ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

M.Sc. THESIS

Cumali ÇELİKTEN

PERFORMANCE AND EMISSION CHARACTERISTICS OF BUTANOL AND GASOLINE MIXTURES IN A SPARK IGNITION ENGINE

DEPARTMENT OF MECHANICAL ENGINEERING

ADANA, 2010

ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

PERFORMANCE AND EMISSION CHARACTERISTICS OF BUTANOL AND GASOLINE MIXTURES IN A SPARK IGNITION ENGINE

Cumali ÇELİKTEN

M.Sc. THESIS

DEPARTMENT OF MECHANICAL ENGINEERING

We certify that the thesis titled above was reviewed and approved for the award of degree of the Master of Science (M.Sc.) by the board of jury on 02/06/2010.

…….....	…….	…….....
Prof.Dr. Kadir AYDIN	Assoc.Prof.Dr. Hüseyin AKILLI	Prof.Dr. Selahattin SERİN
SUPERVISOR	MEMBER	MEMBER

This M.Sc. Thesis is written at the Department of Institute of Natural and Applied Sciences of Çukurova University.

Registration Number:

Prof. Dr. İlhami YEĞİNGİL
Director
Institute of Natural and Applied Sciences

Not: The usage of the presented specific declarations, tables, figures, and photographs either in this thesis or in any other reference without citation is subject to "The law of Arts and Intellectual Products" number of 5846 of Turkish Republic

ABSTRACT

M.Sc. THESIS

PERFORMANCE AND EMISSION CHARACTERISTICS OF BUTANOL AND GASOLINE MIXTURES IN A SPARK IGNITION ENGINE

Cumali ÇELİKTEN

ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF MECHANICAL ENGINEERING

Supervisor :Prof.Dr. Kadir AYDIN
Year: 2010, Pages: 67
Jury :Assoc.Prof.Dr. Hüseyin AKILLI
:Prof.Dr. Selahattin SERİN

Petrol and petroleum based fuels resources are declining and their production costs are increasing rapidly. In addition, these fuels cause several environmental pollutions. For this reason, researches about alternative fuels are increasing in order to reduce production cost, decrease environmental pollution and increase efficiency. LPG, natural gas, biodiesel and some derivatives of alcohol like ethanol and methanol are good examples for alternative fuels. Some of these fuels can be used as pure or as blends with derivatives of petrol.

In this experimental study, affects of fuel blends that are prepared by mixing butanol with gasoline at volumetric rate of 5%, 10% and 15% to performance and exhaust emissions of a petrol engine were investigated. Firstly, pure unleaded gasoline and pure butanol were tested according to ASTM standards, after those fuel properties of fuel blends that are prepared by mixing butanol with gasoline at volumetric rate of 5%, 10% and 15% were measured similarly. By using a commercial 4 stroke, 4 cylinder petrol engines, performance values like torque and power were measured with a computer controlled hydraulic dynamometer, fuel consumption values were measured with computer controlled volumetric flow meter and emission values were measured by the help of exhaust gas analyzer. According to experimental results it was determined that addition of butanol to gasoline decreased engine performance values due to its lower heating value; however, since butanol contains oxygen, it increased combustion efficiency and as a result caused reduction of exhaust emission values at important rates.

Key Words: Butanol, Torque, Power, Fuel Consumption, Emissions.

ÖZ

YÜKSEK LİSANS TEZİ

BÜTANOL VE BENZİN KARIŞIMLARININ BUJİ ATEŞLEMELİ BİR BENZİNLİ MOTORDA PERFORMANS VE EGZOZ EMİSYONLARINA OLAN ETKİLERİNİN İNCELENMESİ

Cumali ÇELİKTEN

ÇUKUROVA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ
MAKİNA MÜHENDİSLİĞİ ANABİLİM DALI

Danışman :Prof.Dr. Kadir AYDIN
Yıl: 2010, Sayfa: 67
Jüri :Doç.Dr. Hüseyin AKILLI
:Prof.Dr. Selahattin SERİN

Petrol ve petrol türevi yakıt kaynakları hızla azalmakta ve bu kaynakların üretim maliyetleri hızla artmaktadır. Ayrıca, bu yakıtlar oldukça fazla çevre kirliliğine sebep olmaktadır. Bu nedenle, günümüzde düşük üretim maliyeti, daha az çevre kirliliği ve yüksek verimlilik için alternatif yakıt araştırmaları artmaktadır. LPG, doğalgaz, biyodizel ile etanol, metanol ve bütanol gibi bazı alkol türevleri alternatif yakıtlar için iyi birer örnektir. Bu yakıtların bazıları saf veya petrol türevi yakıtlara karıştırılarak kullanılabilir.

Yapılan bu deneysel çalışmada, benzine hacimsel olarak %5, %10 ve %15 oranlarında bütanol karıştırılarak hazırlanan yakıt karışımlarının benzinli bir motorun performans ve egzoz emisyonlarına olan etkileri araştırılmıştır. Öncelikle deneylerde kullanılacak saf kurşunsuz benzin ile saf bütanol Amerikan Test ve Malzeme Enstitüsü (ASTM) standartlarına göre test edilmiş, daha sonra bu yakıtlardan benzinin içerisine hacimsel olarak %5, %10 ve %15 oranında bütanol katılarak hazırlanan yakıt karışımlarının yakıt özellikleri benzer şekilde ölçülmüştür. 4 zamanlı ve 4 silindirli ticari bir benzinli motor kullanılarak hazırlanan yakıtların motor performans değerleri olan tork, güç değerleri bilgisayar kontrollü bir hidrolik dinamometre ile, yakıt tüketimi yine bilgisayar kontrollü bir hacimsel debi metre ile ve emisyon değerleri de bir egzoz gaz analiz cihazı yardımıyla ölçülmüştür. Yapılan deneyler sonucu benzine bütanol katkısının bütanolün ısıl değerinin benzine göre düşük olması nedeniyle motorun performans değerlerini bir miktar düşürdüğü ancak bütanolün içeriğinde bulunan oksijen nedeniyle silindir içerisinde yanma verimini yükselttiği ve sonuç olarak egzoz emisyonlarında önemli miktarlarda düşüşe sebebiyet verdiği tespit edilmiştir.

Anahtar Kelimeler: Bütanol, Tork, Güç, Yakıt Tüketimi, Emisyonlar.

ACKNOWLEDGEMENTS

Firstly, I am grateful to my supervisor Prof.Dr. Kadir AYDIN for his extensive advice, guidance and encouragement throughout my thesis. Also, I would like to thanks to Research Assistants Gökhan TÜCCAR, Erinç ULUDAMAR, Ayşen YILMAZ and fuel laboratory technician Songül ATMACA for their help during fuel tests and their interests during the period of thesis.

Specially, I would like to thanks to automotive laboratory technician Cevdet YILDIRIM and Otokoç-Adana technicians of Edip KOCAAĞA, Mahmut YILDIRIM for devotion, support and effort during engine tests.

Finally, I offer loves to my family for their understanding and supports.

CONTENTS **PAGE**

ABSTRACT I
ÖZ II
ACKNOWLEDGEMENTS III
CONTENTS IV
LIST OF TABLES VI
LIST OF FIGURES VII
LIST OF ABBREVIATONS X
l. INTRODUCTION 1
2. PREVIOUS WORKS 3
3. MATERIAL AND METHOD 7
3.1. Materials 7
3.1.1. Butanol 7
3.1.1.1. Production of Butanol 8
3.1.1.2. Distribution of Butanol 10
3.1.1.3. Energy Content and Effects on Fuel Economy 10
3.1.1.4. Common Properties of Butanol and Other Fuels 11
3.1.1.5. Octane Rating of Butanol 11
3.1.1.6. Air-Fuel Ratio 12
3.1.1.7. Specific Energy of Butanol 12
3.1.1.8. Viscosity of Butanol 13
3.1.1.9. Heat of Vaporization 13
3.1.1.10. Advantages and Disadvantages of Butanol 13
3.1.1.11. Possible Mixtures of Butanol 14
3.1.2. Gasoline 15
3.1.2.1. Chemical Analyses and Production 15
3.1.2.2. Density 17
3.1.2.3. Volatility 17
3.1.2.4. Octane Rating 19
3.1.2.5. Energy Content 19

3.1.2.6. Gasoline Blending Agents and Additives.....20
3.1.2.7. Oxygenate Blending……..……24
3.2. Methods.....24
3.2.1. Measuring of Density.....25
3.2.2. Measuring of Octane Numbers.....26
3.2.3. Measuring of Calorific Values.....27
3.2.4. Engine Test Dynamometer……28
3.2.4.1. Cooling System……..…30
3.2.4.2. Magnetic Pick-Up……..…..…30
3.2.4.3. S Type Load Cells……...……...31
3.2.4.4. Sensors Used in Engine Test Equipment……..……31
3.2.4.5. Engine Start and Stop Function……...…...32
3.2.4.6. Dynamometer Control Unit……..…….....32
3.2.5. Engine.....33
4. RESEARCH AND DISCUSSION.....35
4.1. Fuel Properties of Butanol-Gasoline Blends.....35
4.2. Engine Performance Test Results for Gasoline and Fuel Blends.....38
4.2.1. Torque Versus Speed Graphics.....40
4.2.2. Power Versus Speed Graphics.....43
4.2.3. Specific Fuel Consumption (SFC) Versus Speed Graphics.....46
4.3 Exhaust Emissions and Air Fuel Ratio (AFR) Values of Fuel Blends.....49
4.3.1. Carbon Monoxide (CO).....51
4.3.2. Carbon Dioxide (CO_2)……53
4.3.3. HydroCarbon (HC).....56
4.3.4. Air Fuel Ratio (AFR)……..58
5. CONCLUSION.....61
REFERENCES.....65
CURRICULUM VITAE.....67

LIST OF TABLES **PAGE**

Table 3.1. Chemical Compound of Some Alcohols.....7
Table 3.2. Common Properties of Some Fuels…….....11
Table 3.3. Properties of Density-meter.....25
Table 3.4 Properties of Calorimeter.....27
Table 3.5. Dynamometer Identity……..….29
Table 3.6. Dynamometer Technical Specifications……....30
Table 3.7. Cooling Water Requirement of Dynamometer Heat Exchanger...…....30
Table 3.8. Technical Specifications of Load Cell……...31
Table 3.9. Technique Values of Engine…….….33
Table 4.1. The Properties of Butanol and Gasoline Blended Fuels.....35
Table 4.2. Engine Performance Test Results for Pure Gasoline…….38
Table 4.3. Engine Performance Test Results for 5% Butanol Blend……..39
Table 4.4. Engine Performance Test Results for 10% Butanol Blend.....39
Table 4.5. Engine Performance Test Results for 15% Butanol Blend.....40
Table 4.6. Exhaust Emissions of Gasoline……..50
Table 4.7. Exhaust Emissions of 5% Blend.....50
Table 4.8. Exhaust Emissions of 10% Blend……..50
Table 4.9. Exhaust Emissions of 15% Blend……..50

LIST OF FIGURES **PAGE**

Figure 3.1. Schematic Diagram of Dual Stage Butanol Prototype with Adsorption/Desorption Recovery…….....9

Figure 3.2. The Dual Immobilized Reactors with Continuous Recovery (DIRCR™) Process.....….....9

Figure 3.3. A Picture of Density-meter.....26

Figure 3.4. Octane Number Analyzer.....26

Figure 3.5. A Picture of Calorimeter.....28

Figure 3.6. Engine Test Dynamometer…..……..……..29

Figure 3.7. Software Screen of Control and Measurement Unit…….....32

Figure 3.8. Complete Picture of the Test Unit…….....33

Figure 4.1. Densities of Gasoline, Butanol and Their Blends.....36

Figure 4.2. Motor Octane Numbers of Gasoline, Butanol and Their Blends……....36

Figure 4.3. Research Octane Numbers of Gasoline, Butanol and Their Blends……....37

Figure 4.4. Calorific Values of Gasoline, Butanol and Their Blends.....37

Figure 4.5. Torque-Engine Speed Graphic for Gasoline and 5% Butanol Blend……...41

Figure 4.6. Torque-Engine Speed Graphic for Gasoline and 10% Butanol Blend…….42

Figure 4.7. Torque-Engine Speed Graphic for Gasoline and 15% Butanol Blend…….42

Figure 4.8. Torque-Engine Speed Graphics for Gasoline and All Butanol Blends……..43

Figure 4.9. Power-Engine Speed Graphic for Gasoline and 5% Butanol Blend……...44

Figure 4.10. Power-Engine Speed Graphic for Gasoline and 10% Butanol Blend…….45

Figure 4.11. Power-Engine Speed Graphic for Gasoline and 15% Butanol Blend.....45
Figure 4.12. Power-Engine Speed Graphic for Gasoline and All Butanol Blends……..46
Figure 4.13. SFC-Engine Speed Graphic for Gasoline and 5% Butanol Blend……..….47
Figure 4.14. SFC-Engine Speed Graphic for Gasoline and 10% Butanol Blend…….....48
Figure 4.15. SFC-Engine Speed Graphic for Gasoline and 15% Butanol Blend….....48
Figure 4.16. SFC-Engine Speed Graphic for Gasoline and All Butanol Blend……....49
Figure 4.17. CO Emission-Engine Speed Graphic for Gasoline and 5% Butanol Blend……...……51
Figure 4.18 CO Emission-Engine Speed Graphic for Gasoline and 10% Butanol Blend…….…52
Figure 4.19. CO Emission-Engine Speed Graphic for Gasoline and 15% Butanol Blend…….52
Figure 4.20. CO Emission-Engine Speed Graphic for Gasoline and All Butanol Blends…….53
Figure 4.21. CO_2 Emission-Engine Speed Graphic for Gasoline and 5% Butanol Blend……...54
Figure 4.22. CO_2 Emission-Engine Speed Graphic for Gasoline and 10% Butanol Blend…….54
Figure 4.23. CO_2 Emission-Engine Speed Graphic for Gasoline and 15% Butanol Blend.....55
Figure 4.24. CO_2 Emission-Engine Speed Graphic for Gasoline and All Butanol Blends……..55
Figure 4.25. HC Emission-Engine Speed Graphic for Gasoline and 5% Butanol Blend…….……..56

Figure 4.26. HC Emission-Engine Speed Graphic for Gasoline and 10% Butanol Blend……..…57
Figure 4.27. HC Emission-Engine Speed Graphic for Gasoline and 15% Butanol Blend……..…57
Figure 4.28. HC Emission-Engine Speed Graphic for Gasoline and All Butanol Blends…….….58
Figure 4.29. AFR-Engine Speed Graphic for Gasoline and 5% Butanol Blend……...59
Figure 4.30. AFR-Engine Speed Graphic for Gasoline and 10% Butanol Blend…….59
Figure 4.31. AFR-Engine Speed Graphic for Gasoline and 15% Butanol Blend….60
Figure 4.32. AFR-Engine Speed Graphic for Gasoline and All Butanol Blends….60

LIST OF ABBREVIATIONS

A/F	: Air-fuel mass ratio
η	: Efficiency
CR	: Compression ratio
IC	: Internal combustion
MBT	: Maximum brake torque
MON	: Motored octane number
RON	: Research octane number
MEP	: Mean effective pressure
HP	: Hourse power
T	: Torque
SI	: Spark ignited
CC	: Centimeter cube
P	: Pressure
Q	: Heat
Temp	: Temperature
V	: Volume
SFC	: Specific fuel consumtion
g	: Gram
RPM	: Revulation per minute
S	: Speed
CO2	: Carbon dioxide
CO	: Carbon monoxide
HC	: Hydro carbon
°C	: Centigrade degree
Nm	: Newton meter
h	: Hour
s	: Second

1. INTRODUCTION

People have started considering the options of an alternative fuel over petroleum or diesel. Because, fuel resources are not going to be around forever and their extinction is nearly unavoidable with the ever increasing consumption. Also, fossil fuels are not renewable in nature. Currently, the consumption of fossil fuels is very much time faster than their natural production around the world. Also the combustion of fossil fuels emits dangerous gases like sulfur dioxide, carbon monoxide. This harmful gas when released into the atmosphere makes a huge contribution to the greenhouse effect. Also, the development in technology has made it possible to extract fossil fuels in a much easier but more cost effective. So, the rapid depletion of the world's crude oil reserves and environmental considerations has focused on the clean, renewable and sustainable energy systems. The energy crisis and environmental pollution created an incentive to study and evaluate alcohols as a fuel in spark ignition engines

Alcohol fuels and particularly ethanol can be produced from renewable sources, such as sugar cane, cassava, many types of waste biomass materials, corn and barley. Ethanol has some advantages over gasoline, such as the reduction of CO, volatile organic compounds (VOC) and unburned hydrocarbon (UHC) emissions and better anti-knock characteristics, which allow for the use of higher compression ratio of engines. Since ethanol is a liquid fuel, the storage and dispensing of ethanol is similar to that of gasoline. At the present time ethanol is used in spark ignition engines by blending with gasoline at low concentrations without any modification. Pure ethanol can be used in spark ignition engines but necessitates some modifications to the engine (Yücesu and Topgül, 2006).

Biofuels are example to alternative fuels the instead of diesel and gasoline that produced from renewable resources like plants, organic waste. Production of biofuels is booming in our day. Butanol, ethanol and biodiesel are main biofuels. Butanol is a liquid alcohol fuel that can be used gasoline powered internal combustion engines. The properties of butanol make it highly amenable to blending

with gasoline. It is also compatible with ethanol blending and can improve the blending of ethanol with gasoline.

Butanol may be used as a fuel in an internal combustion engines. Because it has got longer hydrocarbon chain, it is more similar to gasoline than ethanol. Butanol has been demonstrated to work in vehicles designed for use with gasoline without modification. It can be produced from biomass as well as fossil fuels. Butanol is less corrosive than ethanol and has a higher energy content than ethanol, similar energy content to gasoline. In comparison to ethanol, butanol is less prone to water contamination. As a result it could be distributed using the same infrastructure used to transport gasoline. It can be used alone however, when taking into account the latent heat of vaporization of these fuels; butanol is less attractive than the others. For port fuel injection systems, when the fuel vaporizes in the inlet port it affects a temperature decrease of the intake charge. Therefore, fuels of higher latent heat of vaporization have larger decreases in temperature of intake charge with complete vaporization in the intake port. This increases the density of combustible mixture and increases the charge mass. Furthermore, the cost of butanol production is higher in comparison with ethanol. However, there are some promising circumstances for butanol production from fermentation process of agricultural feedstock by cellulosic enzymes that have the potential to reduce its production cost (Szwaja, 2009).

