PROPERTIES, PERFORMANCE AND EMISSIONS OF BIOFUELS IN BLENDS WITH GASOLINE

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ABSTRACT

The emission performance of fuels and their blends in modern combustion systems have been studied with the purpose of reducing regulated and unregulated emissions, understanding of exhaust products of fuels such as Gasoline, Ethanol and 2,5-Dimethylfuran and comparison of results. A quantitative analysis of individual hydrocarbon species from exhaust emissions of these three fuels were carried out with direct injection spark ignition (DISI) single cylinder engine. The analysis of hydrocarbon species were obtained using gas chromatography-mass spectrometry (GCMS) connected on-line to SI engine. During this project, novel works have been done including the set up of on-line exhaust emission measurement device for detection and quantification of individual volatile hydrocarbons. Setting of a reliable gas chromatography mass spectrometry measurement system required definition and development of a precise method. Considerable work has been done for development of analysis method, suitable for detection of specific individual hydrocarbon species. Conventional Gasoline, Ethanol and 2,5-Dimethylfuran were used as fuels in single cylinder direct injection spark ignition engines for the purpose of analysis on regulated and unregulated exhaust emissions using online measurement method. Engine operating conditions can be used to reduce the amount of many species in engine exhaust. This revealed that aromatic compounds such as Toluene and Benzene give higher concentrations from DMF addition than from Ethanol addition. The most common exhaust emissions hydrocarbons for the two different engine operating modes are Propylene, 1-Butene, Benzene and Toluene.

Significant reductions in THC and CO were observed for E10 and E30 compared with DMF blends for Gasoline The engine operation modes used are very important for production of many hydrocarbon species such as 1, 3 – Butadiene. At high load, concentration of 1, 3-Butadiene was decreased significantly in exhaust emissions. The concentrations of heavy hydrocarbons were found to be higher at lower engine loads. Benzene and Toluene were found to be the major components of engine exhaust regardless of engine operating conditions and fuels used. These aromatics were significantly reduced by addition of Ethanol.

Lubricity characteristics of biofuels and Gasoline were investigated using High Frequency Reciprocating Rig (HFRR). Results showed great enhancing lubricity characteristics of biofuels when added to conventional Gasoline. 2, 5-Dimethylfuran was found to be the best among the fuels used, addition of this fuel to Gasoline also showed better result compared with Ethanol addition. Aging of the fuels also investigated during this analysis. Aging was also found to be a good lubricity enhancer compared with non-aged fuel blends. Friction coefficient of DMF and Ethanol remained roughly constant during the experiments, in contrast this value showed an increasing trend when Gasoline was used (resulting in poor lubricity of Gasoline).

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I would like to thank Professor Miroslaw L. Wyszynski for his help and guidance during my PhD course, it was greatly appreciated.

I would like to dedicate this thesis to soul of my lovely father, with my love and respect for his help and encouragement in all of my academic aspiration.

To my beloved wife and family, without their support this would not have been possible.

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List of Abbreviations

CAD	Crank Angle Degrees
CAI	Controlled Auto-Ignition
CI	Compression Ignition
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DX	X% by volume DMF in Gasoline-DMF Blend
DI	Direct Injection
DISI	Direct Injection Spark Ignition
DMF	2, 5-Dimethylfuran
EGR	Exhaust Gas Recirculation
ETH	Ethanol
EX	10% by volume Ethanol in Gasoline/ Ethanol Blend
FID	Flame Ionisation Detector
GAS	Gasoline
GC	Gas Chromatography
GCMS	Gas Chromatography Mass Spectrometry
H/C	Hydrogen Carbon Ratio
HFRR	High Frequency Reciprocating Rig
HMF	5-Hydroxymethhylfurfural
IC	Internal Combustion
IMEP	Indicated Mean Effective Pressure
LCV	Lower Calorific Value
LHV	Heat of Combustion

MS	Mass Spectrometry
NOx	Oxides of Nitrogen
PFI	Port Fuel Injection
RON	Research Octane Number
RPM	Engine speed, Revolutions per Minute
SI	Spark Ignition
ULG	Unleaded Gasoline
VOC	Volatile Organic Compounds
°aTDC	Crank angle degrees after Top Dead Centre of Combustion
°bTDC	Crank angle degrees before Top Dead Centre of Combustion

CHAPTER 1

1. INTRODUCTION

Road vehicles are major contributors to air pollution and this is why significant attentions and concerns are being paid to emission from internal combustion (IC) engines. Due to harmful effects of internal combustion emissions, various emissions legislations have been introduced to reduce emissions of greenhouse gases and air pollution. The road vehicles produce large quantities of carbon monoxide (CO), nitrogen oxides (NOx), hydrocarbons (HC), carbon dioxide (CO_2), sulphur oxides (SOx) and many other carcinogen and toxic substances such as Benzene, acetylaldehyde, formaldehyde, 1, 3-Butadiene and Toluene. Each of these emitted emissions can cause serious adverse effects on human health and environment. Due to growth of number of motor vehicles and resulting emissions, it is believed that human health has been damaged significantly in developed countries and this concern is being increased in most of the cities in the world. There are many factors affecting the quantities of these toxic emissions such as properties of fuels being burnt in the engines. Various properties of the fuels used nowadays were found to be the key factor defining the nature of the engine emissions, although there are many other important factors including the combustion conditions. Physical and chemical properties of biofuels make them excellent choice for altering the conventional fossil fuels.

1.1. Research Outline

The research presented in this thesis was carried out at University of Birmingham to investigate effect of chemical and physical properties of Gasoline, Ethanol and 2, 5-Dimethylfuran and their blends on lubricity and also influence of fuels and their blends on exhaust emissions at different engine operating conditions of spark-ignition direct-injection single cylinder engine.

The research is divided into three parts. The first part of this research explains the lubricity properties of Gasoline and its blends with alternative fuels such as Ethanol and 2, 5-Dimethylfuran using a HFRR lubricity test rig. Second part deals with effect of different single cylinder engine operating modes on individual hydrocarbon in exhaust emissions of Gasoline, Ethanol, 2, 5-Dimethylfuran and Isooctane-Toluene (2:1). Third part of this research deals with influence of addition of different percentage (Vol %) of Ethanol and 2, 5-Dimethylfuran in blends with Gasoline on individual hydrocarbon and regulated emissions of exhaust emission at low/high load in spark-ignition direct-injection single cylinder engine.

The regulated emissions such as CO, CO_2, THC and NO_x were measured for all fuel blends in each test. All research in this project was carried out on a single cylinder spark-ignition direct-injection engine which represents similar technology as multi-cylinder Jaguar V8 engine.

1.2. Aims and Objectives

The main goal of this project is to assess concentrations of individual hydrocarbons in exhaust emissions from SI engines for different fuels and their blends. This may assist in production of cleaner fuels with lower level of impurity and toxicity in future. The 2, 5-Dimethylfuran was used due to similar physical properties to unleaded Gasoline.

The other part of this study are to evaluate lubricity property of different fuels and their blends, this is important since introduction of direct-injection Gasoline fuel pump with high injection pressure becoming closer to diesel pumps. Another

1.3. Objectives and Approaches

To achieve the aims of this study, following objectives must be investigated:

- Comparison of lubricity property of fuels Gasoline, Ethanol and 2, 5-Dimethylfuran.
- The beneficial effects of 2, 5-Dimethylfuran and Ethanol addition to Gasoline on lubricity property of Gasoline.
- The influence of various engine operating modes on individual species (C_3-C_7) of exhaust emission fuelled with Gasoline, Ethanol, DMF and Isooctane-Toluene (2:1).
- The effect of addition of different percentages of Ethanol and DMF to Gasoline on regulated emissions such as CO, CO_2, THC and NO_x.
- The influence of Ethanol and DMF addition to Gasoline on individual hydrocarbons from exhaust emission at different engine operating conditions.

1.4. Thesis Outline

This thesis consists of eight chapters that consider the effect of fuel blends with Gasoline on lubricity property and behaviour of individual hydrocarbons at different engine operating modes. A brief description of each chapter is explained below:

Chapter 2-Literature Review

This chapter represents literature review of this study and many significant points are mentioned about author findings and achievements. Main attention is paid to combustion and speciation of fuels and their blends in SI engines. However, lubricity property of fuels and their blends also has been reviewed.

Chapter 3-Experimental Setup and Techniques

The engine, gas chromatography-mass spectrometry and other measuring equipment applied in this research are described comprehensively including their setup method.

Chapter 4-Experimental Investigation on Lubricity of 2, 5-Dimethylfuran blends with Gasoline and Ethanol

This chapter investigates the lubricity of conventional 95 RON Gasoline and compares it with Ethanol and 2.5-Dimethylfuran. Also different blends of Gasoline-biofuel were examined to investigate the effect of biofuels addition in detail.

Chapter 5- GC-MS Speciation and Quantification of 1, 3 Butadiene and Other C_3-C_7 in SI engine Exhaust at 3.5 and 8.5 Bar IMEP

The influence of using bio (oxygenated) fuels on regulated and unregulated emissions in Direct Injection Spark Ignition (DISI) engine is investigated in this chapter. Ethanol and 2, 5-Dimethylfuran as conventional and novel biofuels were tested using the same conditions. Results were compared to 95 RON Gasoline. In order to extend the study on effect of fuel type on exhaust emission, Isooctane and Toluene were blended with the ratio of 2:1 respectively. The blending ratio was set to 2:1 as fuel composition in this ratio is very close to Gasoline.

Chapter 6- Volatile Hydrocarbon (C_3-C_7) Speciation and Quantification of Engine Exhaust Running on 2, 5-Dimethylfuran and Ethanol in blends with Gasoline

Volatile hydrocarbon speciation of exhaust emission running on various fuel blends (95 RON Gasoline, 2, 5-Dimethylfuran and Ethanol) is investigated and compared with the results from 95 RON Gasoline in this chapter. The effect of blending percentages is the main investigation in this chapter.

Chapter 7-Conclusions

According to the results, the conclusions are achieved for each chapter and also recommendations for further studies were mentioned.

CHAPTER 2

2. LITERATURE REVIEW

2.1. Automobile Traffic

Throughout the world, the number of motor vehicles has been gradually increasing and this is considered as global threat due to the large amount of pollutants they emit in the atmosphere daily. It is well known that vehicle emissions are a contributor to global warming and can constitute a risk to human health (Andrews et al. 2007).

Europe, Japan and the United States have the largest amount of traffic, nearly 250 million light vehicles in the United States and Canada in 2002 (MacLean and Lave 2003). China has the fourth place in the largest light vehicle producers ranking and has been ranked as third largest consumer. The number of vehicles and motorcycles was 24.21 million and 59.29 million correspondingly and predictions confirm that this amount will reach 90 million and 192 million by 2020 (Deng 2006).

Fossil fuels are the most common source of the world’s transportation fuel and two major transportation fuels are Gasoline and diesel. In 2004, estimations demonstrate that 2.5×10^{12} litres of Gasoline were devoted to world’s transportation (Wallington et al. 2006). The major environmental concern in automotive industry is to reduce concentration of exhaust emission components.

2.2. Emission Legislation

Motor vehicles are the major contributors for the environmental pollution and global warming (Andrews et al. 2007). Therefore, vehicle emissions should be regulated and car manufacturers must comply with sustained reductions. The countries such as United States, Europe and Japan regulate emissions standards strictly (Delphi 2009). Although the most important plan is to reduce emissions from engines, different standards applied in each of these areas. Europe has introduced two different types of standards, the Economic Commission for Europe (ECE) and the European Union (EU). The emissions regulations are compulsory for countries in the European Union (EU) and all countries must obey these regulations, the other non-European Union countries must follow ECE (Delphi 2009). Figure 2.1 illustrates an overview of the main regulations.

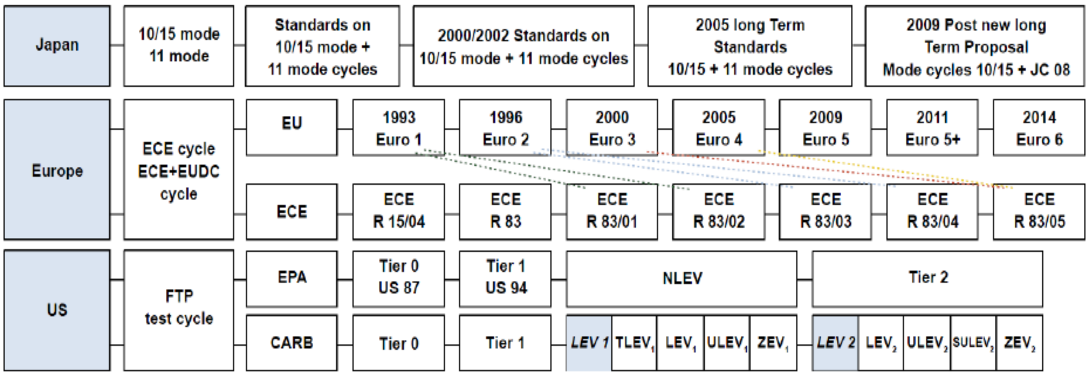


Figure 2.1-Emission Regulations (Delphi 2009)

The main aim of this project is to investigate spark ignition engine emissions. Compression ignition (CI) engines do have the emission regulations for heavy duty and large passenger vehicles (Delphi 2009).

In this section, only European Union will be studied due to the similarities between ECE and EU emission regulations. Emissions regulations have been tightened since Euro1 in 1993 and that is why emissions tests are performed and it is not limited only to tail pipe emission tests. Nowadays, the following approvals must be carried out in emission tests before vehicles meet the emissions standards that are as follows (Delphi 2009). Table 2.1 demonstrates the emission standards tests. Limitations of emissions were described in 1970 (No 1970) and also adjusted for a drive cycle: the New European Drive Cycle (NEDC). The limitations of regulated emissions are presented in Table 2.2 from 2000 to 2015. Figure 2.2 illustrates present combined driving cycle for testing.

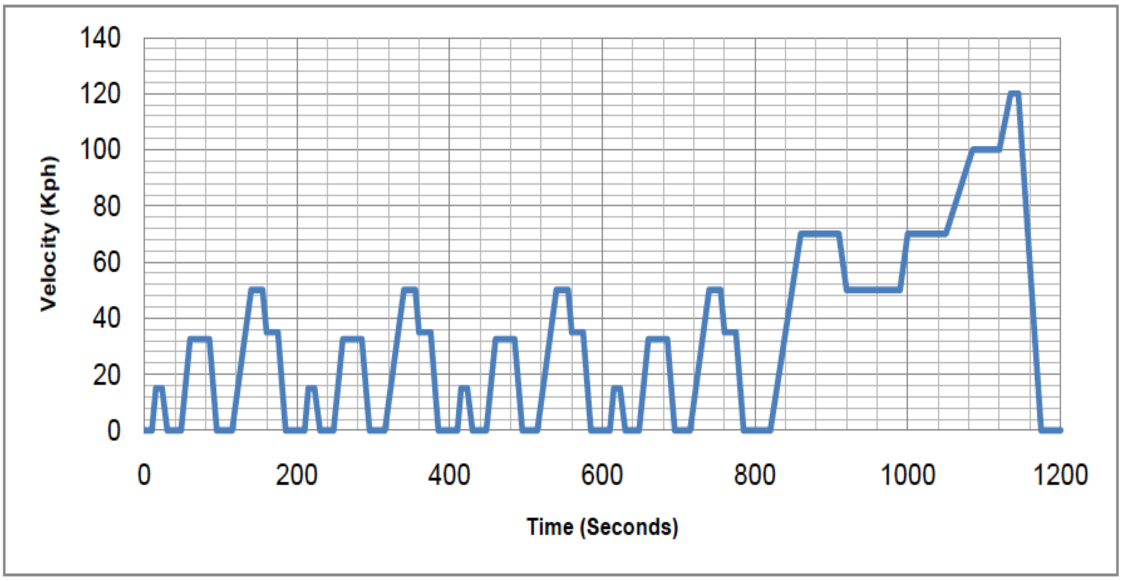


Figure 2.2-Combined EU Test Driving Cycle (DieselNet, 2000)

Table 2.1-Emission Standards Tests

Type I	Tailpipe emissions after a cold start
Type II	CO emission test at idling speed
Type III	Emissions of crankcase gases
Type IV	Evaporative emissions
Type V	Durability of anti-pollution devices
Type VI	Low Temperature Test
----------	On Board Diagnostics (OBD)

Table 2.2- Emissions Legislation (Delphi 2011)

Emissions	**Unit**	**Euro III 2000**	**Euro IV 2005**	**Euro V(a) 2011**	**Euro v(b/b+) 2013**	**Euro VI 2015**
HC	mg/km	200	100	100	100	100
NOx		150	80	60	60	60
CO		2300	1000	1000	1000	1000
PM (mass)		-	-	5	4.5	4.5

In Euro 5, emission legislation has not been restricted to only the total hydrocarbon emissions but also has certain limitations for non-methane hydrocarbons. The term “hydrocarbons” refers to molecules which contain hydrogen and carbon. It also includes the hydrocarbon oxides and other HC based molecules.

To create new regulations, emissions are tested through the normal driving process using vehicles. For European legislation, emission experiments are performed using the combined driving cycle, which contains European extra urban driving cycle and ECE urban driving cycle.

It is believed that the motor vehicles emissions are the reason of 55-58% of human cancer in the USA (US-EPA 1990b). The first smog formation observation due to motor vehicle traffic was reported in LA in 1943. Haagen-Smit (1952) proved that the smog issues in the LA originate from reactions between NOx and hydrocarbons, resulting in photochemical smog and it is appeared during combustion process in vehicle engines. Analysing the smog formation experiences in Los Angeles has made state of California governors to legislate new emission standards for motor vehicle engines (Krier and Ursin 1977). The United Stated government followed the new emission standards for engines in the state of California and then different standards were introduced into the European countries and Japan (see Table 2.3). To respect these legislations and regulations, researchers must do more investigation on improvement of combustion modes and exhaust catalysts.

Table 2.3-US Gasoline engine exhaust emission standards summary 1966 to 1993

Year	Federal (g/mi)			California (g/mi)			
	HCs	CO	NOx	HCs	CO	NOx	PM
1965	-	-	-	10.6	84	4.1	-
1968	6.3	51	6.0	6.3	51	6.0	-
1971	4.1	34	6.0	4.1	34	4.0	-
1972	3.0	28	6.0	2.9	34	3.0	-
1974	3.0	28	3.0	2.9	34	2.0	-
1977	1.5	15	2.0	0.41	9.0	1.5	-
1980	0.41	7.0	2.0	0.39	9.0	1.0	-
1984	0.41	7.0	1.0	0.39	3.4	0.4	0.6
1990	0.41	7.0	1.0	0.39	3.4	0.4	0.08
1993	0.41	3.4	1.0	0.25	3.4	0.4	0.08

The Clean Air Act amendment in 1990 announced that compliance of all light-duty vehicles with federal emission regulations is mandatory. The Tier 1 emission standards emphasize that light-duty vehicles emission such as volatile organic compounds (VOC) and nitrogen oxides must be 30% and 60% respectively less than the US Tier 2 standards which were introduce in 1999 and must be implemented for 2004-2009.

Three different methods are available worldwide to measure emissions of motor vehicles: the US federal test method (FTP-75) with the upcoming new version of the US test method, which has been suggested to adopt with the US06 (US EPA). The second procedure is the European test method (ECE) and the third one is Japanese test method. The biggest difference between these methods and procedures is described in driving vehicle cycle and running cycle for motor vehicle engines. The European test methods are applied in the European countries and also in India and China. The US method is implemented in Brazil, Taiwan, Republic of Korea and North America (see Table 2.4). The Japanese emission standards are used in East Asian nations.

Table 2.4- Progression of US exhausts emission standards for light-duty Gasoline-fuelled vehicles

Year	**CO (g/mi)**	**HCs (g/mi)**	**NOx (g/mi)**
1994-97 (Tier 1)	3.4 (4.2)	0.25a (0.31)	0.4 (0.6)
2004-2009 (Tier 2)	1.7 (1.7)	0.125a (0.125)	0.2 (0.2)

2.3. Composition of Gasoline

The composition of Gasoline changes considerably and quickly in the world and even for different seasons Gasoline must be enhanced with different types of additives. For instance, in winter, various additives must be added to Gasoline to prevent the fuel freezing and to keep its capability to combust at lower temperatures (Elghawi 2009).

Gasoline is divided into various “grades” and the most known types of Gasoline are RON 97 and RON 95 in the United Kingdom, where RON is the Research Octane Number. The Research Octane Number (RON) demonstrates capability of fuel for resisting knock or uncontrolled auto ignition in the engine during compression. It is essential to identify composition of Gasoline therefore behaviour of each individual component of fuels can be considered and analysed for different applications.

Table 2.5 illustrates an example of volume percentages of different components in Gasoline; it was obtained from Future and Fuel Laboratory at University of Birmingham (Ritchie Daniel, PhD Research Student, University of Birmingham). As it is shown, aromatics are considered as the major component in the Gasoline composition. It is essential to mention that aromatics have a Benzene ring and due to carbon-carbon double bonds they are very stable. Investigations (Kaiser et al. 1983) tested a certified Gasoline which contained 60% aromatics and 40% paraffins and speciation was carried out for this composition. Toluene (Methyl-Benzene) is considered as the most suitable to represent the aromatics fraction of blend, as it is the most significant component of aromatics in Gasoline, namely 13% (Elghawi 2009). As shown in Table 2.5, Gasoline composition contain 46% of alkanes including iso-alkanes and 14.43% of alkenes which means over 60% volume of composition of Gasoline constitute of alkanes and alkenes. it can be concluded that 95% of Gasoline by volume are aromatics, alkanes and alkenes. One of the main components is used to characterize alkanes and alkenes is the iso-octane (2,2,4 thrimethylpentane). It is recognized as an appropriate alkane fraction in certification test of Gasoline (Kaiser et al. 1991). The Gasoline composition in Table 2.5 is different from that reported by (Elghawi 2009) of 98% being aromatics, alkanes and alkenes for winter grade Gasoline. This illustrates modifications that can happen in Gasoline composition. Nevertheless, both Gasoline compositions demonstrate aromatics, alkanes and alkenes as the major and main components of Gasoline.

Table 2.5 Typical Composition of Gasoline by % Volume, It was obtained from Future and Fuel Laboratory at University of Birmingham (Ritchie Daniel, PhD Research Student, University of Birmingham)

Component	**% Volume**
Alkanes	11.57
Iso-Alkanes	34.30
Alkenes (including dienes)	14.43
Dienes	0.18
Naphthenes	4.01
Aromatics	34.96
Oxygenates	0.00
Unknowns	0.55
Total	**100.00**

2.3.1. Sources of Emissions in Spark ignition Gasoline Engines

Different pollutants generated by engine are called engine emissions, which are typically divided into main components such as carbon monoxide (CO), carbon dioxide (CO_2), Hydrocarbons (HC), Nitrogen Oxides (NO_x), and Particulate Matter (PM). The main aim of this project is to analyse individual hydrocarbons at different engine conditions

2.3.1.1. Carbon monoxide (CO)

Carbon monoxide is produced during incomplete combustion in the engine. The process of fuel conversion into carbon monoxide can be explained as conversion of fuel to small hydrocarbons, then oxidation of these hydrocarbons and finally conversion to carbon monoxide and also due to dissociation of carbon dioxide at higher temperatures. Incomplete combustion is due to lack of sufficient oxygen in the air/fuel mixture during combustion. During the combustion, there is no enough oxygen to fully oxidise the carbon atoms and convert them into carbon dioxide (CO_2). The higher H/C ratio results in lower concentration of carbon monoxide (Harrington and Shishu 1973).

By adjusting air/fuel ratio in the cylinder, CO emissions can be controlled in the SI engine. Valério et al. (2004), invented a model to obtain the kinetic formation rate of carbon monoxide in a spark ignition engines and also the validation of the model.

2.3.1.2. Hydrocarbon emission (HC)

Hydrocarbon emissions are produced from two types of sources which are unburned hydrocarbons and partially burned hydrocarbons. Unburned HCs can be described as fuel that passes through the chamber and appears in the exhaust emission in its original form. These types of hydrocarbons are usually in a range of C5 to C12 (Elghawi 2009). Partially burned HCs are defined as hydrocarbons that are not fully burnt or combusted in the cylinder and have created chain HCs and carbon dioxide and water (Elghawi 2009).

In this project, analysis of individual hydrocarbons was carried out along with total hydrocarbons (THC) that contain the main hydrocarbons such as alkenes, alkanes and aromatics. The main structure of alkanes consists of single carbon-hydrogen bond that is not able to have additional hydrogen atoms; this kind of hydrocarbons is recognized as a fully saturated structure. Alkanes may include different side chains such as iso-alkanes and it will still appear as saturated structure CnH2n+2 where ‘n’ stands for the number of atoms in a molecule. Alkenes structure also has carbon and hydrogen atoms, but it includes one carbon-carbon double bond. This is known as unsaturated hydrocarbon and its structure is CnH2n. Aromatics contain a ring of carbon atoms with double carbon-carbon bonds that are very stable (Hill and Holman 2000). The most abundant main aromatic hydrocarbons in Gasoline is Toluene.

Andrews et al. (2007) reported that most of the HCs in fuel are fully combusted in the combustion chamber. However, small quantity of hydrocarbons is partially burned during combustion and that will result in lower molecular hydrocarbons and oxidized compounds such as aldehydes appearing in emissions. Aromatics such as Benzene and Toluene may survive process and are emitted in exhaust as unburned hydrocarbons. If combustion does not proceed in a proper way such as when a misfire happens, huge amount of HCs are emitted in exhaust from the combustion chamber. Composition of these hydrocarbons depends on engine design, fuel composition and different operation modes.

There are many different sources of hydrocarbon emissions; the most significant one that produces major amount of HCs in exhaust under fully warmed engine condition is combustion chamber crevice volumes. Cheng (Cheng et al. 1993) classified sources of hydrocarbons emissions according to their relative importance. Combustion chamber crevices produce 38% of the hydrocarbon emissions. Table 2.6 presents estimation of hydrocarbons sources. Nevertheless, (Alkidas et al. 1995) estimated that 50% of emitted HCs originates from combustion chamber crevices.

