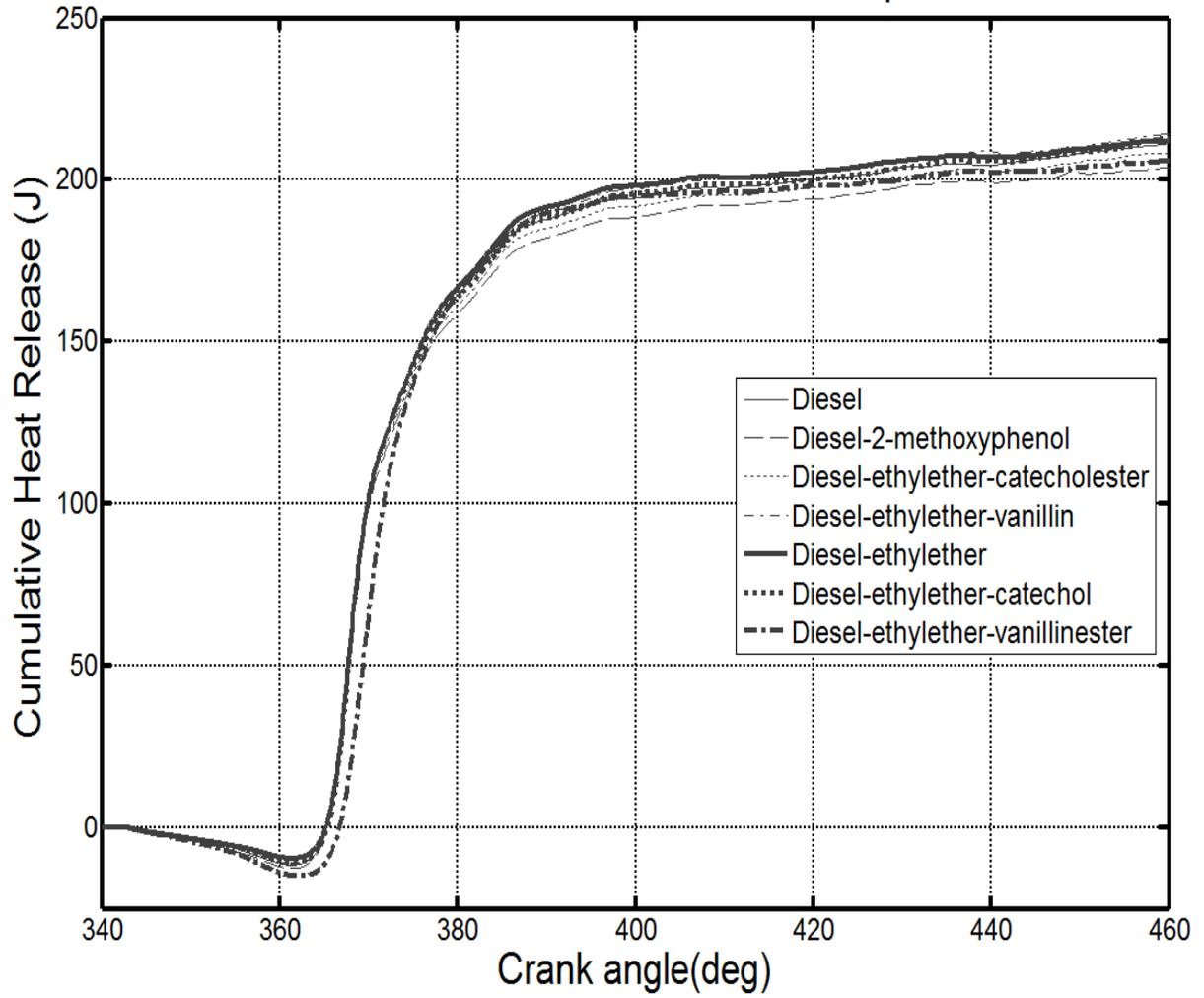


Figure 7.6: Cumulative heat release at 2000 rpm and 1.26 bar BMEP

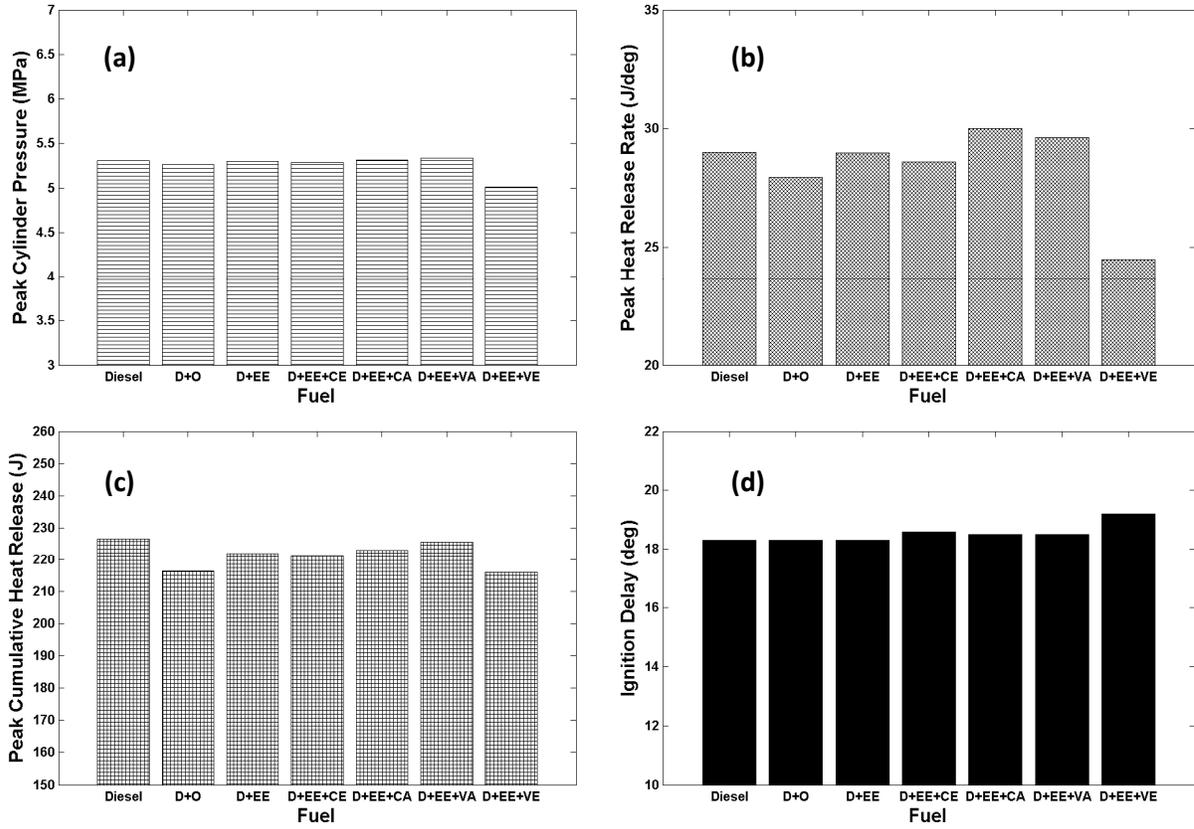


Figure 7.7: (a) Peak in-cylinder pressure (b) Peak heat release rate (c) Peak cumulative heat release (d) Ignition delay at 2000 rpm and 1.26 bar BMEP