The objective of the present study is to investigate the engine performance and emission characteristics of a spark ignition engine using pure unleaded gasoline and unleaded gasoline–butanol blends at 5%, 10% and 15% volumetric based mixture rates. Fuel properties of pure unleaded gasoline, pure butanol and unleaded gasoline-butanol mixtures are measured using ASTM standards. Performance and emissions characteristics are measured using a commercial 4 stroke, 4 cylinder spark ignition engine. Butanol addition to the unleaded gasoline reduced exhaust emissions of the engine significantly.

2. PREVIOUS WORKS

Ethanol is commonly used as oxygenate and Octane improver for gasoline for a long period of time. There are some disadvantages of ethanol like low energy contents, corrosivity and very prone to water contamination. Butanol has many advantages against ethanol. However butanol usage in spark ignition engines is very new therefore there are very few previous works on this subject.

Alcohols, because of their potential to be produced from renewable sources and because of their high quality characteristics for spark-ignition (SI) engines, are considered quality fuels which can be blended with fossil-based gasoline for use in internal combustion engines. They enable the transformation of our energy basis in transportation to reduce dependence on fossil fuels as an energy source for vehicles. The research presented in this work is focused on applying n-butanol as a blending agent additive to gasoline to reduce the fossil part in the fuel mixture and in this way to reduce life cycle CO_2 emissions. The impact on combustion processes in a spark-ignited internal combustion engine is also detailed. Blends of n-butanol to gasoline with ratios of 0%, 20%, and 60% in addition to near n-butanol have been studied in a single cylinder cooperative fuels research engine (CFR) SI engine with variable compression ratio manufactured by Waukesha Engine Company. A real-time combustion analysis system was applied for data acquisition and online analysis of combustion quantities. Tests were performed under stoichiometric air-to-fuel ratios, fixed engine torque, and compression ratios of 8:1 and 10:1 with spark timing sweeps from 18° to 4° before top dead center (BTDC). On the basis of the experimental data, combustion characteristics for these fuels have been determined as follows: mass fraction burned (MFB) profile, rate of MFB, combustion duration and location of 50% MFB. Analysis of these data gives conclusions about combustion phasing for optimal spark timing for maximum break torque (MBT) and normalized rate for heat release. Additionally, susceptibility of 20% and 60% butanol-gasoline blends on combustion knock was investigated. Simultaneously, comparison between these fuels and pure gasoline in the above areas was investigated. Finally, on the basis of these conclusions, characteristic of these fuel

blends as substitutes of gasoline for a series production engine were discussed (Sjawa and Naber, 2010).

n-Butanol is a fuel that has been proposed as an alternative to conventional gasoline and diesel fuels. In order to better understand the combustion characteristics of *n*-butanol, this study presents new experimental data for *n*-butanol in three experimental configurations. Species concentration profiles are presented in jet stirred reactor (JSR) at atmospheric conditions and a range of equivalence ratios. The laminar flame speed obtained in an *n*-butanol premixed laminar flame is also provided. In addition, species concentration profiles for *n*-butanol and *n*-butane in an opposed-flow diffusion flame represented. The oxidation of *n*-butanol in the aforementioned experimental configurations has been modeled using an improved detailed chemical kinetic mechanism (878 reactions involving 118 species) derived from a previously proposed scheme in the literature. The proposed mechanism shows good qualitative agreement with the various experimental data. Sensitivity analyses and reaction path analyses have been conducted to interpret the results from the JSR and opposed-flow diffusion flame. It is shown that the main reaction pathway in both configurations is via H-atom abstraction from the fuel followed by β-scission of the resulting fuel radicals. Several unimolecular decomposition reactions are important as well. This study gives a better understanding of *n*-butanol combustion and the product species distribution (Sarathy et all., 2009).

An experimental investigation is conducted to evaluate the effects of using blends of butanol with conventional diesel fuel, with 8% and 16% (by vol.) butanol on the performance and exhaust emissions of a fully instrumented, six-cylinder, water-cooled, turbocharged and after-cooled, heavy duty, direct injection (DI), Mercedes-Benz engine, installed at the authors' laboratory, which is used to power the mini-bus diesel engines of the Athens Urban Transport Organization sub-fleet. The tests are conducted using each of the above fuel blends, with the engine working at two speeds and three loads. Fuel consumption, exhaust smokiness and exhaust regulated gas emissions such as nitrogen oxides, carbon monoxide and total unburned hydrocarbons are measured. The differences in the measured performance and exhaust emissions of the two butanol diesel fuel blends from the baseline

operation of the engine, i.e. when working with neat diesel fuel, are determined and compared. It is revealed that this fuel, which can be produced from biomass butanol, is a very promising bio-fuel for diesel engines. The differing physical and chemical properties of butanol against those for the diesel fuel, aided by sample cylinder pressure and heat release rate diagrams, are used to interpret the observed engine behavior (Rakopoulos et all., 2010).

Experimental study was conducted to investigate the influence of the diesel fuel n-butanol content on the performance and emissions of a heavy duty direct injection diesel engine with multi-injection capability. At fixed engine speed and load, exhaust gas recirculation rates were adjusted to keep NOx emission at 2.0 g/kW h. Diesel fuels with different amounts (0%, 5%, 10% and 15% by volume) of n-butanol were used. The results show that the n-butanol addition can significantly improve soot and CO emissions at constant specific NOx emission without a serious impact on the break specific fuel consumption and NOx. Early pilot injection reduces soot emission, but a result in a dramatic increase of CO. Post injection reduces soot and CO emissions effectively. Under each injection strategy, the increase of fuel n-butanol content leads to further reduction of soot. A triple-injection strategy with the highest n-butanol fraction used in this study offers the lowest soot emission (Yao et all, 2010).

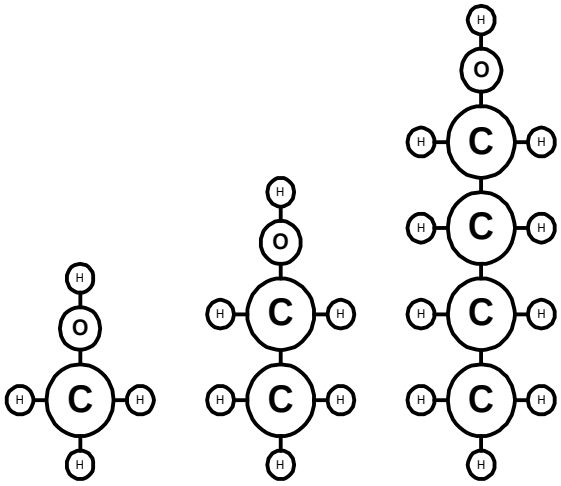
3. MATERIAL AND METHOD

3.1. Materials

3.1.1. Butanol

Butanol is a four-carbon alcohol (C_4H_9OH), a clear neutral liquid with a strong characteristic odor. It is miscible with most solvents (alcohols, ether, aldehydes, ketones, and aliphatic and aromatic hydrocarbons), is sparingly soluble in water (water solubility 6.3%) and is a highly refractive compound (Minter, 2006). Butanol is produced efficiently from sugar or starch by anaerobic fermentation. It can use corn, grain, potatoes, sugar beets, grass, leaves, trees or agricultural waste.

Table 3.1. Chemical Compound of Some Alchols (Ramey and Yang, 2004)



	Methanol	Ethanol	Butanol	Gasoline
	CH3OH	C2H5OH	C4H9OH	
Energy Density (MJ/L)	16	19.6	29.2	32
Motor Octane	104	96	78	88
Air to Fuel Ratio	6.6	9	11-12	12-15

3.1.1.1. Production of Butanol

Production of butanol by fermentation utilizes bacteria, typically of the genus Clostridium. In addition to butanol, these organisms also produce acetone and ethanol, so the process is often referred to as the "ABE fermentation". The process was first practiced on an industrial scale in Britain during World War I, in order to produce acetone which was vital for the production of military ammunition. Prior to the war, the acetone had been supplied from Germany. Although the advent of cheap petroleum and the development of the petrochemical industry later rendered fermentatio obsolete, the process continued in countries such as China and South Africa into the 1980's, with butanol being the primary product. In recent years, higher oil prices and environmental concerns have led to a renewed interest in fermentation processes. Many research groups are attempting to increase the butanol yield of the process to improve the economics (Ramey and Yang, 2004).

The difference from ethanol production is primarily in the fermentation of the feedstock producing butanol rather than ethanol like primary fermentation product and minor changes in distillation. The feed stocks are the same as for ethanol energy crops such as sugar beets, sugar cane, corn grain, wheat and cassava as well as agricultural byproducts such as straw and corn stalks. One of the effective butanol production process is dual stage butanol production, in the first step of this process Butric Acid is produced and in the second stage butanol is produced from butric acid. Schematic diagram of dual stage butanol production with adsorption/desorption recovery is shown in Figure 3.1 (Ramey and Yang, 2004).

The two-step fermentation process was tested first with a small laboratory unit to fine-tune some of the process parameters. Later, a small pilot scale process was built and tested to evaluate the feasibility and performance of the process for butanol production form glucose (dextrose) and butyrate. The design also was modified to an extractive fermentation operation for the butanol production step shown in Figure 3.2 (Ramey and Yang, 2004).

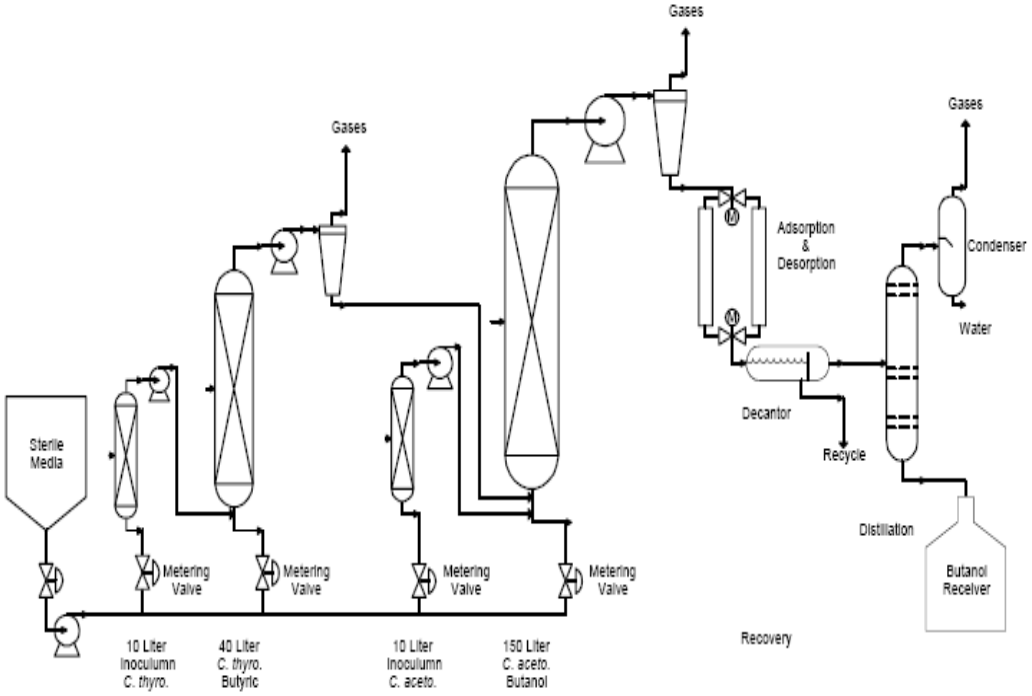


Figure 3.1. Schematic Diagram of Dual Stage Butanol Prototype with Adsorption/Desorption Recovery (Ramey and Yang, 2004)

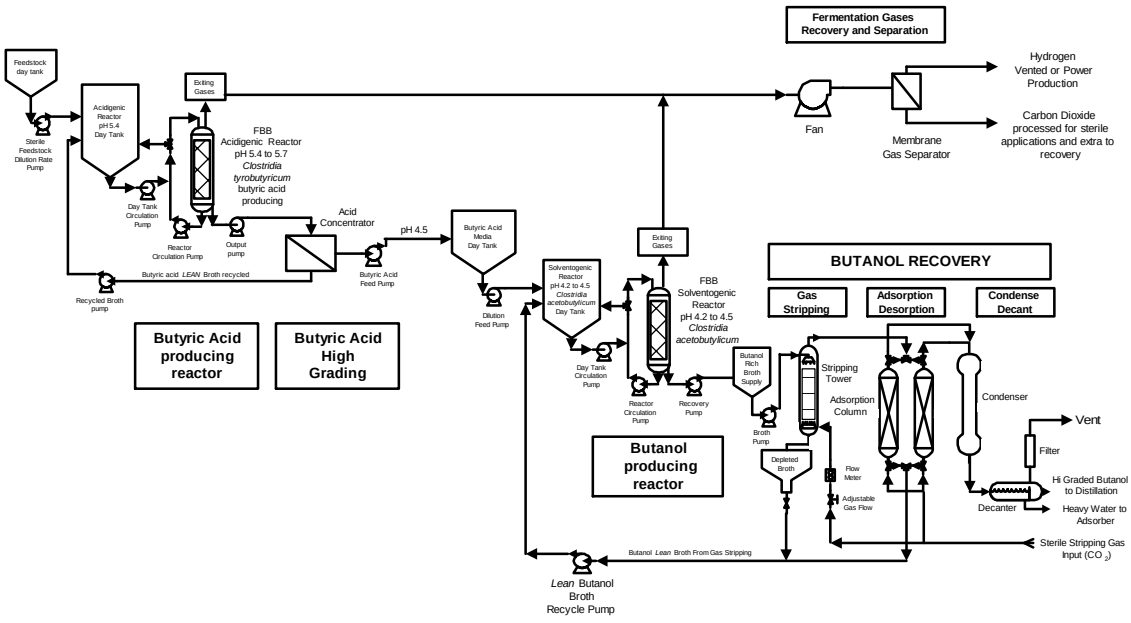


Figure 3.2. The Dual Immobilized Reactors with Continuous Recovery (DIRCR™) Process (Ramey and Yang, 2004)

The Dual Immobilized Reactor with Continuous Recovery (DIRCR™) Process for the production of butanol consists of a seven-stage process:

1. Dry or wet milling
2. Conversion of biomass into usable sugars
3. Butyric acid and hydrogen fermentation (acidiogenic)
4. Butanol fermentation (solventogenic)
5. High grading: gas-stripping/adsorption/desorption/condensing/decantation
6. Distillation: high purity
7. By-product recovery

Any front-end material handling technology that is applicable to biorefinery production can be used in the DIRCR™ process. When whey permeate is used as a feedstock, steps 1 and 2 are eliminated and 23% savings in capital equipment costs for feedstock preparation is not required. When whey is used another 40% in overheads for the cost of corn as in industrial fermentations are removed making the process very economical (Ramey and Yang, 2004).

3.1.1.2. Distribution of Butanol

Butanol better tolerates water contamination and is less corrosive than ethanol and more suitable for distribution through existing pipelines for gasoline. In blends with diesel or gasoline, butanol is less likely to separate from this fuel than ethanol if the fuel is contaminated with water. There is also a vapor pressure co-blend synergy with butanol and gasoline containing ethanol, which facilitates ethanol blending. This facilitates storage and distribution of blended fuels. No infrastructure for fueling vehicles with biobutanol currently exists in the world (Smith and Workman, 2007, http://www.afdc.energy.gov/afdc/fuels/emerging_biobutanol_distribution).

3.1.1.3. Energy Content and Effects on Fuel Economy

Switching a gasoline engine over to butanol would in theory result in a fuel consumption penalty of about 10% but there is no scientific study yet which butanol

effects on fuel consumption for the commercial vehicles. While the energy density for any mixture of gasoline and butanol can be calculated, tests with other alcohol fuels have demonstrated that the effect on fuel economy is not proportional to the change in energy density (Minter, 2006).

3.1.1.4. Common Properties of Butanol and Other Fuels

Common fuel properties like energy density, air-fuel ratio, specific energy, heat of vaporization, RON, MON and kinematics viscosity of fuel used for spark ignition engines are given in the Table 3.2 (Minter, 2006). Form this table, it can be said that butanol is the best alternative for the gasoline from the point of view of fuel properties. Energy density and air-fuel ratio properties are very similar comparing to the other alcohol fuels (http://www.bioenergywiki.net/index.php/Butanol).

Table 3.2. Common Properties of Some Fuels (Minter, 2006)

Fuel	Energy Density MJ/L	Air-Fuel Ratio	Specific Energy MJ/kg air	Heat of Vaporization MJ/kg	RON	MON	Kinematic Viscosity at 20°C cSt
Gasoline	32	14.6	2.9	0.36	91–99	81–89	0.4-0.8
Butanol	29.2	11.2	3.2	0.43	96	78	3.64
Ethanol	19.6	9.0	3.0	0.92	130	96	1.52
Methanol	16	6.5	3.1	1.2	136	104	0.64

3.1.1.5. Octane Rating of Butanol

The octane rating of n-butanol is similar to that of gasoline but lower than that of ethanol and methanol. n-Butanol has a RON (Research Octane Number) of 96 and a MON (Motor Octane Number) of 78 while t-butanol has octane ratings of 105 RON and 89 MON. t-Butanol is used as an additive in gasoline but cannot be used as

a fuel in its pure form because its relatively high melting point of 25.5 °C causes it to gel and freeze near room temperature (Saraty et all., 2009).

A fuel with a higher octane rating is less prone to knocking (extremely rapid and spontaneous combustion by compression) and the control system of any modern car engine can take advantage of this by adjusting the ignition timing. This will improve energy efficiency, leading to a better fuel economy than the comparisons of energy content different fuels indicate. By increasing the compression ratio, further gains in fuel economy, power and torque can be achieved. Conversely, a fuel with lower octane rating is more prone to knocking and will lower efficiency. Knocking can also cause engine damage (Collins, 2007).