Table 2.6-Hydrocarbon sources and their relative magnitude in SI engine (Cheng et al. 1993)

Source	**% HC**
Combustion-chamber crevices	38
Single-wall flam quenching	5
Oil film layers	16
Combustion-chamber deposits	16
Exhaust-valve leakage	5
Liquid fuel	20

Largest source of hydrocarbon emission result from unburned fuel stored in chamber crevice volumes in the engine cylinder and propagation of flame is not possible for narrow entrances into crevice volumes and stored fuel is not combusted and remains unburned. This is inevitable for all operating modes and conditions. During expansion stroke, major amounts of hydrocarbons are converted into carbon monoxide (CO) and carbon dioxide (CO_2) in the hot combusted gases in the cylinder and exhaust system. The rest of emissions that are part of stored hydrocarbons in crevice volumes, are divided into organic products and unburned fuel which are produced from partial combustion (Kaiser et al. 1994). Combustion of stored hydrocarbons in the exhaust system plays vital role in concentration of emitted hydrocarbon species.

Fuel films are produced by wall wetting liquid which is not evaporated and combusted in the cylinder when flame is passing. Fuel films are evaporated during cylinder gases cooling, which cause hydrocarbon emission increase. However, wall wetting does not produce any hydrocarbon emission when the engine is fully warm (Kaiser et al. 1994).

Combustion chamber deposits can have significant effect on production of HC emission. Hydrocarbons are pushed into pores during air/fuel mixture compression. Therefore, when combustion happens, the fuel does not burn. Nevertheless, during exhaust stroke, these hydrocarbons are emitted into the exhaust stream (Kaiser et al. 1994).

Wall quenching occurs as the combustion flame front burns up to the relatively cool walls of the combustion chamber. This cooling extinguishes the flame before all fuels are burned in the cylinder and allows HCs to be emitted through the exhaust valve. The main source of hydrocarbon emission originates from this phenomenon in four-stroke engines.

Over the past 30 years, the main focus of all research throughout the world was to reduce the HCs emissions from spark ignition engines. The oxidation catalyst produced significant reductions of HC emissions in tailpipe in 1970s. In conclusion, as many articles mentioned during decades, any element that cause to have more oxygen or the temperature rise to the post flame region result in less hydrocarbon emission.

2.3.1.3. Oxides of Nitrogen (NOx)

High temperatures combustion flame cause production of nitrogen oxides (NOx) during combustion. In spark ignition engines, nitric oxide (NO) is considered as the main part of these oxides along with tiny amount of nitrogen diooxide (NO_2). Oxides of nitrogen are considered as NOx when nitric oxide (NO) and nitrogen dioxide (NO_2) appear together. Usually above 90% of the NOx consists of nitric oxide (NO) (Stone 1985).

The most part of NOx production is obtained from oxidation of atmospheric nitrogen originated from reaction with oxygen atoms:

$O + N_2 \rightarrow NO + N$ (1)

$N + O_2 \rightarrow NO + O$, and (2)

$N + OH \rightarrow NO + H$. (3)

This method is identified as the Zeldovich mechanism (Zeldovich 1946). Production of nitric oxides (NO) increases dramatically with temperature when oxygen atoms are formed via the thermal decomposition of molecular oxygen.

To limit NOx production from engine, it is necessary to decrease the combustion temperature. One of the best methods to reduce NOx emissions is the exhaust gas recirculation (EGR), which introduces part of the exhaust emission to the intake manifold. The influence of dilution and the use of CO_2 and H_2O exhaust gases instead of air cause temperature reduction in combustion process and finally less production of NOx.

2.3.1.4. Carbon Dioxide (CO_2)

One of the main combustion components is carbon dioxide (CO_2), which is a greenhouse gas. It is also one of the most important components responsible for global warming through the greenhouse effect. However, most of emission limitations require a decrease of carbon dioxide (CO_2) emissions from automobiles (Johnson 2010). Although Carbon dioxide emissions are proportional to fuel consumption and combustion efficiency, in an optimised engine the effects on CO_2 are inversely related. Higher combustion efficiency will result in higher carbon dioxide emissions and decreasing fuel consumption will cause lower carbon dioxide emissions. Investigations show that oxygenated fuels produce more carbon dioxide emissions (Owen and Coley 1995) and the reason is explained in having higher combustion efficiency and lower low heating value, which results in higher fuel consumption.

2.3.1.5. Unregulated Engine-out Emissions

Toxic components such as 1, 3-Butadiene, Benzene and aldehydes are emitted from the spark ignition engines. 1, 3-Butadiene is recognized as a product of partial combustion and originates from the aromatic and alkane components of fuel (Filser and Bolt 1984). Many articles have presented carcinogenic properties of 1,3-Butadiene, which cause human cancer (Huff et al. 1985). One of the main components in the Gasoline engine exhaust is Benzene. Benzene is originated from de-alkylation of aromatic compounds such as Toluene.

Both of these hydrocarbons are considered as carcinogens. According to epidemiological evidence, International Agency for Research on Cancer (IARC) has introduced Benzene as a human carcinogen group 1 (IARC 1987). Many studies in the United States has shown that motor vehicles are the main reason for human exposure to toxic pollutants such as Benzene and 1,3-Butadiene (US-EPA 1990b).

Aldehydes are those types of HCs, which contain additional oxygen atoms. These hydrocarbons appear during combustion process of fuel with high oxygen content. Incomplete combustion and also thermal decomposition are the main reasons of aldehydes formation in the cylinder. Formaldehyde forms 50-75% of aldehydes in exhaust emission of Gasoline fuel and are considered as one of the most reactive organic chemicals. For alcoholic fuels such as Ethanol and Methanol, due to oxidation reactions in acetaldehydes, formaldehyde and benzaldehyde, significant concentration of these carcinogen components in the exhaust emissions are expected.

2.3.1.5. Ozone Formation

Concerns about air pollution have generated special attention to research about fuels and engine effects on emissions. A critical component of these investigations is to fully understand atmospheric impact of emitted hydrocarbons from motor vehicles. The atmosphere contains 79% nitrogen and 21% oxygen by volume and is extremely oxidizing environment. Oxidization of engine exhaust components is carried out in a various series of reactions in atmosphere.

Ozone plays a vital role in the earth atmosphere and it is considered as a pollutant at ground altitude. Existing oxygen, nitrogen oxides and hydrocarbons help to form ozone in atmosphere under sun radiation effects. Carter et al. (1998) have introduced a method to measure ozone formation potential of hydrocarbons. Two methods have been discovered, chemical kinetic models and smog chamber experiments.

Maximum incremental reactivity is a measure of the increase in ozone formation per unit weight of a hydrocarbon when added to the atmosphere. Each of exhaust emission hydrocarbons demonstrates various photochemical reactivities. Table 2.7 illustrate hydrocarbons with their maximum incremental reactivity (MIR) that was developed by Carter (1998). The speciation factors of individual hydrocarbons multiplication by maximum incremental reactivity (MIR) scale makes this possibility to avoid calculation of ozone formation potential of exhaust emissions. The negative amount of MIR demonstrates ability of oxidation compounds for reacting with NO2 and it eliminates NOx from the exhaust system. The low maximum incremental reactivity means lower reaction.

Table 2.7-Maximum incremental reactivity factor for selected Hydrocarbon species (Carter 1998)

Compounds	MIR [g ozone/ g HC]
Methane	0.01
Ethane	0.35
n-Butane	1.44
n-Pentane	1.74
n-Hexane	1.69
n-Heptane	1.43
n-Octane	1.24
Iso-butane	1.56
Iso-pentane	1.93
Iso-Octane	1.69
Ethylene	9.97
Propylene	12.44
1-Butene	10.8
1-Pentene	8.16
1-Hexene	6.3
Iso-Butene	6.81
1,3-Butadiene	13.09
Formaldehyde	9.12
Acetaldehyde	7.27
Acrolein	8.09
Benzaldehyde	-0.5
m-,o-,p- Tolualdehyde	-0.44
Benzene	1
Toluene	4.19
Ethyl benzene	2.97
Styrene (vinyl benzene)	2.52
m-Xylene	11.06
o-Xylene	7.83
p-Xylene	4.44
1,3,5-Trimethyl benzene	11.1
Naphthalene	3.05
Furan	17.25

2.4. Developments in Speciation and Quantification of Hydrocarbons (review)

The major source of high atmospheric hydrocarbon release is motor engines in many urban areas. This poses serious environmental and health hazards in the society. Photochemical smog is an example of health hazards emerging from the higher concentration of exhaust gases released by the combustion engines (Loh et al. 2007). In a research study, it was reported that 48 to 54 % of cancer prevalent in USA is due to the presence of high amounts of toxic gases in the environment (US-EPA 1990b).

In recent years, most of the energy used in the world originates from fossil fuels and due to high cost of fossil fuels; clean energy demands have been increasing rapidly (Mousdale 2008). Studies have shown other renewable sources of energy such as vegetable oil, biogas, biofuels and natural gas besides the traditional fossil fuels sources (Bechtold 1997). These studies have shown Ethanol obtained from the biomass as a potential alternative of fossil fuels. It is considered as the most efficient fuel because of its high heat of evaporation and octane number, which improves the engine operation and reduces exhaust gases release (Das L.M 1996, Yücesu et al. 2006). High miscibility of Ethanol is observed with water in contrast to Gasoline (Kelly et al. 1996, Koç et al. 2009).

Many studies have been conducted to produce more efficient biofuels e.g. 2,5-dimethyfuran (Román-Leshkov et al. 2007). Conversion of fructose and glucose to 5-hydroxymethhylfurfural and 2,5-Dimethylfuran were made through a novel catalytic biomass liquid process and fuel showed improved efficiency and yield (Dumesic et al. 2007). Some more studies reported the production of high yields of

HMF with non-acid conversion bioprocess (Zhao et al. 2007). Cellulose can also be converted to 5-(chromethyl) furfural and later upon homogenization it can be further converted to DMF fuel. Due to improved manufacturing process of DMF, it has shown a considerable potential to substitute Gasoline in automobile industry (Mascal and Nikitin 2008).

DMF exhibit volumetric energy density (31.5 MJ/l) which is the same as Gasoline and it is 40% greater than the one exhibited by Ethanol (23 MJ/l). The DMF feature which makes it an ideal alternative of Gasoline in comparison with Ethanol is its high boiling point ($92^{o}C$) as it confers low volatility and thus makes it a potential alternative fuel.

Due to the newly discovered and currently being developed production methods of DMF, it has become more attractive biofuel candidate. Higher energy density and octane number of DMF compared with Ethanol lead to higher compression ratio, improvement in fuel consumption and engine performance makes this fuel an alternative for Ethanol. Furthermore, DMF has practically zero water solubility, which eliminates the water absorption problem. (Rothamer and Jennings 2012).

Suitable Gasoline alternatives and their compositions can be identified via hydrocarbon speciation process. Individual study on each hydrocarbon can impart photochemical effect and toxicities. Compound which is studied up till now through new regulatory mechanisms is 1,3- Butadiene and aldehyde (Kao 1994).

Gas chromatography was reported to be the most effective process for individual hydrocarbon study as mentioned by Jensen et al. (1992) and Siegl (1993) and through this method 140 hydrocarbons have been analyzed up till now (Jensen et al. 1992, Siegl et al. 1993).

Kaiser studied the impact of some of the fuels on environment due to their emission and he also investigated the effect of unburned hydrocarbons on total HC released. The fuels he used were six paraffin fuels, two naphtene fuels, two aromatic fuels and also unleaded and olefin fuels. The aromatic emissions from both naphtene fuels contribute significantly to the emitted hydrocarbons and the experiments demonstrate that substantial quantities of aromatic species were observed from non-aromatic fuels. However, for olefin fuels, four alkenes such as ethylene, 1-Butene, 1-hexene and di-isobutylene were used as fuels in a single cylinder engine and the results illustrates that the total hydrocarbons emissions increased with increasing the molecular weight of the fuel as was investigated previously for alkanes.(Kaiser et al. 1991, Kaiser et al. 1992, Kaiser et al. 1993, Andrews et al. 2007).

In many countries, increasing air pollution and greenhouse gas emissions caused by fossil fuels has encouraged the use of alternative fuels. The reasons such as depletion of world’s crude oil and its increasing wholesale price as well as the energy crisis have created an incentive to use alcohols as alternative fuels (Wagner et al. 1980, Mielenz 2001 and Al-Baghdadi 2003). This trend is motivated by three primary factors: global climate change, energy security, and economics. To improve engine performance and exhaust emissions, many additives can be added to fuel.

Oxygenates are one family of additives that can be used to enhance engine efficiency and exhaust emissions (Jia et al. 2005). Biofuels play an increasingly vital role in the supply of renewable energy and can help to reduce greenhouse gas emissions. The renewable energy demands will increase in the future with the development of new generation biofuels which are more efficient and do not compete with the food chain. Due to these developments, 2,5-Dimethylfuran (DMF) is assumed as an alternative fuel (Aden and Foust 2009).

In the United States, large-scale production of Ethanol has made it possible to exceed the 10% Ethanol content requirements for Gasoline blend nationwide. In recent years, use of larger percentage of Ethanol (up to 15%) in blend with Gasoline is allowed by US Environmental Protection Agency (EPA) in new light duty vehicles. Higher percentage of Ethanol requires an EPA waiver in terms of emissions and performance considerations (US-EPA 1990b).

Among various oxygenates, Ethanol is the most suitable fuel for spark ignition engines (SI) and the main benefit of Ethanol as an SI engine biofuel is that it can be produced from renewable energy source such as sugar cane, cassava and various types of waste biomass materials (Bayraktar 2005, Topgül et al. 2006).

Most attractive properties of Ethanol over Gasoline as a fuel are high evaporation heat, high octane number and flame speed which allow positive effect on the engine efficiency and higher compression ratios. Nowadays, Ethanol-Gasoline blends are more desirable fuels, with better anti-knock characteristic than pure Gasoline (Yücesu et al. 2006) which allows increasing the compression ratios. Moreover, the main advantages of using Ethanol and Gasoline blends are reduction of CO, volatile organic compounds (VOC) and unburned hydrocarbons emissions (Topgül et al. 2006).

Blending Gasoline with low levels of Ethanol has the advantage of no need for changes on current engines. Also it offers increase in overall octane number of the fuel blend; this increase in octane number can result in increase in efficiency by advancing spark timing (Rothamer and Jennings 2012).

Recently, Ethanol is used mostly as alternative liquid biofuel (Agarwal 2007, Fatih Demirbas 2009). In some regions like Brazil, Ethanol is used as a neat engine fuel or in different blends with Gasoline (Román-Leshkov et al. 2007, Mousdale 2008).

Daniel et al. (2011) investigated the performance and emissions of DMF compared with Ethanol and commercial Gasoline. They reported that all of the standard emissions were reduced for Ethanol and slightly decreased for DMF. Rothamer et al. (2012) reported the effect of DMF and Ethanol in blends with Gasoline on combustion properties and emissions, their findings were in agreement with Daniel's work. Also they reported that for direct injection operation Ethanol is more effective than DMF for reducing engine knock for the same blend percentages.

Graham et al. (2008) found that 10% Ethanol blend has considerably increased acetaldehyde emissions (108%) and produced insignificant changes in formaldehyde emissions. Hsieha et al. (2002) tested Ethanol-Gasoline blend with various blended rates (0%, 5%, 10%, 20% and 30% by volume). Furthermore, the influence of Ethanol content on the exhaust emissions from SI engines has been studied. Addition of Ethanol decreased CO and total hydrocarbon (THC) significantly; NOx emissions are dependent on engine operating condition rather than on Ethanol content.

Al-Hasan (2003) studied effect of using unleaded Gasoline-Ethanol blends on engine performance and exhaust emission. The results indicated that CO and HC emissions reduced approximately 46.5% and 24.3% respectively. The study mentioned that 20% Ethanol addition to Gasoline had the best results of the exhaust emissions.

Hasan et al. (2011) investigated the effect of composite after treatment catalyst on hydrocarbon speciation from Gasoline engine; they found that hydrocarbon speciation is heavily dependent on engine operation and combustion mode. Elghawi et al. (2009) reported the same concept as Hasan et al. Also they have reported that for SI mode about one half to two thirds of total HC emissions comes from the C_6-C_{12} range.

2.5. Investigations on Lubricity of fuels using HFRR (review)

Exposure of the fuel to the fuel pump and internal combustion injection system provides lubrication of these components. Aeronautical industry was the first to report the problems of insufficient lubricity problems of fuels in the 60s (Margaroni 1998). The same problem was reported when low sulphur fuel was fed to light-duty diesel engine The literature shows highly polar fuel compounds were found as the causes of good lubrication due to the formation of protective layer on the surface of metal (Safran 1994). This investigation shows the protection could increase for the fuels containing nitrogen and oxygen. Anti-wear additives are used to improve the lubricity properties of the fuel because the fuel processing may lead to elimination of surface active polar compounds (Nikanjam 1992, Barbour and Elliott 2000).

The necessities of lubricity improvement for diesel fuels are much higher than Gasoline counterparts due to high pressure operation of diesel fuel’s pumps. There have been some reports on failure of fuel pumps in Gasoline; some of these failures are reported to be because of poor Gasoline lubricity (Spikes et al. 1996, Wei et al. 1996, Rovai et al. 2005).

To enhance the catalyst life and performance in Gasoline engines, the reduction of fuels compounds such as sulphur contents were considered as a requirement for high pressure injections pumps of direct injection Gasoline engines, therefore the investigation of lubricity property of Gasoline fuels became a significant issue (Eleftherakis et al. 1994). Fuels must provide adequate lubrication of the moving parts in the fuel supply system, thus research on the effect of specification of fuel compositions on lubricity is of paramount importance (Danping and Spikes 1986).

In engine fuel systems components such as fuel pumps, flow-control valves and injectors, fuel lubricity is important for the lubricating behaviour of the fuel itself. There are many investigations published on diesel and biodiesel fuel lubricity characteristics, but there is lack of data on lubricity of Gasoline and Gasoline type bio-fuels. Most Gasoline fuel injection systems inject fuel into the inlet port upstream of the inlet valves; consequently the operation is at much lower pressure compared to diesel pumps (Heywood 1985, Aden and Foust 2009). This reduction in operation pressure results in lower lubricity requirements for Gasoline compared with diesel (Ping and Korcek 1996). It was discovered that Gasoline which has higher sulphur content, has good lubricity. It is believed that this good lubricity is a result of polar-type compounds which absorb themselves into the alloy and form a protective film coating (Childs and Stobart 2004).

Ping et al. (1996) was the first groups researching the lubricity of Gasoline. They modified the High Frequency Reciprocating Rig (HFRR) which is mainly used as the instrument for measuring the lubricity of diesel fuel for testing the Gasoline. They reported that the Gasoline without additives gave higher wear than highly refined Class I diesel fuels. Also they reported that adding detergent additives to

Gasoline decreases the wear. Lapuerta et al. (2009) reported that adding Ethanol to biodiesel blends resulted in loss of lubricity at high concentrations of Ethanol in blend. Agudelo et al. (2011) reported that adding different percentages of Ethanol to Gasoline (E20-E85) did not impact significantly the blend lubricity, but that addition of hydrated Ethanol slightly improved blend lubricity in comparison with adding anhydrous Ethanol.

2.6. Summary

In summary, the literature review discusses the regulated and unregulated exhaust emissions. The major areas contain the discussion of different sources of emission in spark ignition engines and the effect of composition of fuels on emission of individual hydrocarbons.

The effect of new alternative oxygenated fuels in SI engines also discussed. The main concentration of the literature review is on 2, 5-Dimethylfuran (DMF) that has become popular as a biofuel candidate among researchers due to newly developed production methods. Advances in production of DMF, conversion of fructose using a catalytic biomass liquid process have created this possibility for DMF to be considered as an alternative for Gasoline. Nowadays, many investigations have reported the anti-knock characteristics of DMF which makes properties of biofuel similar to Gasoline. The effect of oxygenated fuels blends with Gasoline on regulated and unregulated emissions were discussed. Ethanol reduces the amount of CO and THC significantly due to oxidisation of unburned hydrocarbons.

The effect of lubricity of diesel and Gasoline fuel's pump in SI engines explained. The diesel engines require more attention for lubrication of moving parts in fuel system due to high pressure of operation in diesel fuel's pump. Lack of publications in lubricity of Gasoline and oxygenated fuels give an incentive to investigate about this property of fuels.

The major motivation of thesis was introduced in the literature review, which is to describe comparison of regulated and unregulated emissions of different fuels and their blends in single cylinder spark ignition engine.

CHAPTER 3

3. EXPERIMENTAL SETUP

3.1. Lubricity experimental setup

Over the decades, various experimental methods have been applied to investigate and study the lubricants and lubricity of fuels. The most two common test procedures are as follows:

- High frequency reciprocating rig (HFRR) ASTM D 6079-99 and ISO 12156-1
- Scuffing Load Ball on Cylinder Lubricity Elevator (SBOLCE) ASTM 6078-99

Due to high repeatability of HFRR method, it is more popular than SBOLCE and it was used in this study.

3.1.1. HFRR (High Frequency Reciprocating Rig)

The high frequency reciprocating rig (HFRR) experiment is performed according to European standards for the measurement of lubricity. In short, HFRR rig use a metal ball to scratch on a metal plate with constant frequency while it is immersed in the fuel. Figure 3.1 shows schematic diagram of High Frequency Reciprocating rig (HFRR). After the experiment, the wear scar appears on the metal ball and must be measured in accordance with the BS EN 590. To obtain accurate and consistent results for lubricity of different fuels, some factors and parameters requires to be constant and must be within a permitted range. The HFRR rig is controlled by a computer and provides reliable analysis of lubricity results. The HFRR rig is attached to a controller/processor (see Figure 3.2) and this processor communicates with a PC as the interface between the user and the device.

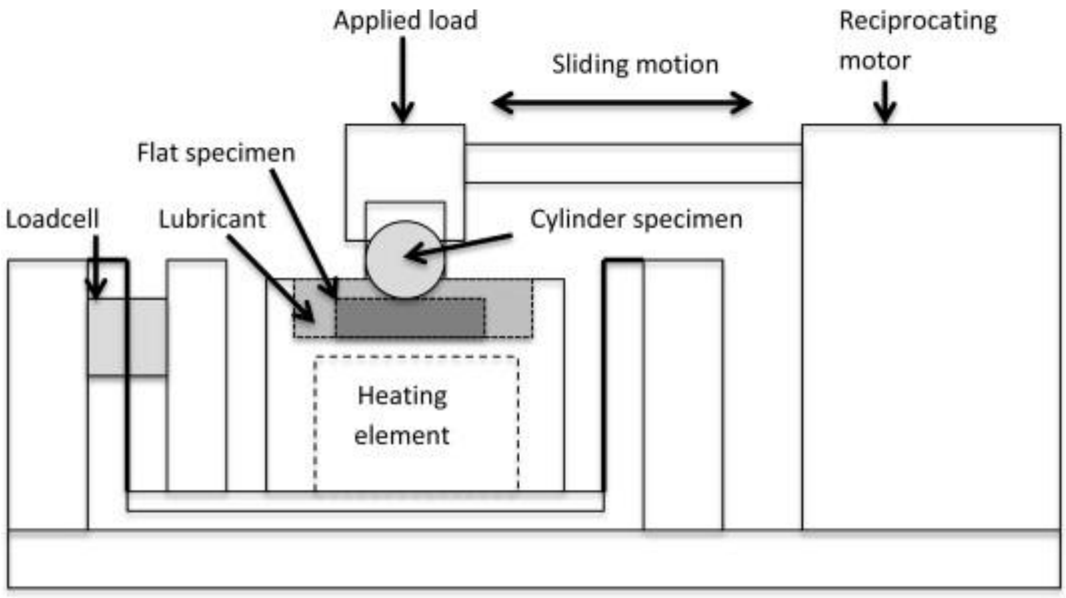


Figure 3.1-HFRR Schematic Diagram

Figure 3.2-HFRR instrument (PCS Instrument Company)

At the first stage, the HFRR must be calibrated to confirm accurate functioning of the test rig. It is recommended that the device to be calibrated after every five experiment to achieve reliable and repeatable results for the future experiment. To attain the best performance for the rig, the wear scar for high and low lubricity reference fuel must be measured.

There are many different methods and procedures for the tests and various standards are used in many countries. In the EU, the most common and popular method is described in the standard BS EN ISO 12156 -1. The test conditions in this research are explained in the Table 3.1.

Table 3.1-HFRR Test Conditions

Parameter	Value
Fluid Volume, ml	2 ± 0.2
Stroke length, mm	1 ± 0.02
Frequency, Hz	50 ± 1
Fluid temperature, degC	60 ± 1
Test load mass, g	200
Test duration, min	75 ± 0.1

Each experiment takes about 75 minutes to be finished and the test specimens and accessories must be cleaned carefully by Acetone and Toluene straightaway after each test. The volume of 2ml fuel sample is located in the reservoir with a constant temperature of 60° C during the test. A stainless steel ball is fixed in the ball holder and is mounted on metal plate vertically in the reservoir loaded with a hanging load.

The vibrating motion is carried out by the HFRR machine with stroke length of 1mm and a frequency of 50 Hz.

The atmosphere condition during the test has significant effect on the result of the experiment and the wear scar. The acceptable ranges of atmosphere conditions and relative humidity percentage are shown in Figure 3.3.