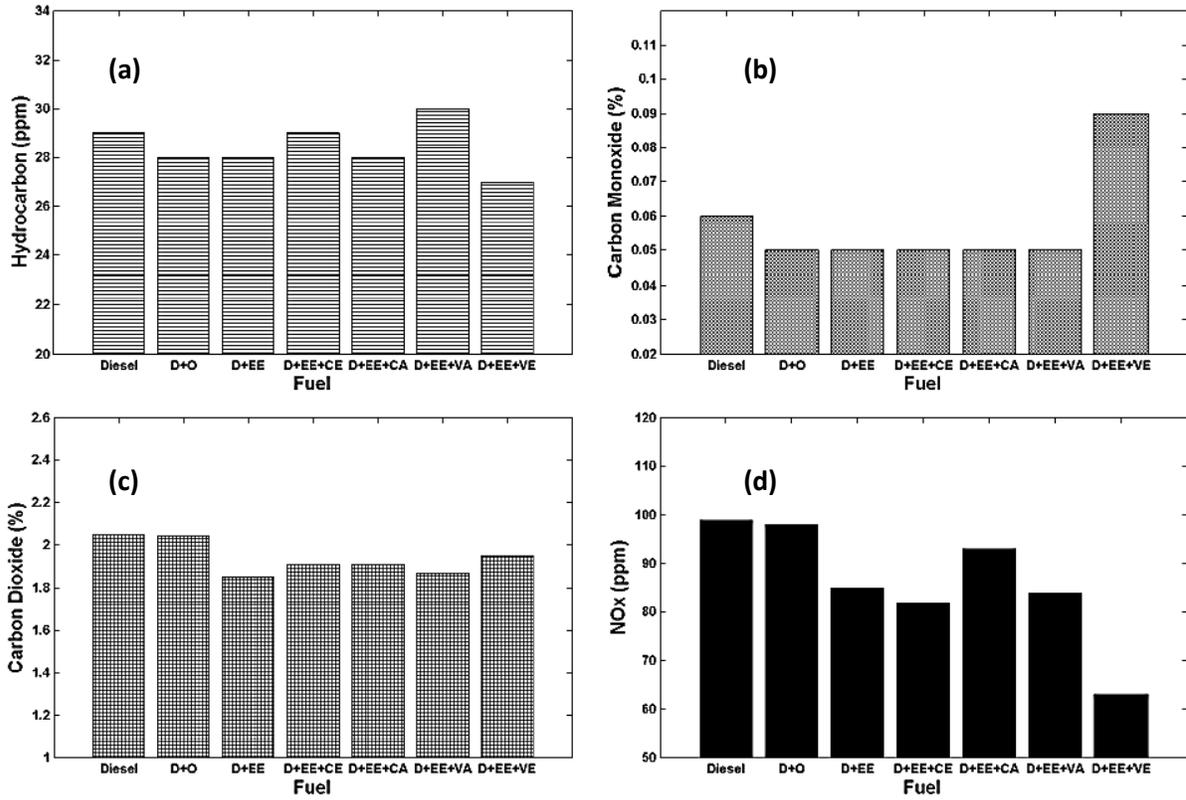


Figure 7.8: (a) Hydrocarbon (b) Carbon Monoxide (c) Carbon Dioxide (d) NOx emissions at 2000 rpm and 25% load

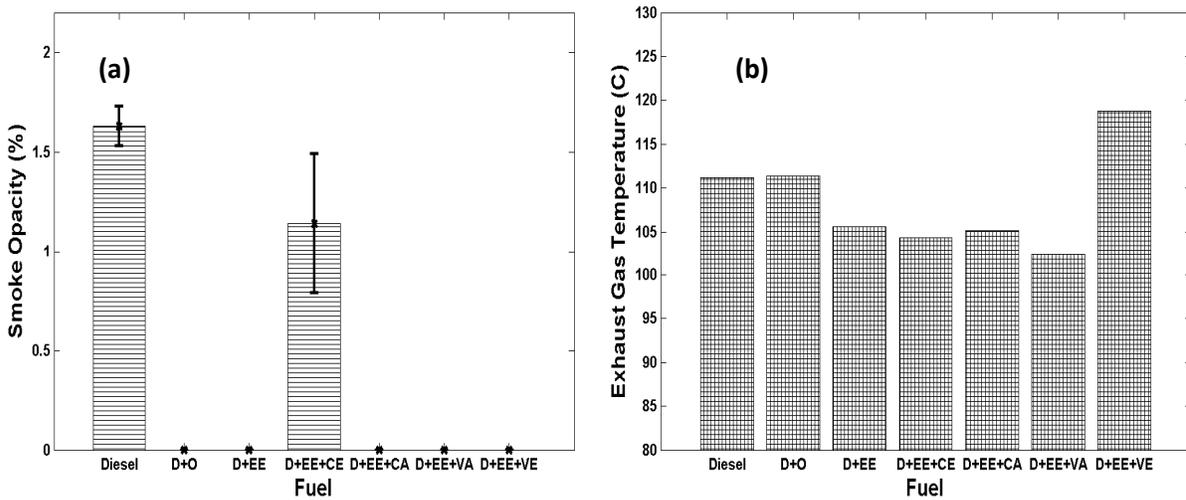


Figure 7.9: (a) Smoke opacity (b) Exhaust gas temperature at 2000 rpm and 25% load

CHAPTER 8

CONCLUSION

The works discussed here were performed in a compression-ignition engine. The main objective was to test the viability of emerging alternative fuels and additives in a diesel engine. Four sets of experiments based on two second generation biofuels, a fuel emulsion using a renewable surfactant, and renewable additives were investigated in this work.

In the first set of experiments, the performance, combustion and emissions from an engine running renewable diesel was investigated. From this experiment, it was determined that diesel engines running renewable diesel had lower mechanical efficiency and lower brake specific fuel consumptions when compared to conventional diesel. The engine running these fuels also had similar brake thermal efficiencies to when fossil diesel was used as such the overall performance of the engine on green diesel was roughly the same as when used with conventional diesel. Combustion wise, renewable diesel fuels had shorter ignition delays, lower in-cylinder pressures and lower peak heat release rates when compared with conventional diesel. Engine emissions when running renewable diesel were also observed to be lower for most of the renewable diesel fuels when compared to fossil diesel with the exception of HC emissions. Based on this study, it can be concluded that renewable diesel can be used as viable fuel alternatives to oil diesel.

The second set of experiments involved the use of a different second generation biofuel called biomass to liquid fuel (BTL). This fuel was compared to diesel

fuel and a first generation biodiesel. It was determined from the result of this experiment that running the diesel engine on BTL resulted in lower brake specific fuel consumption and higher brake thermal efficiency. The use of BTL also resulted in a slight increase in indicated work as engine load increased but a slightly lower engine mechanical efficiency. BTL was found to have shorter ignition delays when compared to oil diesel but longer ignition delays when compared to biodiesel. Overall, the diesel engine running on BTL had lower engine emissions with the exception of NO_x when compared to oil diesel. It can be concluded then that BTL is a feasible substitute for conventional diesel fuel.