3.1.1.6. Air-Fuel Ratio

Alcohol fuels, including butanol and ethanol, are partially oxidized and therefore need to run at richer mixtures than gasoline. Standard gasoline engines in cars can adjust the air-fuel ratio to accommodate variations in the fuel, but only within certain limits depending on model. If the limit is exceeded by running the engine on pure butanol or a gasoline blend with a high percentage of butanol, the engine will run lean, something which can critically damage components. Compared to ethanol, butanol can be mixed in higher ratios with gasoline for use in existing cars without the need for retrofit as the air-fuel ratio and energy content are closer to that of gasoline (http://en.wikipedia.org/wiki/Butanol_fuel).

3.1.1.7. Specific Energy of Butanol

Alcohol fuels have less energy per unit weight and unit volume than gasoline. To make it possible to compare the net energy released per cycle a measure called the fuels specific energy is sometimes used. It is defined as the energy released per air fuel ratio. The net energy released per cycle is higher for butanol than ethanol or methanol and about 10% higher than for gasoline (http://www.butanol.com).

3.1.1.8. Viscosity of Butanol

The viscosity of alcohols increases with longer carbon chains. For this reason, butanol is used as an alternative to shorter alcohols when a more viscous solvent is desired (http://en.wikipedia.org/wiki/Butanol_fuel). The kinematics viscosity of butanol is several times higher than that of gasoline and about as viscous as high quality diesel fuel (Rakopoulos et all., 2010).

3.1.1.9. Heat of Vaporization

The fuel in an engine has to be vaporized before it will burn. Insufficient vaporization is a known problem with alcohol fuels during cold starts in cold weather. As the heat of vaporization of butanol is less than half of that of ethanol, an engine running on butanol should be easier to start in cold weather than one running on ethanol or methanol (Alasfour, 1997).

3.1.1.10. Advantages and Disadvantages of Butanol

- Due to its low vapor pressure it can be easily blended with gasoline but does not have to be blended with fossil fuels.
- It contains nearly as much energy as gasoline (ethanol only contains 66% as much).
- It separates less easily in the presence of water it is better adapted to be used in the present distribution system than ethanol.
- It is less corrosive; it is also expected to be more suitable for use in existing oil pipelines.
- Butanol when consumed in an internal combustion engine yields no SO_X, NO_X or carbon monoxide all environmentally harmful by products of combustion. CO_2 is the combustion by product of butanol, and is considered environmentally 'green'.

- Butanol solves the safety problems associated with the infrastructure of the hydrogen supply. Reformed butanol has four more hydrogen atoms than ethanol, resulting in a higher energy output and is used as a fuel cell fuel (http://www.lightparty.com/Energy/Butanol.html).
- While ethanol and methanol have lower energy densities than butanol, their higher octane number allows for greater compression ratio and efficiency. Higher combustion engine efficiency allows for lesser greenhouse gas emissions per unit motive energy extracted.

  On the other hand it has some potential problems with the use of butanol are similar to those of ethanol:
- To match the combustion characteristics of gasoline, the utilization of butanol fuel as a substitute for gasoline requires fuel-flow increases (though butanol has only slightly less energy than gasoline, so the fuel-flow increase required is only minimal, maybe 10%).
- Alcohol-based fuels are not compatible with some fuel system components.
- Alcohol fuels may cause erroneous gas gauge readings in vehicles with capacitance fuel level gauging.

3.1.1.11. Possible Mixtures of Butanol

Standards for the blending of ethanol and methanol in gasoline exist in many countries, including the EU, the US and Brazil. Approximate equivalent butanol blends can be calculated from the relations between the stochiometric fuel-air ratio of butanol, ethanol and gasoline. Common ethanol fuel mixtures for fuel sold as gasoline currently ranges from 5% to 10%. The share of butanol can be 60% greater than the equivalent ethanol share, which gives a range from 8% to 16%. "Equivalent" in this case refers only to the vehicle's ability to adjust to the fuel. Other properties such as energy density, viscosity and heat of vaporization will vary and may further limit the percentage of butanol that can be blended with gasoline. Consumer acceptance may be limited due to the offensive smell of butanol (Minter, 2006).

3.1.2. Gasoline

Gasoline or petrol is petroleum derived liquid mixture which is primarily used as a fuel in internal combustion engines. It is also used as a solvent, mainly known for its ability to dilute paints. It consists mostly of aliphatic hydrocarbons obtained by the fractional distillation of petroleum, enhanced with iso-octane or the aromatic hydrocarbons toluene and benzene to increase its octane rating. Small quantities of various additives are common, for purposes such as tuning engine performance or reducing harmful exhaust emissions. Some mixtures also contain significant quantities of ethanol as a partial alternative fuel. Most current or former Commonwealth countries use the term petrol, abbreviated from petroleum spirit. In North America, the word gasoline is the common term, where it is often shortened in colloquial usage to simply gas (although petrol is also accepted and used to a lesser extent in Canada). It is not a genuinely gaseous fuel (unlike, for example, liquefied petroleum gas, which is stored under pressure as a liquid.

In aviation, mogas, short for motor gasoline, is used to distinguish automobile fuel from aviation gasoline, or avgas. In British English, gasoline can refer to a different petroleum derivative historically used in lamps, but this usage is relatively uncommon. Before gasoline was used as fuel for engines, it was sold in small bottles as a treatment against lice and their eggs. This treatment method is no longer common because of the inherent fire hazard and the risk of dermatitis. In the United States, gasoline was also sold as a cleaning fluid to remove grease stains from clothing. Before dedicated filling stations were established, early motorists bought gasoline in cans to fill their tanks. Gasoline was also used in kitchen ranges and for lighting, and is still available in a purified form, known as camping fuel, white gas or Coleman fuel, for use in lanterns and portable stoves.

3.1.2.1. Chemical Analyses and Production

Gasoline is produced in oil refineries. Material that is separated from crude oil via distillation, called virgin or straight-run gasoline, does not meet the required

specifications for modern engines (in particular octane rating; see below), but will form part of the blend. The bulk of a typical gasoline consists of hydrocarbons with between 4 and 12 carbon atoms per molecule (Yeni, 2005).

Many of the hydrocarbons are considered hazardous substances and are regulated in the United States by the Occupational Safety and Health Administration. The material safety data sheet for unleaded gasoline shows at least fifteen hazardous chemicals occurring in various amounts, including benzene (up to 5% by volume), toluene (up to 35% by volume), naphthalene (up to 1% by volume), trimethylbenzene (up to 7% by volume), MTBE (up to 18% by volume, in some states) and about ten others.

The various refinery streams blended together to make gasoline all have different characteristics. Some important streams are:

- Reformate, produced in a catalytic reformer with a high octane rating and high aromatic content, and very low olefins (alkenes).
- Cat cracked gasoline or cat cracked naphtha, produced from a catalytic cracker, with a moderate octane rating, high olefins (alkenes) content, and moderate aromatics level.
- Hydrocrackate (heavy, mid, and light) produced from a hydrocracker, with medium to low octane rating and moderate aromatic levels.
- Virgin or straight-run naphtha, directly from crude oil with low octane rating, low aromatics (depending on the grade of crude oil), some naphthenes and no olefins (alkenes).
- Alkylate, produced in an alkylation unit, with a high octane rating and which is pure paraffin (alkane), mainly branched chains.
- Isomerate (various names) which is obtained by isomerising the pentane and hexane in light virgin naphthas to yield their higher octane isomers.

  Overall, a typical gasoline is predominantly a mixture of paraffins (alkanes), naphthenes (cycloalkanes), and olefins (alkenes). The exact ratios depend on:
- The oil refinery that makes the gasoline, as not all refineries have the same set of processing units.
- The crude oil feed used by the refinery.

- The grade of gasoline, in particular the octane rating.

Currently, many countries set limits on gasoline aromatics in general, benzene in particular, and olefin (alkene) content. Such regulations led to increasing preference for high octane pure paraffin (alkane) components, such as alkylate, and is forcing refineries to add processing units to reduce benzene content.

Gasoline can also contain other organic compounds such as organic ethers (deliberately added), plus small levels of contaminants, in particular sulfur compounds such as disulfides and thiophenes. Some contaminants, in particular thiols and hydrogen sulfide, must be removed because they cause corrosion in engines (Collins, 2007).

3.1.2.2. Density

The specific density of gasoline ranges from 0.71–0.77 kg/L, higher densities having a greater volume of aromatics. (719.7 kg/m^3). Gasoline floats on water; water cannot generally be used to extinguish a gasoline fire, unless used in a fine mist.

3.1.2.3. Volatility

Gasoline is more volatile than diesel oil, Jet-A or kerosene, not only because of the base constituents, but because of the additives that are put into it. The final control of volatility is often achieved by blending with butane. The Reid Vapor Pressure (RVP) test is used to measure the volatility of gasoline. The desired volatility depends on the ambient temperature: in hotter climates, gasoline components of higher molecular weight and thus lower volatility are used. In cold climates, too little volatility results in cars failing to start. In hot climates, excessive volatility results in what is known as "vapor lock" where combustion fails to occur, because the liquid fuel has changed to a gaseous fuel in the fuel lines, rendering the fuel pump ineffective and starving the engine of fuel. (This effect mainly applies to camshaft-driven (engine mounted) fuel pumps that also lack a fuel return line. Vehicles with fuel injection require the fuel to be pressurized, to within a set range.

Because camshaft speed is very near zero before the engine is started, an electric pump is used; it is located in the fuel tank so that the fuel may also cool the high pressure pump. Pressure regulation is achieved by returning unused fuel to the tank, thus vapor lock is almost never a problem in a vehicle with fuel injection.)

In the United States, volatility is regulated in large urban centers to reduce the emission of unburned hydrocarbons. In large cities, so-called reformulated gasoline that is less prone to evaporation, among other properties, is required. In Australia, summer petrol volatility limits are set by State Governments and vary between capital cities. Most countries simply have a summer, winter and perhaps intermediate limit.

Volatility standards may be relaxed (allowing more gasoline components into the atmosphere) during emergency anticipated gasoline shortages. For example, on 31 August 2005 in response to Hurricane Katrina, the United States permitted the sale of non-reformulated gasoline in some urban areas, which effectively permitted an early switch from summer to winter-grade gasoline. As mandated by EPA administrator Stephen L. Johnson, this "fuel waiver" was made effective through 15 September 2005.

Besides lowering the volatility of the fuel, other means of controlling the emission of unburned hydrocarbons, for environmental concerns, exist and are used. All vehicles sold in the United States (since at least the 1980s, probably the 1970s or earlier) are required to have a fuel evaporative control system (called an EVAP system in automotive jargon) which collects expanding fuel vapor from the fuel tank in a charcoal-lined canister while the engine is stopped and then releases the collected vapors (through a "purge valve") into the engine intake for burning when the engine is running (usually only after it has reached normal operating temperature.) The fuel evaporative control system is also required to include a gasket filling cap which seals the fueling inlet to prevent vapors from escaping directly from the tank through it. Modern vehicles with OBD-II emissions control systems will turn on the MIL (Malfunction Indicator Light, a.k.a. "check engine" light) if it is detected that the gas cap is missing or loose and so not sealing.

3.1.2.4. Octane Rating

An important characteristic of gasoline is its octane rating, which is a measure of how resistant gasoline is to the abnormal combustion phenomenon known as pre-detonation (also known as knocking, pinging, spark knock, and other names). Deflagration is the normal type of combustion. Octane rating is measured relative to a mixture of 2,2,4-trimethylpentane (an isomer of octane) and n-heptanes There are a number of different conventions for expressing the octane rating; therefore, the same fuel may be labeled with a different number, depending upon the system used (Yeni, 2005).

The octane rating became important in the search for higher output powers from aircraft engines in the late 1930s and the 1940s as it allowed higher compression ratios to be used.

3.1.2.5. Energy Content

Gasoline contains about 32.0 MJ/L (8.89 kW·h/L) or 12.9 kWh/kg in comparison to batteries. This is an average; gasoline blends differ, and therefore actual energy content varies from season to season and from batch to batch, by up to 4% more or less than the average, according to the US EPA. On average, about 74 L of gasoline are available from a 160 L barrel of crude oil (about 46% by volume), varying due to quality of crude and grade of gasoline. The remaining residue comes off as products ranging from tar to naphtha.

Volumetric and mass energy density of some fuels compared with gasoline:

A high octane fuel such as liquefied petroleum gas (LPG) has lower energy content than lower octane gasoline, resulting in an overall lower power output at the regular compression ratio an engine ran at on gasoline. However, with an engine tuned to the use of LPG (i.e. via higher compression ratios such as 12:1 instead of 8:1), this lower power output can be overcome. This is because higher-octane fuels allow for a higher compression ratio—this means less space in a cylinder on its combustion stroke, hence a higher cylinder temperature which improves efficiency

according to Carnot's theorem, along with fewer wasted hydrocarbons (therefore less pollution and wasted energy), bringing higher power levels coupled with less pollution overall because of the greater efficiency.

The main reason for the lower energy content (per liter) of LPG in comparison to gasoline is that it has a lower density. Energy content per kilogram is higher than for gasoline (higher hydrogen to carbon ratio). The weight-density of gasoline is about 740 kg/m³.

Different countries have some variation in what RON (Research Octane Number) is standard for gasoline, or petrol. In the UK, ordinary regular unleaded petrol is 91 RON (not commonly available), premium unleaded petrol is always 95 RON, and super unleaded is usually 97-98 RON. However both Shell and BP produce fuel at 102 RON for cars with hi-performance engines, and the supermarket chain Tesco began in 2006 to sell super unleaded petrol rated at 99 RON. In the US, octane ratings in unleaded fuels can vary between 86-87 AKI (91-92 RON) for regular, through 89-90 AKI (94-95 RON) for mid-grade (European Premium), up to 90-94 AKI (95-99 RON) for premium (European Super).

3.1.2.6. Gasoline Blending Agents and Additives

Gasoline additives have been used commercially in the U.S. since 1923 to enhance performance or to solve engine operating problems. Literally hundreds of compounds have been used as gasoline blending agents or additives. Typically, an additive is added to gasoline in parts per million levels, while a blending agent is added in percent levels. The following discussion is limited to some of the most widely used and important additives and blending agents.

Lead Additives: As automobile designers improved engine power and efficiency, they encountered a problem with noisy combustion, commonly termed knocking. Engine knock was found to be associated with low-octane gasoline. Tetraethyl lead (TEL) was the first widely-accepted gasoline additive for reducing engine knock. TEL, developed as an anti-knock agent in December 1921 by Thomas Midgeley and Thomas Boyd of General Motors Research Corporation, was

first marketed on February 1, 1923 in Dayton, Ohio. Four months later, TEL supplemented fuel was used by the top three finishers in the 1923 in Indianapolis.

The Ethyl Gasoline Corporation was formed by General Motors and Standard Oil of New Jersey in August 1924 to bring TEL to the mass market. However, a series of accidents in experimental laboratories and TEL manufacturing facilities in

1924 and 1925 caused numerous illnesses and approximately 15 fatalities. The incidents caused international concern, and resulted in local bans and generally declining sales. In May 1925, the U.S. Surgeon General suspended the use of TEL due to safety concerns; however, the ban was lifted one year later after further studies were completed and new regulations were developed.

TEL was used only in premium gasoline until 1933, when the Ethyl Corporation introduced the Q Brand. TEL remained the only lead additive widely used in the US until 1960, when Standard Oil Company (later Chevron) introduced tetra methyl lead (TML). TEL and TML were used in combination with each other and with other lead alkyls including tetra methyl ethyl lead (TMEL), dimethyl diethyl lead (DMDEL), and methyl tetraethyl lead (MTEL).

Lead emissions from gasoline engine exhaust prompted a gradual transition to unleaded gasoline. In 1973, Environmental Protection Agency (EPA) required that lead concentrations in leaded gasoline be reduced from 0.5 to 0.8 grams per liter to 0.026 grams per liter by 1986. However, catalytic converters, which were designed to reduce carbon monoxide and unburned hydrocarbon emissions, were blinded by leaded fuels. Therefore, the introduction of catalytic converters in late 1974 hastened the acceptance of unleaded gasoline, which first appeared on a large scale in the early 1970s. It has been estimated that 3.2 million kilograms of lead additives were used in the U.S. between 1923 and 1986.

Ethylene Dibromide (EDB) and Ethylene Dichloride (EDC): Early work with TEL in gasoline uncovered a serious operating problem. Lead oxide formation in the combustion chamber was found to erode spark plugs and burn exhaust valves. This problem was solved by the use of lead scavengers, which reacted with

the deposited lead and vented it to the atmosphere. EDB and EDC were found to be suitable scavengers, but supplies of bromine available as of 1926 were not sufficient to meet the anticipated demand for EDB. The sole producer of bromine at the time, Dow Chemical, developed and implemented a process to extract bromine from seawater. EDB and EDC were reportedly used commercially as lead scavengers beginning in

1928. In 1978, the National Cancer Institute found that EDB caused several forms of cancer in rates and mice. The use of EDB and EDC in gasoline decreased in tandem with leaded gasoline.

Methyl-Tert-Butyl Ether (MTBE): MTBE was initially used as an octane booster for unleaded gasoline. The Atlantic Richfield Company (ARCO) obtained EPA approval to add up to 7.0% MTBE to unleaded gasoline in 1979. The approved percentage was increased to 11% in 1981 and 15% in 1988. Between 1980 and 1986, MTBE use increased approximately 40% per year. By 1984, it was one of the top 50 chemicals produced in the U.S. Between 1979 and the mid-1980s, MTBE was most commonly used in the eastern states.

The use of MTBE increased further due to the 1990 Clean Air Act amendments, which required the use of oxygenated fuels (also known as reformulated gasoline or RFG) to attain clean air standards. As a result of the amendments, the use of MTBE increased in areas where carbon monoxide and/or ozone standards were not met. The requirements became effective in November 1992 for carbon monoxide non-attainment areas, and in January 1995 for ozone non- attainment areas.

The accidental release of MTBE due to spillage and leaking storage or dispensing systems led to its increased detection in water supplies across the country. The earliest cases of MTBE contamination of water supplies were reported in the mid-1980s. In 1996, two water supply wells in Santa Monica, California were shut down due to high MTBE concentrations, resulting in the loss of 80% of the city's water supply, and an annual expense of over 3 million dollars to purchase water from an alternative source.

Tert-Butyl Alcohol (TBA): In 1979, Atlantic-Richfield Company (ARCO)

obtained EPA approval to use TBA as an octane enhancer in unleaded gasoline at concentrations up to 7.0% by volume. That same year, Sun Oil Company received approval to use a methanol/TBA blend in unleaded gasoline. Prior to EPA's approval, TBA had been used as an octane enhancer since at least 1969.