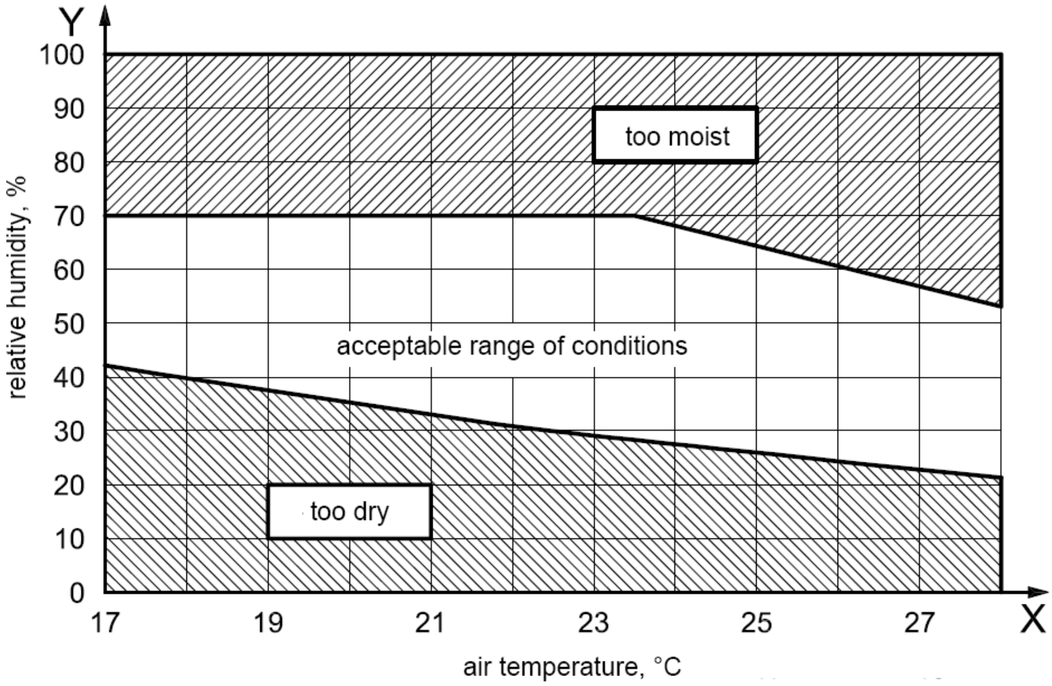


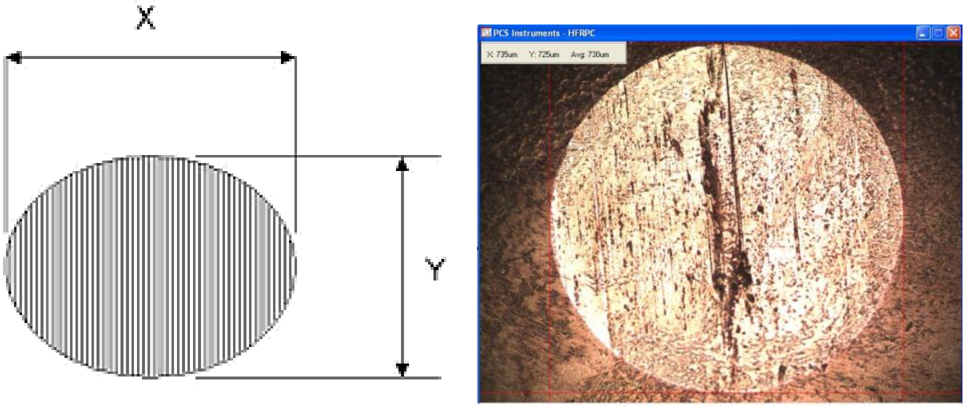
Figure 3.3-Acceptable Test Conditions (ISO 12156 -1)

The HFRR Humidity Controlled Cabinet (HFRHCAB) is applied as an accessory for the HFRR to permit the experiments to be performed at constant room temperature and relative humidity. The humidity control cabinet increases repeatability and reliability of the tests (see Figure 3.4).

Figure 3.4-HFRR Atmosphere Control Cabinet (PCS Instrument Company)

Figure 3.5 demonstrates the wear scar measurement under the microscope. The wear scar was measured using a microscope (see Figure 3.6). The wear scar diameter is observed in both X and Y directions. Mean wear scars were calculated as follows:

$$\text{Mean Wear Scar} = \frac{\text{Wear Scar Diameter in X axis} + \text{Wear Scar Diameter in Y axis}}{2}$$



X: 735um Y: 725um Avg: 730um

Figure 3.5-Wear Scar Measurement after HFRR Test

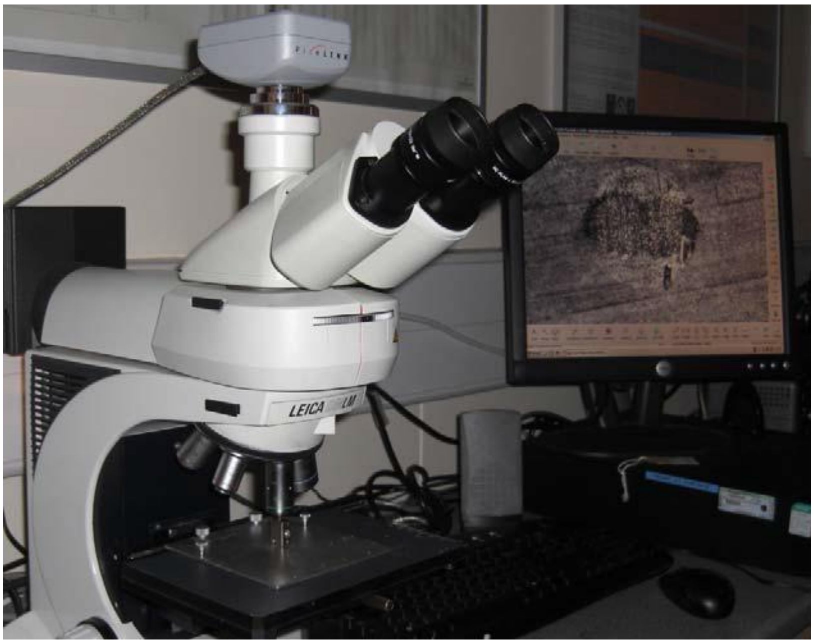


Figure 3.6-Microscope

In order to prevent evaporation of fuels such as Gasoline, Ethanol and DMF, Gasoline Conversion Kit has been used (see Figure 3.7).

Figure 3.7-Gasoline Conversion Kit (PCS Instrument Company)

3.2. Exhaust Emission Measurement

This chapter provides information on equipment applied in this research, including equipment setup and operation. The Gas Chromatography Mass Spectrometry method development for different applications is described in this section.

3.2.1. Single Cylinder Engine

The single cylinder four-stroke engine used in this research is fitted with a four valves spray guided direct injection cylinder head. The basic engine specifications are shown in the Table 3.2. In order to even-out the pressure in the intake and exhaust ducts, it is required that the engine is connected to both the intake and exhaust plenums. The engine is connected to a DC dynamometer, which in the experiments presented here has a constant speed of 1500 RPM. When engine operates at stable condition, the speed can be maintained within ±20 RPM but it reaches to ±200 RPM at unstable operation. Before any research is carried out, the engine must be warmed up at low load in SI mode until water and oil operating temperature reaches to 95±3 °C and 85±3 °C respectively. Figure 3.8 shows schematic diagram of single cylinder engine used in this study which is connected to the GCMS using heated line.

Table 3.2-Basic Engine Geometry

Bore (mm)	90.0
Stroke (mm)	88.9
Swept Volume (cm^3)	565.5
Connecting Road Length (mm)	160.0
Compression Ratio	11.5:1

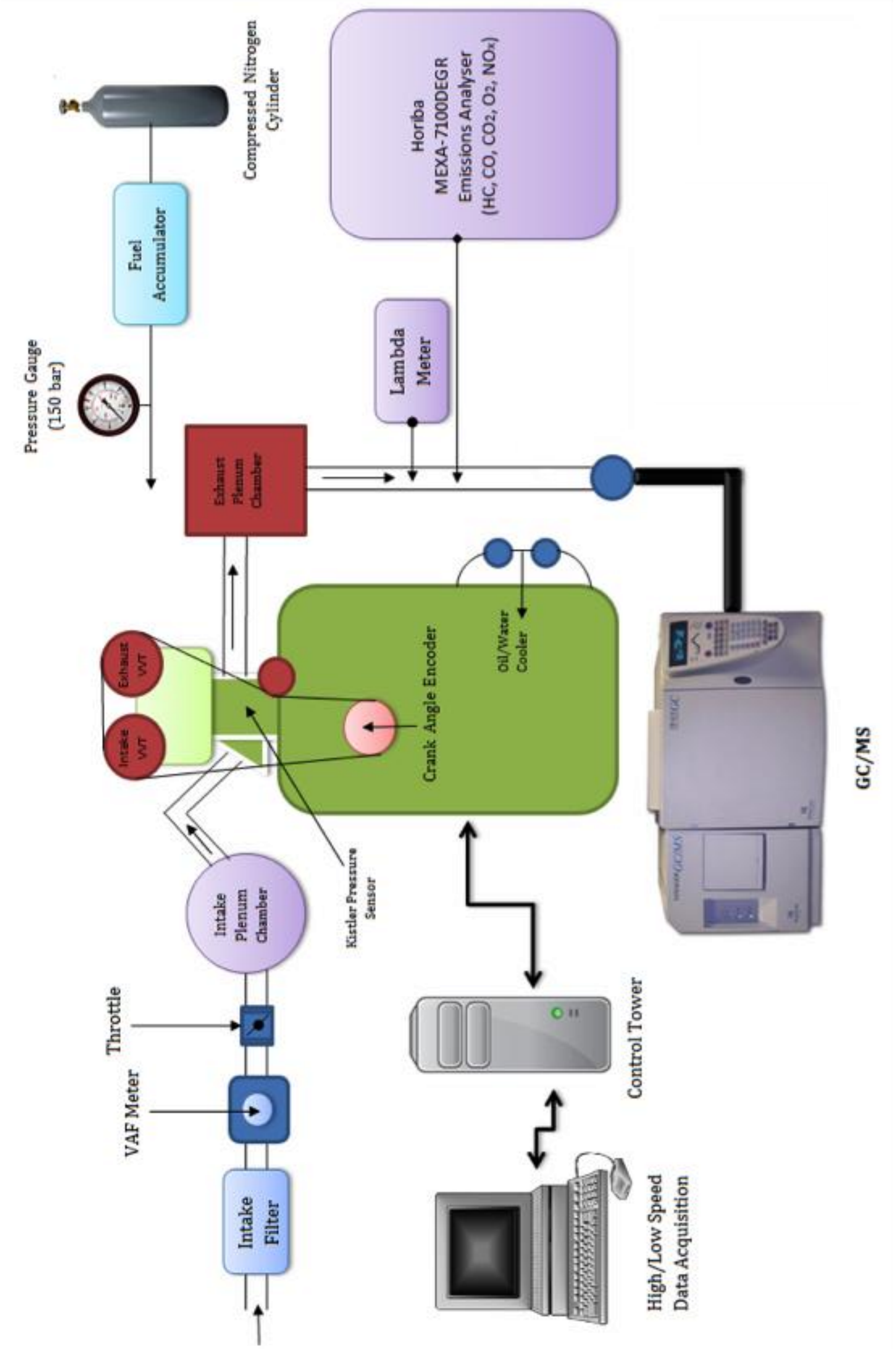


Figure 3.8- Schematic of the laboratory setup used this study

3.2.1.1. Combustion System

As demonstrated in Figure 3.9 the combustion system of this engine contains a centrally fitted injector having six injection holes; the spark plug is connected next to the injector at an angle of 18 degrees relative to the axis of the cylinder. The pattern of the nozzle contains two groups of three holes and the symmetric line of these holes is coincident with the crankshaft axis.

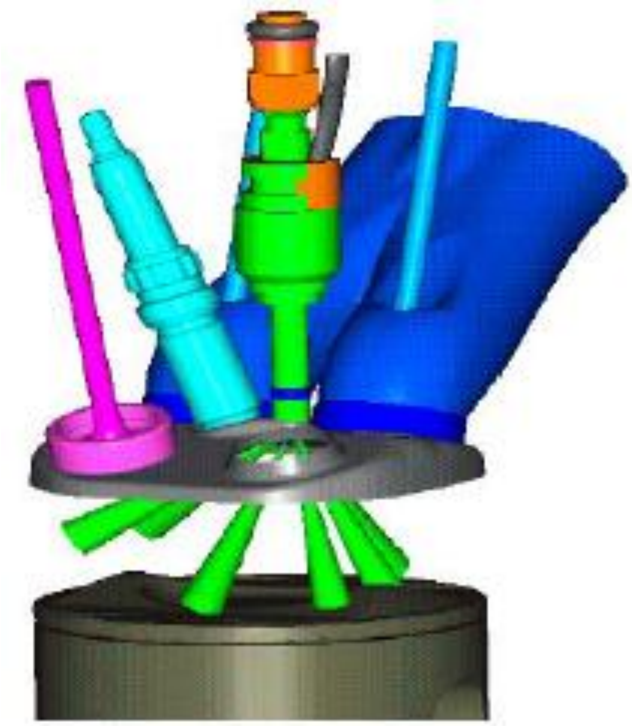


Figure 3.9-Layout of combustion system

3.2.1.2. Crankshaft Encoder Assembly

The timing signal produced by the crankshaft encoder must be precisely recognized as it is utilized by the engine control software package and the variable valve timing software for spark timing. The timing of this signal (relative to combustion TDC) is acquired by adjusting a spark timing of 0º bTDC in the engine software, and evaluating the real location of the spark by operating a stroboscope and the one degree markings on the flywheel of engine. Once this balance is achieved it can be inserted into the engine control software therefore the 0º bTDCCOMB spark appears at TDC. The one/degree markings on the engine flywheel are confirmed by measurement of the piston location (relative to TDC) at different positions and evaluating the angular distance from the crankshaft geometry.

3.2.1.3. Variable Cam Timing

The variable cam timing system (VCT) attached to the single cylinder engine applies lubricating oil pressure to modify the camshaft offset relative to the camshaft pulley. The camshaft timing may be delayed up to 50 crank angle degrees for both camshafts (intake and exhaust). A LABVIEW program is used to control variable cam timing system, the software shows the camshaft location once a cycle and every two revolutions for crankshaft and performs adjustments to the cam timing by modifying the signal pulse width which is sent to Variable Camshaft Timing Oil Control Solenoid. Generally, for maintaining stable engine condition and operation, the camshaft position must be kept within ±0.1 CAD.

3.2.1.4. Fuel System

The single cylinder engine applied in this research is connected to direct injection (DI) system and a port fuel injection system (PFI). The PFI system is used to warm up the engine, but it can be applied to evaluate the mixture preparation performance of direct injection system. The DI system is constructed with a free piston accumulator. An electric pump helps to deliver fuel from day-tank to the volume in the top of accumulator, which is located above the piston. The DI injector is attached to top of the cylinder. Using oxygen-free nitrogen supplied by BOC, the area under the piston is pressurized. The system is equipped with a circuit to return all unused fuel to the tank, with ability to flush the entire system using the nitrogen cylinder. The system is made of ¼ inch stainless steel tube and fittings; the fuel pressure in all experiments is 150 bar gauge.

3.2.1.5. Lambda Meter System

The lambda meter system applied in the experiments is an ETAS Lambda Meter (Model LA3) with Bosch heated wide-band oxygen sensor. This special lambda meter device permits the preprogrammed fuel properties to be modified to match the fuel in the engine. These fuel properties are stoichiometric air fuel ratios, H/C and O/C ratios. These properties and parameters become important when oxygenated fuels are applied to the engine. The lambda control must be open loop where engine operator sets the injection pulse width to obtain appropriate value.

3.2.1.6. Control

The LABVIEW software controls all parameters such as injection and spark timing in the engine using a National Instruments counter timer card (model 6602). While the engine is running at stable operating condition, the injection and spark timing can be adjusted in real time. The software has the potential of monitoring two separate injections with different pulse width per cycle.

Load settings for SI are obtained by adjusting a butterfly throttle valve that is located in the inlet. The indicated mean effective pressure (IMEP) is measured online from in-cylinder pressure using high-speed data acquisition program and IMEP also is measured using a Kistler water-cooled pressure transducer type 6041A, flush connected to the cylinder head wall, attached to the data acquisition system by a Kistler 5011 charge amplifier.

The intake and exhaust temperatures and other temperatures such as engine oil and coolant were all obtained by type “K” thermocouples. The engine coolant temperature is adjusted with Proportional Integral Derivative (PID) to control solenoid valve that set the cold water flow through a heat exchanger.

3.2.2. Gas Chromatography

The main aim of gas chromatography is to separate and detect individual components of a mixture that are gas or liquid. To analyze the exhaust gas samples, GCMS is connected to an engine exhaust outlet. To vaporize the liquid sample, the sample inlet (injection point of the sample) must be heated.

The gas chromatograph is divided into five main parts (McNair and Miller 2011), which are as follows:

- Carrier Gas
- Sample inlet
- Column
- Thermostatic Oven
- A Detector

All gas chromatographs contain these five main parts and they are the same for both gas and liquid sampling.

Separation process (chromatography) of solute mixture is done by distribution of mixture into mobile and stationary phases. The stationary phase is solid and is packed within the column and it is described with a large surface area that includes particles with 150µm diameters or less, creating a porous surface and finally providing absorption (Elghawi 2009). The mobile phase contains a carrier gas that pushes the vaporized components in the column and into the mass spectrometer detector. Each compound travels across the column in a specific time due to its unique molecular structure (McNair and Miller 2011). The certain time for each compound to leave the GC is called its retention time.

The gas chromatograph applied in this study contains an automatic oven temperature control that performs precise control of the oven and consequently column temperature. The gas chromatograph has the capability of different temperature ramping profiles therefore temperature can be modified at various preset rates.

A chromatogram is always generated by the gas chromatographs and form of chromatograms can be slightly different due to different type of detectors that can be used. It is important to mention that all chromatograms in this research have the same layout. The X-axis illustrates retention times for each compound, while the Y-axis demonstrates the percentage of signal intensity that has been received by the detector for each compound. The signals have the form of Gaussian shape on the chromatograms. To perform quantitative analysis of the sample, the peaks are used to identify each components existing in the original sample. For the quantitative analysis, the relative areas under the peaks must be calculated to find out how much of a specific component exists in the original sample. However, the quantification of components requires calibration of gas chromatography mass spectrometry (GCMS) using mixture of pure gases with a certain quantities.

3.2.2.1. Carrier Gas

The main aim of the carrier gas is to transfer the injected sample through the column and push into the mass spectrometer. The carrier gas selection is important and it must be chosen correctly, depending upon the compounds that need to be analyzed, the temperature profiles and the detector that is going to be used. A wrong carrier gas could directly affect the separation process of components, detector performance and finally results. The carrier gas can be helium or hydrogen but other available gases such as nitrogen and argon can be used. The most appropriate carrier gas for use in this research is helium as a carrier gas since all compounds present in this study contain hydrogen. A hydrogen carrier gas could interfere with separation and detection process of compounds. Helium is pumped away easily by mass spectrometer vacuum pump and the sensitivity of detector is low for the helium; in general, helium reduces its effect on the analysis of results.

The flow rate of carrier gas has significant importance in separation of components. For the best separation of compounds, the optimum flow rate must be chosen. The flow rate of carrier gas depends on the inlet pressure at head of gas chromatograph column.

Flow control is essential in GCMS, and the flow rate should be maintained at constant pressure during components separation to prevent fluctuations of chromatogram baseline, which affect quantitative analysis of results. The reason of these fluctuations during temperature programming of GC is due to changes of flow rate, as viscosity of helium will increase with temperature. However, decrease in flow rate affects appropriate separation of components and their retention times. The changes in retention time result in some difficulties for identification of compounds. Controlling of flow to keep the constant flow rate within temperature profile is essential.

3.2.2.2. Sample Inlet Injection

The exhaust gas sample injection to the GC column head has significant importance in having accurate results. This must be obtained rapidly without having any contamination and directly into the column. The gas samples are introduced by sampling valves and loops while liquid samples are introduced into the GC using septum seal.

3.2.2.3. Liquid Sample Inlet

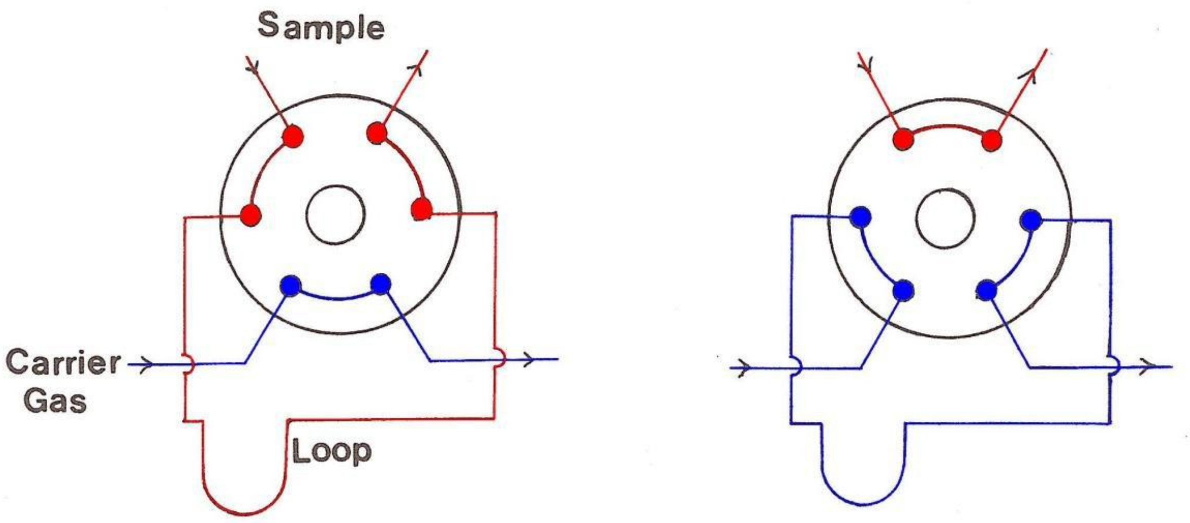
Sample inlet must be heated for injection of liquid samples to vaporise the sample immediately and mix it with carrier gas flow. To create sharp peaks of compounds on chromatogram, the liquid sample injection must be performed quickly. Slow injection of the sample will produce wider peaks, which could cause some difficulties in identification of compounds. The introduction of sample to the GC is performed by micro syringe as small amount of sample is needed due to expansion of the sample when it is vaporised from liquid to gas. Sample volumes are usually only a few micro litres (μL). It is also essential not to overheat the sample since it causes decomposition of components that affect in appropriate detection of the components.

Liquid injection is divided into two different techniques that are:

- Split Injection- after injection and vaporization of the sample, only small quantity of the sample enters the column. This phenomenon is carried out by split or purge valve to determine what proportion of the sample enters into the column and how much is purged from the sample. This technique is performed due to having high-resolution separation of peaks for more accurate analysis of the results. This method also determines ratios in the range of 10:1 to 1000:1, but these extremes are unlikely to be used (Elghawi 2009). The major advantage of this technique is explained when the split ratio needs easily to be adjusted by a valve and the disadvantage of the split injection is that the detector may not be able to detect and identify the compounds as only small quantities of the sample are injected into the column.
- In Split-less Injection the injection is made as in split injection but the sample is not purged, it means that the entire injected sample enters into the column. This method is used to improve sensitivity of components with low concentration.

3.2.2.4. Gaseous Sample Inlet

Gaseous samples are injected directly into column using a sampling loop. Figure 3.10 demonstrates a schematic diagram of six port Valco switching valve that was used in this study. When the Valco valve is in the LOAD position, the gas sample is introduced into the sample loop. In the LOAD position, sample flows through the loop and then is vented through the atmosphere and helium as a carrier gas enters into the gas chromatograph directly. The other position is the VENT position in which the excess sample will flow out through the vent port directly and helium gas will push the samples within the loop toward the column. Figure 3.11 shows the six port Valco valve used in this study.



LOAD Position **VENT Position**

Figure 3.10-Six Port Valco Valve Assembly

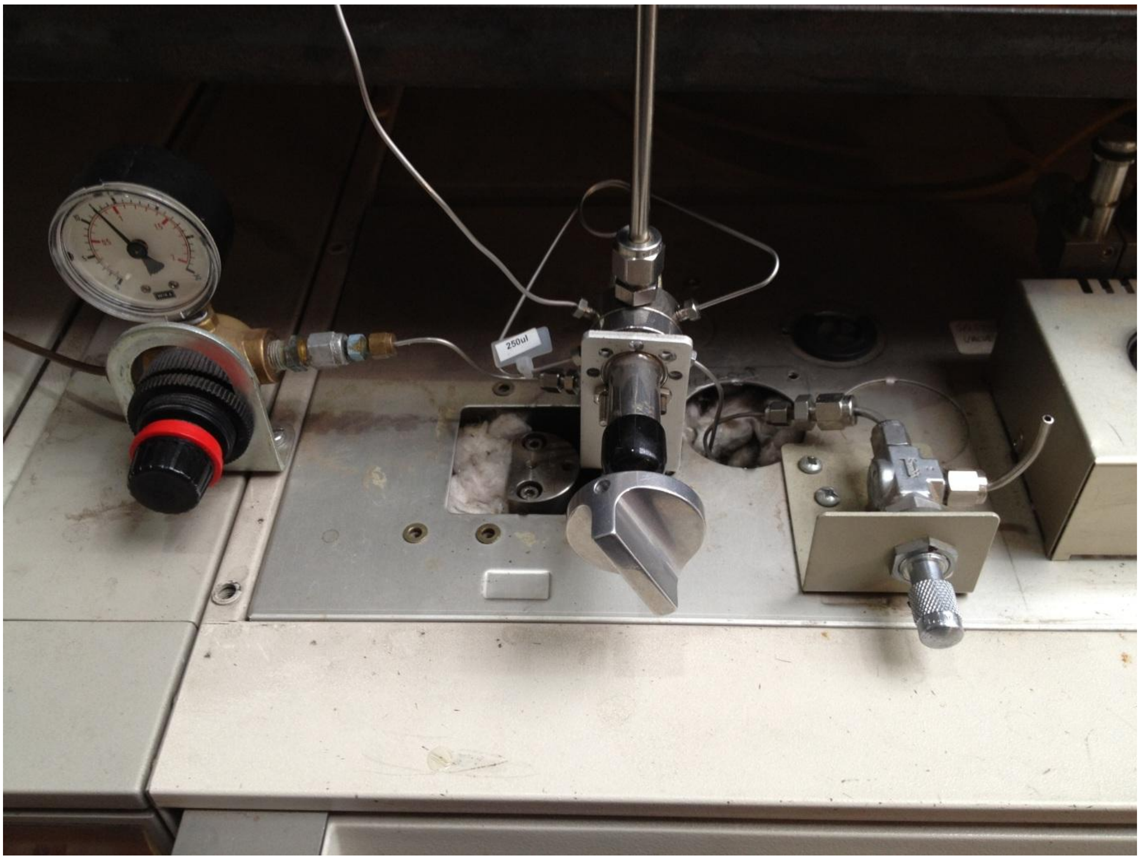


Figure 3.11-GCMS Sampling Set

Many different experiments were performed using different volumes of loops (1 ml and 100 μL) to improve the sensitivity of the gas chromatography analysis. Small sample size will result in lower concentration of compounds, weaker peaks in chromatogram and also cause minor compounds of the sample to become undistinguishable from the column bleed and column coating.

In general, the Valco valve mechanism has the capability of reducing carrier gas pressure fluctuations as the valve switches to INJECT position when helium enters into the column via six-port valve.

3.2.2.5. The GC Column

One of the most important parts of the gas chromatography instrument is the column. It contain stationary phase that cause separation of different compounds in the sample. Usually, there are two different types of column that can be applied in the GC which are: the conventional packed columns with diameter of 2 to 4 mm and with the length of 0.6 to 4 meters and packed with appropriate adsorbent (Braithwaite et al. 1985). The other type of column is the open tubular column that is produced from fused silica (McNair and Miller 2011). Internal diameter of this column ranges from 100 μm to 500 μm and with 10m to 100m long. The open tubular column is divided into two different categories of (a) Porous Layer Open Tube (PLOT) and (b) Walled Coated Open Tube (WCOT).