The third set of experiment involved the use of oil in water emulsion made with a renewable surfactant (carboxymethylated Kraft Lignin) as a fuel source for the diesel engine. Three different oils, diesel, biodiesel and jet fuel were used in making the fuel emulsion. The use of fuel emulsion in the engine led to a decrease in indicated work, an increase in brake thermal efficiency and brake specific fuel consumption when compared to the oils used. By factoring only the quantity of oil used in the emulsion, the brake thermal efficiency of the engine increases significantly while the brake specific fuel consumption decreases significantly. Fuel emulsions were also observed to generally have higher peak cylinder pressure, heat release rates and cumulative heat release when compared to their base oil. They also had longer ignition delays in general. The effect of fuel emulsions on engine emissions was determined to be affected by the base fuel and the engine operating conditions. Based on this study, it may be concluded that for specific engine parameters, oil in water emulsions can be used as fuels in diesel engines.

The final experiment focused on the use of renewable fuel additives. These additives, catechol, vanillin, guaiacol, vanillin ester, catechol ester were obtained from the pyrolysis of lignin a renewable compound. The compounds were dissolved in ethyl ether before blending with diesel fuel for use as a fuel additive. The use of these additives resulted in slightly higher brake specific fuel consumption, an increase in mechanical efficiency but a decrease in brake thermal efficiency. The only exception was vanillin ester blend which had a higher brake thermal efficiency than pure diesel oil. The combustion profile for all the compounds looked very similar to diesel fuel with the exception of the vanillin ester blend which had a longer ignition delay, lower cylinder pressure and lower peak heat release rate when compared to diesel oil. Engine emissions when using these additives proved to be lower than when diesel oil alone is used. The only instances that differed were vanillin blend which had higher hydrocarbon emissions and vanillin ester blend which had a higher CO emission. While the pure diesel oil used in this experiment contained some other additives, positive results have been observed with the use of these compounds as fuel additives.

The results of these experiments are promising seeing as not only do the fuels and additives reduce in one form or another dependency on fossil oil, they for the most part also result in lower exhaust emissions than conventional diesel fuel. For all of these fuels and additives, further research in passenger and heavy duty vehicles would be needed for validating their effectiveness in practical transportation applications.

CHAPTER 9

FUTURE WORK

Several experiments were discussed in this dissertation. In the first two experiments, second generation biofuels were discussed. The two fuels were shown to have a positive impact by reducing engine emissions without significant performance differences compared with conventional fuels and in some cases offered better engine performance. Oil in water emulsions were examined as a means of reducing engine emissions which they did to an extent. Finally, in the last study, lignin derived compounds were used as fuel additives to successfully reduce engine emissions and performance.

Two future experiments have been planned for lignin based compounds. The first experiment involves the use of blended phenolic compounds derived from lignin as additives to help tackle engine emissions. The second experiment involves a study on the engine characteristic differences from the use of carboxymethylated Kraft lignin as a surfactant compared to more commercially available surfactants. Additional work is being considered to test some of this alternative fuels in an optical engine so as to better understand the combustion properties of these fuels.

It would be interesting to study the effect of changing the concentration of additives used in this study as well as proper testing of all the fuels and additives under more comprehensive engine operating conditions or in vehicles over practical operating conditions.

REFERENCES

1. United States Vehicle Registration 2012 Statistics. Accessed July 25, 2014, from <http://www.statista.com/statistics/183505/number-of-vehicles-in-the-united-states-since-1990/>
2. Stacy C. Davis, Susan W. Diegel, Robert G. Boundy, Sheila Moore. 2013 Vehicle technologies Market Report. Oak Ridge National Laboratory.
3. Meeting Emissions - The Cummins Solution. Accessed July 25, 2014 from <http://cumminsengines.com/cummins-aftertreatment-system>
4. Dominik Rutz, Rainer Janssen. (2007). Biofuel Technology Handbook. WIP Renewable Energies.
5. Angelo Young . Here are the December 2013 'Big Eight' US Auto sales Numbers: Gm, Ford, Chrysler, Toyota, Honda, Nissan, Volkswagen, Kia/Hyundai. International Business Times. Accessed July 25, 2014 from <http://www.ibtimes.com/here-are-december-2013-big-eight-us-auto-sales-numbers-gm-ford-chrysler-toyota-honda-nissan-1525492>
6. The Associated Press. Auto Sales reach six year high of 15.6 million vehicles sold, Ford F-series takes the lead. NY Daily News. Accessed July 25, 2014 from <http://www.nydailynews.com/autos/auto-sales-reach-six-year-high-demand-peaked-article-1.1567645>.
7. G. Knothe, J. Van Gerpen, J. Krahl, The biodiesel handbook. Champaign, Illinois. AOCS Press 2005.