Methyl Cyclopentadienyl Manganese Tricarbonyl (MMT): The discovery of MMT, a trademark of the Ethyl Corporation, was announced in June 1957, along with results indicating a 20% power gain in aircraft engines. MMT, temporarily sold as AK-33X, was first mass-marketed in 1959. This compound was found to be an effective anti-knock when used either alone or in combination with TEL. MMT became more widely used in the US and Canada in the mid-1970s, when the use of leaded gasoline was being phased out. Beginning in 1974 and continuing until 1978, MMT was used in the US without TEL. However, government intervention resulted when a large-scale fleet test found that MMT caused increased exhaust emissions by interfering with catalytic converters and oxygen sensors. The Clean Air Act amendments of 1977 limited the use of MMT in unleaded gasoline, and EPA required that unleaded gasoline be manganese-free as of October 1978. MMT was banned in Canada in 1997, but the ban was lifted in July 1998 when the Ethyl Corporation successfully challenged the Canadian government under the terms of the North American Free Trade Agreement (NAFTA).

Although MTBE is by far the most commonly used oxygenate in the US, several other chemicals have also been used. First among these is ethanol, which was used as a blending agent in gasoline since the 1950s. Due to gasoline shortages in the 1970s, ethanol saw increased use in Gasohol, a gasoline/ethanol blend containing about 9.5% ethanol. As of 1991, Gasohol comprised 7% of total U.S. gasoline use. Other oxygenates include methanol (typically used with a TBA cosolvent), ethyl-tert- butyl ether (ETBE), tert-amyl methyl ether (TAME), and diisopropyl ether (DIPE). The first commercial TAME plant began production in 1986 (Yeni, 2005).

3.1.2.7. Oxygenate Blending

Oxygenate blending add oxygen to the fuel in oxygen-bearing compounds such as MTBE, ETBE and ethanol, and so reduces the amount of carbon monoxide and unburned fuel in the exhaust gas, thus reducing smog. In many areas throughout the US oxygenate blending is mandated by EPA regulations to reduce smog and other airborne pollutants. For example, in Southern California, fuel must contain 2% oxygen by weight, resulting in a mixture of 5.6% ethanol in gasoline. The resulting fuel is often known as reformulated gasoline (RFG) or oxygenated gasoline (Yeni, 2005).

3.2. Method

In this study, firstly fuel properties of 95 Octane unleaded gasoline and butanol were measured used measured in the Fuel Quality Analysis Laboratory which is belongs to Çukurova University, Department of Mechanical Engineering, Automotive Division. Later unleaded gasoline and butanol blended with the ratio of 5% (95% unleaded gasoline and 5% butanol by volume), 10% (90% unleaded gasoline and 10% butanol by volume) and 15% (85% unleaded gasoline and 15% butanol by volume) in different bottles. After that, fuel properties of blends were measured using ASTM standards.

During the engine test period, a 1389 cc, 16 valves, four stoke, gasoline engine, which was manufactured by Opel Company, was used. Firstly, this engine was mounted on a chassis frame. After, all electrical components and cables were connected to the engine. Engine control unit was programmed again because of there is no immobilizer on the engine for test cases. All injectors were checked, cleaned and fuel supply system was connected to the engine. A computer controlled hydraulic dynamometer, which was manufactured by Netfren Company, was connected to the engine. All the sensors of engine and dynamometer as well as exhaust gas temperature sensor and fuel flow measurement system were connected to the computer control and data logging system. A Sun MGA 1200 exhaust gas

analysis unit was also connected to the exhaust system of the engine to measure exhaust CO, CO_2, HC emissions. All safety considerations have been considered to prevent any injury. For noise and emissions which can cause problem on the human health, special earlaps and noise filter have been used during the tests.

During the test period, firstly engine was heated up until the cooling water temperature was reached to 90 ^oC without applying any load at the idle position. Later, engine speed was increased up to 5,000 rpm then; the engine was loaded by dynamometer. The throttle of the engine was positioned fully open, engine speed set up to the 5,000 rpm. When the test started, engine was loaded slowly and engine torque, power, engine speed, specific fuel consumption, AFR, exhaust temperature, CO, CO_2 and HC emissions were stored at the data logging system. All this operations and measurements were continued with pure unleaded gasoline, 5%, 10%, and 15% unleaded gasoline-butanol blends.

3.2.1. Measuring of Density

Densities of blends are measured by KYOTO DA-130 Portable density meter. This analyzer gives density values converting them to their amount which is in temperature of 16 °C. It is not important how ambient temperature because the analyzer converts the values with using their software database which loaded in when it is produced. These measurements repeated five times for every blend and their averages were calculated and used. Some properties of density meter are listed in Table 3.3. and a picture of density meter has been shown in Figure 3.3.

Table 3.3. Properties of density meter

Range	0.0000 to 2.0000 g/cm^3
Precision	±0.001 g/cm^3
Resolution	0.0001 g/cm^3
Temperature range	0 to 40 °C
Display content	Density, temperature compensated density, specific gravity, temperature compensated specific gravity, Brix %, alcohol concentration, sulfuric acid concentration, API degree, etc.



Figure 3.3. A Picture of density meter

3.2.2. Measuring of Octane Numbers

Octane numbers are measured by Zeltex ZX-440 liquid fuel analyzer. It's measurement principle is based on Near Infra-Red (NIR) technology. Light energy that enters the sample is scattered and absorbed within the sample. The ZX 440 measures the spectra exiting the sample, and directly displays the product's constituent concentrations. The picture octane number analyzer is given in figure 3.4.



Figure 3.4. Octane Number Analyzer

3.2.3. Measuring of Calorific Values

Calorific values of the blends were measured by IKA C2000 basic bomb calorimeter. In this analyze, nearly 0.45 grams of blends was put in a small metal cup which was settled in a bomb. Oxygen was sent in to bomb and when temperature equalizing has been get by water circulation, blends was burned. The calorimeter is a combustion calorimeter for determining gross calorific values of liquid and solid samples. A high level of automation with extremely simple handling characterizes this instrument. In addition to the isoperibolic measurement procedure (static jacket), a dynamic (reduced time) working method is also available. Properties of calorimeter are given in Table 3.4 and picture of calorimeter is given in Figure 3.5.

Table 3.4. Properties of Calorimeter

Technical Data			
Measuring range max. [J]	40000	Measuring mode adiabatic 22°C	no
Measuring mode isoperibol 22°C	no	Measuring mode dynamic 25°C	yes
Measuring mode isoperibol 25°C	yes	Measuring mode dynamic 30°C	yes
Measuring mode isoperibol 30°C	yes	Measuring mode double dry (ISO 1928)	no
Measuring time dynamic approx. [min]	7	Measuring time isoperibol approx. [min]	22
Reproducibility dynamic (1g benzoic acid NBS39i) [%RSD]	0.1	Reproducibility isoperibol (1g benzoic acid NBS39i) [%RSD]	0.05
Working temperature max. [°C]	30	Temperature measurement resolution [K]	0.0003
Cooling medium temperature min. [°C]	12	Cooling medium temperature max. [°C]	28
Cooling medium permissible	1.5	Cooling medium	water
Type of cooling	flow	Flow rate min. [l/h]	60
Flow rate max. [l/h]	70	Oxygen operating pressure max. [bar]	40
Interface ext. monitor	yes	Interface ext. keyboard	yes
Oxygen filling	yes	Degasification	no
Decomposition detection	yes	Decomposition vessel C 5010	yes
Decomposition vessel C 5012	no	Decomposition vessel C 7010	no
Decomposition vessel C 7012	no	Decomposition vessel C 62	no



Figure 3.5. A Picture of Calorimeter

3.2.4. Engine Test Dynamometer

A computer controlled hydrodynamic dynamometer for measuring of speed, torque, and consequently the engine power of internal combustion engines has been used. Hydrodynamic dynamometer consists of stator and rotor. Rotor is constructed for mounting to engine flywheel by cardan shaft between rotor and stator is water. System works without requiring an external lubrication. Dynamometer's drive shaft is 316 type stainless steel. Standard flanges can be connected directly. Rotor and stator are made from stainless steel and resistance to high corrosion. The dynamometer is equipped with many sensors, like engine speed sensor, temperature sensors, load cell, pressure sensors and pressure valves etc. and actuators. All these sensors and actuators are connected to the control unit of dynamometer for the measurement of torque, power and speed of the test engine.

The hydrodynamic dynamometer identity used in this thesis is given in the Table 3.5 and picture of the dynamometer is illustrated in Figure 3.6. Technical specifications of dynamometer are shown in Table 3.6.

Table 3.5. Dynamometer Identity

Trademark:	Netfren
Type:	FM 150
Serial Number:	12009150
Production Year:	2009

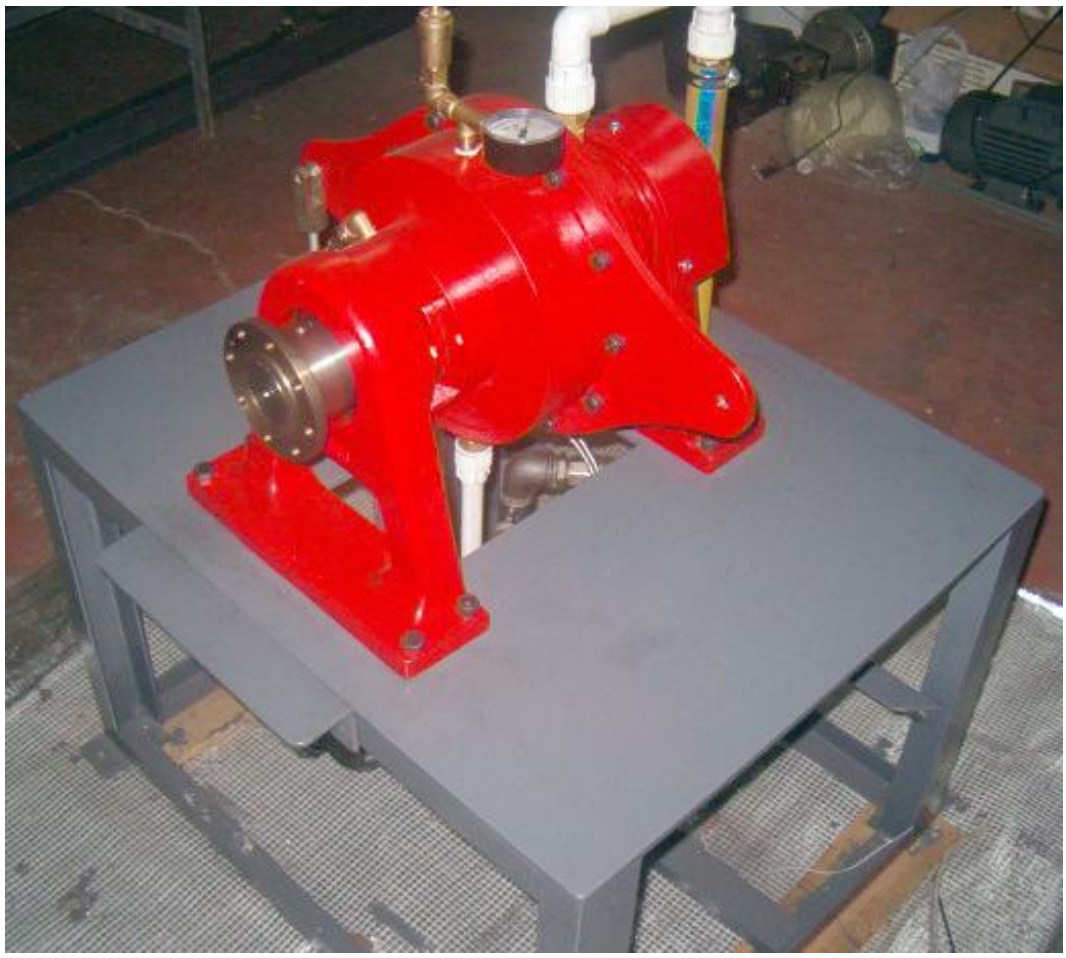


Figure 3.6. Engine Test Dynamometer

Table 3.6. Dynamometer Technical Specifications

Braking Torque Range:	0-1700 Nm Range is infinite and accuracy of ± 1
Working speed:	0-7500 rpm
Body weight:	45 kgf
Total Weight:	110 kgf
Body Diameter:	350 mm
Torque Arm Length:	350 mm and the symmetrical structure.

3.2.4.1. Cooling System

Braking power of dynamometer is converted to heat energy, so a cooling system is used to cool the oil of the dynamometer. Cooling system is composed by heat exchanger with stainless steel plate with the capacity of 300 kW. According to the engine power, cooling water requirement is given in Table 3.7.

Table 3.7. Cooling Water Requirement of Dynamometer Heat Exchanger

Engine power (HP)	60	80	120	180	240	300	400
Cooling water quantity (m^3/h)	0.8	1.2	1.8	2.7	3.5	4.4	6.2

3.2.4.2. Magnetic Pick-Up

Magnetic Pick-up measures to rotation of the engine or dynamometer with counting the gear teeth on shaft of dynamometer during rotation. It produces a pulse for each tooth which passes permanent magnet sensor. Rotation of engine is measured by counter which is connected a computer.

3.2.4.3. S Type Load Cells

S type load cell is used to measure the torque of the dynamometer. Load cell is connected to torque arm. Braking torque of dynamometer or engine torque is described by measuring of effective force on the load cell. Engine power is calculated by transmitted values to computer. Technical specifications of S type load cell are given in table 3.8.

Table 3.8. Technical Specifications of Load Cell

Materials:	Stainless steel, according to OIML R60 Norm, IP66
Accuracy:	C3 1 / 3000
Measurement range:	0-250 or 0-500 daN
Overload:	350 or 750 daN
Cable length:	5 m

3.2.4.4. Sensors Used in Engine Test Equipment

- Engine Oil Pressure Sensor: It measures to pressure of engine. It is 1% accuracy in the range of 00-10 bar.
- Engine Oil Temperature Sensor: It measures to the temperature of engine oil. PT100 type thermocouples are used.
- Engine Water Temperature Sensor: It measures to the temperature of engine coolant water. PT100 type thermocouples are used.
- Exhaust Gas Temperature Sensor: It measures to the temperature of exhaust gases. K type thermocouples are used.
- Fuel Consumption Measurement: It measures to fuel consumption of internal combustion engine, according to the load at unit time. Measurements are denominated cc/s, gr/s, kg/h and gr/kW.h on the screen and saved into test file at the same time.

3.2.4.5. Engine Start and Stop Function

The start and stop functions of engine can controlled by buttons on the engine control board. Also engine can be stopped in emergency conditions automatically by control computer, when the motor temperature and oil pressure are out of limits.

3.2.4.6. Dynamometer Control Unit

Dynamometer control unit is used for measurement of desired parameters during engine test by coming signals from sensors. If the measured value is out of boundary, dynamometer control unit gives warning to operator with alert. If the measured values show dangerous situation, control unit halts to the system. On the other hand, dynamometer control unit adjusts to the speed of test engine and the weight of the dynamometer. A software screen of the control and measurement unit is given in Figure 3.7. A complete picture of test equipment is illustrated

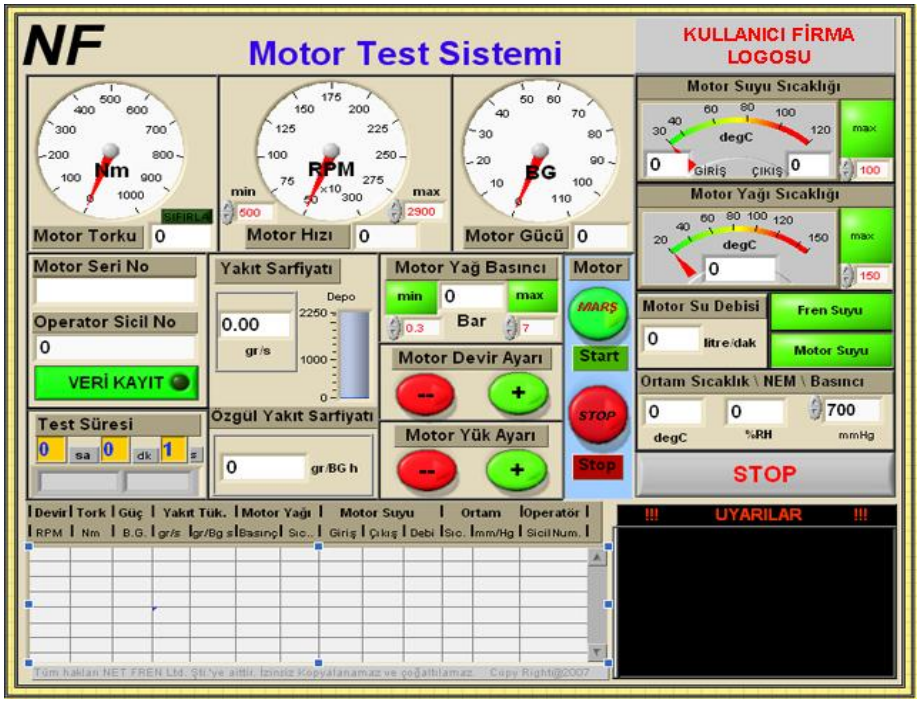


Figure 3.7. Software Screen of Control and Measurement Unit

3.2.5. Engine

A 1389 cc, four strokes, four cylinders, 16 valves gasoline engine manufactured by Opel Company was used in this thesis. Some technical values of the engine is shown in Table 3.9.

Table 3.9. Technique Values of Engine

Valves	Cylinder capacity (cc)	Number of Valves	Comp. Ratio	Max. Power (HP) at rpm	Max. Torque (Nm) at rpm	Bore and Stroke (mm)	Production year
DOHC	1389	16	10.5:1	84/6000	125/4000	77.6x73.4	1998

Finally a complete picture of the test unit used in this thesis is illustrated in Figure 3.8 shown below.