Many parameters must be considered for choosing the appropriate column since the type of the column has a direct effect on retention times of the sample in the column. Longer columns can provide better separation of compounds within the column but also the analysis time of the GCMS becomes longer (McNair and Miller 2011). Other factors such as column temperature and carrier gas flow rates can help the column to be optimised for the sample (Elghawi 2009). Hasan et al. (2011) used this column to do speciation of hydrocarbons in his investigation.

After many experiments, the column may be contaminated when the sample passes through it. Therefore, there is a need to bleed the column with the high temperature of 220 ^{o}C and leave it for a day or less to clean any contaminants of the column and to keep the accuracy of the column during the experiments. In this study the highest appropriate temperature for bleeding the column is 220°C. Columns have limited life and after a while must be replaced, but column bleeding can help to increase the life of the column. The column used in this study is PoraPlot Q type (see Figure 3.12). The column specifications were shown in Table 3.3.

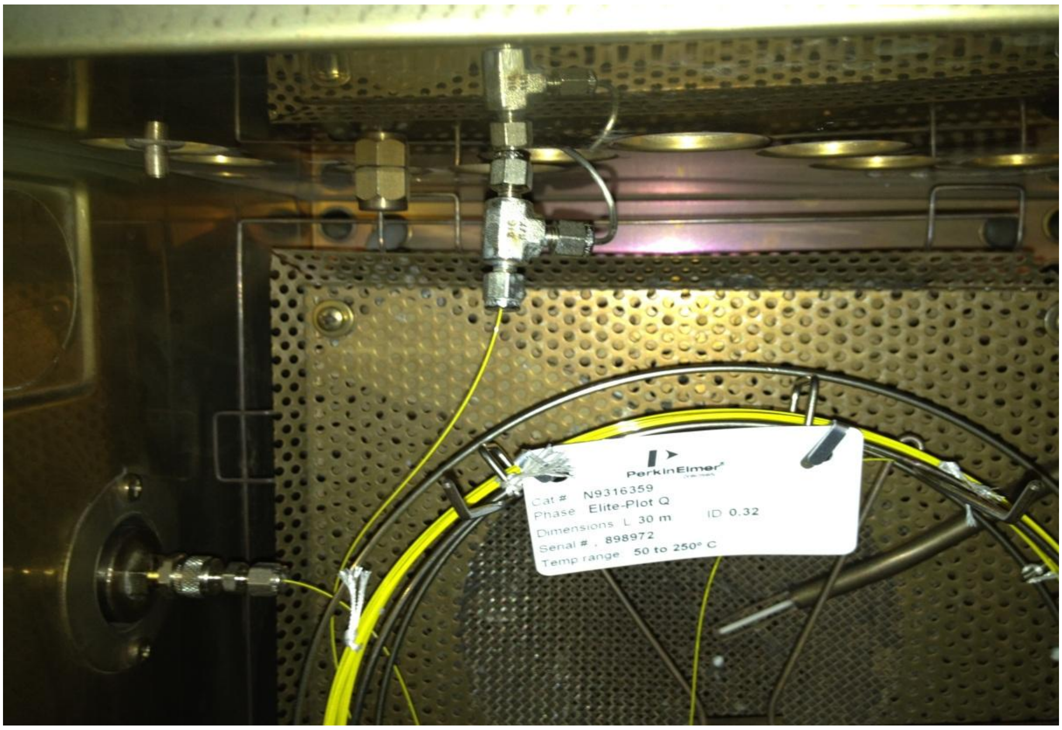


Figure 3.12-PoraPLOT Q Column (PerkinElmer Company)

Table 3.3-Column Specifications

Column	**PoraPLOT Q**
Length (m)	25
Internal Diameter (mm)	0.32
Film (μm)	10

3.2.2.6. Thermostatic Oven

One of the most important factors for better separation of the components is the temperature of the GC column. The GC oven controls the column temperature precisely and it can be varied in range of 25°C to 350°C. The GC oven is programmed to heat up temperature with time. It increases the programmed temperature profile at a linear rate. All temperature settings are adjusted by the users. For adjusting the oven temperature, the oven must be set at 35°C firstly; it must be held at this temperature for two minutes; when temperature starts to rise the carrier gas expands. Then temperature increases at a certain rate (in these experiments the rate is 8°C/minute) and it heats up until the temperature reaches 220°C and at the final stage it remains at 220°C for few minutes to flush the column. Finally the oven is cooled down to 35°C again to before any subsequent experiment is carried out.

A slower temperature increase rate will generally perform better separation of components in the sample but it takes a longer time to carry out the analysis.

3.2.2.7. The GC Detectors

There are different types of detectors that are applied to perform identification of sample components. The most common detectors are:

- Catalytic combustion detector (CCD)
- Electron capture detector (ECD)
- Flame ionization detector (FID)
- Thermal conductivity detector (TCD)
- Helium ionization detector (HID)
- Electrolytic conductivity detector (ELCD)
- Fourier Transform Infrared (FTIR)
- Mass Spectrometer (MS)

In this research, mass spectrometer detector has been used to detect hydrocarbon compounds.

3.2.3. Mass Spectrometry

Mass spectrometry analysis is described as dominant method that performs identification of HC components in different applications such as engine exhaust emission analysis, drugs and pharmaceuticals, clinical chemistry, petroleum and oil products, environmental investigations. A mass spectrometry performs ionization of the sample when it enters into the MS source in gaseous phase. The MS source applies the electron impact principle of operation to create fragment and molecular ions for each compound as a small quantity of gaseous sample at low presser of 10^{-4} mm Hg using the vacuum pump. The electron beam is placed perpendicular to gaseous sample entrance. The filament temperature controls number of electrons accurately and the electrons are conducted to the body of chamber using positive charged beam. A source of mass spectrometry operates at 70 V and supplies enough energy to ionize the fragments of molecules. Fragmentation of molecules helps to identify the unknown components and can be in large or small scale of the original molecules. The fragments masses divided by their electrical charge are called mass to charge ratio (M/Z). The acceleration of ions is required before passing through a quadrupole mass-charge filter. The detection and identification of unknown compounds are obtained by measurement of the charge of the ion and the mass is related to that ion. Very small potential differences of the electrons make it necessary to use an amplifier in order to produce measurable current for the detectors.

3.2.4. Gas Chromatography-Mass Spectrometry (GCMS)

The gas chromatography (GC) for separation of components and the mass spectrometer (MS) for detection of compounds are combined to produce very powerful instrument for identification of present components in each sample. Figure 3.13 shows the GCMS used in this study. It is not easily possible to use these instruments individually for different applications. Heated transfer line is used to prevent condensation of sample while it reaches the GCMS. The main concern is the carrier gas pressure during the experiment in the GC and MS. When the sample exits the GC the pressure must be at vacuum in the MS inlet (McNair and Miller 2011). This is achieved on the Fisons MD8000 instrument using the vacuum pump. Figure 3.14 illustrate the basic components of GCMS.

Figure 3.13-Gas Chromatography-Mass Spectrometry Instrument

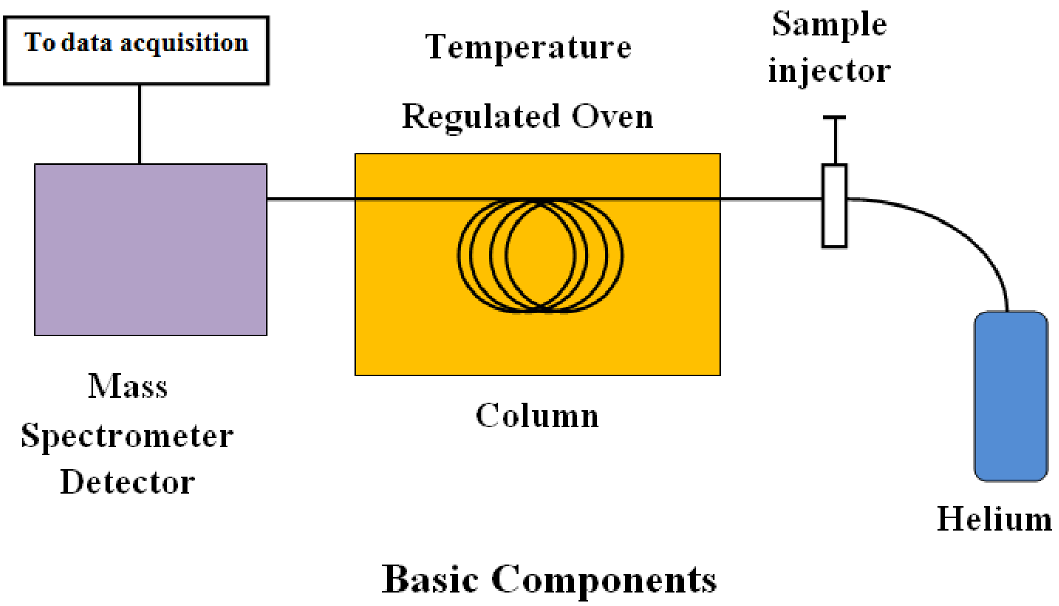


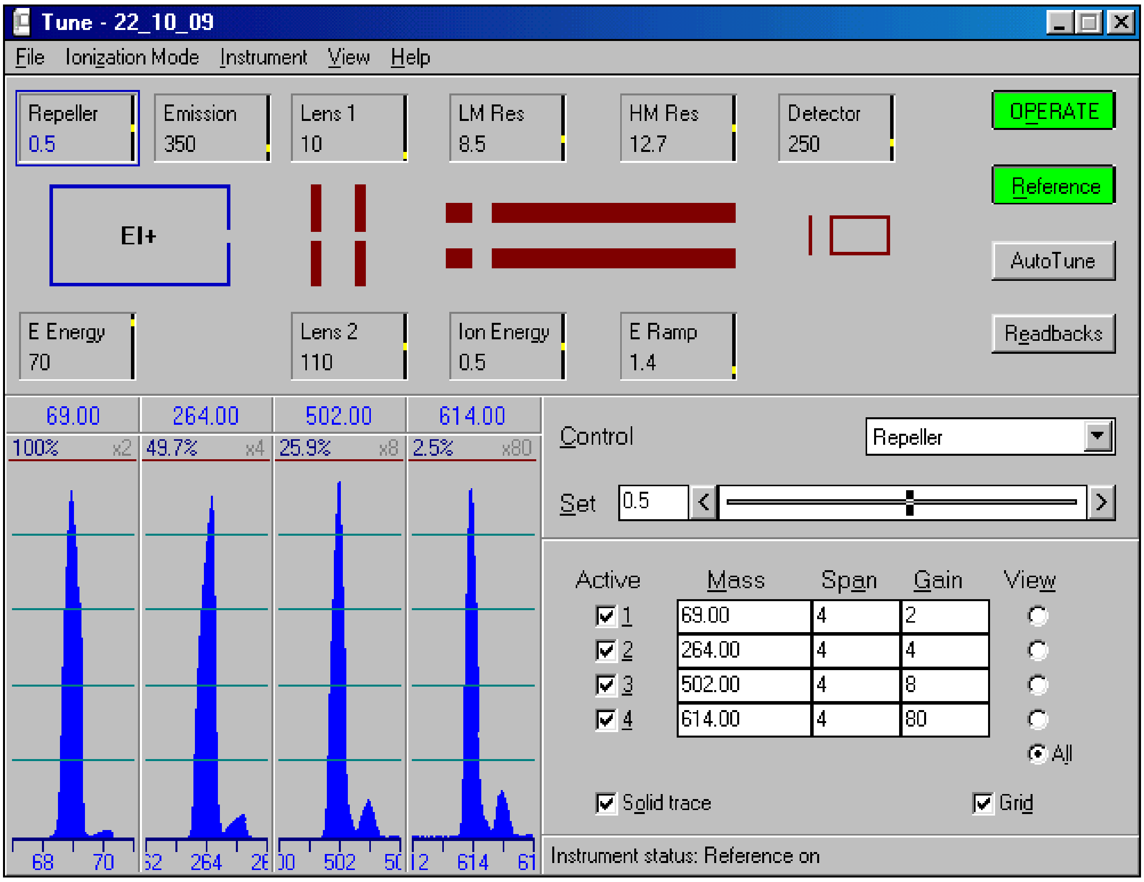
Figure 3.14-Fundamental Component of GC-MS

To have very accurate and reliable results, mass spectrometer is combined with an online gas chromatograph. For the precise identification of various compounds using mass spectrometer, the GCMS must be calibrated.

3.2.4.1. Calibration of Gas inlet GC-MS

The first step to calibrate GCMS is to apply the tuning process that contains adjustments for mass spectrometer (MS) to scan reference components (internally located in the MS). These components have the molecular masses of 69, 264, 502 and 614. This is used to optimize ion source parameters such as voltage and temperature. The tuning process can be acquired manually for the best intensity for ion peaks. The tuning page screenshot is illustrated in Figure 3.15. There are four peaks at the bottom of the page. Figure 3.15 shows that all peaks are completely tuned for MS and display best intensity. Changing the “Gain” for each peak can modify peak's intensity and shape. The peak size increased as the gain will rise. Mass spectrometer over sensitivity will appear if the gain is too large and peak size is beyond the window. If the gain value is too small and the peak size is really small, low sensitivity will appear in comparison with the ideal tuning process.

However, the MS tuning process can be performed automatically using MassLab if the manual tuning is not possible and this option is named “Auto Tune” that is shown in Figure 3.15. The MS Autotuning concentrates on the adjustment and optimization of mass spectrometer for the reference components to provide ideal intensity of the peaks.



Tune - 22_10_09

Repeller 0.5
Emission 350
Lens 1 10
LM Res 8.5
HM Res 12.7
Detector 250
E Energy 70
Lens 2 110
Ion Energy 0.5
E Ramp 1.4

Control: Repeller
Set: 0.5

Active	Mass	Span	Gain	View
☑ 1	69.00	4	2	○
☑ 2	264.00	4	4	○
☑ 3	502.00	4	8	○
☑ 4	614.00	4	80	○
				● All

☑ Solid trace
☑ Grid

Instrument status: Reference on

Figure 3.15- MassLab Software Tuning Page screenshot

During the optimization of mass spectrometer, two parameters of stability and sensitivity of the peaks must be considered accurately. To perform accurate quantitative analysis and obtain repeatability for the results, stability is needed. There is a possibility to maximize sensitivity of the MS, but for performing identification of species and not for quantifications. This research is concerned with both quantification and identification of different species; therefore, the MS must be tuned for the ideal intensity of peaks to have the accurate results for both identification and quantification.

3.2.4.2. Species Identification

The gas chromatography mass spectrometry is attached to a PC and is controlled using the MassLab software. The software has the capability of controlling temperature profile and ramps in the GC and also provides manual and automatic tuning process for the MS. The Masslab creates a real time chromatograph while connected to the mass spectrometer. However, it is possible to analyze different peaks of chromatogram in the mass sepctra page. The mass spectrum contains a graph of “Mass/Charge ratio (M/Z)” in the X-axis against “Abundance Percentage” in the Y-axis. The software allows identifying of different components using scans of mass spectrum in the library. The four existing libraries in the GCMS are as follows:

- National Institute of Standards and Technology (NIST)
- Wiley
- NBS
- Libtx

Various factors must be considered during scanning process, but the main technique is to find the highest six peaks and then it scans the peaks in the MS library. Furthermore, the MassLab provides a list of 18 to 20 probable components related to the MS fragmentation in order of highest probability for possible matches. It is possible for the user to compare the real spectra with the components in the library and find the best possible matches as recognized by MassLab.

3.2.4.3. Calibration Procedures

This research has focused on 14 hydrocarbon species C_3-C_7 presented in the exhaust emissions from various fuels in an SI engine.

In order to prepare the equipment for experiments, a best method must be provided to have the repeatable and consistent results. This includes the development of temperature profile for the flow rates and the column. To have good separation of components, best temperature program and ramping must be established.

The best capillary column that permits the good separation of volatile hydrocarbons is the PoraPLOT Q with the specification of 25 meter long x 0.32 mm i.d and 10 μm film thickness. The PoraPLOT Q allows the detection and identification of both polar and non-polar components at the same time.

The capillary column is connected to the GC and column head pressure is adjusted to 11 psi. The GCMS parameters applied in this research are shown in Table 3.4. The temperature profile and ramping method used in this project is the best possible method for the separation of hydrocarbons from C_3-C_7. In order to perform quantitative and qualitative analysis, the standard gas bottle must be used which contains alkanes and alkenes mixture from C_3 to C_7 with a certain concentrations. The equipment must be calibrated daily using the standard gas mixture bottle to maintain the device in a good condition. The certified standard gas bottle was supplied by AirLiquid Company.

Each experiment takes 29 minutes to be completed and all hydrocarbons were detected by their retention times (Table 3.5). The area of each peak in chromatogram demonstrates the concentration of each hydrocarbon component related to that peak. Figure 3.16 illustrates the standard components in C_3 to C_7 range applied in this study and this chromatogram was used as a reference to identify and perform quantitave analysis of individual hydrocarbons from exhaust emission. The MS detector used in this research is Fisons MD800. The MassLab provides the gas chromatographic data for each experiment.

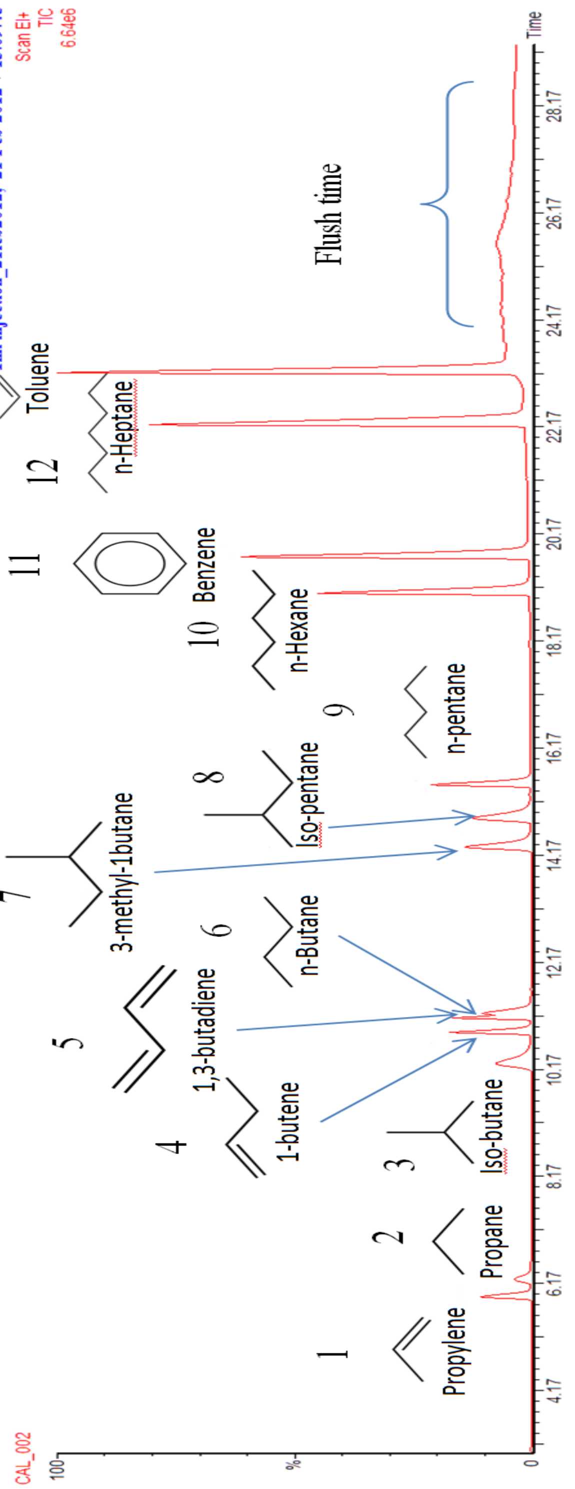


Figure 3.16-Standard Hydrocarbons Chromatogram

Table 3.4-GCMS Operating Parameters

Instrument Parameters	MD800mass spectrometry/GC8000 gas chromatograph
Column	PoraPLOT Q 25 m; 0.32 mm ID; 10 μm film
Detector	MS, MD800-1 Source 200 ^{o}C ; 10:150 amu
Oven ramp	ramp 35 ^{o}C initial; 2 minutes hold 8 ^{o}C /minute to 220 ^{o}C 4 minute final hold (Flush)
Flow rate	6 ml / minute; He

Table 3.5-Standards Species Retention Time

Peak number	Compound	Retention time (min)
1	Propylene (C_3H_6)	5.802
2	Propane (C_3H_8)	6.182
3	Iso-butane(C_4H_{10})	10.215
4	1-Butene(C_4H_8)	10.532
5	1,3-Butadiene (C_4H_6)	11.178
6	n-Butane (C_4H_{10})	11.238
7	3-Methyl-1-Butane (C_5H_{12})	14.225
8	Iso-pentane (C_5H_{12})	14.798
9	n-Pentane (C_5H_{12})	15.425
10	n-Hexane (C_6H_{14})	19.085
11	Benzene (C_6H_6)	19.786
12	n-Heptane (C_7H_{16})	22.245
13	Toluene (C_7H_8)	23.264

3.3. Fuel Used in this Research

The chemical and physical properties of fuels used in this study are listed in Table 3.6. It must be mentioned that when the fuels such as Ethanol and 2, 5-Dimethylfuran are blended with Gasoline no effort is applied to keep the original properties of the unleaded Gasoline such as octane number. It must be mentioned that DMF provided in this research is produced from crude-oil rather than a bio-source, but it still has the same properties of the bio-derived fuel. The test fuels used in this study were 97 research octane number (RON) Commercial Gasoline and the Bio-Ethanol both supplied by Shell Global Solutions UK. The DMF with purity of 99.8% was provided by Shijiazhuang Lida Chemical Co. LTD in China. Also, the experiments were carried out with blending of Isooctane (C_8H_{18}) and Toluene ($C_6H_5CH_3$) in volumetric fraction (2:1 blending ratio). The Isooctane was chosen as a primary reference fuel and it is representative of alkanes and supplied by ACROS Company. The Toluene was chosen as a representative of aromatics and supplied by Fisher Chemicals.

Table 3.6-Fuel chemical and physical properties

Properties	DMF	Ethanol	Gasoline	Isooctane	Toluene
Chemical formula	C_6H_8O	C_2H_6O	C_2-C_{14}	C_8H_{18}	$C_6H_5.CH_3$
Molecular mass (kg/kmol)	96.13	46.07	100-105	114.23	92.14
H/C ratio	1.333	3	1.795	2.25	1.14
O/C ratio	0.167	0.5	0	0	0
Gravimetric oxygen content (%)	16.67	34.78	0	0	0
Density at 20°C (kg/m3)	889.7[a]	790.9[a]	744.6	692	870
Research Octane Number (RON)	reported 119[b] 101.3[c]	106	96.8	100	121
Stoichiometric air-fuel ratio (kg/kg)	10.72	8.95	14.46	15.02	13.41
LHV (MJ/kg)	33.7 [a]	26.9 [a]	42.9	-	-
LHV (MJ/l)	30 [a]	21.3 [a]	31.9	-	-
Heat of vaporization (kJ/kg)	332	840	373	308	351
Initial Boiling Point(°C)	92	78.4	32.8	99	110.6

a. Measured at University of Birmingham
b. Román-Leshkov, Barrett et al. (2007), Yanowitz, Christensen et al. (2011)
c. Wang, Xu et al. (2012)

3.4. Summary

In summary, this chapter describes the experimental test facilities applied in this research. All experiments were performed in single cylinder spark ignition engine with compression ratio of 11.5:1 and variable valve timing (intake and exhaust) system.

The gas chromatography mass spectrometry (GCMS) was used to identify individual hydrocarbons. The GCMS must be calibrated by performing the tuning process that includes adjustments for MS to scan reference components with molecular masses of 69, 264, 502 and 614.

An appropriate method was developed to separate and detect standard calibration hydrocarbons with maximum sensitivity in the GCMS. The PoraPLOT Q column has been chosen to detect volatile organic compounds (VOC) and the temperature profile was used to obtain best separation of components.

The six port valco valve was used to inject 1ml exhaust emission sample into the GCMS. The volume of sample is 1ml to get strong peaks.

Finally, the test facilities were discussed in detail. The each experiment was carried out in three times to validate reliable and repeatable results.

CHAPTER 4

4. LUBRICITY OF FUELS

4.1. Introduction

Spark ignition engines fuelled with alternative fuels are the topic of many studies. As alternatives for Gasoline, Ethanol and recently 2, 5 - Dimethylfuran (DMF) have been investigated for their different properties. Lubricity analysis of fuels in fuel systems is vital because of the lubricating role of fuel in the fuel pumps and injectors. Lubricity of Gasoline and its alternatives became important since introduction of direct-injection Gasoline fuel pump with high injection pressure becoming closer to diesel pumps. Therefore, this work examines the lubricity properties of Gasoline and its blends with alternative fuels using a HFRR lubricity test rig. Results of lubricity experiments showed that DMF as an additive to Gasoline improved the lubricity of blends; this effect was increasing with the percentage of DMF. These results can be compared with DMF-Ethanol blends which displayed the same pattern but with lower enhancing role of DMF. The DMF fuel was kept in storage for seven months and then the same experiments were repeated (DMF Ageing). Smaller wear scar and better lubricity effects were achieved by using the aged DMF. These results highlight the potential of DMF to become an additive for Gasoline and its alternatives.

4.2. Results and Discussions

In the HFRR lubricity test, for pure DMF, Ethanol and Gasoline results have been obtained after 75 minutes of test and by measuring wear scar under the microscope; the results show that the largest wear scar is for Gasoline - 714µm and the lowest one is for DMF - 238.5µm (see Table 4.1). Therefore, DMF has the best lubricity in comparison with Ethanol and Gasoline.

Table 4.1- Pure Fuels Wear Scar Sizes

Pure Fuels	**Wear Scar (µm)**
DMF	238.5
Ethanol	596
Gasoline	714

Figures 4.1 and 4.2 illustrate how friction coefficient and lubrication film of DMF, Ethanol and Gasoline change with time at 35-45% relative humidity and 25˚C. The friction coefficient values and lubrication film percentages data were transferred to the computer software using data acquisition system and all analysis were carried out by data stored on computer.

The study of pattern of changes of the friction coefficient of fuel during the HFRR test is one of the most important factors in the test in order to investigate how properties of fuel can have an effect on the wear scar and lubricity of fuel. The graph in Figure 4.2 illustrates the behaviour of friction coefficient of the three fuels during test. Among the tested fuels, Gasoline displays biggest changes and large fluctuations in friction coefficient during the test, and this is why it has the largest wear scar.