8. Willard W. Pulkrabek. (2003). Engineering Fundamentals of the Internal Combustion Engine. Prentice Hall; Second Edition.
9. J.B. Heywood. (1988). Internal Combustion Engine Fundamentals. McGraw – Hill, Inc.
10. Kenneth k. Kuo. (2005). Principles of Combustion. Wiley-Interscience; second edition
11. ED Dearnley. Reducing Particulate Matter Emissions from Diesel Vehicles and Equipment. Black Carbon Campaign. <http://www.clientearth.org/reports/bcc-retrofit-guidance.pdf>. Accessed July 2014
12. A.K. Agarwal, Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion science 33 (2007) 233-271.
13. Yusuf Ali, Milford A. Hanna & Louis I. Leviticus. Emissions And Power Characteristics Of Diesel Engines On Methyl Soyate And Diesel Fuel Blends. Bioresource Technology Vol. 52, pp.185-195, 1995
14. Bhupendra Singh Chauhan, Naveen Kumar, Haeng Muk Cho. A Study on the performance and Emission of a Diesel Engine Fueled with Jatropha Biodiesel Oil And its Blends. Progress in Energy and Combustion science Vol. 33, pp.233-271, 2007.
15. C.D. Rakopoulos, D.C. Rakopoulos, D.T. Hountalas, E.G. Giakoumis, E.C. Andritsakis. Performance and Emissions of Bus Engine Using Blends of Diesel Fuel with Bio-diesel of Sunflower or Cottonseed Oils Derived from Greek Feedstock. Fuel Vol. 87 pp.147-157, 2008.
16. Baljinder Singh, Jagdeep Kaur, Kashmir Singh. Biofuels Production Of Biodiesel From Used Mustard Oil and Its Performance Analysis in Internal Combustion Engine. Department of Biotechnology Panjab University, Chandigarh

17. T.Ganapathy, R.P. Gakkhar, K. Murugesan. Influence of Injection Timing On Performance, Combustion and Emission Characteristics of Jatropha Biodiesel Engine. Applied Energy Vol. 88.pp.4376-4386, 2011.
18. N. Thapaliya, Study, Optimization and Scale-up of Liquid Phase Deoxygenation of Free Fatty Acids to n-Alkanes over 5% Pd/C for Biofuel Production. Master's Thesis, North Carolina State University, Raleigh, 2012.
19. W.L. Roberts IV, H.H. Lamb, L.F. Stikeleather, T.L. Turner, Process for conversion of biomass to fuel. US patent publication number US7816570B2; 2010
20. W.C. Wang, N. Thapaliya, A. Campos, L.F. Stikeleather, W.L. Roberts. Hydrocarbon fuels from vegetable oils via hydrolysis and thermo-catalytic decarboxylation. Fuel 95(2012) 622-629.
21. T. Kalnes, T. Marker, D.R. Shonnard. Green Diesel: A second Generation Biofuel, International Journal of Chemical Reactor Engineering. Volume 5, Article A48, 2007.
22. G. Onyestyak, S. Harnos, A. Szegedi, D. Kallo, Sunflower oil to green diesel over Raney-type Ni- Catalyst. Fuel 102 (2012) 282-288.
23. Olav A. Opdal, Oyvind Skreiberg. Production of synthetic biodiesel via Fischer-Tropsch synthesis. Zero Emission Resource Organization. 2006
24. Henry Ng, Munidhar Biruduganti, Kevin Stork. Comparing the Performance of SunDiesel and Conventioal Diesel in a Light-Duty Vehicle and a Heavy-Duty Vehicle. SAE 2005-01-3776.

25. Khan, Mohammed Yahaya, Z.A. Abdul Karim, Ftwi Yohaness Hagos, A.Rashid A Aziz, Isa M Tan,. Current Trends in Water-in-Diesel Emulsion as a Fuel. The Scientific World Journal. Volume 2014, Article ID 527472.
26. Fahd, M.Ebna, Wenming Yang, P.S Lee, S.k. Chou, Christopher R. Yap .Experimental investigation of the performance and emission characteristics of direct injection diesel engine by water emulsion diesel under varying engine load conditions. Applied Energy 102 (2013) 1042-1049
27. Abu-Zaid, M. Performance of single cylinder, direct injection Diesel engine using water fuel emulsions. Energy Conversion and Management 45 (2004)697-705
28. Lin, Cherng-Yuan, Kuo-Hua Wang. Diesel engine performance and emission characteristics using three-phase emulsions as fuel. Fuel 83 (2004)537-545
29. Saravanan, M., A. Anbarasu, B.M. Gnanasekaran. Study of performance and emission characteristics of IC engines by using diesel-water emulsion. Int J Adv Manuf Technol (2013)69:2531-2544
30. Alahmer, A., J. Yamin, A. Sakhrieh, M.A. Hamdan. Engine performance using emulsified diesel fuel. Energy Conversion and Management 51 (2010) 1708-1713
31. Lin, Cherng-Yuan, Li-Wei Chen. Engine performance and emission characteristics of three –phase diesel emulsions prepared by an ultrasonic emulsification method. Fuel 85 (2006) 593-600
32. M.F. Fuller. (2004). The Encyclopedia of Farm Animal Nutrition. Cambridge Ma: CABI Publishing