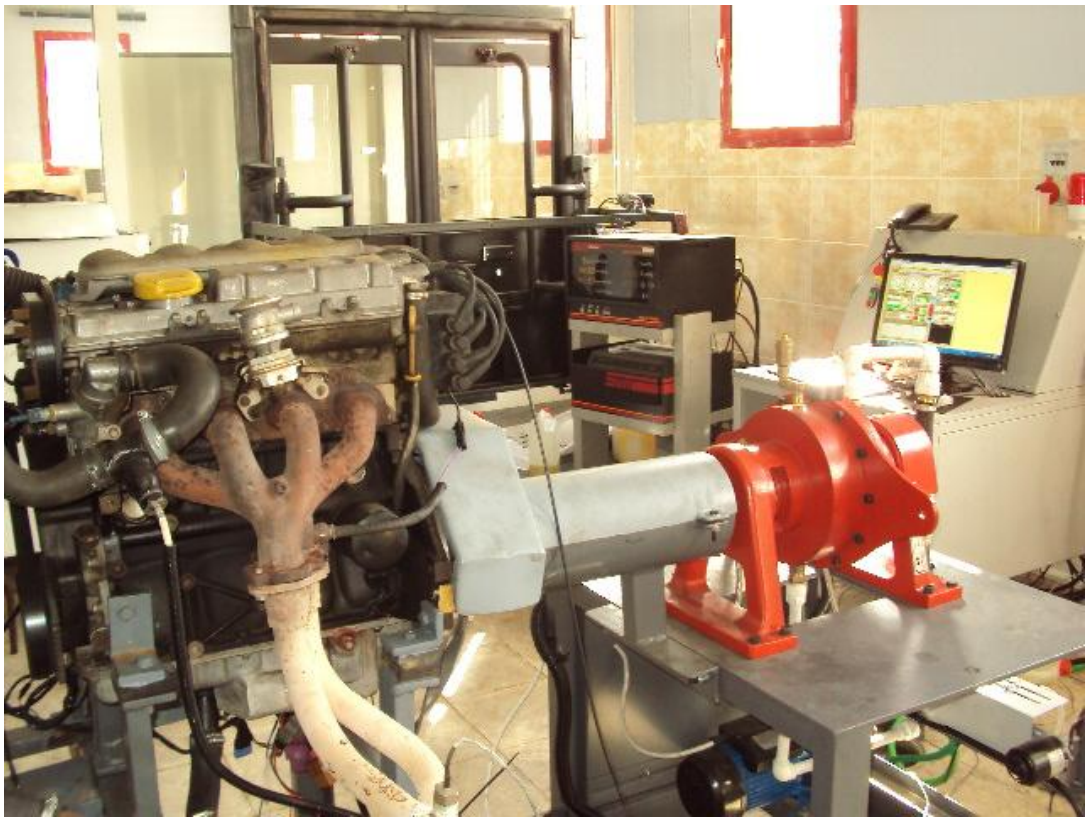


Figure 3.8. Complete Picture of the Test Unit

4. RESEARCH AND DISCUSSION

4.1. Fuel Properties of Butanol-Gasoline Blends

In this experimental study, affects of fuel blends that are prepared by mixing butanol with unleaded gasoline at volumetric rate of 5%, 10% and 15% to performance and exhaust emissions of a petrol engine were investigated. Firstly, pure unleaded gasoline and pure butanol were tested according to ASTM standards, after those fuel properties of fuel blends that are prepared by mixing butanol with gasoline at volumetric rate of 5%, 10% and 15% were measured similarly. All measurements are performed three times and average values are given. The result of the ASTM analysis, some of the combustion related properties have been summarized in Table 4.1. The table shows the variations of density, Motor Octane Number (MON), Research Octane Number (RON) and calorific values of base fuels (unleaded gasoline and butanol) and prepared blend fuels.

Table 4.1. The Properties of Butanol and Gasoline Blended Fuels

The Properties of Butanol and Gasoline Blended Fuels				
Fuel Type	Density (g/cm^3)	MON	RON	Calorific Value (cal/g)
5% Blend	0.750	86.90	98.39	9,121
10% Blend	0.754	86.68	97.62	8,420
15% Blend	0.757	86.35	97.20	8,350
Gasoline	0.749	87.54	98.76	9,400
Butanol	0.814	76.30	82.13	8,247

As it seen from Table 4.1 and Figure 4.1, the density of gasoline is less than butanol. The density of butanol is 0.814 g/cm^3, in spite of this the density of gasoline is 0.749 g/cm^3. Therefore, densities of the blends are dependent of the butanol content in the blend directly.

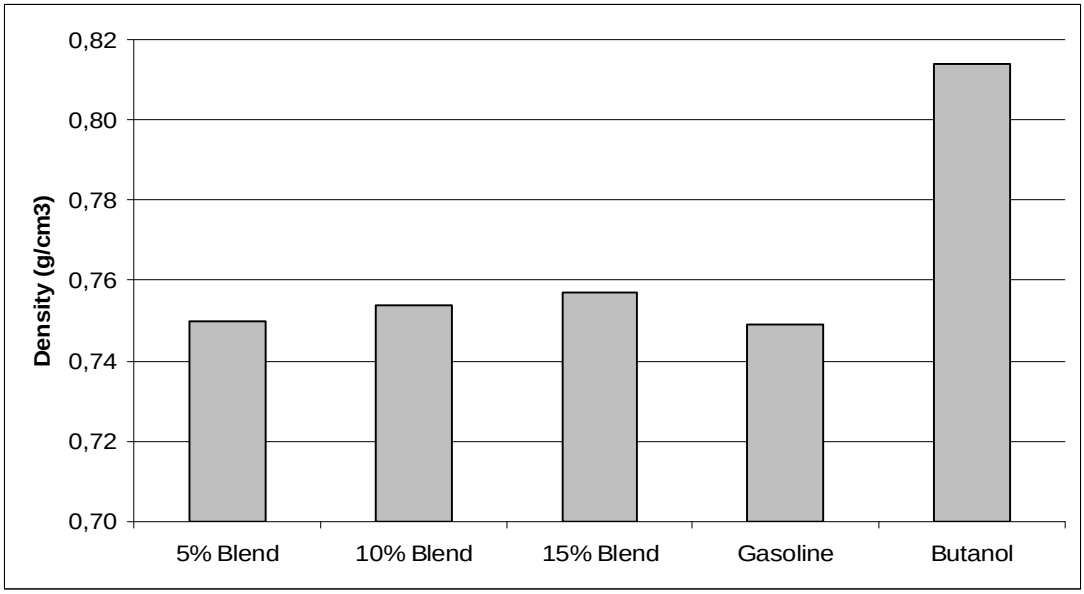


Figure 4.1. Densities of Gasoline, Butanol and Their Blends

Variations of Motor Octane Number (MON) of gasoline, butanol and their blends are shown in Table 4.1 and Figure 4.2. MON of pure butanol is very low compared to gasoline (76.3 instead of 87.54). However, butanol blends with gasoline have given better results; therefore pure butanol used in this study is not suitable for spark ignition engines.

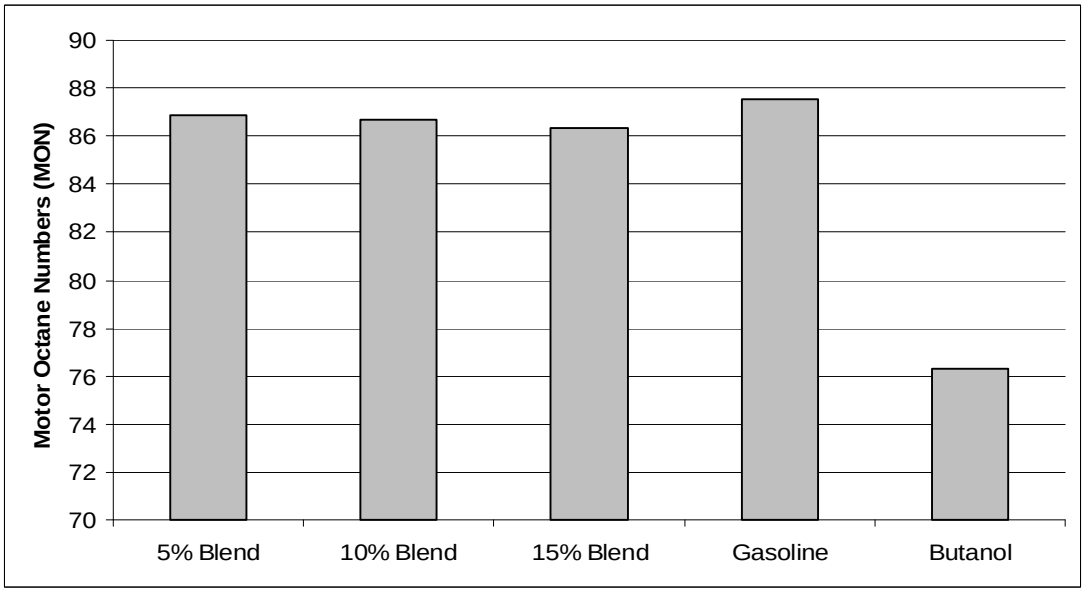


Figure 4.2. Motor Octane Numbers (MON) of Gasoline, Butanol and Their Blends

Similar those of the MON results, Research Octane Numbers (RON) of gasoline, butanol and their blends are illustrated in Table 4.1 and Figure 4.3. RON of butanol is 82.13 compared to gasoline of 98.76. RON of butanol used in this study is low and it has to be blended with gasoline at the ratio of maximum of 25%.

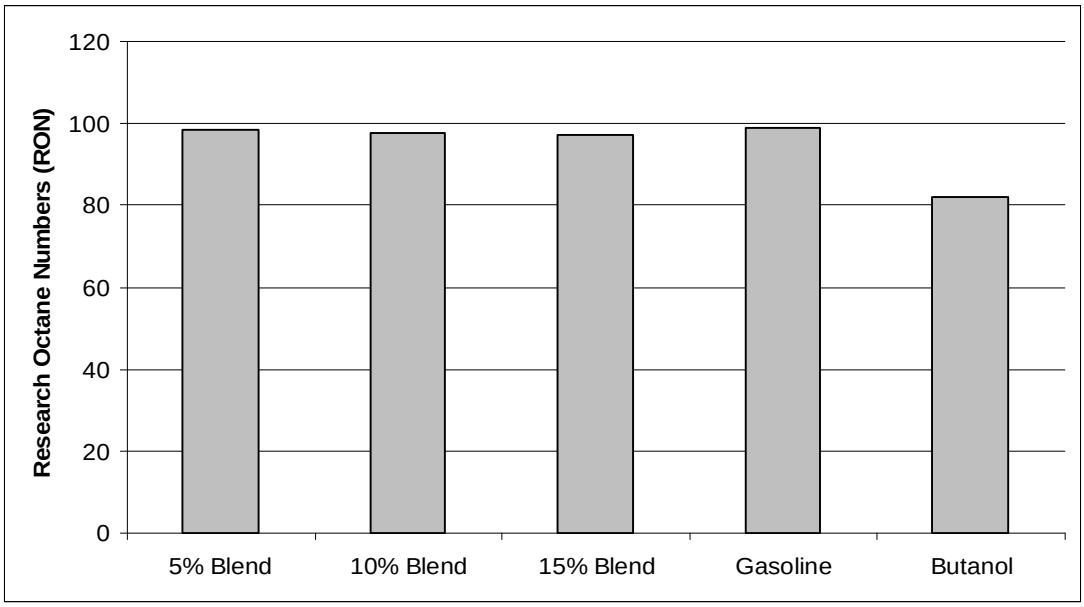


Figure 4.3. Research Octane Numbers (RON) of Gasoline, Butanol and Their Blends

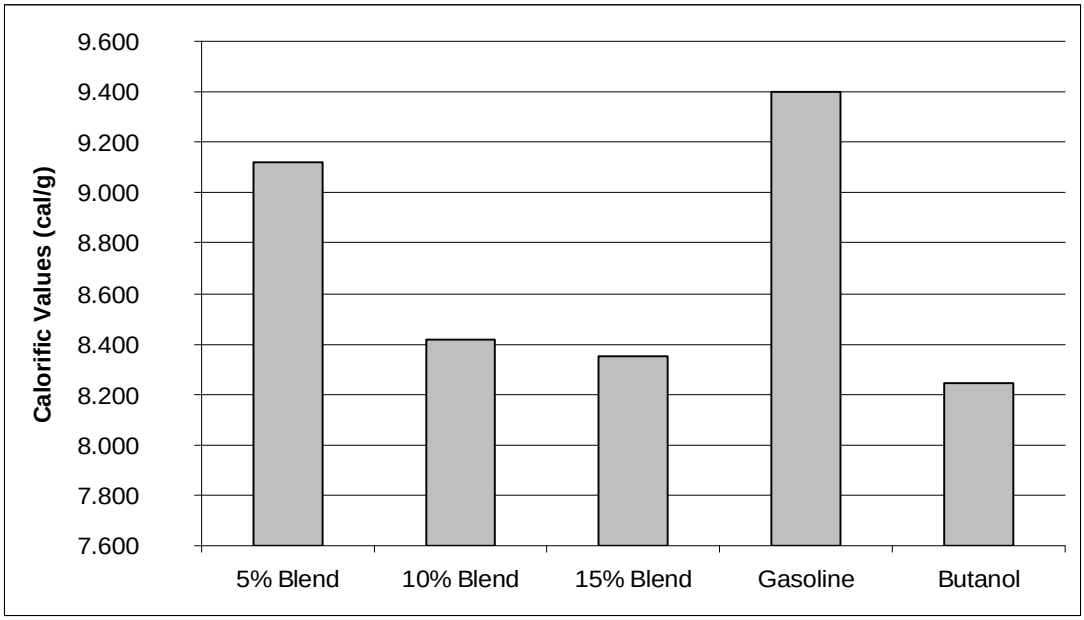


Figure 4.4. Calorific Values of Gasoline, Butanol and Their Blends

Calorific value of butanol used in this study is low (8,247 cal/g) compared to gasoline (9,400 cal/g) given in Table 4.1 and Figure 4.3. The value shows that butanol used in this study contains water (purity 96%) and butanol has to be dehydrated before any usage in spark ignition engines

4.2. Engine Performance Test Results for Gasoline and Fuel Blends

Experimental study of engine performance tests have been performed three times with pure gasoline (Table 4.2) and other ethanol blends (5% butanol blends in Table 4.3, 10% butanol blends in Table 4.4, 15% butanol blends in Table 4.5) and average values are given below in the following tables. Butanol blends engine performance test results are compared with pure gasoline in the following sections.

Table 4.2. Engine Performance Test Results for Pure Gasoline

Engine Speed rpm	Engine Torque Nm	Engine Power HP	Fuel Consumption g/s	Specific Fuel Consumption (SFC) g/HP.h	Exhaust Gas Temp. °C
5085	41.90	27.96	1.63	230.32	406.68
5351	56.84	39.37	2.94	246.81	422.69
5259	63.56	45.99	2.94	244.14	433.60
4933	76.97	53.07	3.64	234.67	441.50
4488	81.74	53.15	3.64	225.51	448.77
4188	84.63	51.14	3.64	229.51	455.50
3900	88.32	50.22	3.42	262.19	470.11
3674	93.10	49.46	2.81	265.50	483.90
3033	95.33	44.11	2.81	268.09	495.28
2648	97.73	38.61	2.81	274.83	496.27
2050	101.94	32.56	2.40	290.95	492.88
1758	99.06	26.91	1.78	285.35	489.93
1610	98.03	23.31	1.78	296.16	486.52
1253	92.41	17.26	1.22	347.70	452.67
1104	90.27	14.17	1.06	449.04	438.26

Table 4.3. Engine Performance Test Results for 5% Butanol Blend

Engine Speed rpm	Engine Torque Nm	Engine Power HP	Fuel Consumption g/s	Specific Fuel Consumption (SFC) g/HP.h	Exhaust Gas Temp. °C
5009	39.44	26.55	1.23	246.13	372.98
5041	43.35	30.06	1.23	255.87	381.27
5046	62.93	34.26	1.23	256.20	389.76
4545	75.16	49.88	3.71	248.44	398.93
4126	79.14	48.84	3.71	248.33	408.85
3922	82.17	48.87	1.68	263.93	419.31
3531	89.29	47.06	3.39	273.38	442.63
3242	91.64	43.85	3.39	282.13	449.57
2928	91.31	39.67	3.39	288.40	454.74
2657	93.95	36.88	1.32	278.85	458.81
2447	96.62	34.18	1.32	269.45	459.54
2314	99.63	33.01	1.79	268.21	459.78
2142	101.62	32.10	1.79	272.28	459.32
1817	99.28	26.90	1.55	326.14	457.37
1589	98.67	22.77	1.55	325.41	451.64

Table 4.4. Engine Performance Test Results for 10% Butanol Blend

Engine Speed rpm	Engine Torque Nm	Engine Power HP	Fuel Consumption g/s	Specific Fuel Consumption (SFC) g/HP.h	Exhaust Gas Temp. °C
5409	54.17	35.30	2.25	220.95	398.27
5275	62.40	45.85	2.53	217.23	408.89
4771	72.53	48.96	2.92	200.99	444.09
4128	80.53	47.59	2.63	211.16	499.98
3833	86.43	47.39	2.80	209.77	509.83
3595	91.27	47.66	2.78	226.73	512.86
3386	92.22	45.29	2.46	235.36	515.26
3212	93.71	43.98	2.46	232.72	516.50
2741	95.91	38.49	2.53	225.76	515.95
2438	97.98	35.69	2.53	207.21	512.97
2206	102.29	33.27	2.53	215.13	509.32
1838	98.42	29.23	1.89	214.54	505.26
1479	98.29	21.27	1.42	221.24	495.84
1337	95.95	19.01	1.42	238.09	485.27
1096	93.55	14.80	0.88	247.34	449.50

Table 4.5. Engine Performance Test Results for 15% Butanol Blend

Engine Speed rpm	Engine Torque Nm	Engine Power HP	Fuel Consumption g/s	Specific Fuel Consumption (SFC) g/HP.h	Exhaust Gas Temp. °C
4748	33.38	21.07	1.76	211.97	451.97
4829	41.50	24.74	1.76	216.19	454.37
5081	48.10	32.71	2.15	211.14	457.87
5018	54.51	36.52	2.15	234.99	462.49
4849	64.05	42.84	2.15	234.25	469.05
4272	72.96	44.87	2.65	225.85	519.80
4175	75.43	45.13	2.65	212.25	521.82
3992	78.27	44.39	2.90	215.36	518.60
3677	82.00	42.82	2.56	224.00	534.68
3435	82.00	43.50	2.71	240.15	534.54
2891	80.03	40.58	2.71	262.54	534.37
1931	83.78	24.81	2.60	276.78	528.76
1310	65.18	15.14	2.60	317.50	522.27

4.2.1. Torque Versus Speed Graphics

Variations of engine torque with engine speed are given in the following figures. Each graphics are given with butanol blends and pure gasoline results to compare each other. Also 2^{nd} and 3^{rd} order polynomials are fitted to the experimental results to indicate experimental error.