The friction coefficients of DMF are relatively stable and constant during the experiment in comparison with Gasoline and Ethanol which display increasing trends, particularly visible for Ethanol.

Figure 4.1 demonstrates that the average friction coefficient of DMF is 0.271 which is almost 42% lower than that of Gasoline (0.466) and over 20% lower than that of Ethanol (0.355). That is why DMF has the best lubricity among three fuels. Also, the average percentage of lubrication film coverage of the three fuels has been illustrated in Figure 4.2 where DMF average lubrication film coverage is 68% while this value is 53% and 46% for Gasoline and Ethanol respectively. High film coverage of DMF can result in smaller wear scar. Highest value of film coverage for DMF is 83% during experiment.

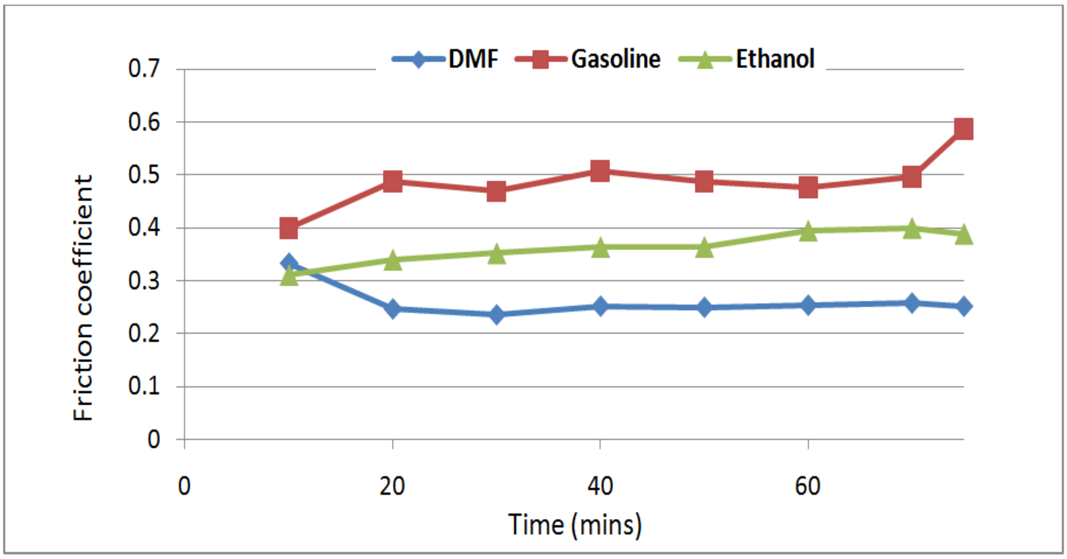


Figure 4.1-Friction coefficient comparison of pure fuels during experiment (75 minutes)

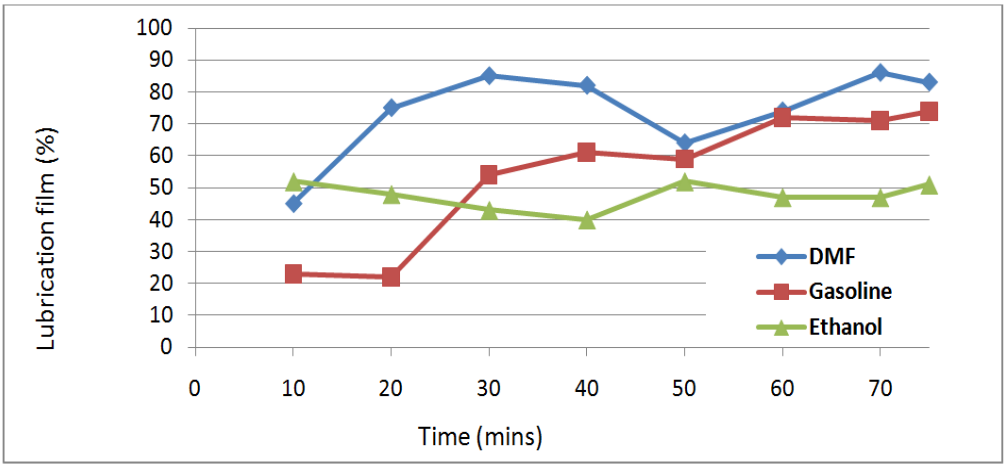


Figure 4.2-Lubrication film comparison of pure fuels during experiment (75 minutes)

4.2.1. DMF Blends with Gasoline and Ethanol

Figures 4.3 demonstrate the effect of DMF concentration in blends with Gasoline on the values of friction coefficient and lubrication film coverage. It can be seen that friction coefficient decreases gradually for larger percentages of DMF and lubrication film coverage has an increasing trend with larger concentration of DMF in the blends. For 0% to 70% DMF blends, some irregularities can be seen in the lubrication films results since DMF is oxygenated fuel, reaction may take place at high temperature and can enhance Gasoline lubricity property; these kinds of errors can have a direct effect on the lubrication film coverage. It can be concluded that there is a decreasing trend in wear and friction coefficient at low concentration of DMF in blends with Gasoline. By addition of 10% of DMF the wear scar size is reduced by almost 34% to 472µm from 714µm at 0% DMF. Larger concentrations of DMF in blends can further decrease the wear scar size. At 90% DMF, the wear scar size reduced to 278µm. Table 4.2 shows the results of DMF blending with gasoline.

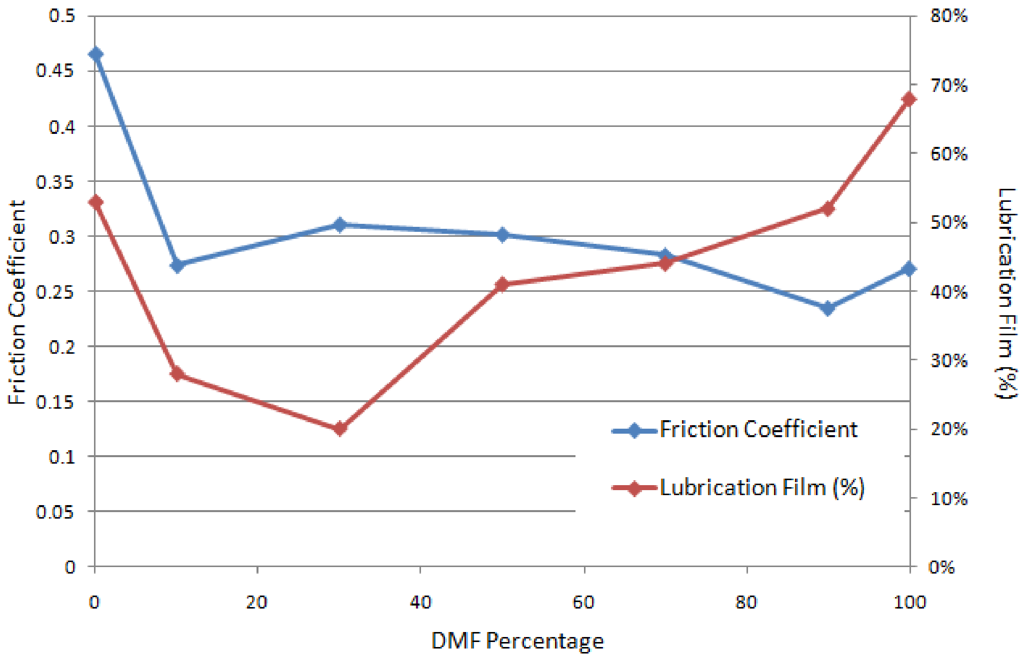


Figure 4.3-Friction coefficient and lubrication film coverage - effect of DMF and Gasoline Blends

Table 4.2-Test results for 2, 5-Dimethylfuran (DMF) and Gasoline blends

Fuel Blend	**Average Wear Scar(µm)**	**Average Friction Coefficient**	**Average Lubrication Film Coverage**
100GAS	714	0.466	53%
10DMF90GAS	472	0.274	28%
30DMF70GAS	539.5	0.311	20%
50DMF50GAS	429	0.302	41%
70DMF30GAS	322	0.283	44%
90DMF10GAS	278	0.235	41%
100DMF	238.5	0.271	68%

Figure 4.4 indicates friction coefficient and lubrication film coverage of different percentages of DMF and Ethanol blends. It was realized that by increasing the percentage of DMF, the friction coefficient and lubrication film coverage varied differently and as percentage of DMF was increased the friction coefficient of blends changed slightly. This friction coefficient remained relatively constant by increasing the concentration of DMF in the blend. Investigation on lubrication film coverage and friction coefficient in DMF Ethanol blends showed better lubricity properties and wear scar by increasing percentages of DMF in blends. There is a reduction in wear scar and friction coefficient in lower DMF concentration of blends with Ethanol. Also, DMF concentration in blends with Gasoline enhanced lubricity more than Ethanol blends.

The lubrication film coverage was decreased by 28% upon addition of 10% DMF after which it fluctuates upon further addition. In DMF and Ethanol blends, 10% DMF reduced the wear by 12% from 596 μm to 521.5 μm compared to the 38% reduction in Gasoline. Also by adding more percentages of DMF, the wear scar was decreased to 447 μm at 90% DMF. It is obvious that increase in DMF concentration in blends with Ethanol resulted in better wear scar compared with Gasoline blends. The analysis of results indicates that small amount percentages of DMF to Gasoline can improve the lubricity of Gasoline more significantly than that of Ethanol. Table 4.3 demonstrate the results obtained for DMF blends with Ethanol.

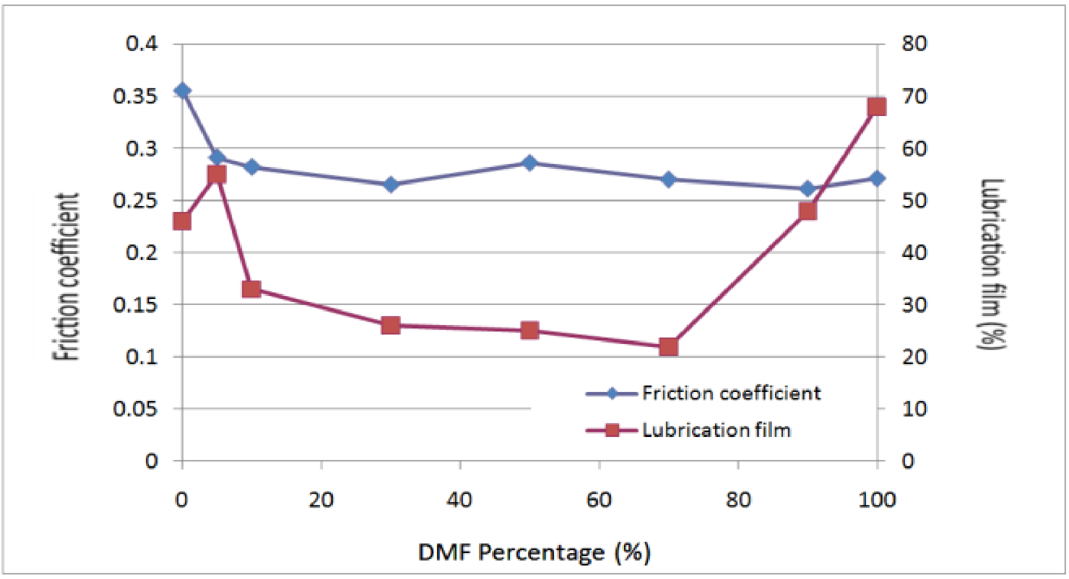


Figure 4.4- Effect of DMF and Ethanol blends on friction coefficient and lubrication film

Table 4.3-2, 5- Dimethylfuran and Ethanol blend test results

Fuel Blend	**Average Wear Scar(μm)**	**Average Friction Coefficient**	**Average Lubrication Film Coverage**
100ETH	596	0.355	46%
10DMF90ETH	521.5	0.282	33%
30DMF70ETH	515.5	0.265	26%
50DMF50ETH	485	0.286	25%
70DMF30ETH	534.5	0.27	22%
90DMF10ETH	447	0.261	48%
100DMF	238.5	0.271	68%

In general, the study of friction coefficient of DMF in blends with Ethanol and Gasoline illustrates important role of DMF for enhancement of Gasoline lubricity properties. As it is illustrated in the results, DMF has better effect on Gasoline lubricity properties in comparison with the effect on Ethanol. Figure 4.5 represents inverse relationship of lubrication film coverage and friction coefficient in DMF Ethanol blend (50DMF 50ETH). As the friction coefficient is increased, the percentages of lubrication film coverage is decreased and this issue proves that lubrication film and friction coefficient of fuel have inverse relationship.

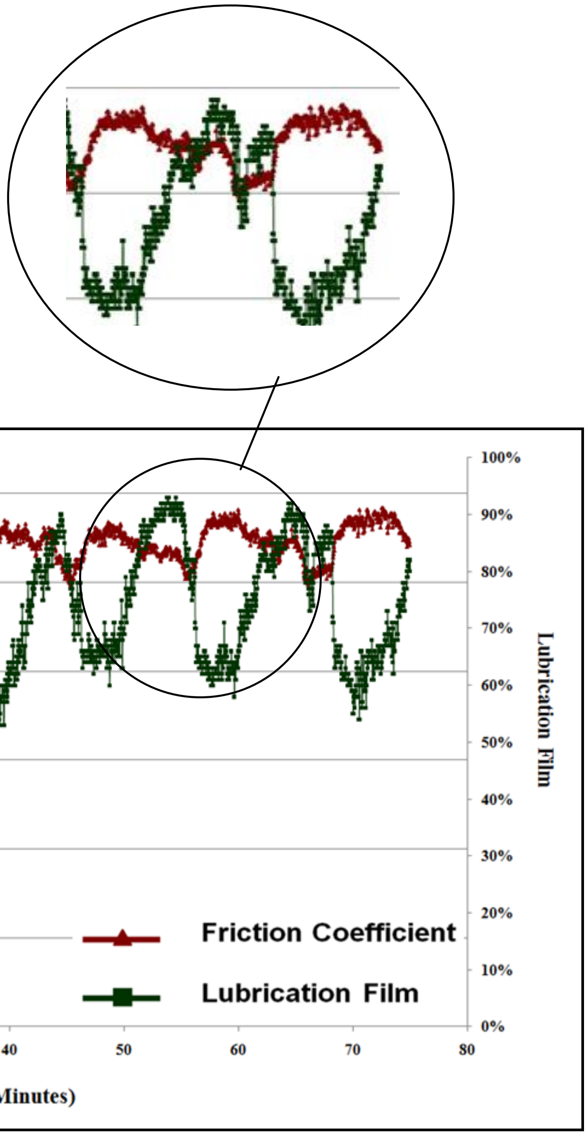


Figure 4.5-Inverse Relationship of Friction Coefficient and Lubrication Film coverage

2, 5-Dimethylfuran was stored in a dark cupboard at atmospheric condition for seven months to investigate on changes of lubricity properties of fuel after storage. Results on same DMF after seven months showed that the DMF lubricity properties were changed during storage. Results demonstrate lower average wear scar which means better lubricity properties for DMF. Figures 4.6 and 4.7 illustrate the friction coefficient and lubrication film percentage of the non-aged and aged sample of DMF with respect to time at 35–45% relative humidity and 25 ˚C.

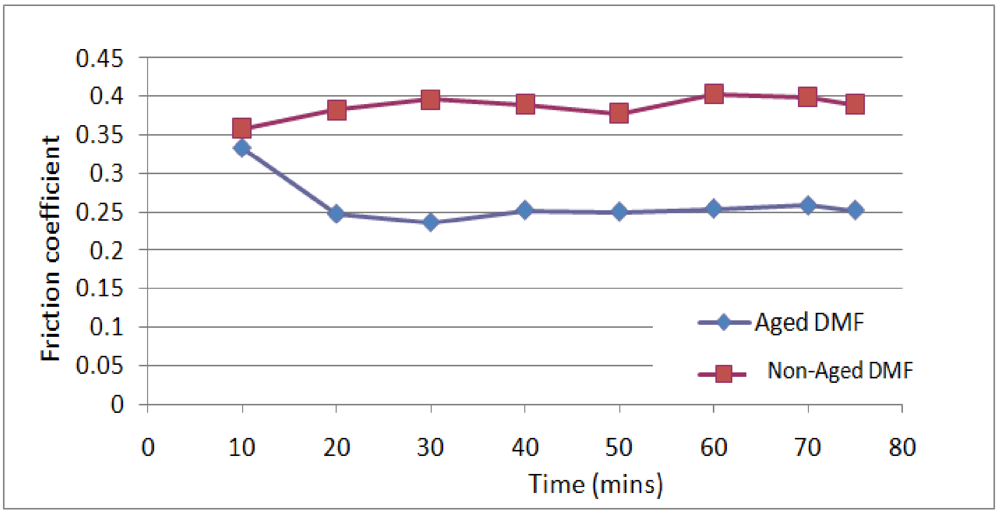


Figure 4.6-Comparison of friction coefficient of Non-Aged DMF and aged DMF

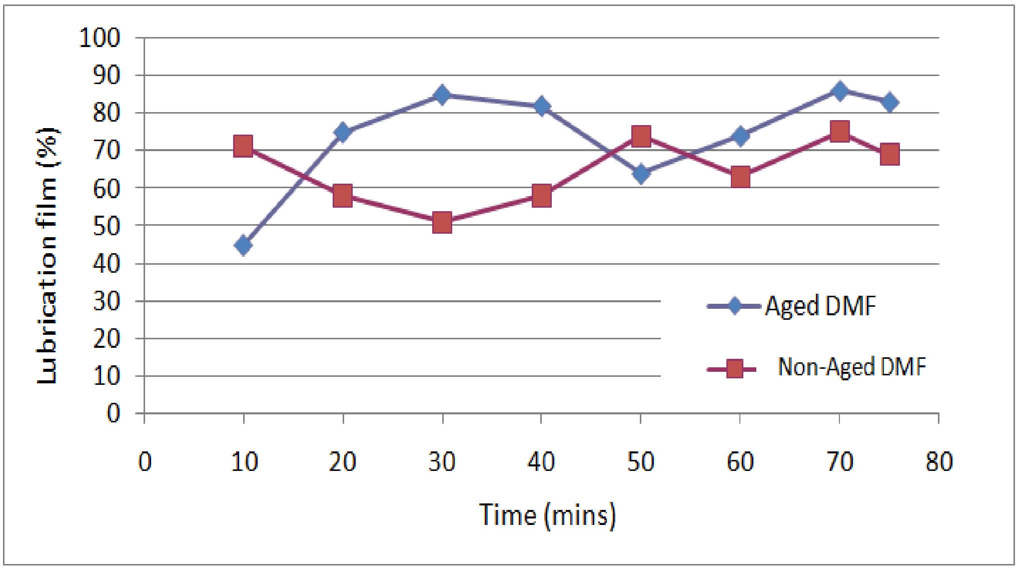


Figure 4.7-Comparison of lubrication film coverage of Non-Aged DMF and Aged DMF

The average lubrication film coverage has varied slightly from 65% to 68% and the average friction coefficient has decreased considerably by almost 30% after the seven months storage. The main reason for these chemical properties changes is likely to be the high volatility of DMF and also the effect of air-trapped in the bottle in which the DMF was stored. The wear scar was improved after seven months and for the aged DMF it is 28% smaller than for the non-aged DMF.

4.3. Validation of Results

In order to have report the correct data from the experiments all tests have been done three times and the average of the data was reported as the main result. Percentage of the error in the data was set to less than 5% and if the data from each test was out of the range the experiment was repeated. For illustration results of friction coefficient from DMF and Gasoline blends obtained from three different tests are shown in Figure 4.8. As it is illustrated the percentage of error is less than 5% and data were acceptable for report.

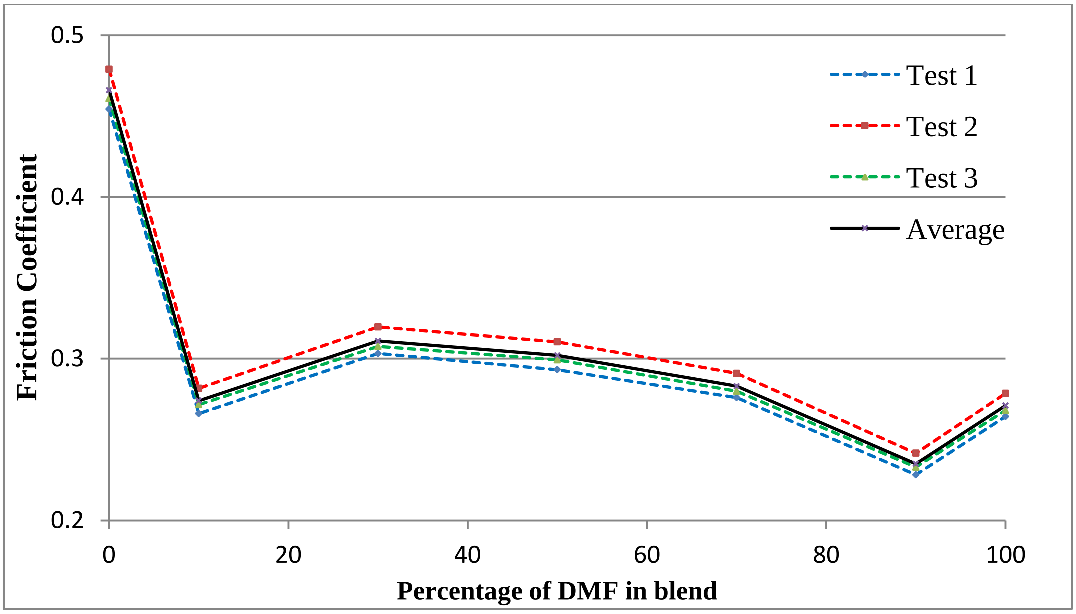


Figure 4.8-Illustration of error percentage in friction coefficient of DMF blends with Gasoline

Results obrained from experiments at University of Birmingham are in very good agreement with the results reported by Agudelo et al. (2011). They reported all tested Gasoline fuels had a wear scar diameter in the range of 700-850 μm and Ethanol wear scar diameter is 605 μm which are really close to the results obtained at University of Birmingham.

4.4. Summary

This chapter investigates comparison of lubricity of different fuels such as Gasoline, Ethanol and 2, 5-Dimethylfuran using High Frequency Reciprocating Rig (HFRR). Moreover, the effect of addition of different percentages of DMF (by volume) as a biofuel to Gasoline and Ethanol on lubricity property of these fuels were carried out

The results illustrate that DMF has the best lubricity among three fuels and friction coefficient was almost constant for pure DMF and Ethanol during the experiment.

The friction coefficient has an increasing trend for the Gasoline during the lubricity experiment that confirms poor lubricity of Gasoline.

Additions of DMF and Ethanol have improved lubricity of Gasoline drastically due to being oxygenated fuels. The DMF has enhanced lubricity of Gasoline more than Ethanol.

Inverse relationship between friction coefficient and lubrication film percentages was observed.

Aging of fuels were studied for their influence on lubricity. The aging of biofuels improved the lubricity more than non-aged fuels in the blends.

CHAPTER 5

5. GC-MS QUANTIFICATION OF C_3-C_7 HYDROCARBONS IN SI ENGINE EXHAUST FUELLED WITH ETHANOL, DMF, GASOLINE AND ISOOCTANE-TOLOUENE BLEND

5.1. Introduction

This chapter is focused on the impact of pure fuels which are used in engine for combustions such as Ethanol, DMF, unleaded Gasoline, Ethanol and Isooctane-Toluene blend The gases emitted on their combustion and their impact were extensively investigated and the engine used for this study was a single cylinder four stroke spark engine at two different indicated mean effective pressures i.e. 3.5 and 8.5 bar. The speed of engine was set at 1500 rpm and the engine was run at stoichiometric condition of $\lambda=1$. Quantitative analyses of gases were performed using gas chromatography/ mass spectrometry techniques and the species investigated were Propylene, Iso-Butene, 1-Butene, 1,3-Butedine, n-Butane, 3-Methyl-1Butane, Iso-pentane, n-Pentane, n-Hexane, Benzene and Toluene. A HORIBA-7100DEGR gas tower was used to identify the NO_x and THC concentrations presence in the exhaust gas. Exhaust samples were taken 0.3 m downstream of the exhaust valve and pumped via a heated line (maintained at 191 °C) to the analyzer.

Direct connection using a heated line to engine was made with GC/MS for exhaust gas sample transfer and an online method was employed. Changes of concentration of individual hydrocarbons (C_3-C_7) observed in results from various engine conditions and fuels used.

5.2. Results and Discussions

In Table 5.1, it is possible to see the illustrations of the NOx, total hydrocarbons (THC) and CO engine out emissions that were obtained for different fuels in two engine loads. By conducting repeated experiments, it was possible to extract reliable and constant HC emissions. The various kinds of fuels fed at operating engine conditions have the ability to affect the amount of total hydrocarbons. The lowest hydrocarbons emission can be observed for Ethanol at the two operating conditions. More NOx is produced if the combustions temperatures are set higher (Stone 1985) which is why it is believed that higher engine loads have the ability to produce higher isNOx (indicated specific NOx) (Payri et al. 2009).

The results also indicate that lower levels of isNOx are produced by Ethanol as compared to DMF and Gasoline. This is because of lower temperature levels and burning rate that takes place in the engine. The DMF has the ability to burn at a higher rate than Ethanol along with having a high combustion temperature which then produces isNOx emissions for 2, 5- Dimethylfuran which are near to those from Gasoline fuelling. The H/C ratio and isNOx amount could also prove to have an inverse relationship with each other. The lowest H/C ratio is present in DMF, which is why it could produce the highest levels of isNOx. On the other hand, Ethanol has been found to have the highest H/C ratio. Harrington and Shishu are the first researchers who came across this issue and reported it (Harrington and Shishu 1973).