33. Independent Statistics and Analysis, Short Term Energy Outlook. U.S. Energy Information Administration. www.eia.gov accessed June 2013
34. United States Environmental Protection Agency. EPA Proposes Tier 3 Motor Vehicle Emission and Fuel Standards. Office of Transportation and Air Quality, EPA-420-F-13-016A, March 2013.
35. Independent Statistics and Analysis, Biofuels Issues and Trends. U.S. Energy Information Administration. Accessed October 2012
36. D.H. Qi, H. Chen, L.M. Geng, Y.Z. Bian. Experimental studies of the combustion characteristics and performance of a direct injection fueled with biodiesel/diesel blends. *Energy conversion and management* 2010; 51: 2985-2992.
37. O. Ozener, L. Yuksek, A.T. Ergenc, M. Ozkan. Effect of soybean biodiesel on a DI diesel engine performance, emission and combustion characteristics. *Fuel* 2014; 115: 875-883
38. A.P. Carlucci, F.F. Chiara, D. Laforgia. Analysis of the relation between injection parameter variation and block vibration of an internal combustion diesel engine. *Journal of Sound and Vibration* 2006; 295: 141-164.
39. C.D. Rakopoulos, K.A. Antonopoulos, D.C. Rakopoulos, E.G. Giakoumis. Study of combustion in a divided chamber turbocharged diesel engine by experimental heat release analysis in its chambers. *Applied Thermal Engineering* 2006; 26: 1611-1620.
40. T. Fang, Y.C. Lin, T.M. Foong, and C.F. Lee. Biodiesel combustion in an optical HSDI diesel engine under low load premixed combustion conditions. *Fuel* 2009; 88(11): 2154-2162.

41. J. Zhang, W. Jing, W.L. Roberts, T. Fang. Soot Temperature and KL Factor for Biodiesel and Diesel Spray Combustion in a Constant Volume Combustion Chamber. *Applied Energy* 2013; 107: 52-65.
42. M. Lapuerta, O. Arnas, J.R. Fernandez. Effect of biodiesel fuels on diesel engine emissions. *Progress in energy and combustion science* 2008; 34: 198-223
43. S.H. Yoon, C.S. Lee. Experimental Investigation on the combustion and exhaust emission characteristics of biogas-biodiesel dual – fuel combustion in a CI engine. *Fuel Processing Technology* 2011; 92: 992-1000.
44. T. Fang, Y.C. Lin, T.M. Foong, and C.F. Lee. Reducing NO_x from the biodiesel-fuelled engine by low-temperature combustion. *Environmental Science & Technology* 2008; 42 (23): 8865-8870
45. G. Knothe, C.A. Sharp, T.W. Ryan III. Exhaust Emissions of Biodiesel, Petrol diesel, Neat Methyl Esters and Alkanes in a New Technology Engine. *Energy and Fuels* 2006; 20: 403-408.
46. C.J. Mueller, A.L. Boehman, G.C. Martin. An experimental investigation of the origin of increased NO_x emissions when fueling a heavy-duty compression-ignition engine with soy biodiesel. *SAE Paper* 2009; 2009-01-1792
47. M. Shahabuddin, A.M. Liaquat, H.H. Masjuki, M.A. Kalam, M. Mofijur. Ignition delay, combustion and emission characteristics of diesel engine fueled with biodiesel. *Renewable and Sustainable Energy Reviews* 2013; 21: 623-632.
48. J. Xue, T.E. Grift, A.C. Hansen. Effect of biodiesel on engine performances and emissions. *Renewable and sustainable Energy Reviews* 2011; 115: 1098-1116.

49. P.C. Chen, W.C. Wang, W.L. Roberts, T. Fang. Spray and Atomization of Diesel Fuel and its Alternatives from a Single-Hole Injector Using a Common Rail Fuel Injection System. *Fuel* 2013; 103: 850-861.
50. M. Snare, I. Kubickova, P. Maki–Arvela, D. Chichova, K. Eranen, D. Yu. Murzin. Catalytic deoxygenation of unsaturated renewable feedstocks for production of diesel fuel hydrocarbons. *Fuel* 2008; 87: 933-945.
51. A.D. Puckett, B.H. Caudle. Ignition qualities of hydrocarbons in the diesel-fuel range. U.S. Dept. of the interior, Bureau of Mines, 1948
52. Piedmont Biofuels Certificate of Analysis of B100. Report date October 29, 2012.
53. J. Bacha, J. Freel, et al. Diesel Fuels Technical Review. Chevron Products Company, San Ramon, CA. 2007.
54. G. Hemighaus, T. Boval, J. Bacha, et al. Aviation Fuels Technical Review (FTR-3) Chevron Products Company, San Ramon, CA. 2006.
55. A. Majewski, H. Jääskeläinen, Smoke Opacity calculator, www.dieslnet.com/calculator/smoke1.html, Revision 2013.07 Accessed 8-10-2013.
56. Independent Statistics and Analysis, Biofuels Issues and Trends. U.S. Energy Information Administration. <http://www.eia.gov>. Accessed October 2012
57. Kalghatgi, G. (2014). *Fuel/Engine Interactions*. Warrendale, Pa: SAE International
58. Mponzi, P. (2011) *Production of Biofuels by Fischer Tropsch Synthesis*. Master's thesis. Lappeenranta University of Technology.