Torque-speed curves of the fuel blends are similar to the torque-speed curve of pure gasoline. Only, torque values of 15% blend is lesser than the others. 5% butanol blend achieved the maximum of 101.62 Nm torque value at 2142 rpm (Table 4.3 and Figure 4.5) compared to the 10% butanol blend achieved the maximum of 102.29 Nm torque value at 2206 rpm (Table 4.4 and Figure 4.6) and 15% butanol blend achieved the maximum of 82 Nm torque value at 3435 rpm (Table 4.5 and Figure 4.7). Pure gasoline achieved the maximum of 101.94 Nm torque value at 2050 rpm (Table 4.2). Calorific value of butanol is lesser than the calorific value of gasoline therefore it is expected that any butanol addition to the gasoline reduces the torque output of the engine. However oxygen content of butanol improves the

combustion in the cylinder and with the 5% and %10 butanol blends similar value are achieved with gasoline.

As you see from the results, the torque increases up to the maximum torque point. And then, torque curve begins to go down. Viscous friction effects increase quadratically with engine speed. So, the torque curve decrease at high engine speeds. Since, the torque will depend on the product of air-fuel ratio and delivery ratio. When the two variables are increased simultaneously there will be large change in the torque.

At low engine speeds, heat losses increases so that torque drops. At high engine speeds, the combustion efficiency is very low. Because, due to the high engine speeds, there is not enough time for complete combustion or it becomes more difficult to ingest full charge of air. So, the air-fuel ratio is no adequate for perfect combustion and the torque curve decreases when speed goes up.

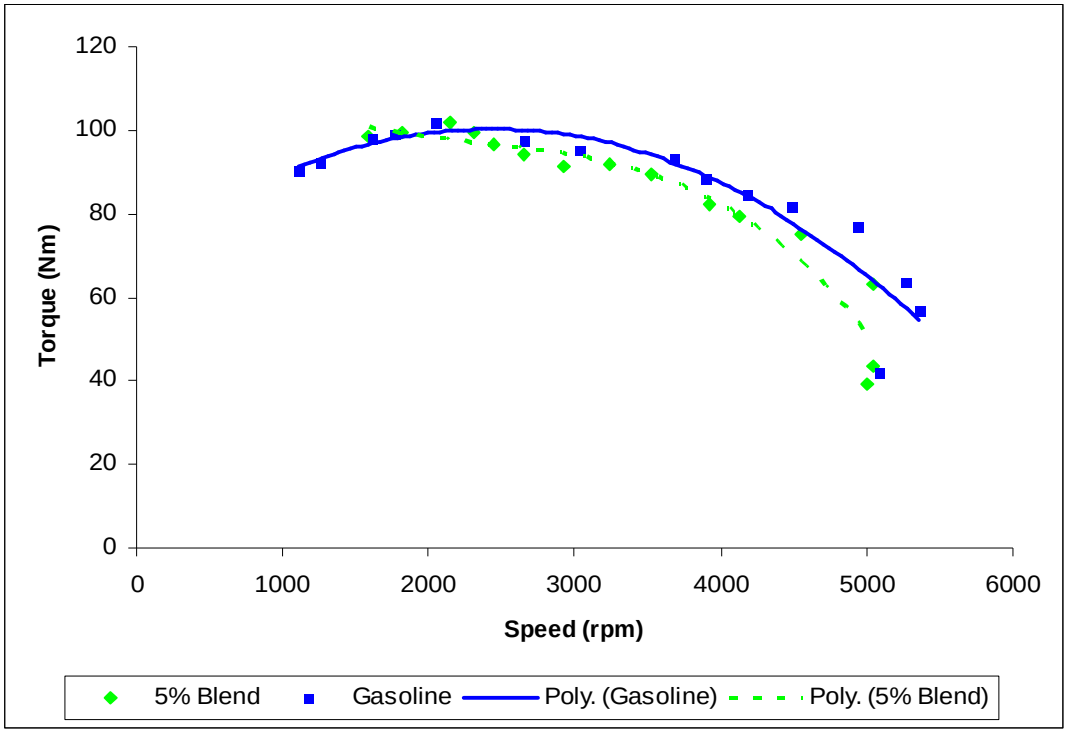


Figure 4.5. Torque-Engine Speed Graphic for Gasoline and 5% Butanol Blend

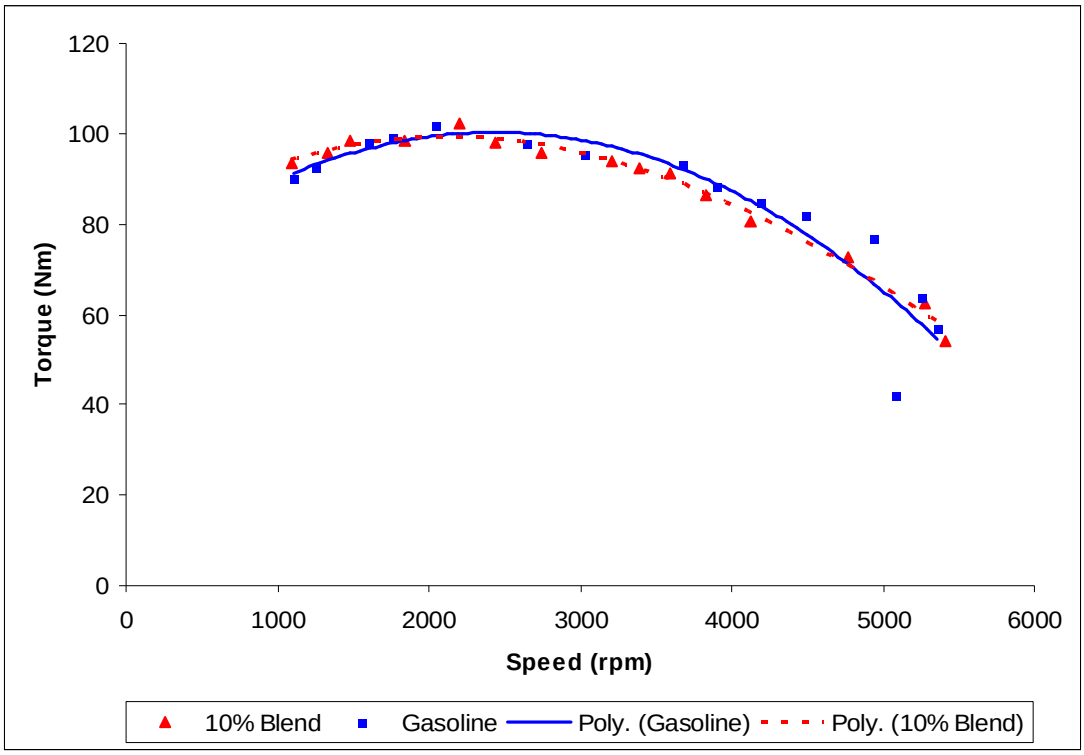


Figure 4.6. Torque-Engine Speed Graphic for Gasoline and 10% Butanol Blend

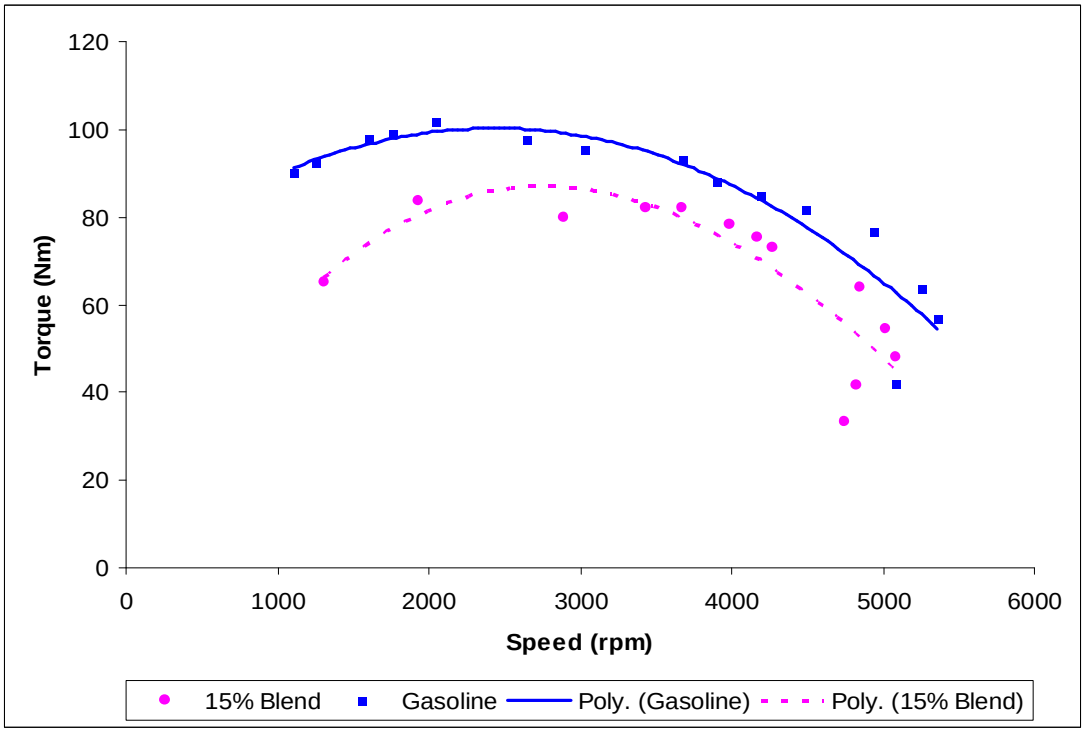


Figure 4.7. Torque-Engine Speed Graphic for Gasoline 15% Butanol Blend

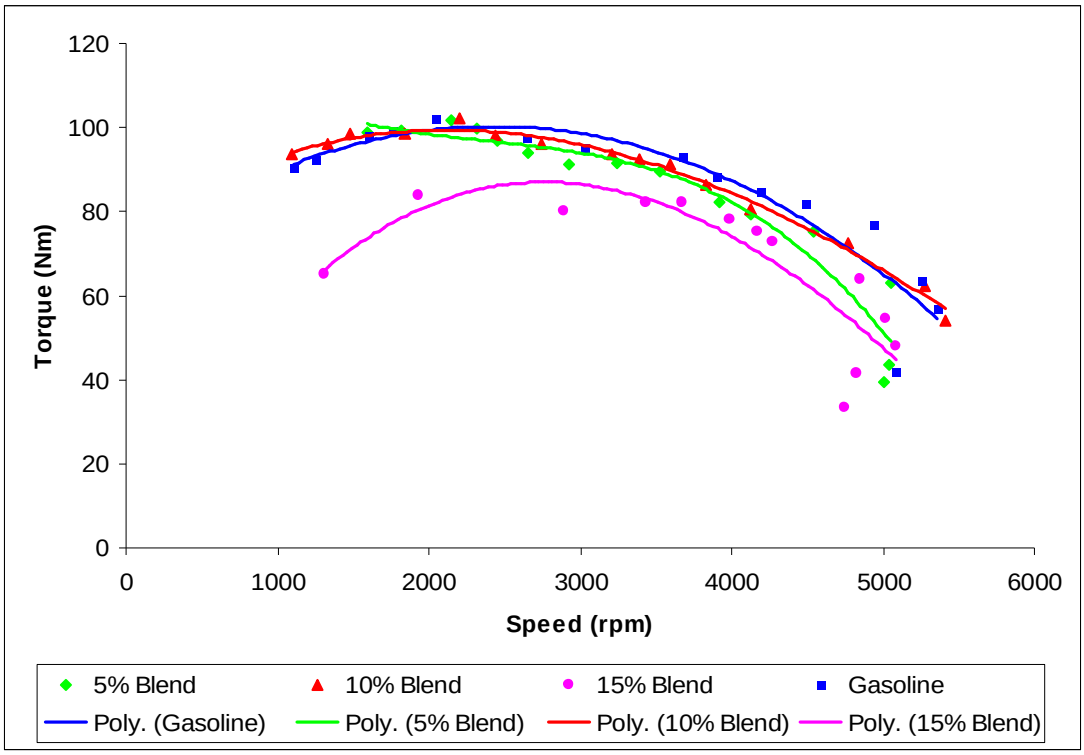


Figure 4.8. Torque-Engine Speed Graphics for Gasoline and All Butanol Blends

4.2.2. Power Versus Speed Graphics

Variations of engine power with engine speed are given in the following figures. Each graphics are given with butanol blends and pure gasoline results to compare each other. Also 2nd and 3rd order polynomials are fitted to the experimental results to indicate experimental error.

Engine power versus engine speed graphs show a hyperbolic curve for each fuel blends. Like in the torque-speed graphs, the power-speed graphs are similar to each other. 5% butanol blend achieved to the maximum of 49.88 HP power value at 4545 rpm (Table 4.3 and Figure 4.9) compared to 10% butanol blend achieved the maximum of 48.96 HP power value at 4771 rpm (Table 4.4 and Figure 4.10) and 15% butanol blend achieved the maximum of 45.13 HP power value at 4175 rpm (Table 4.5 and Figure 4.11). Pure gasoline is achieved the maximum of 53.15 HP power value at 4488 rpm (Table 4.2).

The speed where maximum power is obtained is higher than the speed where the maximum torque is obtained. The formula of the power-torque explains to this result. A falling off in volumetric efficiency at the higher speeds causes the falling off of the indicated power at high speed. The indicated power is not decreasing as fast as it would if the volumetric efficiency were the only parameter changing with speed.

Butanol addition to the gasoline does not affect engine power significantly, but especially at high engine speed (over 4500 rpm) there is a sharp reduction the power curves compared to pure gasoline (Figure 4.12). The reason of this reduction can be affected by the low calorific value of butanol. Higher purity butanol (99.8% purity) has to be used for fuel blend instead of technical butanol (96% purity) used in this study or dehydration process has to be applied to the technical butanol before any use in spark ignition engines.