Table 5.1-Measured emissions from exhaust at different loads (octane numbers should be given – earlier info does not mention Isooctane-Toluene)

Fuel	IMEP (bar)	CO (%)	isCO (g/kWh)	CO2 (%)	isCO2 (g/kWh)	HC (ppm)	isHC (g/kWh)	NOx (ppm)	isNOx (g/kWh)
ETH	3.561	0.563	21.697	14.420	860.872	291.724	1.846	412.407	1.816
	8.594	0.678	23.531	14.1	768.365	313.599	1.786	1452.573	5.757
ULG	3.554	0.731	33.645	15.813	825.564	615.275	7.685	1205.380	6.882
	8.461	0.721	30.856	14.630	758.661	488.636	5.215	1654.595	9.058
DMF	3.604	0.744	26.899	16.668	947.058	458.874	5.689	1120.103	4.630
	8.623	1.081	35.193	16.240	831.062	339.153	3.787	2504.388	9.320
Iso tol	3.565	0.723	27.197	14.822	876.176	537.553	14.877	559.683	2.406
	8.632	0.903	30.420	14.548	770.183	452.710	11.220	2781.131	10.707

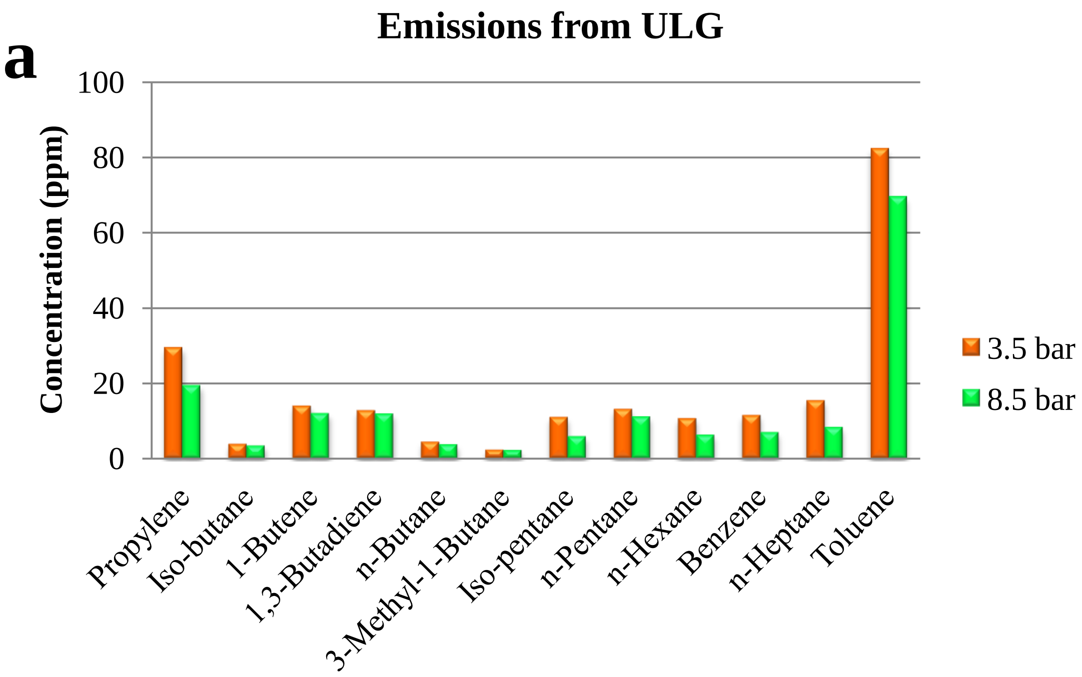
In the results that have been obtained for DMF, indicated specific total hydrocarbon emissons (isTHC) are very similar to those of Gasoline. Meanwhile, the isTHC emissions for Ethanol are much lower because of higher oxygen content in comparison with DMF which helps in oxidation of unburned hydrocarbons. Due to increased combustion temperature, the isTHC is reduced with increase of load from 3.5 to 8.5 bar IMEP for Ethanol. The only way possible to increase the efficiency of combustion is through the high rate of oxidation of hydrogen and carbon molecules. The results indicate that the trends of isTHC are similar to those of specific carbon monoxide (isCO2), as a conclusion it can be mentioned that as load increases, the isCO2 emissions become lower. Lower isCO emissions are produced due to high oxygen content present in Ethanol.

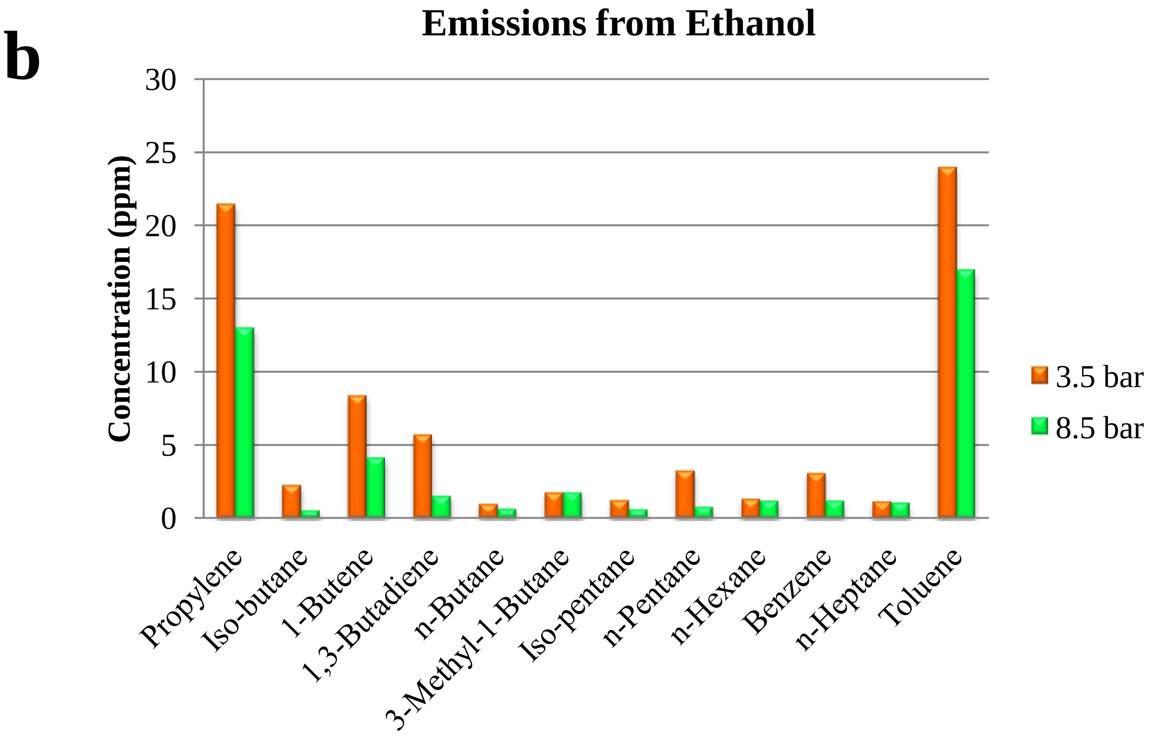
Carbon dioxide is a non-toxic gas, but it has the ability to affect global warming. Hence it is considered essential to analyze isCO_2 during the experiment. CO_2 emissions are reduced if load is increased and the biofuels can produce larger isCO_2 emissions as compared to Gasoline.

The n-Hexane, Propylene and n-Butane are the common compounds present in all the samples (Figure 5.1). Due to the fact that the exhaust gas has higher temperature at higher loads, the presence of 1-ButeneButene and 1, 3-Butadiene has been found there at lower levels. For lower loads, the NOx emissions are reduced and due to incomplete combustion, the HC emissions increase to a large extent.

It is generally believed that Benzene emissions are carcinogenic. Hence it is important to thoroughly analyze this component during the experiment. When engine load has been increased from 3.5 to 8.5 bar, the Benzene concentration present in the exhaust is reduced for all fuels. This can be clearly observed in Figure 5.1. The Ethanol usually produces lower level of Benzene emissions compared to ULG.

When compared to other kinds of fuels, it was found for the Ethanol combustion that Iso-pentane, n-Heptane, n-Hexane and n-Butane components have the lowest concentration level. When the load was increased, it is observed that nearly all components in emissions are reduced. However, the 3-Methyl-1-Butane and n-Hexane remained constant. Propylene and Toluene have shown high levels of concentration compared to other hydrocarbons for emissions from this fuel, which is present at both 3.5 and 8.5 engine loads. Table 5.2 presents individual hydrocarbon concentratios for each fuel at different engine conditions.


a
Emissions from ULG
Concentration (ppm)
100
80
60
40
20
0
Propylene
Iso-butane
1-Butene
1,3-Butadiene
n-Butane
3-Methyl-1-Butane
Iso-pentane
n-Pentane
n-Hexane
Benzene
n-Heptane
Toluene
3.5 bar
8.5 bar


b
Emissions from Ethanol
Concentration (ppm)
30
25
20
15
10
5
0
Propylene
Iso-butane
1-Butene
1,3-Butadiene
n-Butane
3-Methyl-1-Butane
Iso-pentane
n-Pentane
n-Hexane
Benzene
n-Heptane
Toluene
3.5 bar
8.5 bar

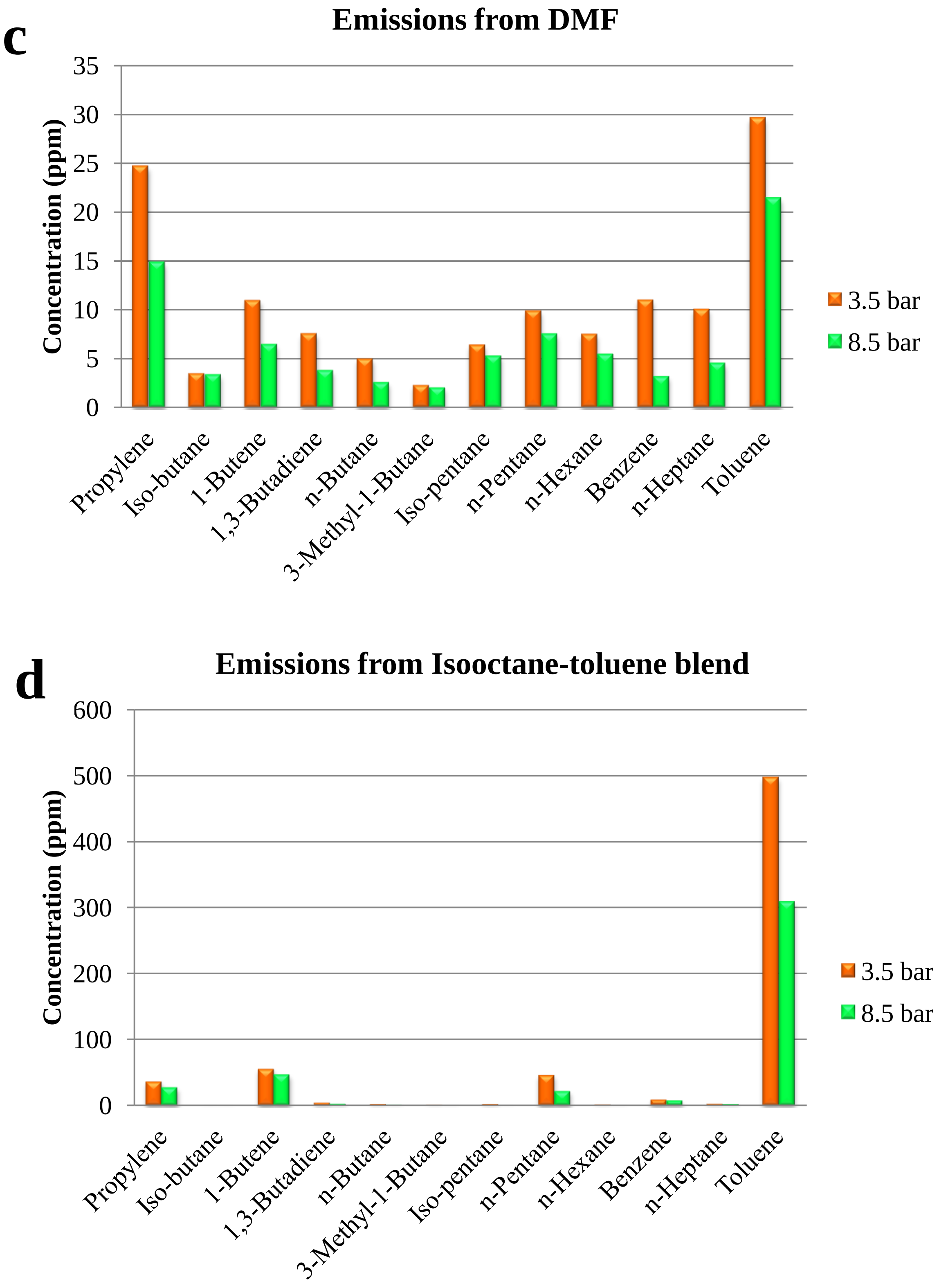


Figure 5.1-Measured hydrocarbon species for different fuels (a) Gasoline, (b) Ethanol, (c) DMF and (d) Isooctane-Toluene Blend

Table 5.2-Individual hydrocarbon concentrations for each fuel at low and high engine load (all in ppm)

	Ethanol		**DMF**		**ULG**		**Isooctane-Toluene blend**	
	3.5 bar	**8.5 bar**	**3.5 bar**	**8.5 bar**	**3.5 bar**	**8.5 bar**	**3.5 bar**	**8.5 bar**
Propylene	21.437	12.973	24.670	14.858	29.468	19.480	36.563	27.845
Iso-butane	2.294	0.579	3.498	3.378	3.919	3.471	0.716	0.651
1-Butane	8.408	4.159	10.962	6.469	14.013	12.057	55.526	47.195
1,3-Butadiene	5.737	1.565	7.573	3.813	12.811	11.943	4.347	2.833
n-Butane	1.010	0.686	4.99	2.573	4.466	3.7693	2.138	1.213
3-Methyl-1-Butane	1.807	1.792	2.279	2.053	2.366	2.238	1.290	0.913
Iso-pentane	1.274	0.632	6.405	5.297	11.000	5.897	2.336	0.737
n-Pentane	3.286	0.814	9.909	7.554	13.125	11.213	46.462	22.043
n-Hexane	1.363	1.223	7.523	5.467	10.668	6.380	1.629	0.845
Benzene	3.117	1.239	10.997	3.212	11.564	7.083	8.9633	8.018
n-Heptane	1.193	1.098	10.078	4.572	15.475	8.372	2.671	2.415
Toluene	23.925	16.911	29.624	21.421	82.176	69.457	497.267	308.752

The DMF tests that have been carried out show that for a 3.5 bar IMEP load highest levels of concentration were present for Propylene, 1-Butene, Benzene and Toluene. On the other hand, for 8.5 bar IMEP the lowest levels of concentration were present for n-Butane and 3-Methyl-1-Butene. Generally, the Toluene and Propylene concentrations were highest in the exhaust gas, followed by 1-Butene, n-Pentane and n-Heptane components at both loads.

The highest concentrations of individual hydrocarbons in exhaust gas were present with Gasoline fuelling, which is the most common fuel for petrol engines. It is observed in the results that this fuel generates higher levels of most individual HC gaseous emissions as compared to others. A downward trend is observed when the engine load is increased and a 46% decrease is observed in the emission of n-Heptane and Iso-pentane components.

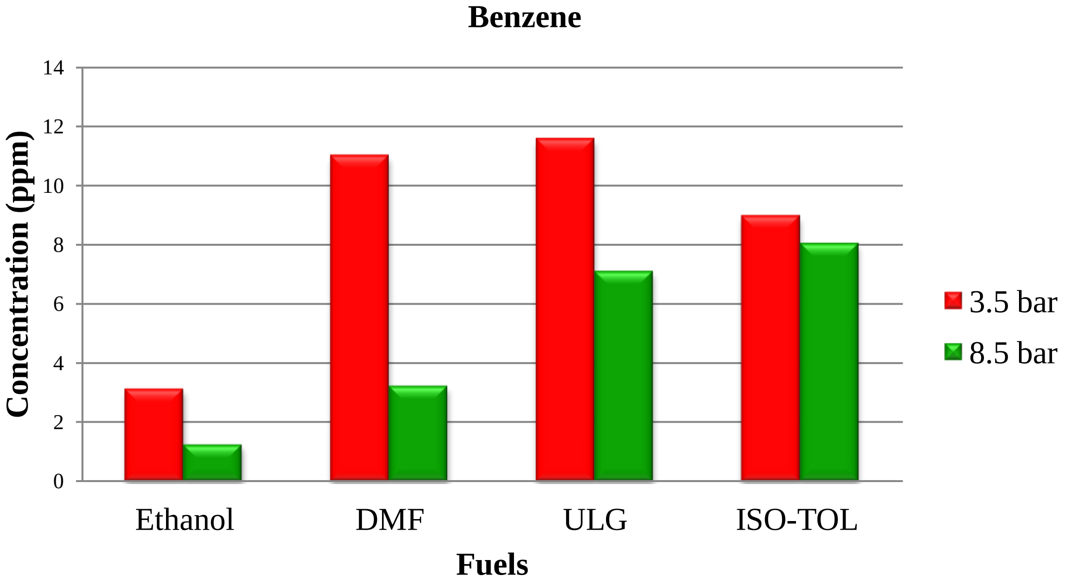
The Toluene concentration in the Isooctane-Toluene blend was much higher than the rest of the fuels.

The incomplete combustion of alkanes in the fuel causes an increase in alkenes like Propylene and 1-Butene in the exhaust. The results provided by Hasan et al. (2011) explain that due to higher combustion temperatures, the concentrations of Propylene at 8.5 bar were greater than during 3.5 bar engine load. This is because of the higher temperatures that cause the transformation of the paraffinic species into olefins by the abstracting of the H-atom.

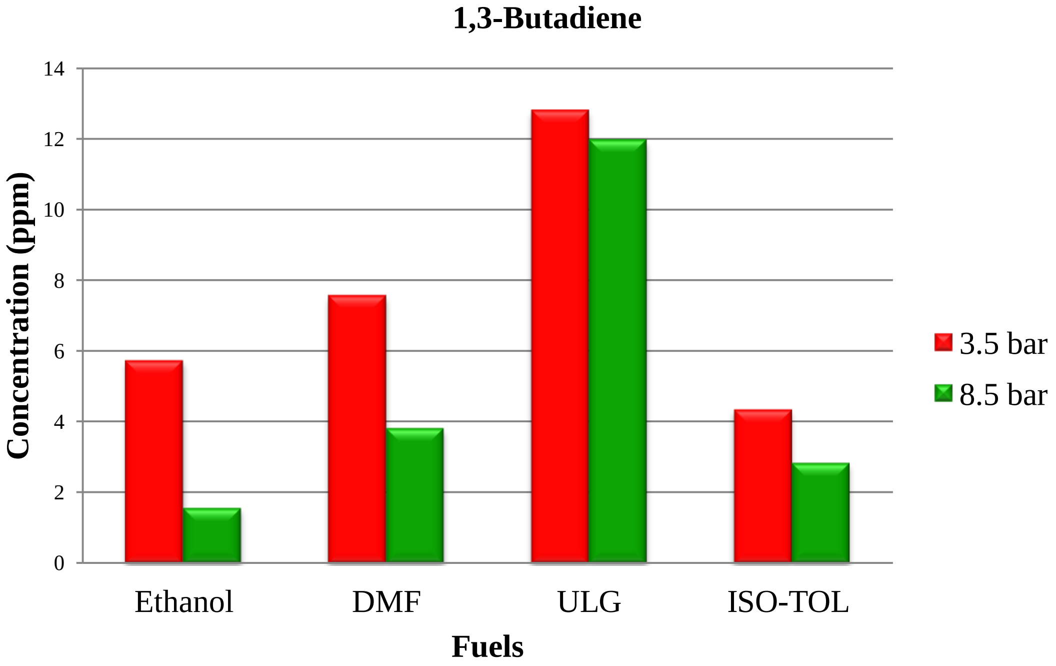
A by-product of partial HC oxidation is the 1, 3-Butadiene. The 1, 3-Butadiene is a photo-chemically reactive unregulated hydrocarbon. This reactivity is a unique property of it as other hydrocarbons do not display it.

Figure 5.2 demonstrate comparison of concentrations of hydrocarbons for different fuels and operating conditions.

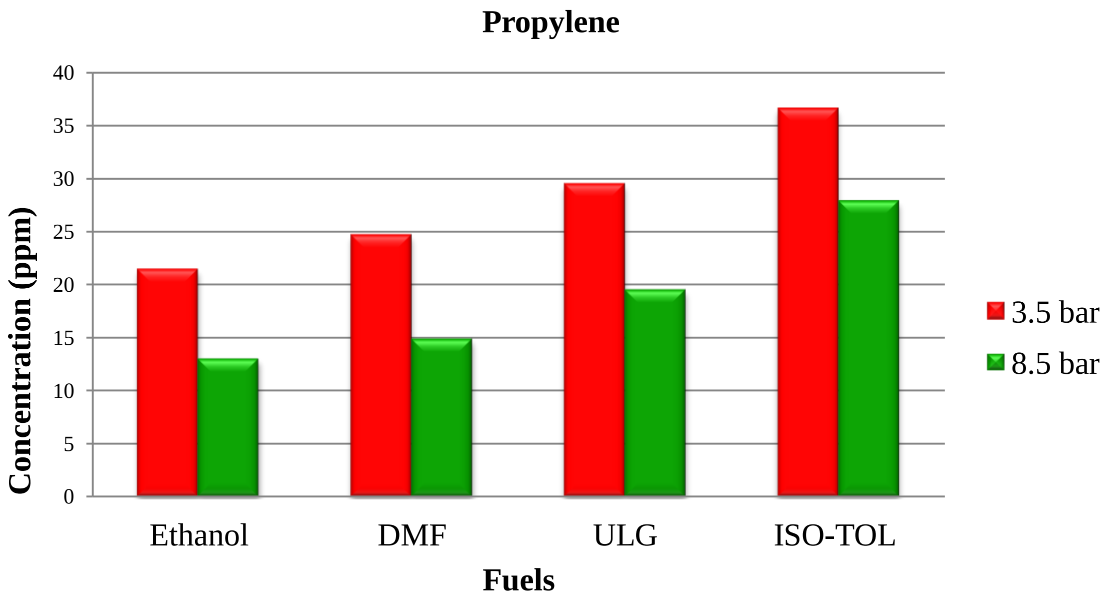
a


Benzene
Concentration (ppm)
14
12
10
8
6
4
2
0
Ethanol
DMF
ULG
ISO-TOL
Fuels
3.5 bar
8.5 bar

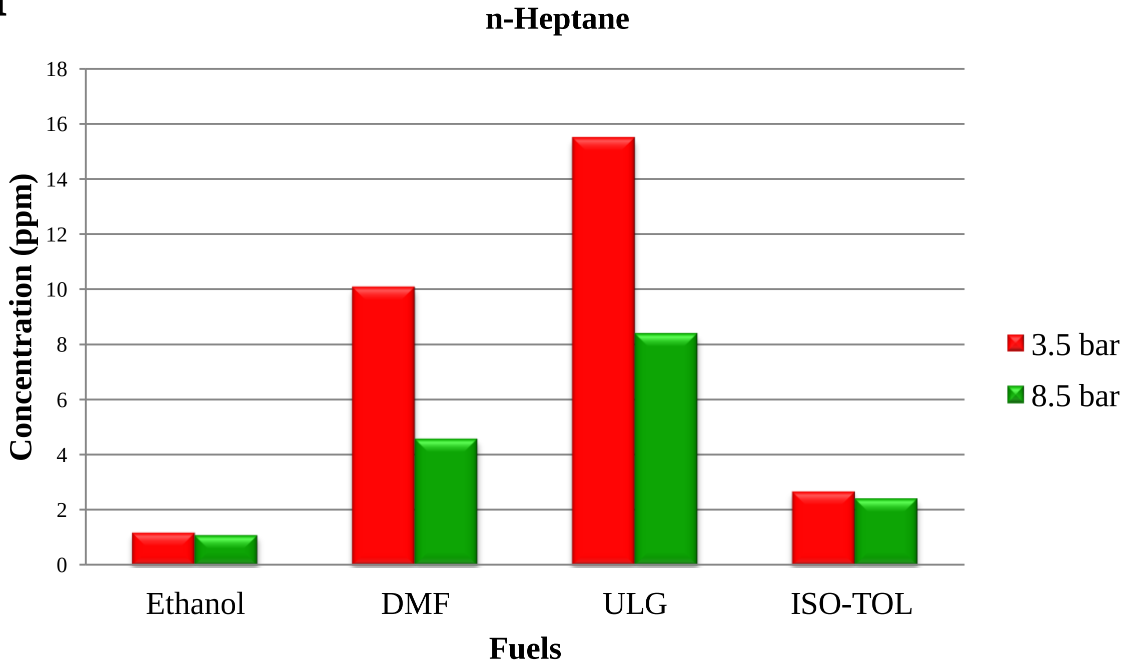
b

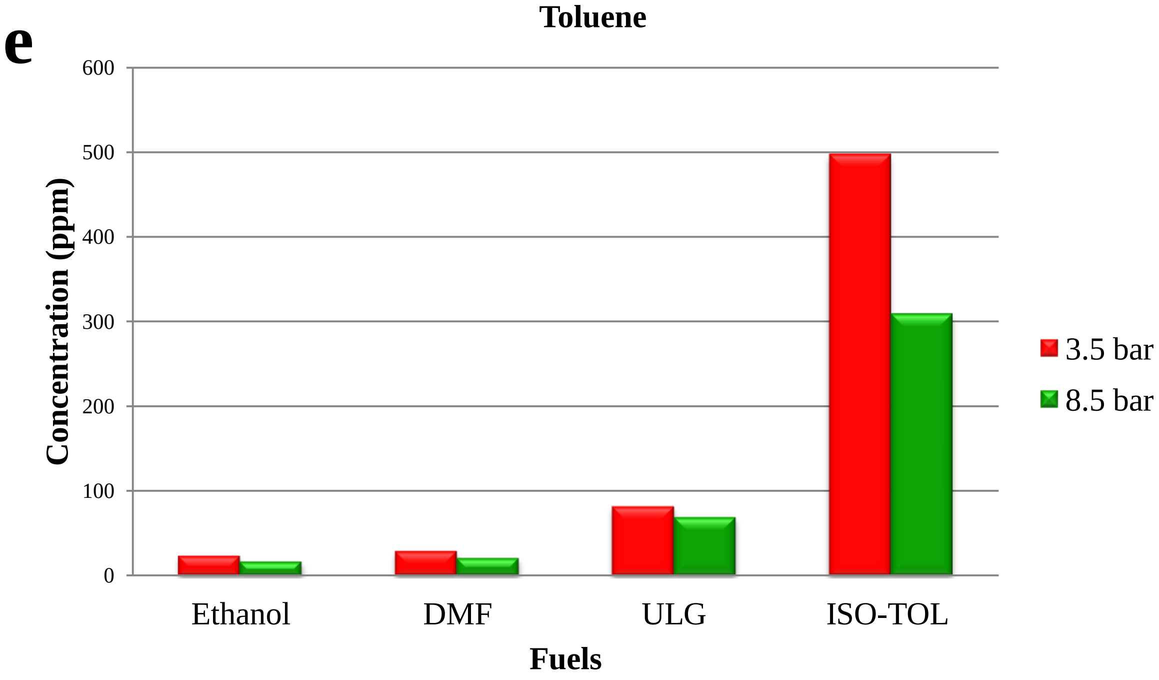

1,3-Butadiene
Concentration (ppm)
14
12
10
8
6
4
2
0
Ethanol
DMF
ULG
ISO-TOL
Fuels
3.5 bar
8.5 bar

c


Propylene
Concentration (ppm)
40
35
30
25
20
15
10
5
0
Ethanol
DMF
ULG
ISO-TOL
Fuels
🟥 3.5 bar
🟩 8.5 bar

d


n-Heptane
Concentration (ppm)
18
16
14
12
10
8
6
4
2
0
Ethanol
DMF
ULG
ISO-TOL
Fuels
🟥 3.5 bar
🟩 8.5 bar