59. Sunde, K. Brekke A, B. Solberg. Environmental impacts and costs of woody Biomass-to Liquid (BTL) production and use- A review. *Forest Policy and Economics* 12 (2011) 591- 602
60. Moon, G, Y. Lee, K. Choi, D. Jeong. Emission Characteristics of diesel, gas to liquid and biodiesel-blended fuels in a diesel engine for passenger cars. *Fuel* 89 (2010) 3840-3846
61. Li, X, Z. Huang. Emission reduction potential of using gas –to-liquid and diemethyl ether fuels on a turbocharged diesel engine. *Science of The Total Environment* 407 (2009) 2234-2244
62. Abu-Jrai, A, J.R. Fernandez, A. Tsolakis, A. Megaritis, K. Theinnoi, R. F. Cracknell, R.H. Clark. Performance, combustion and emissions of a diesel engine operated with reformed EGR, Comparison of diesel and GTL fuelling. *Fuel* 88 (2009) 1031-1041
63. Abu-Jrai, A, A. Tsolakis, K. Theinnoi, R. Cracknell, A. Megaritis, M.L.Wyszynski and S.E. Golunski. Effect of Gas-to –Liquid Diesel Fuels on Combustion Characteristics, Engine Emissions, and Exhaust Gas fuel Reforming. Comparative Study. *Energy & Fuels* 2006, 20, 2377-2384.
64. Clark, N, M. Gautam, D. Lyons, C. Atkinson and W. Xie. On-Road Used of Fischer-Tropsch Diesel Blends SAE paper 1999-01-2251
65. Lapuerta, M, O. Armas, J.J. Hernandez, A. Tsolakis. Potential for reducing emissions in a diesel engine by fuelling with conventional biodiesel and Fischer-Tropsch diesel. *Fuel* 89(2010) 3106-3113

66. Wang, H, H. Hao, X. Li, K. Zhang, M. Ouyang. Performance of Euro III common rail heavy duty diesel engine fueled with Gas to Liquid. *Applied Energy* 86 (2009) 2257-2261.
67. Swain, P.K, L.M. Das, S.N. Naik, Biomass to liquid: A prospective challenge to research and development in 21st century. *Renewable and Sustainable Energy Reviews* 15 (2011) 4917-933
68. Alternative Fuels Data Center. Fuel Properties Comparison. www.afdc.energy.gov Accessed September 2014.
69. Zhang, J, W. Jing, W.L. Roberts, T. Fang. Soot measurements for diesel and biodiesel spray combustion under high temperature highly diluted ambient conditions. *Fuel* 135(2014) 340-351
70. Cowart, J.S, Sink E.M, Slye P.G, Caton P.A, Hamilton L.J. Performance, efficiency and emissions comparison of diesel fuel and a Fischer Tropsch synthetic fuel in a CFR single cylinder diesel engine during high load operation. SAE paper 2008-01-2382
71. Emulsion." *Encyclopaedia Britannica*. *Encyclopaedia Britannica Online Academic Edition*. Encyclopædia Britannica Inc., 2014. Web. 16 Oct. 2014. <<http://www.britannica.com/EBchecked/topic/186307/emulsion>>.
72. M. Senthil Kumar, M. Jaikumar. A comprehensive study on performance, emission and combustion behavior of a compression ignition engine fuelled with WCO (waste cooking oil) emulsion as fuel. *Journal of the Energy Institute* 87 (2014) 263-271
73. M. Senthil Kumar, A. Kerihuel, J. Bellettre, M. Tazerout. Ethanol animal fat emulsions as a diesel engine fuel – Part 2: Engine test analysis. *Fuel* 85 (2006) 2646-2652