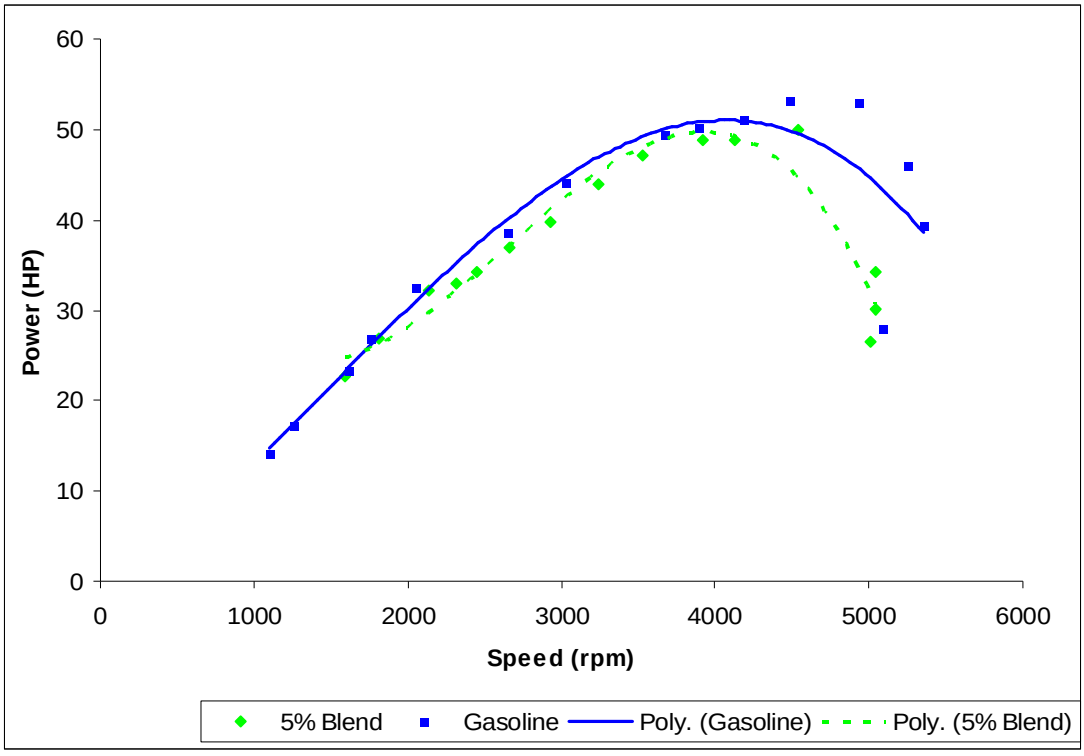


Figure 4.9. Power-Engine Speed Graphic for Gasoline and 5% Butanol Blend

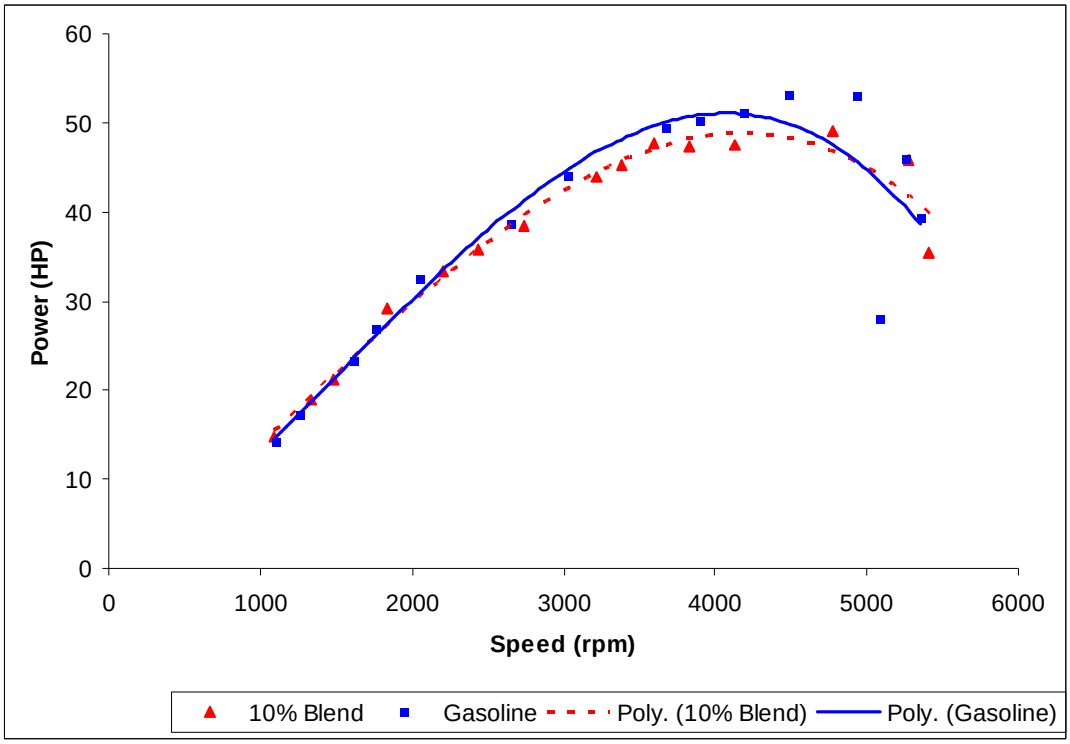


Figure 4.10. Power-Engine Speed Graphic for Gasoline and 10% Butanol Blend

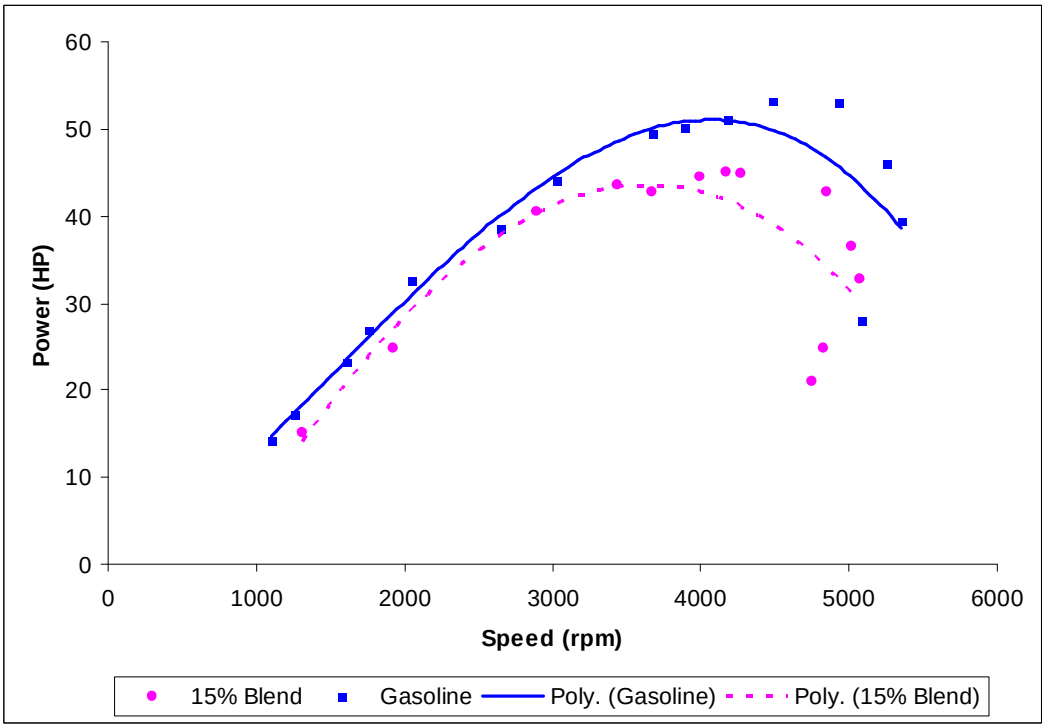


Figure 4.11. Power-Engine Speed Graphic for Gasoline and 15% Butanol Blend

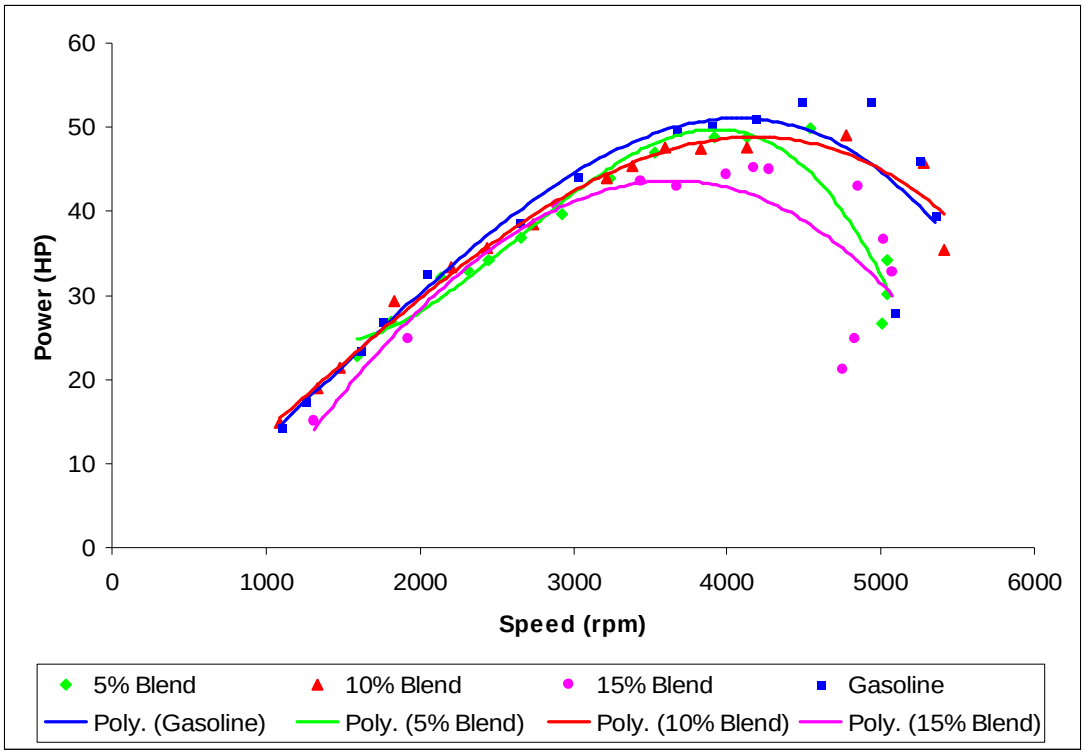


Figure 4.12. Power-Engine Speed Graphic for Gasoline and All Butanol Blends

4.2.3. Specific Fuel Consumption (SFC) Versus Speed Graphics

Variations of specific fuel consumption (SFC) with engine speed are given in the following figures. Each graphics are given with butanol blends and pure gasoline results to compare each other. Also 2nd and 3rd order polynomials are fitted to the experimental results to indicate experimental error.

Specific fuel consumption, abbreviated SFC, compares the ratio of the fuel used by an engine to a certain force such as the amount of power the engine produces. Specific fuel consumption allows engines of all different sizes to be compared to see which is the most fuel efficient. There are different types of specific fuel consumption. TSFC, thrust specific fuel consumption, and BSFC, brake specific fuel consumption, are two of the most common BSFC is used to calculate and compare how fuel efficient a reciprocating engine is. While it allows engines of all

sizes to be compared, resulting in a chart that shows the most efficient engine, it can also leave out other important factors.

Minimum values are desired for the SFC versus engine speed graphs because of the minimum fuel consumption per HP.h results better economy for the engine. It is expected that higher SFC values for butanol blends because of low calorific value of butanol. However similar SFC values for all fuel types were measured. Especially, SFC of 10% butanol blend gives the best result. SFC versus engine speed graphs of gasoline fluctuates compared to the butanol blends. 5% butanol blend achieved to the minimum of 246.13 g/HP.h SFC value at 5009 rpm (Table 4.3 and Figure 4.13) compared to 10% butanol blend achieved the minimum of 200.99 g/HP.h SFC value at 4771 rpm (Table 4.4 and Figure 4.14) and 15% butanol blend achieved the minimum of 211.14 g/HP.h SFC value at 5081 rpm (Table 4.5 and Figure 4.15). Pure gasoline is achieved the min. of 225.51 g/HP.h SFC value at 4488 rpm (Table 4.2).

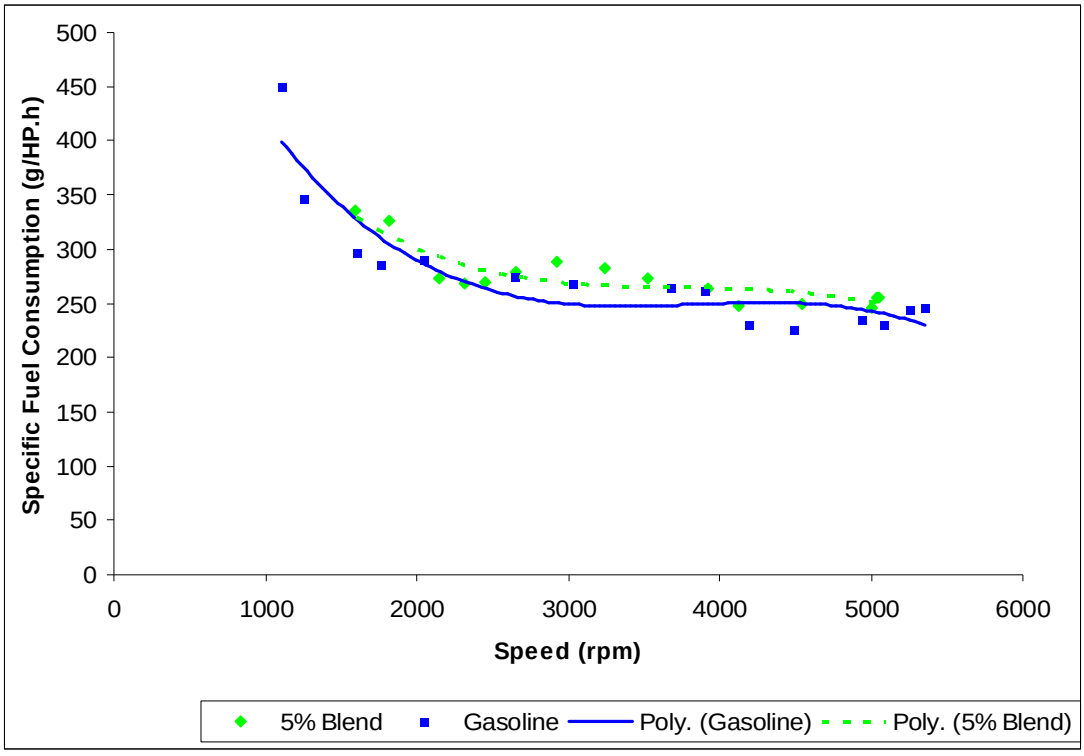


Figure 4.13. SFC-Engine Speed Graphic for Gasoline and 5% Butanol Blend

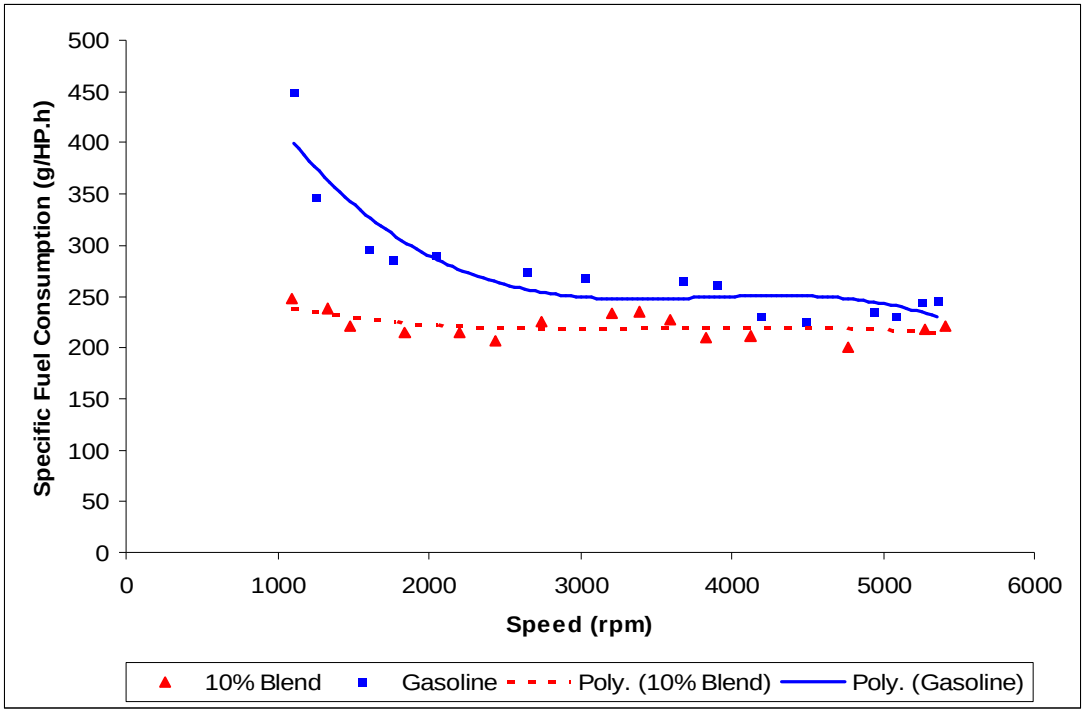


Figure 4.14. SFC-Engine Speed Graphic for Gasoline and 10% Butanol Blend

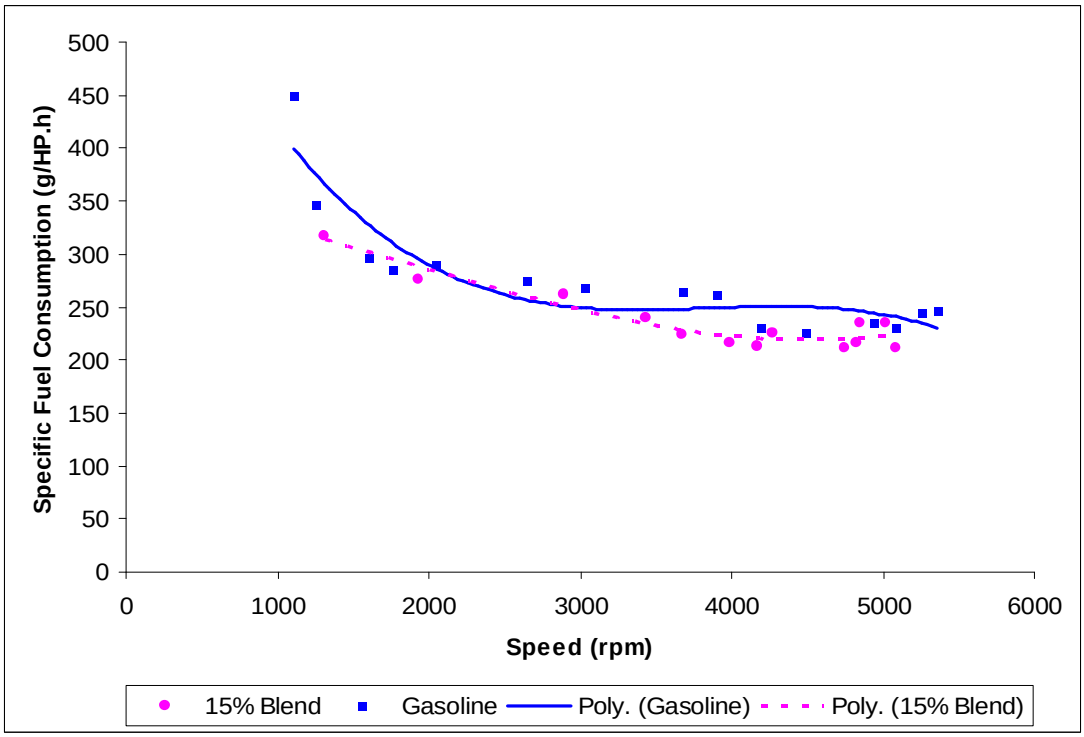


Figure 4.15. SFC-Engine Speed Graphic for Gasoline and 15% Butanol Blend

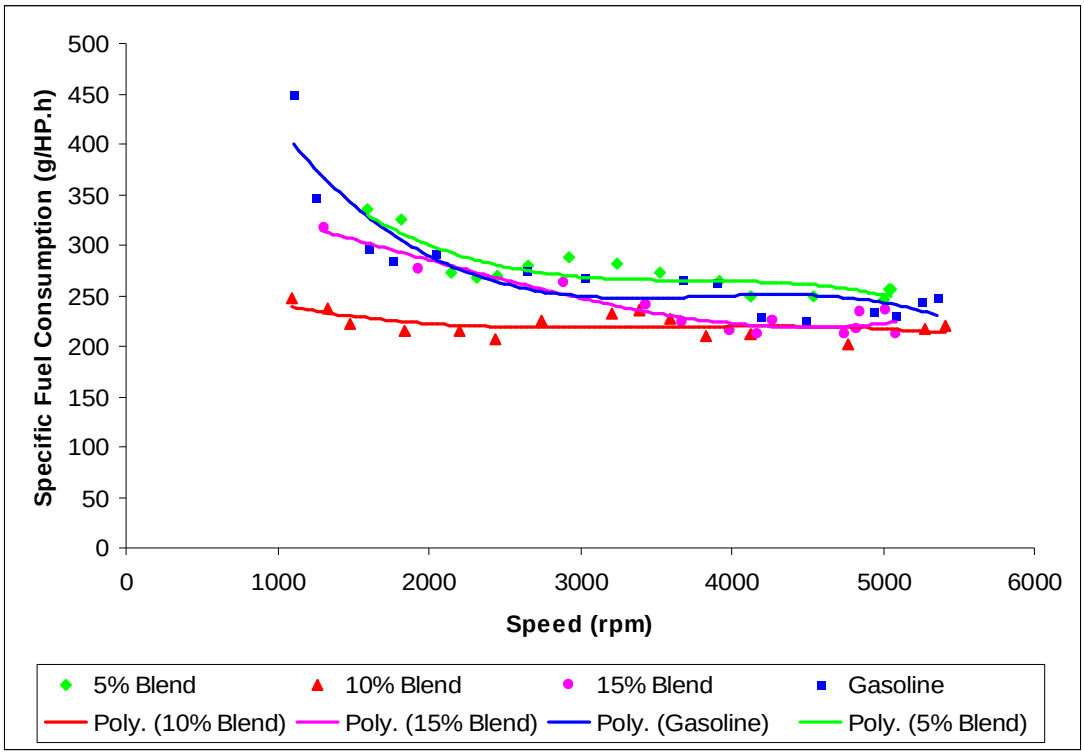


Figure 4.16. SFC-Engine Speed Graphic for Gasoline and All Butanol Blends

4.3. Exhaust Emissions and Air Fuel Ratio (AFR) Values of Fuel Blends

Fuels consist of Hydrogen (H) and Carbon (C) molecules. During the combustion period in the engine cylinder, these C and H molecules react with oxygen (O_2) in the air and converted to the CO, CO_2, HC. These exhaust tail emissions are harmful for health and environmental pollution. Exhaust emissions were measured by SUN MGA-1200 exhaust gas analyzer. There was not any connection to the data logging unit, therefore during the engine test exhaust emission values are recorded manually. Engine speed results of performance test can be different with exhaust emissions test because performance test results were recorded by data logging unit while emission results read by taken photograph of exhaust emission analyzer screen. Measured emission values of pure gasoline (Table 4.6) and 5% (Table 4.7), 10% (Table 4.8), 15% (Table 4.9) butanol blendes are shown in following tables below.