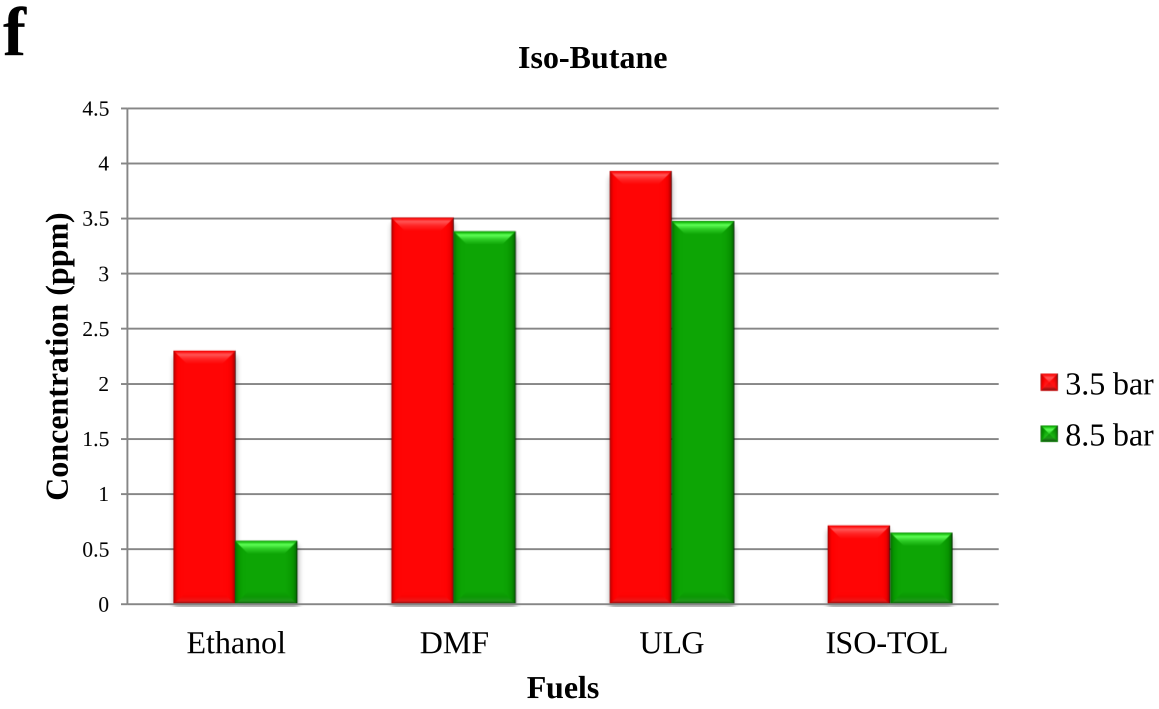


Figure 5.2-Comparison of individual hydrocarbon concentrations for different fuels at low and high engine load (a) Benzene, (b) 1, 3-Butadiene, (c) Propylene, (d) n-Heptane, (e) Toluene, (f)Iso-butane

This photo-chemical reactivity of 1,3-Butadiene is a unique property of it as other unregulated hydrocarbons does not possess it (Filser and Bolt 1984). In the engine exhaust, 90% of the 1, 3-Butadiene comes from general alkanes and aromatic content present in the fuel. According to the classification by the US environmental protection agency (EPA), the 1,3-Butadiene is considered as a probable human carcinogen because it is grouped as B2 carcinogen (US-EPA 1990b). The alkenes are not effectively oxidised or decomposed when combustion temperature is relatively low. Therefore, the maximum 1,3-Butadiene evolved during the lower engine load operation as the temperatures of combustion were comparatively lower at 8.5 bar IMEP load.

The incomplete combustion of Toluene, alkylbenzenes and xylenes results in dealkylation which produces Benzene (Johnson et al. 2007). The chances of acute myeloid leukaemia increases when 1-5 ppm is exposed for many years in ambient air according to the conclusion of the risk assessment conducted by Johnson and his team (2007). Benzene is said to be a human carcinogen (group 1), taking into the consideration the epidemiological evidence by IARC, the international agency for research on cancer (IARC 1987). Higher post-flame oxidation results in highest concentrations of Benzene. Therefore, at higher loads Benzene formation is preferential for Toluene combustion (Johnson et al. 2007). This is proven by the evidence that in the engine operating at 3.5 bar, engine fuelled with Gasoline, the Benzene concentration ranged from 1 ppm to 11.5 ppm (shown in Table 5.2, as the post-flame oxidation increased. This concentration is the highest for such an engine operation (Villinger et al. 2002).

The influences over health of short-term exposure for Toluene are not yet identified, however, long-term exposure effects are well-recognized (Kostrzewski and Piotrowski 1991). As the structure of Toluene is similar to that of aromatic structure, thus its formation is generally related to Benzene, despite the fact that Toluene is a non-carcinogen (category: 3A). Evidence by Schuetzle (1994) supports it as when the Toluene or Xylene is added to the Gasoline fuel, the Benzene emissions are witnessed.

The Toluene quantities in emissions ranged between 17 ppm and 497 ppm. These highest and lowest points of the Toluene emissions were observed in the Isooctane-Toluene blend at 3.5 bar and Ethanol at 8.5 bar, respectively. As compared to the other compounds of this group, the concentration of Toluene remained constantly higher throughout various tests.

The quantities of every constituent of the exhaust helped in calculating the percentage changes of the sum of speciated 12-components emissions in various fuels at 3.5 bar and 8.5 bar engine load. The outcomes for fuels were 30% decrease for unleaded Gasoline, with 70%, 60% and 56% decrease for Ethanol, DMF and Isooctane-Toluene blend respectively. Therefore, it shows that for Ethanol, the alteration of the engine load is of greater significance compared to other fuels (see Figure 5.3).

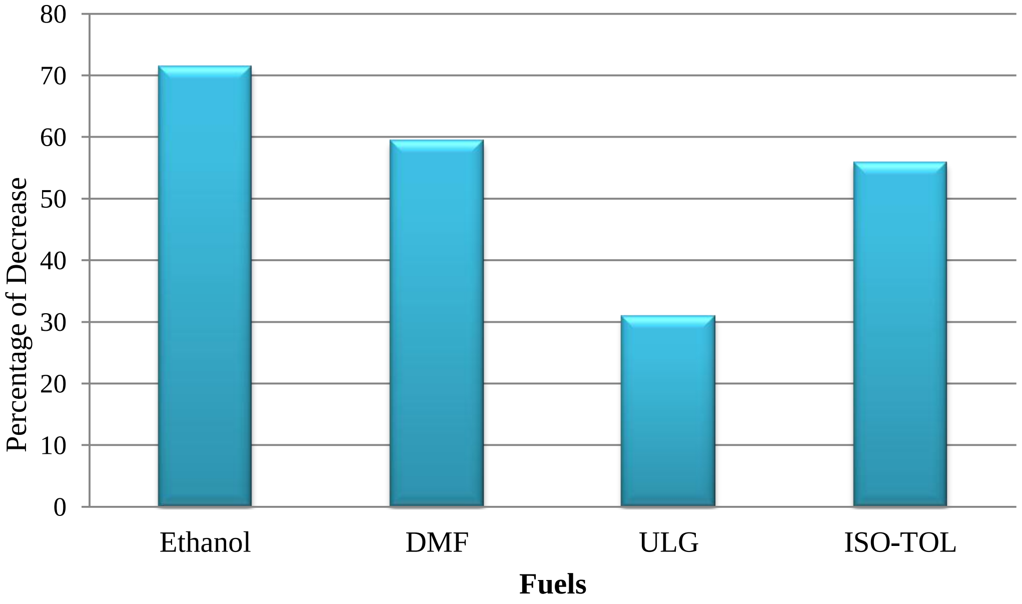


Figure 5.3-Percentage of total emissions decrease between 3.5 and 8.5 bar IMEP engine loads

At lower loads, Ethanol produces low amounts of CO. The level of CO emissions trend is similar for DMF. At higher engine load as the heating value of Ethanol is relatively lower (and enthalpy of vaporization is much greater) , thus, greater time is required to mix large quantity of Ethanol with air, otherwise the mixture of Ethanol and air will not be of good quality. A thorough mixing is required within a short span of time when the fuel is injected. The mixing process with even more Ethanol remains poorer due to weak turbulence level in the cylinder at low engine speeds (1500) and low loads (Zhong et al. 2010). This has been observed by many researchers (Zhong et al. 2010, Daniel et al. 2011). However, the emissions by Ethanol were the lowest, throughout the tests. Lower combustion temperature produces lower THC emissions indicating complete combustion. The importance of using oxygenated biofuels is shown in Table 5.1 by the level of CO emissions. The CO emitted level of Gasoline is higher than that of the DMF.

Lower emissions of engine running on Ethanol can be expressed by the fact that the combustion temperature is lower and it is more complete.

Also lower indicated specific CO level was measured compared with Ethanol when oxygenated biofuel (DMF) was applied As mentioned before, lower total hydrocarbon (THC) emissions were measured at low engine loads when Ethanol was used this can be compared with the result from Gasoline and DMF. These numbers increased rapidly by increase in engine load. Increase in engine load will result in higher in-cylinder temperature and subsequently oxidation of unburned Gasoline and DMF compounds. Lower HC level in exhaust emission when using Ethanol can be expressed by more complete combustion and promoted oxidation reaction which are because of excess oxygen in the fuel. As DMF contains 16.67% oxygen by mass, the level of total unburned hydrocarbons in the exhaust is between Gasoline and Ethanol. High combustion temperatures result in the formation of NOx. Table 5.1 shows the NOx emissions for the DMF, Gasoline and Ethanol. The total HC emissions and NOx emissions are inversely related to each other.

The overall temperature behavior in the experiment finally results in the engine-out NOx emission (Zhong et al. 2010). Low NOx emissions are produced by the Ethanol combustion in the overall full-load range. The higher NOx emissions are a result of the lower heat of vaporization of the DMF when compared to Ethanol. Thus according to Table 5.1, the lower NOx concentration is related to the lower cylinder pressures and exhaust temperatures associated with Ethanol.

5.3. Validation

It is essential that the experiments are performed in a way in which the obtained results and conclusions drawn can be considered acceptable and reliable.

5.3.1. Validating the Experimental Process

The procedure of obtaining the results has been comprehensively described within the sections of this project; still there is a possibility that errors may occur. Extra care was taken to make sure that fuel samples did not become contaminated with more impurities or combined with other fuels. Compressed air was used to clean all of the equipment. The contamination of the fuel used within the engine was more difficult to prevent because the engine lab could not be controlled as easily. The reason can be explained as the engine being used for various types of fuel testing. The adverse impact of the fuel would be within injectors and cylinder of the engine as this area was unreachable for nitrogen purging and evaporation of fuel using the compressed air. However, as fuel was pressurized when using the GDI system, these impurities and remaining fuels would not be able to travel back along the pipe to reach the fuel source within the tank. For that reason, as the engine was run for more than ten minutes prior to each test being carried out, any remained fuel within these areas would already passed through pipes and burn in the engine and would have been pumped out of the exhaust manifold. Therefore, contamination of the fuel is very unlikely, and any corruption that did occur would not have affected the results.

Moreover, prior to each test, the heated line and sample loop and the multiport Valco valve were cleaned to remove pervious test samples. Before injecting the sample in GC-MS,5 minute delay was used considered to be sufficient for all heated line and sample loop areas to become full of the tested exhaust gas sample. Due to mentioned reasons, the results obtained are considered to be accurate and valid.

5.3.2. Validating the analysis of the Results

Much care considered to ensure correct identification of the mass spectra as misidentification could result in inaccurate conclusions being drawn from the experiment. The most accurate and popular method is the use of a reference gas (calibration gas), this would contain known compounds (13 compounds) and of known quantities (50 ppm of each).

This would be quick and reliable way to identify compounds through comparison of retention times; moreover, it would enable quantitative analysis as exact quantities of the various compounds within the reference gas would be known. Thus prior to each daily test, the GC-MS was calibrated by using standard gas bottle with known components.

In general, it is considered that all of the compounds that were identified so correctly as shown in Figure 3.17. The main reason for this is use of the most reliable method that is using a reference gas and comparing retention times.

5.4. Summary

This chapter highlights comparison of the regulated and unregulated emission of different fuels such as Gasoline, Ethanol, 2, 5-Dimethylfuran and isooctane toluene blend (2:1) in single cylinder spark ignition engines.

The results showed that regulated emissions of pure Gasoline such as CO, CO_2 and THC were really similar to DMF emissions. Higher oxygen content of Ethanol results in oxidization of unburned hydrocarbons and lower HC. The most important factors in production of highly toxic hydrocarbons are engine operating modes.

The results demonstrate that at higher load individual species such as Benzene, 1-Butene and 1, 3-Butadiene were present in emitted hydrocarbons with concentrations up to 30ppm.

Aromatics have a ring structure with carbon-carbon double bond that makes them stable during combustion process and aromatics components such as Toluene remains unburned fuel in exhaust emission.

The major hydrocarbons at lower load are alkanes and the main components at higher load are alkene. Aromatics or heavier hydrocarbons such as Toluene and Benzene were found to be more stable at lower load due to lower combustion temperature.

The results were validated using standard gas bottle, reliable and repeatable method.

CHAPTER 6

6. VOLATILE HYDROCARBON (C_3-C_7) SPECIATION AND QUNATIFICATION OF ENGINE EXHUST RUNNING ON 2, 5-DIMETHYLFURAN AND ETHANOL IN BLENDS WITH GASOLINE

6.1. Introduction

The purpose of this part of the study is to experimentally investigate the effect of Ethanol and 2, 5-Dimethylfuran (DMF) addition to Gasoline on regulated and unregulated exhaust emissions from single cylinder direct-injection spark ignition engine. Experiments were conducted with blends containing 10 and 30 volume percentages of Ethanol or DMF. The single cylinder engine was operated at low and high loads (3.5 and 8.5 bar IMEP), constant speed of 1500 rpm and stoichiometric air/fuel ratio for each blend. This study has mainly focused on speciation and quantitative analysis of individual hydrocarbons in the range C_3-C_7 in exhausts emissions using gas chromatography-mass spectrometry (GC-MS).

6.2. Fuels and their blends

Table 3.5 presents the properties of fuels in this study. The test fuels used in this study were 97 research octane number (RON) commercial Gasoline and the bio-Ethanol both supplied by Shell Global Solutions UK. The DMF with purity of 99.8% was provided by Shijiazhuang Lida Chemical Co. LTD in China. The blends tested include DMF blends of 10% and 30% by volume (denoted as D10 and D30), and

Ethanol blends of 10% and 30% (E10 and E30). The fuels used are all relatively high-octane. The octane number of Ethanol used in this study is reported to be larger than Gasoline around 106. Blend octane number generally decreases with increasing octane number of the base fuel and with increasing blend percentage of the additive (Nisbet 1946). The experiments were performed at constant injection timing of 280 °bTDC and stoichiometric air/fuel ratio (λ=1) and fixed valve timing (see Table 3.2). In this study, free piston accumulator, which was used to deliver the fuel, was pressurized to150 bar with nitrogen (oxygen free) bottle. The ETAS LA4 lambda meter is used to set fuel stoichiometric AFR, H/C and O/C ratios as mentioned in Table 3.5.

6.3. Results and Discussion

6.3.1. CO Emissions

Generally, the indicated specific carbon monoxide emissions (isCO) decrease as load increases. At 8.5 bar IMEP, the Ethanol-Gasoline blends (for all contents of Ethanol) have the lowest isCO emissions in comparison with 2, 5-Dimethylfuran (DMF) at the same load, this is due to higher oxygen content and combustion efficiency of Ethanol (Daniel et al. 2011). Figure 6.1 illustrates the indicated specific (is) CO emissions for three different percentage contents of Ethanol and DMF in the Gasoline, investigated in both low and high engine load (3.5 and 8.5 bar IMEP). It is obvious from Figure 6.1 that the isCO (in g/kWh) decreases with increase in content of DMF and Ethanol percentage. As shown in Figure 6.1, the CO emissions at low load using D10, D30, E10 and E30 decreased by 10.76%, 15.06%, 13.91% and 18.60% respectively in comparison with Gasoline. At high engine load (8.5 bar

IMEP) the isCO emissions of D10, D30, E10 and E30 decreased by 8.27%, 9.45%, 14.61% and 15.98%, respectively.

Table 6.1 illustrates the results for indicated specific emissions of CO, CO_2, THC and NOx measured using Horiba MEXA 7100 and recalculated for g/kWh (indicated work).

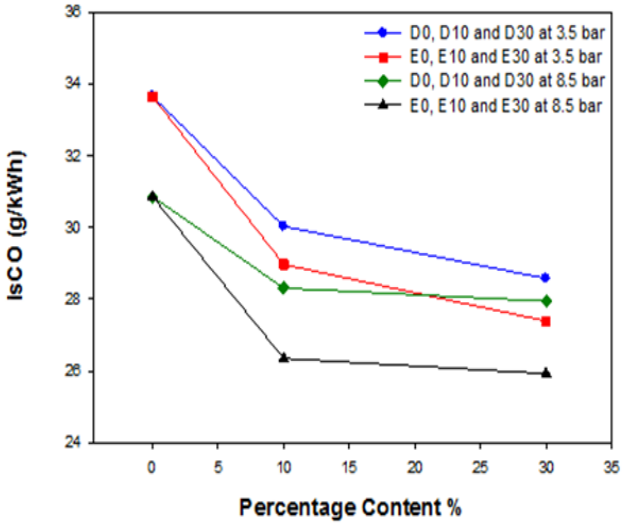


Figure 6.1- Indicated specific emissions of carbon monoxide (CO) for three percentage contents (volumetric) of DMF (D0, D10, D30) and Ethanol (E0, E10, E30) at two different loads (3.5 and 8.5 bar IMEP)

6.3.2. CO_2 emission

Carbon dioxide is not considered as a toxic gas and pollutant engine emission, but it is one of the main components that contribute to greenhouse effect. At 3.5 bar IMEP, The $isCO_2$ emissions of DMF-Gasoline blends decreased with increasing content of DMF and Ethanol. Figure 6.2 represents the relation between the $isCO_2$ emissions and three different percentages (Vol%) of Ethanol and DMF blended with Gasoline. It is evident from Figure 6.2 that, the specific $isCO_2$ emissions decrease as the Ethanol and DMF percentage in fuel blends increases. At low engine load, the $isCO_2$ emissions for D10, D30, E10 and E30 decrease by 0.6%, 3.4%, 2.61% and 4.58%, respectively.

The indicated specific CO_2 emissions at high load (8.5 bar IMEP) using D10, D30, E10 and E30 blends are reduced by 1.5%, 2.89%, 2.61% and 7.64%, respectively.

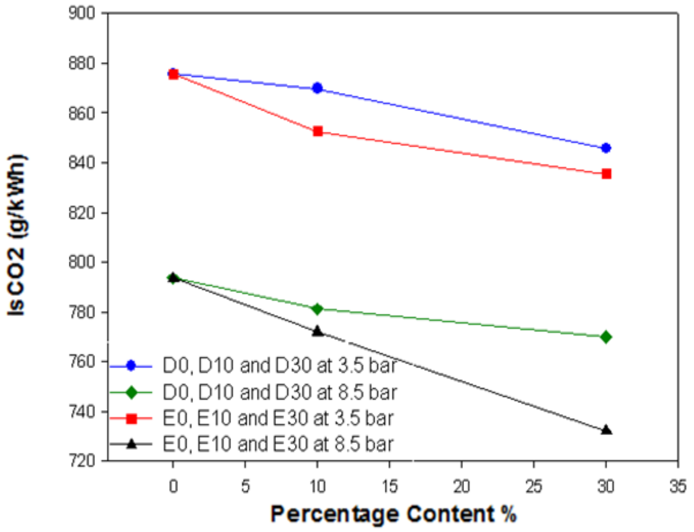


Figure 6.2- Indicated specific emissions of carbon dioxide (CO_2) for three percentage contents (volumetric) of DMF (D0, D10, D30) and Ethanol (E0, E10, E30) at two different loads (3.5 and 8.5 bar IMEP)

6.3.3. THC Emissions

Ethanol contains higher oxygen content compared with DMF and that is why Ethanol-Gasoline blends caused to produce the lowest isTHC emissions. The THC emissions decrease with increase of load; this is due to higher combustion temperature at higher load. HC emissions for three different percentage contents of DMF and Ethanol in Gasoline, at both low and high engine load are illustrated in Figure 6.3. It can be seen that when the Ethanol and DMF percentages increase, the specific emissions of unburned HC decrease. As illustrated in Figure 6.3, HC emissions at low load using D10, D30, E10 and E30 decreased by 3.75%, 5.87%, 9.32% and 19.5%, respectively in comparison with pure Gasoline.

The HC concentrations at high load using D10, D30, E10 and E30 decreased by 3.43%, 13.05%, 9.69% and 24.79%, respectively relative to pure Gasoline.

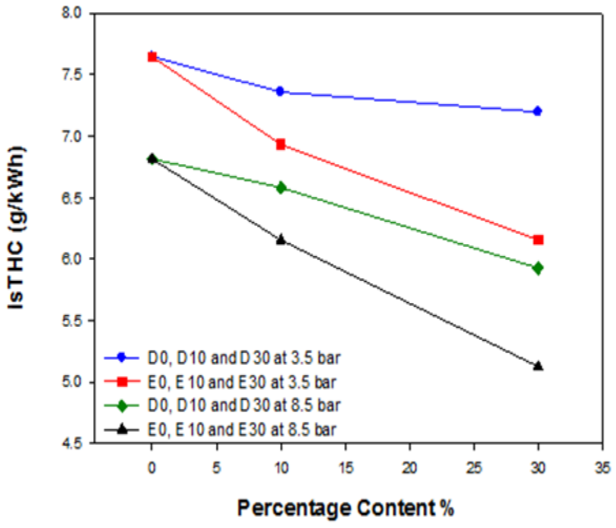


Figure 6.3- Indicated specific emissions of carbon dioxide (CO2) for three percentage contents (volumetric) of DMF (D0, D10, D30) and Ethanol (E0, E10, E30) at two different loads (3.5 and 8.5 bar IMEP)

6.3.4. NOx Emissions

It is obvious that NOx production increases with load. The isNOx emissions are directly associated with combustion temperature. (Laowagul and Yoshizumi 2009). At each load the addition of Ethanol caused to produce lowest isNOx emissions due to lower combustion temperature of Ethanol.in comparison to Gasoline and DMF. Ethanol decreased NOx emission for E10 and E30 by 2.96% and 6.21%, respectively, in comparison to Gasoline. Considering the NOx emission from DMF blends, Figure 6.4 demonstrates that the isNOx emissions increase with the increase of DMF percentage in the blend. Indicated specific NOx emissions increase with load. The specific NOx emissions at low load using D10 and D30 DMF blends are increased by 3.97%, 11.26% respectively compared with pure Gasoline. The NOx emissions at high load using D10 and D30 are increased by 7.65% and 11.99% respectively relative to Gasoline. In contrast, E10 and E30 decreased isNOx emissions by 1.33% and 4.10% respectively. Table 6.1 illustrate indicated specific regulated emissions at 3.5 and 8.5 bar IMEP.

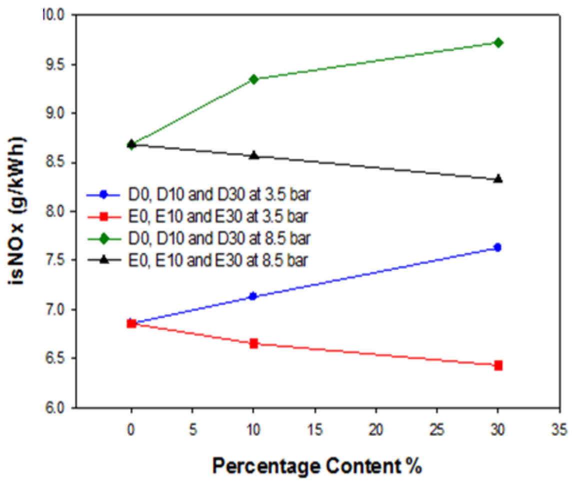


Figure 6.4- Indicated specific emissions of oxides of nitrogen (NOx) for three percentage contents (volumetric) of DMF (D0, D10, D30) and Ethanol (E0, E10, E30) at two different loads (3.5 and 8.5 bar IMEP)

Table 6.1- Indicated specific regulated emissions at different loads

Fuel blends	isCO (g/kWh)		isCO2 (g/kWh)		isTHC (g/kWh))		isNOx (g/kWh)	
	3.5 bar	8.5 bar	3.5 bar	8.5 bar	3.5 bar	8.5 bar	3.5 bar	8.5 bar
Gasoline	33.64512	30.85642	875.5640	792.6615	7.64541	6.81545	6.85452	8.68111
E10	28.96282	26.34583	852.6275	771.9443	6.93264	6.15496	6.65133	8.56536
E30	27.38481	25.92282	835.4582	732.0734	6.15451	5.12565	6.42815	8.32475
D10	30.02227	28.30268	869.7878	781.1364	7.35807	6.58607	7.12648	9.345485
D30	28.57543	27.93979	845.6275	769.7445	7.19604	5.92559	7.62666	9.72212

6.3.5 Speciation of C3-C7 Hydrocarbons

Figure 6.5(a) compares the concentration of hydrocarbons species for Gasoline, D10 and E10 blends for low engine load (approximately 3.5bar). It is clear that addition of 10% DMF to Gasoline decreased the concentration of all individual hydrocarbons (the results were noticeably below those for Gasoline). The highest reduction occurs for n-Pentane by approximately 16.5% and the lowest decrease was for Toluene (nearly 4.44%). According to results presented in Figure 6.5(a), the concentrations of exhaust species dropped significantly for the 10% Ethanol-Gasoline blend as compared with Gasoline. The highest decrease happened for n-Pentane - by 68.11% and the lowest was for 3-methyl-1Butane (approximately 1.35%). Figure 6.5(b) illustrates the results of hydrocarbon speciation in emissions for the same fuel blends at higher engine load (8.5 bar IMEP). These results present the effect of engine conditions on exhaust hydrocarbon speciation. It is found that the concentrations of all individual hydrocarbons for the 10% DMF-Gasoline blend diminish significantly when compared with Gasoline. The biggest reduction occurs for n-Pentane with reduction of 48.92% and the lowest decrease is for 1-Butene (about 3.78%).