74. M. Senthil Kumar, J. Bellettre, M. Tazerout. The use of biofuel emulsions as fuel for diesel engines: a review. Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy 2009 223:729
75. Fu Weibiao, Gong Jingsong & Hou Lingyun. There is no micro-explosion in the diesel engines fueled with emulsified fuel. Chinese Science Bulletin 2006 Vol.51 No.10 1261-1265.
76. Arnas, O., R. Ballesteros, F.J. Martos, J.R. Agudelo. Characterization of light duty Diesel engine pollutant emissions using water-emulsified fuel. Fuel 84 (2005) 1011-1018
77. Lin, Cherng-Yuan, Kuo-Hua Wang. Effects of a combustion Improver on Diesel Engine Performance and Emission Characteristics when Using Three-Phase Emulsions as an Alternative Fuel. Energy & Fuels 2004, 18, 477- 484
78. M.P. Ashok (2012). Role of Emulsified fuel in the Present IC- Engines - Need of Alodine EC Ethanol Corrosion Resistant Coating for Fuel Injection. Fuel Injection in Automotive Engineering, Intech.
79. Javier N. Ballester, Noberto Fueyo, Cesar Dopazo. Combustion characteristics of heavy oil-water emulsions. Fuel 75 (1996) 695-705
80. Hagos, Ftwi Y, A.Rashid A Aziz, Isa M Tan. Water-in-Diesel Emulsion and its Micro-Explosion Phenomenon-Review. Communication Software and Networks (ICCSN), 2011 IEEE 3rd International Conference (2011)314-318
81. Mustafa Ertunc Tat, Jon H. Van Gerpen, Paul S. Wang. Fuel Property Effects on Injection Timing, Ignition Timing and Oxides of Nitrogen Emissions from Biodiesel-Fueled Engines. 2004 ASAE/CSAE annual international meeting.

82. T. Kadota, H. Yamasaki. Recent advances in the combustion of water fuel emulsion. *Progress in Energy and Combustion Science* 28 (2002) 385 – 404
83. Independent Statistics and Analysis, Liquid Fuel Supply and Disposition. U.S. Energy Information Administration. <http://www.eia.gov/forecasts/aeo/pdf/tbla11.pdf> accessed February 2014
84. “What is Lignin?” Lignoworks. Western University Institute for Chemicals and Fuels from Alternative Resources. <http://www.lignoworks.ca/content/what-lignin>. Accessed March 2014.
85. F.G. Calvo- Flores, Jose A. Dobado, Lignin as Renewable Raw Material. *Minireviews*. Doi 10.1002/cssc.201000157
86. William O.S Doherty, Payam Mousavioun, Christopher M. Fellows, Value-adding to cellulosic ethanol: Lignin polymers. *Industrial Crops and Products* 33 (2011) 259-276
87. Art Ragauskas, “Overview of Lignin Applications” Georgia Tech Institute of Paper Science and Technology http://www.ipst.gatech.edu/faculty/ragauskas_art/technical_reviews/Lignin%20Applications2.pdf. Accessed March 2014.
88. Joseph Shabtai, Wlodzimierz Zimierczak, Esteban Chornet, David K. Johnson, Conversion of Lignin. 2. Production of High – Octane Fuel Additives. https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/44_2_ANAHEIM_03-99_0267.pdf. Accessed March 2014.

89. Dmitri A. Bulushev, Julian R.H. Ross, Catalysis for conversion of biomass to fuels via Pyrolysis and gasification: A review. *Catalysis Today* 171 (2011)1-13.
90. Jean-Paul Lange, Richard Proce, Paul M. Ayoub, Jurgen Louis, Leo Petrus, Lionel Clarke, Hans Gosselink, Valeric Biofuels: A platform of cellulosic Transportation Fuels. *Angewandte Chemie*. Doi:10.1002/anie.201000655
91. T.Scheper. Biofuels. *Advances in Biochemical Engineering/Biotechnology*. Springer 2007
92. Madhav Prasad Pandey, Chang Soo Kim, Lignin Depolymerization and conversion: A Review of Thermochemical Methods. *Chemical Engineering Technology* 34 (2011) No.1, 29-41
93. Manuel Garcia-Perez, Jun Shen, Xiao Shan Wang, Chun-Zhu Li, Production and fuel Properties of fast pyrolysis oil/bio-diesel blends. *Fuel Processing Technology* 91 (2010) 296-305
94. Antonio M. Mourao, Texaco Inc. Diesel Oil containing Monoalkoxylated Nonyl Phenol Characterized by Decrease in Visible Smoke in Exhaust Gases. U.S. Patents 4,549,884, Oct.29,1985
95. Wei Mu, Haoxi Ben, Art Ragauskas, Yulin Deng, Lignin Pyrolysis Components and upgrading- Technology Review. *Bioenergy Research* (2013) 6:1183-1204
96. Elmer B. Ledesma, Nathan D. Marsh, Alyssa k. Sandrowitz, Mary J. Wornat, An Experimental Study on the Thermal Decomposition of Catechol. *Proceedings of the Combustion Institute* 29 (2002) 2299-2306

97. Eun-Jae Shin, Mark R. Nimlos, Robert J. Evans. A Study of the Mechanisms of Vanillin Pyrolysis by Mass Spectrometry and Multivariate Analysis. *Fuel* 80 (2001) 1689-1696
98. Wahyudiono, Mitsuru Sasaki, Motonobu Goto. Thermal Decomposition of Guaiacol in Sub- and Supercritical Water and Kinetic Analysis. *J Mater Cycles Waste Manag* (2011) 13:68-79
99. Glazer, A. W., and Nikaido, H. (1995). *Microbial Biotechnology: fundamentals of applied microbiology*. San Francisco: W. H.