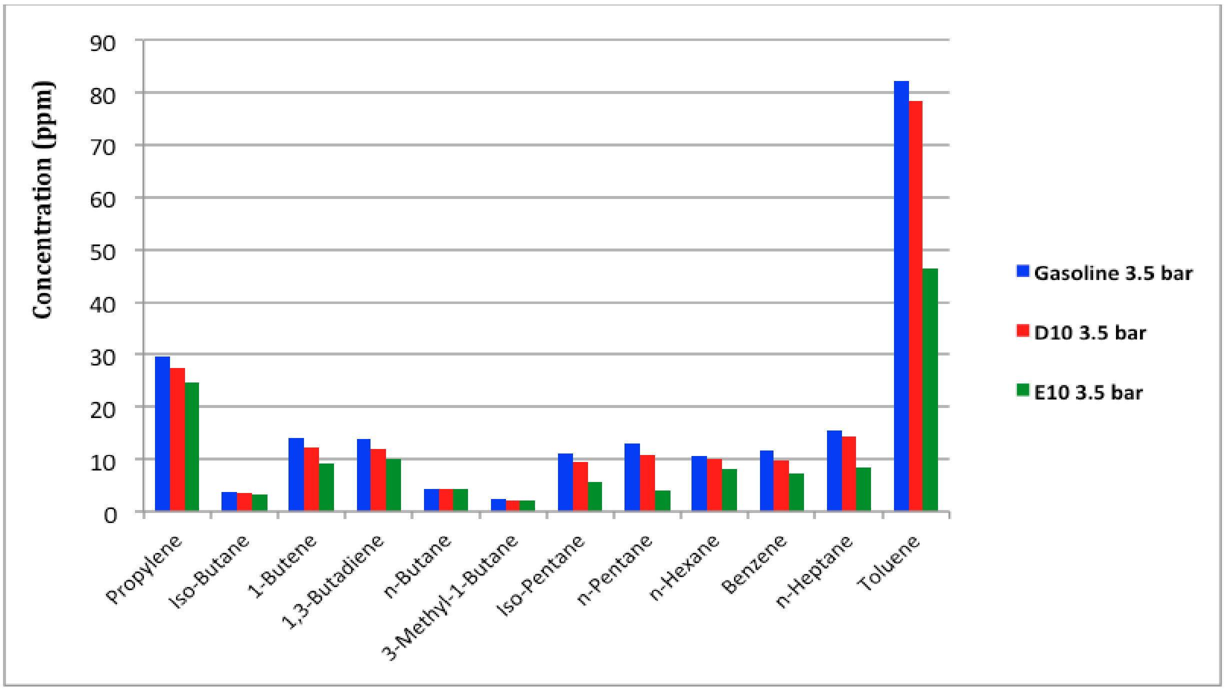
Adding 10% Ethanol to Gasoline resulted in dramatic reduction in concentration of all hydrocarbons; the highest reductions happen for Toluene and n-Pentane with the amount of 71.36% and 69.48% respectively and the lowest decrease is for n-Butane and n-hexane (just under 8%). It was concluded that for both high and low engine loads addition of Ethanol and DMF resulted in change of concentrations in hydrocarbon species. Both the DMF and Ethanol blends decreased concentration of all hydrocarbons for low and high loads. Reductions in concentrations were more significant with the addition of Ethanol to the blends and it was found that for high engine loads these concentrations decreased even more compared with results from low engine loads. Addition of just 10% DMF to the blends was found to be less effective in terms of reduction of speciated hydrocarbons.

Figure 6.5(c) represents the concentration of hydrocarbons for Gasoline, D30 and E30 blends at low engine load (3.5bar IMEP). It can be observed that by adding 30% DMF to Gasoline the concentration of all individual hydrocarbons fall noticeably, except for n-Butane, which displays a rise of 14.6%. The biggest reductions occur for Propylene, Iso-pentane and n-Pentane with 42% drop and the lowest decrease is for 3-methyl-1Butane (approximately 11.76%).

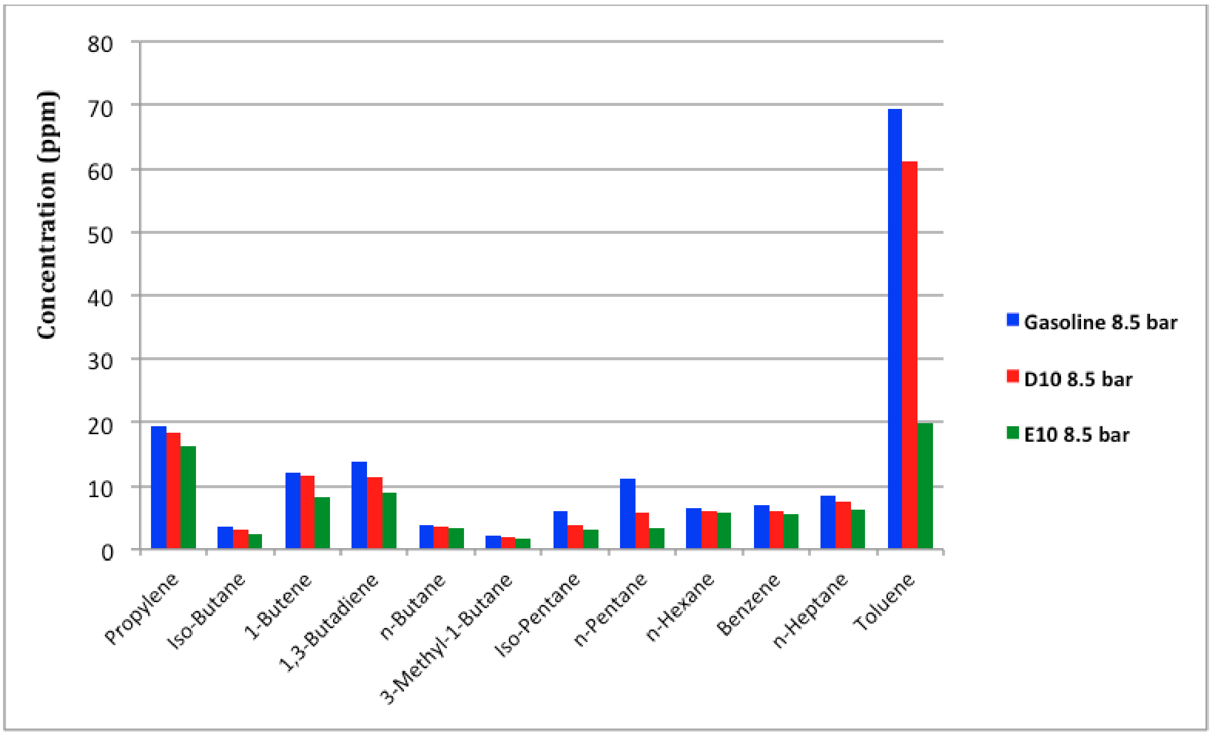
The concentrations of same hydrocarbons for the 30% Ethanol-Gasoline blend reduced considerably compared with those for Gasoline fuelling. The highest decreases happen for 1-Butane and Benzene with the amount of 96% and 94.5% respectively (the values of concentrations of these hydrocarbons changed to almost zero in exhaust), and the lowest reduction is for 3-methyl-1Butane (approximately 22.44%).

Figure 6.5(d) demonstrates the results of speciation for blends of 30% DMF and 30% Ethanol with Gasoline at high engine load. Addition of DMF resulted in a slight decrease in concentration of hydrocarbons with the exception of n-Butane which shows an increase of 9.4%. The largest change was seen for n-Pentane with a reduction of 58.26% and lowest decrease was an almost negligible change for Benzene. Adding 30% Ethanol to Gasoline caused the concentration of all hydrocarbons to drop dramatically, the highest decreases happened for 1-Butane and Benzene with the amounts of 98% and 95.3% respectively, and the lowest decrease was for n-hexane (nearly 27%). In conclusion, addition of higher percentage of DMF does not have significant effect as compared with adding 10%. But Ethanol as an additive to Gasoline showed great reduction in concentration of each hydrocarbon; as it was shown before some of these hydrocarbons almost disappear in the exhaust of engine running on high percentages of Ethanol. Table 6.2 shows the concentration of hydrocarbon species for different fuels and operating engine conditions.

a


Concentration (ppm)
90
80
70
60
50
40
30
20
10
0
Propylene
Iso-Butane
1-Butene
1,3-Butadiene
n-Butane
3-Methyl-1-Butane
Iso-Pentane
n-Pentane
n-Hexane
Benzene
n-Heptane
Toluene
Gasoline 3.5 bar
D10 3.5 bar
E10 3.5 bar

b


Concentration (ppm)
80
70
60
50
40
30
20
10
0
Propylene
Iso-Butane
1-Butene
1,3-Butadiene
n-Butane
3-Methyl-1-Butane
Iso-Pentane
n-Pentane
n-Hexane
Benzene
n-Heptane
Toluene
Gasoline 8.5 bar
D10 8.5 bar
E10 8.5 bar

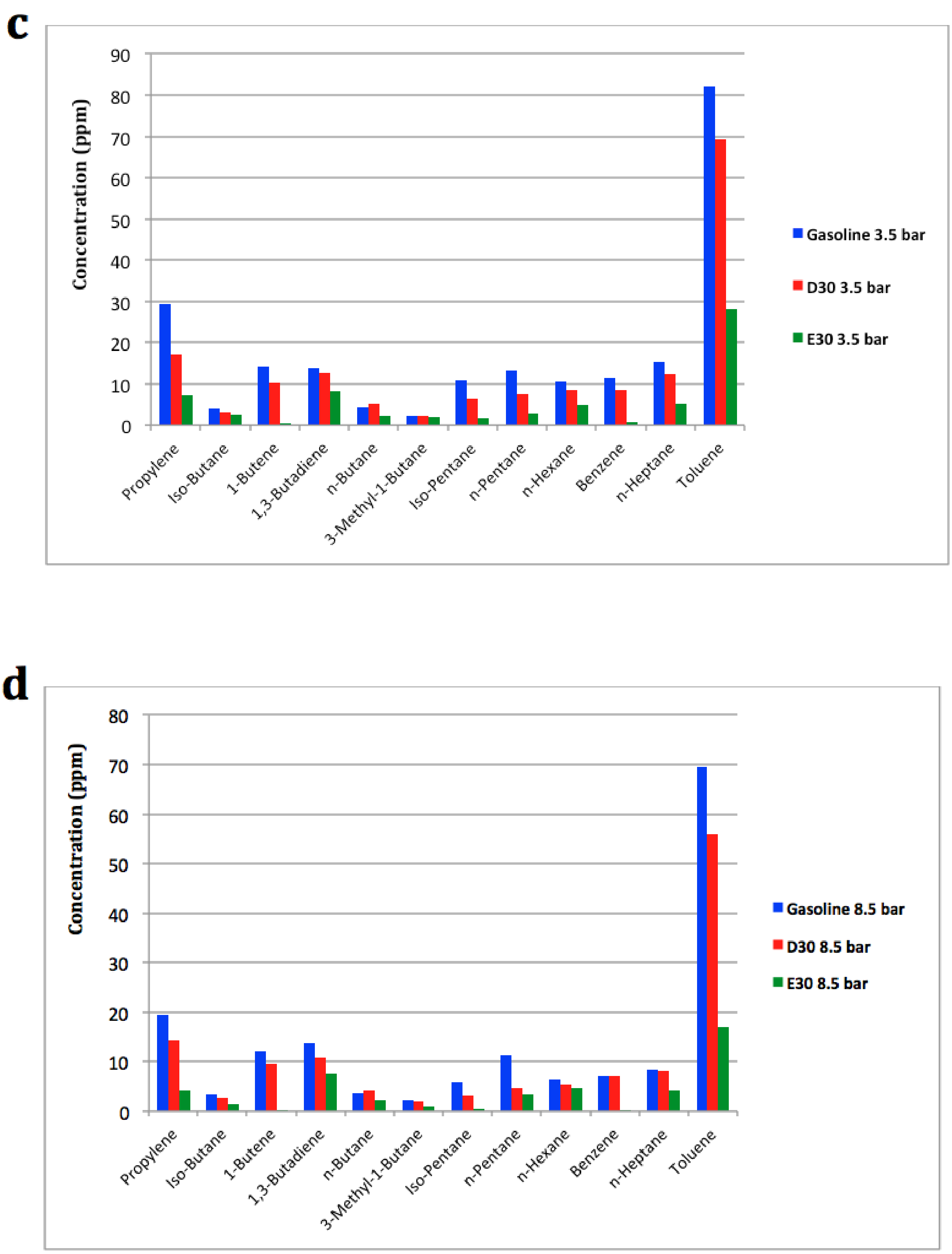


Figure 6.5-C3-C7 hydrocarbons speciation (a) E10, D10 at 3.5 bar (b) E10, D10 at 8.5 bar (c) E30, D30 at 3.5 bars and (d) E30, D30 at 8.5 bar

,

Table 6.2-Hydrocarbons C3-C7 concentrations in engine exhaust at 1500 rpm (λ=1)

Compound	**Gasoline at 3.5 bar (ppm)**	**Gasoline at 8.5 bar (ppm)**	**E10 at 3.5 bar (ppm)**	**E10 at 8.5 bar (ppm)**	**E30 at 3.5 bar (ppm)**	**E30 at 8.5 bar (ppm)**	**D10 at 3.5 bar (ppm)**	**D10 at 8.5 bar (ppm)**	**D30 at 3.5 bar (ppm)**	**D30 at 8.5 bar (ppm)**
Propylene	29.46	19.48	24.62	16.28	7.39	4.18	27.29	18.48	17.07	14.20
Iso-butane	3.91	3.47	3.15	2.35	2.54	1.35	3.66	3.14	2.98	2.64
1-Butene	14.01	12.05	9.34	8.10	0.55	0.23	12.23	11.60	10.26	9.49
1,3-Butadiene	13.82	13.82	10.05	8.81	8.21	7.66	11.81	11.24	12.81	10.94
n-Butane	4.46	3.76	4.40	3.45	2.29	2.12	4.37	3.52	5.12	4.12
3-Methyl-1-Butane	2.36	2.23	2.13	1.62	1.83	1.01	2.15	1.80	2.08	2.03
Iso-pentane	11.00	5.89	5.67	3.18	1.64	0.52	9.40	3.88	6.27	3.24
n-Pentane	13.12	11.21	4.18	3.42	2.71	3.45	10.95	5.72	7.54	4.68
n-Hexane	10.66	6.38	8.21	5.86	4.82	4.63	9.92	6.01	8.48	5.36
Benzene	11.56	7.08	7.42	5.42	0.62	0.33	9.81	6.03	8.48	7.050
n-Heptane	15.47	8.37	8.35	6.16	5.15	4.12	14.51	7.53	12.39	8.19
Toluene	82.17	69.45	46.26	19.88	28.18	17.06	78.52	61.03	69.33	55.95

6.3.6. Further discussion on C_3-C_7 hydrocarbon speciation

6.3.6.1. Alkanes

Engine-out emissions of propane, Iso-butane, n-Butane, Iso-pentane, n-Pentane, n-hexane and n-Heptane were all within the range of 0–12 ppm for engine running on pure Gasoline at 8.5 bar IMEP engine load. The concentrations of these saturated hydrocarbons increased as the engine load and combustion temperatures were reduced (0-16 ppm for engine load of 3.5 bar IMEP and Gasoline as the main fuel).

By introducing even the low percentages of Ethanol (10%) to engine fuel, the concentrations of most of these species were reduced to less than 7ppm for high engine loads (8.5 bar IMEP), presumably as a result of higher oxygen content of the fuel enhancing the oxidation of unburned hydrocarbons. Decrease in engine load resulted in an increase of concentration of these hydrocarbons, although changes were moderate between the two engine loads. Increase in percentage of Ethanol in fuel blends (to 30%) resulted in significant reductions of total hydrocarbons and specially alkanes in engine exhaust.

As an alternative to Gasoline DMF was introduced to the engine at low blends (D10 and D30). Alkanes in the exhaust of engine running on DMF-Gasoline blends showed slight changes compared with pure Gasoline. It is clear that all of these hydrocarbons were decreased for both engine conditions, but these changes were not as big as changes in hydrocarbons when Ethanol was added to the blends.

It can be summarised that adding DMF to Gasoline showed lower reduction in alkanes compared with Ethanol (particularly at higher blends 30%).

6.3.6.2. Alkenes, (Propylene, 1-Butene)

Concentration of Propylene followed the same pattern as total hydrocarbons (decrease in concentration was found as a result of increase in load). Also the addition of Ethanol showed significant change in concentration of Propylene, particularly for higher blends. These changes were present for DMF addition as well but were less significant, 1-Butene as another alkene present in engine exhaust showed reduction in concentration for increased engine load and with addition of DMF and Ethanol. Again changes in concentration when adding DMF were very small and even at high percentages the results were close to those for pure Gasoline, but significant change was noticed when concentration of Ethanol in the blends was increased to 30%. In this case the amount of 1-Butene in exhaust dropped to around zero for both the low and high engine loads.

6.3.6.3. 1, 3-Butadiene

The 1, 3-Butadiene is considered the most toxic hydrocarbon among volatile organic compounds (VOCs) and it has low reactivity with ozone in air in comparison to other alkenes. Investigation on mechanisms of 1, 3-Butadiene carcinogenicity showed that it may increase cancer risks in humans. The highest trace of 1, 3-Butadiene was detected when DMF was added to the fuel blends and changes in engine load did not have major effect on the concentration. 1, 3-Butadiene is considered as highly reactive and hazardous pollutant which is transformed into reaction quickly and produces toxic pollutants. (Duffy, Nelson et al. 1998, Bond and Medinsky 2001, Laowagul and Yoshizumi 2009).

6.3.6.4. Aromatics

Benzene is considered as one of the most toxic substance of exhaust gases and carcinogenicity of Benzene generates particular concern, which causes a range of health problems. Inhalation exposure to Benzene may cause leukaemia risks in occupational environments. Generally, main source of Benzene emission is considered as dealkylation product of alkylbenzene, Toluene and xylene while incomplete combustion occurs. (Stone 1985, Kaiser et al. 1991, Kaiser et al. 2005). In this study, the concentration of Benzene ranged from almost 0 ppm to 12 ppm with the highest concentration being for the engine operating with pure Gasoline and at low loads due to the increased post-flame oxidation, which describes the reason of preference of Benzene formation in SI engines over Toluene (Johnson et al. 2007). The concentration of Benzene in exhaust was significantly reduced by addition of high percentages of Ethanol to the fuel blends (Concentrations decreased to almost zero for both engine loads).

In this work, Toluene was present at relatively high concentrations compared with the rest of the measured compounds in this group. The highest and lowest Toluene traces of 83 ppm and 17 ppm were found in engine running on pure Gasoline at 3.5bar IMEP and E30 at 8.5 bar IMEP engine load respectively.

6.4. Summary

In summary this chapter demonstrated the effect of addition of oxygenated fuels such as Ethanol and 2, 5-Dimethylfuran to Gasoline on regulated and unregulated exhaust emission from spark ignition engines.

Higher heat of evaporation and oxygen content of Ethanol have reduced total hydrocarbon emission (THC) and carbon monoxide (CO) considerably for both E10 and E30 in comparison with DMF blends.

The engine operating conditions play vital role in concentrations of individual hydrocarbons. 1, 3-Butadiene concentration was decreased in exhaust emission by increasing the load.

At higher load, alkanes concentrations were decreased. Concentrations of heavier hydrocarbons were decreased at higher load.

Regardless of engine operating modes, Benzene and Toluene were main components of exhaust emissions. Addition of Ethanol reduced concentration of aromatics drastically.

CHAPTER 7

7. CONCLUSION AND FUTURE WORK

7.1. Main Contribution

7.1.1. Methodology Concept

In order to investigate the fuels lubricity properties the well known HFRR rig was used. The process is discussed in details in Chapter 3 of this thesis. Also in order to prevent any data loss and inappropriate reporting of the results all of the experiments were repeated three times in the same condition (same day) and any results with more than 5 percent error were deleted and average data of all experiments were reported as the final results in this thesis. Also for data validation, results obtained from Gasoline and Ethanol were compared with the literature and as they were in very good agreement with them, results were accepted and reported in this thesis.

For study on emissions and the possible effect of fuels properties on engine exhaust, novel works have been done. For measurement of regulated emissions commercial cutting edge equipments in this field have been used. For analysis of unregulated hydrocarbons in engine exhaust gas chromatography equipped with mass spectrometer have been modified. Engine exhaust was transferred directly from engine into the measurement point using heated lines at elevated temperature to prevent any hydrocarbon loss due to leakage and condensation in the pipes. Special valve (six port Valco valve) was employed with the capability of control on the injected sample using sampling loop. Another main effort during this project was to apply a proper method of analysis on GCMS. This method was developed over long period of time with several runs. And finally after getting the desired peaks of chromatogram, a special calibration gas bottle with 13 types of hydrocarbons have been used to quantify the results. As the concentration of each hydrocarbon in the gas bottle is set to a known value.

7.1.2. Lubricity of fuels

The vital role of fuels lubricating characteristics in new spark ignition engines was analyzed using the HFRR for conventional 95 RON Gasoline and other biofuels as additives.

Friction coefficient as an important factor in lubricity analysis maintained almost constant value during the 75 minute tests for pure 2,5-Dimethylfuran and Ethanol, but this value showed an increasing trend for Gasoline confirming poor lubricity of Gasoline compared with these biofuels.

Addition of 2, 5-Dimethylfuran and Ethanol to Gasoline enhanced the lubricity of the blend significantly. This increase was clearer for DMF.

Inverse relation of lubrication film coverage and friction coefficient was clearly observed.

Aging of the fuels was also investigated for their effect on the lubricity; it was found that ageing of biofuels enhanced the lubricity even more than using non-aged fuels in the blends.

7.1.3. GC-MS Quantification of C_{3}-C_{7} Hydrocarbons in SI Engine Exhaust Fuelled with Ethanol, DMF, Gasoline and Isooctane-Toluene Blend

Regulated emissions of engine exhaust running on pure fuels showed that for 95 RON Gasoline emissions of CO, HC and NO_x were similar to those for DMF. Lower CO was measured using Ethanol as the fuel due to lower maximum in-cylinder temperature and complete combustion, also higher oxygen content of Ethanol resulted in complete combustion and lower HC. NOx emission showed reduction when Ethanol was used.

Engine operating conditions found to be very important in production of highly carcinogenic species. At higher loads it was found that species like Benzene, 1-Butene and 1,3-Butadiene were present in the exhaust in concentrations up to 30 ppm.Due to high stability of the aromatic structure of Toluene there was high fraction of unburned fuel in the engine exhaust compared with iso-octane.

Alkanes were found to be the major components in the exhaust at lower loads and alkenes were found to be the major component for higher loads, again confirming the important role of engine operating conditions on exhaust. Heavier hydrocarbons such as Toluene, n-Heptane and Benzene found to be more prominent at lower engine load.

7.1.4. Volatile Hydrocarbon (C_3-C_7) Speciation and Quantification of Engine Exhaust Running on 2, 5-Dimethylfuran and Ethanol in blends with Gasoline

The significant reduction in total hydrocarbons (THC) and carbon monoxide (CO) emission were generally observed for both E10 and E30 in compared with DMF blends with Gasoline and this is due to higher heat of evaporation and oxygen content of Ethanol addition.

The engine operation modes used are very important for production of many hydrocarbon species such as 1, 3 – Butadiene. At high load, concentration of 1, 3-Butadiene was decreased significantly in exhaust emissions, which is believed to be due to its high reactivity in presence of NOx emission.

Alkanes such as propane, Isobutane, n-Butane, Iso-pentane, n-Pentane, n-hexane and n-Heptane were found to reduce in concentration with increase the engine load. The concentrations of heavy hydrocarbons were found to be higher at lower engine loads.

Benzene and Toluene were found to be the major components of engine exhaust regardless of engine operating conditions and fuels used. Concentrations of aromatics significantly reduced by addition of Ethanol.

7.2. Recommendations and Future Work

Further analysis of lubricity of fuels can be carried out by changing the test conditions. New additives can be added to the fuels for further enhancement of lubricity o the blends (Specially Gasoline).

Exhaust emission speciation can be expanded to heavier hydrocarbons in the range of C_7+ using a new set of standard gases, giving a better idea of the nature of engine exhaust for various engine conditions and fuels.

Monocyclic aromatic hydrocarbons (MAH) and even Polycyclic aromatics hydrocarbons (PAH) for both vapour phase and particulate matter can be investigated for the same conditions using liquid chromatography and thermogravimetric analysis (TGA).

Exhaust emission analysis can be extended to carbonyls using other measurement devices (HPLC)

It would also be beneficial to analyse the fuels in liquid form before the combustion and compare the hydrocarbons with those in the exhaust emissions.

AUTHOR’S PUBLICATION

F. Eslami, M.L.Wyszynski, A. Tsolakis, H. Xu, S. Norouzi, K. Dearn, Experimental Investigation on Lubricity of 2, 5 –Dimethylfuran Blends, Combustion Engines PTNSS Kongress 2012- 1/2012 (148)

F. Eslami, M.L.Wyszynski, Ch. Wang, H. Xu, S. Norouzi, A. Tsolakis, F. Eslami, Volatile Hydrocarbon (C_3-C_7) Speciation and Quantification of Engine Exhaust Emissions Running on 2,5-Dimethylfuran and Ethanol in blends with Gasoline (submitted in Elsevier Fuel Journal)

S. Norouzi, F. Eslami, A. Tsolakis, M.L. Wyszynki, Corrosion Effects of RME in Blends with ULSD on aluminium and Copper, Fuel Processing Technology Elsevier 104 (2012) 204–210

F. Eslami, M.L.Wyszynski, S. Norouzi, A. Tsolakis, F. Eslami, H. Vafamehr,Speciation and Quantification of individual hydrocarbons of Gasoline, Ethanol and 2, 5 Dimethylfuran in Spark Ignition Single Cylinder Engine using GC-MS (Preparation)

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