Table 4.6. Exhaust Emissions of Gasoline

Speed (rpm)	CO % vol	CO2 % vol	HC ppm vol	AFR
5351	9,56	8,09	445	11,9
4933	9,38	9,5	434	12,1
4488	8,65	9,6	427	12,67
4188	8,03	9,5	411	12,85
3674	7,65	9,43	400	13,12
3033	6,03	9,56	398	13,45
2648	5,8	9,6	389	13,67
2050	6,5	9,54	376	13,5
1253	7	9,5	370	13,6

Table 4.7. Exhaust Emissions of 5% Blend

Speed (rpm)	CO % vol	CO_2 % vol	HC ppm vol	AFR
5275	4,23	11,1	325	15,2
4771	4,28	10,92	315	15,11
4128	4,35	10,88	306	15
3833	4,41	10,93	293	15,22
3212	4,48	11,04	287	15,28
2741	4,53	11,1	282	15,33
2206	4,55	11,24	279	14,87
1838	4,6	11,31	275	14,54
1096	4,62	11,35	270	14,26

Table 4.8. Exhaust Emissions of 10% Blend

Speed (rpm)	CO % vol	CO2 % vol	HC ppm vol	AFR
4829	3,81	12,23	310	14,58
5018	3,88	11,9	312	14,56
4272	3,9	11,87	309	14,55
3992	3,99	11,92	297	14,5
3677	4,03	11,76	291	14,46
3435	4,21	11,64	285	14,4
2891	4,29	11,45	279	14,32
1931	4,35	11,32	275	14,28
1310	4,38	11,01	270	14,2

Table 4.9. Exhaust Emissions of 15% Blend

Speed (rpm)	CO % vol	CO_2 % vol	HC ppm vol	AFR
5041	4,45	12,41	395	15,03
4545	4,39	12,35	384	14,97
3922	4,56	12,31	377	14,91
3242	4,78	12,27	361	14,86
2928	4,81	12,21	350	14,81
2657	4,79	12,14	348	14,8
2142	4,7	12,05	339	14,78
1817	4,68	11,98	326	14,77
1589	4,6	12,04	320	14,75

4.3.1. Carbon Monoxide (CO)

Variations of CO emissions with engine speed are given in the following figures. Each graphics are given with butanol blends and pure gasoline results to compare each other. Also 2nd and 3rd order polynomials are fitted to the experimental results to indicate experimental error.

Carbon Monoxide (CO) is colorless, odorless, tasteless gas which is lighter than air. It is highly toxic to humans and animals in higher quantities.

As shown graphics below those CO values of 5% (Figure 4.17), 10% (Figure 4.18) and 15% (Figure 4.19) butanol blendes are quite lower than gasoline (Figure 4.20), because of nearly 15% oxygen contents of butanol. CO emissions are very high in especially high engine speed in gasoline. On the other hand, the amount of CO is stable and low for all butanol blends. The amount of CO emissions for gasoline is in between 7-10 % volume while amount of CO emissions for butanol blends are in between 4-5 % volume. There is almost 80% reduction of CO emission with adding butanol to the gasoline.

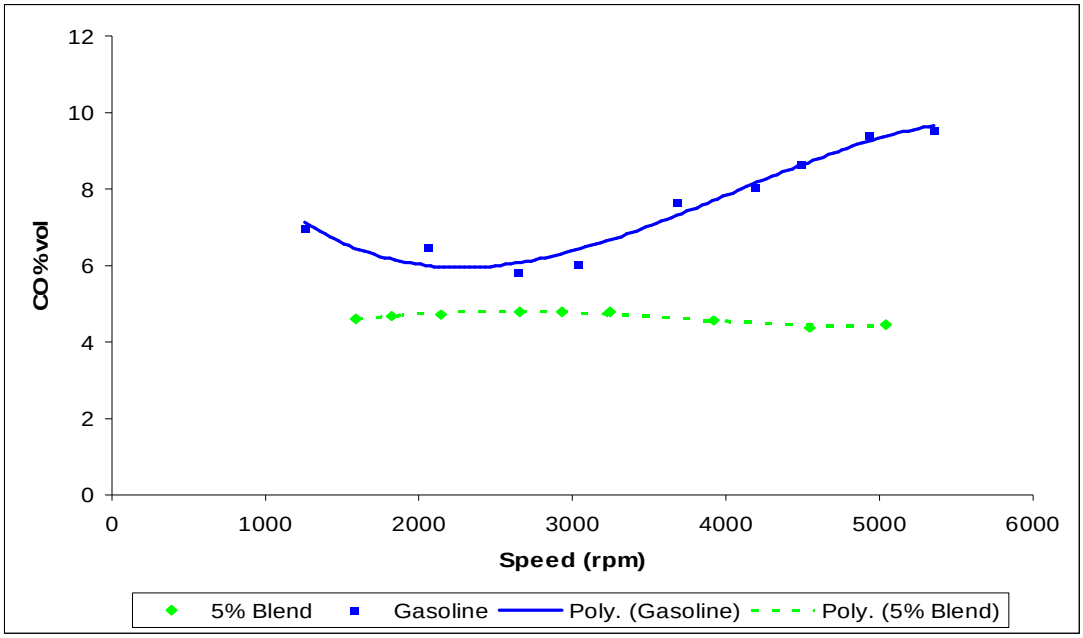


Figure 4.17. CO Emission-Engine Speed Graphic for Gasoline and 5% Butanol Blend

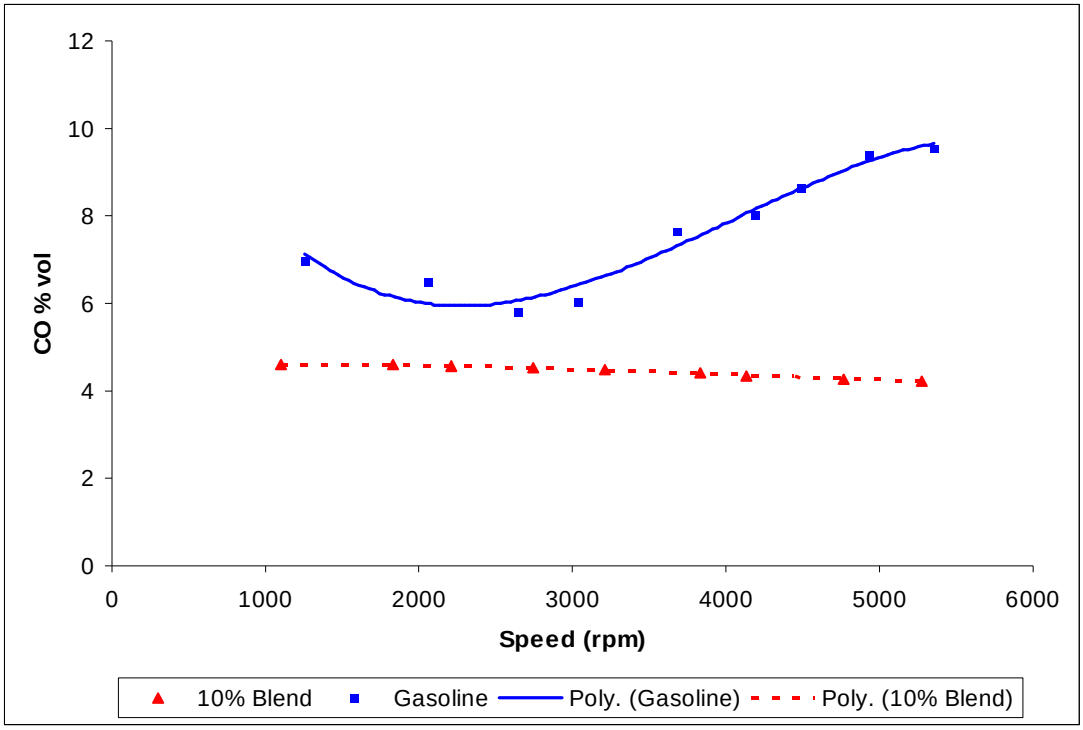


Figure 4.18. CO Emission-Engine Speed Graphic for Gasoline and 10% Butanol Blend

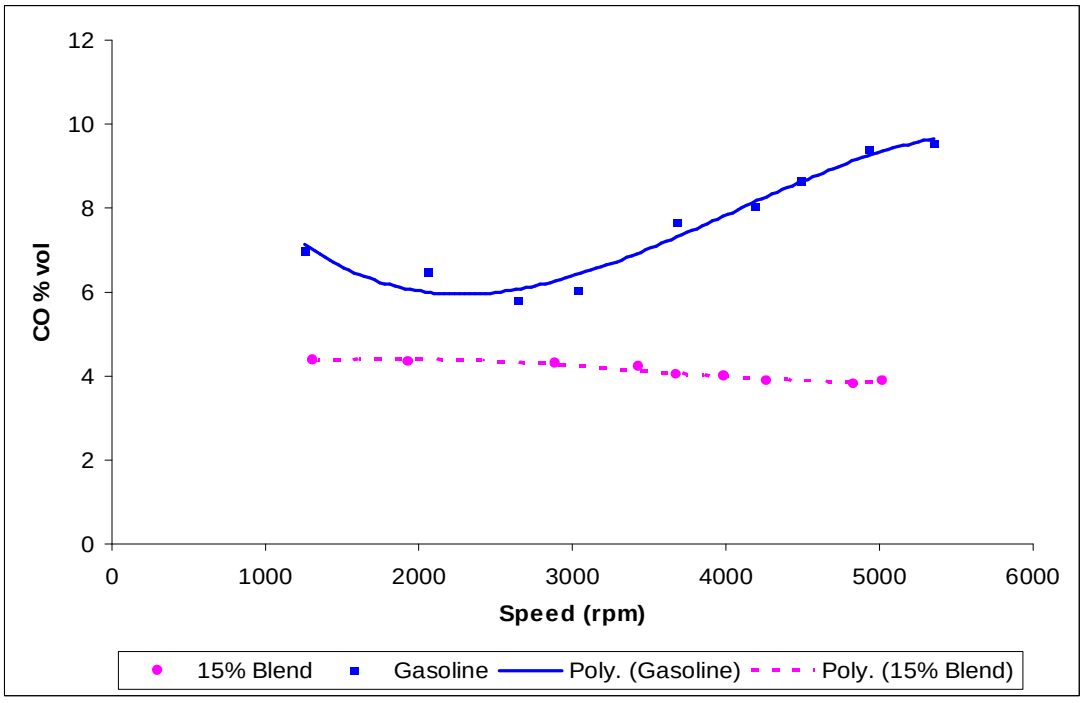


Figure 4.19. CO Emission-Engine Speed Graphic for Gasoline and 15% Butanol Blend

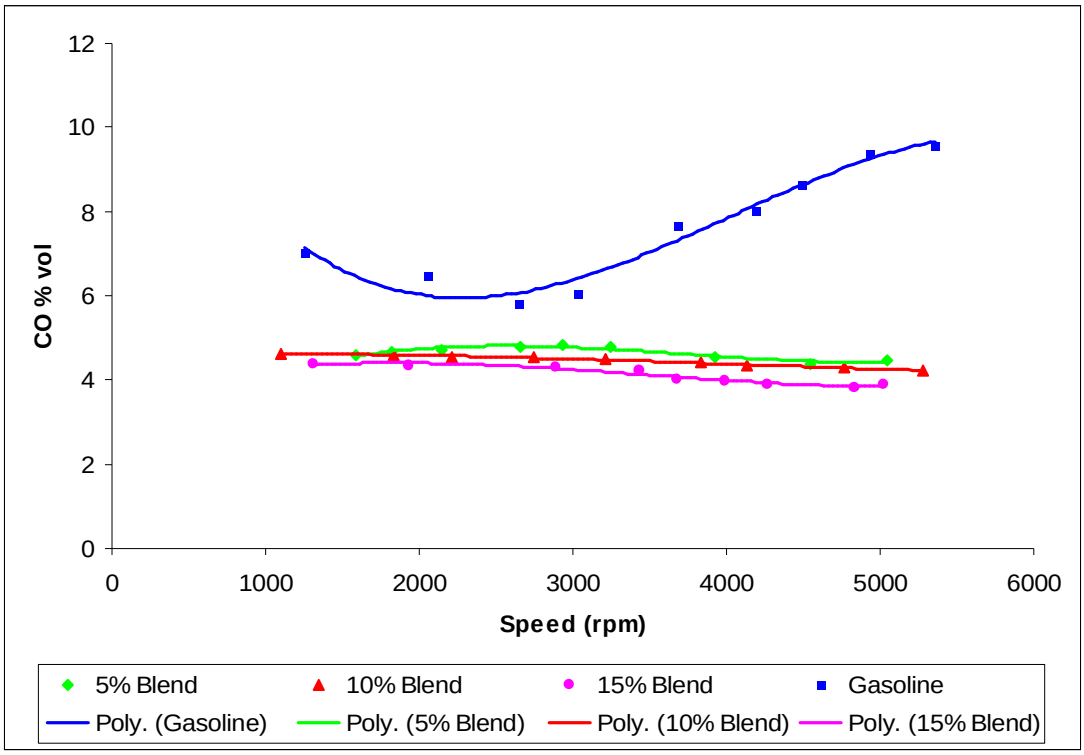


Figure 4.20. CO Emission-Engine Speed Graphic for Gasoline and All Butanol Blend

4.3.2. Carbon Dioxide (CO_2)

Variations of CO_2 emissions with engine speed are given in the following figures. Each graphics are given with butanol blends and pure gasoline results to compare each other. Also 2^{nd} and 3^{rd} order polynomials are fitted to the experimental results to indicate experimental error.

CO_2, which is a greenhouse gas, is very lesser harmful to the environment from CO and HC gases. All hydrocarbon fuels contain carbon, therefore after the combustion CO or CO_2 some gases have to be emitted and CO_2 is preferred instead of more harmful gas for the human health of CO.

As shown graphics below, CO_2 emissions are more in all butanol blends (Figure 4.21-Figure 4.23) compared to the gasoline (Figure 4.24) because of oxygen contents of butanol results complete combustion. The amount of CO_2 emissions for gasoline is in between 8-10 % volume while amount of CO_2 emissions for butanol blends are in between 11-12 % volume.

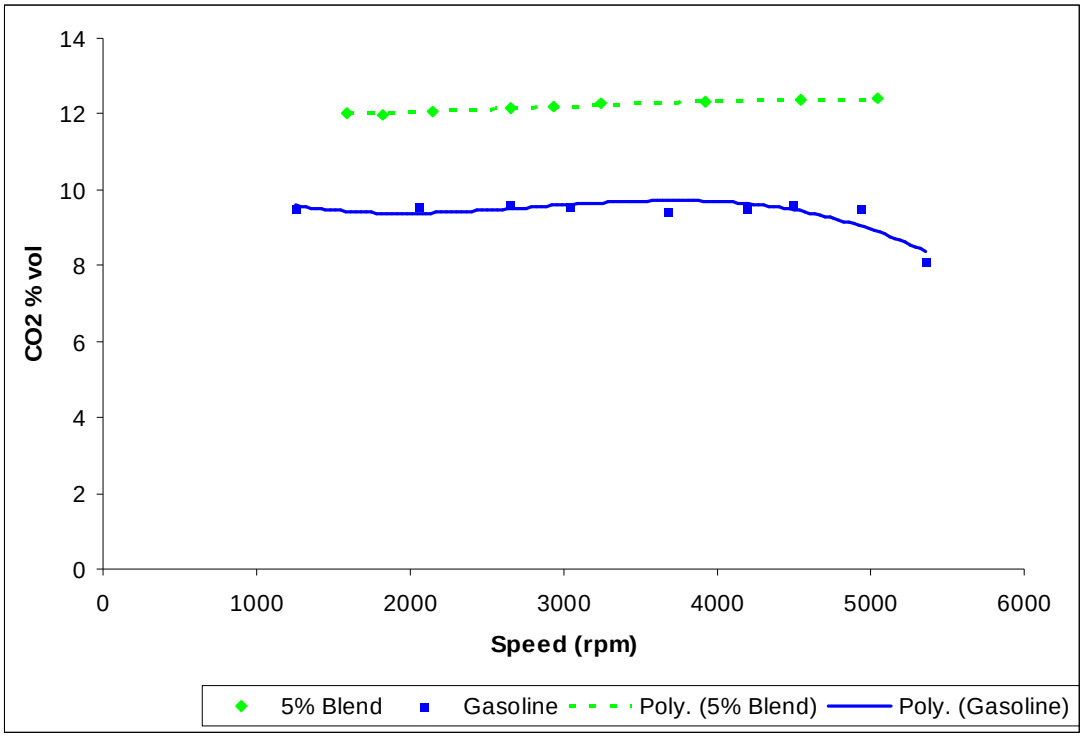


Figure 4.21. CO_2 Emission-Engine Speed Graphic for Gasoline and 5% Butanol Blend

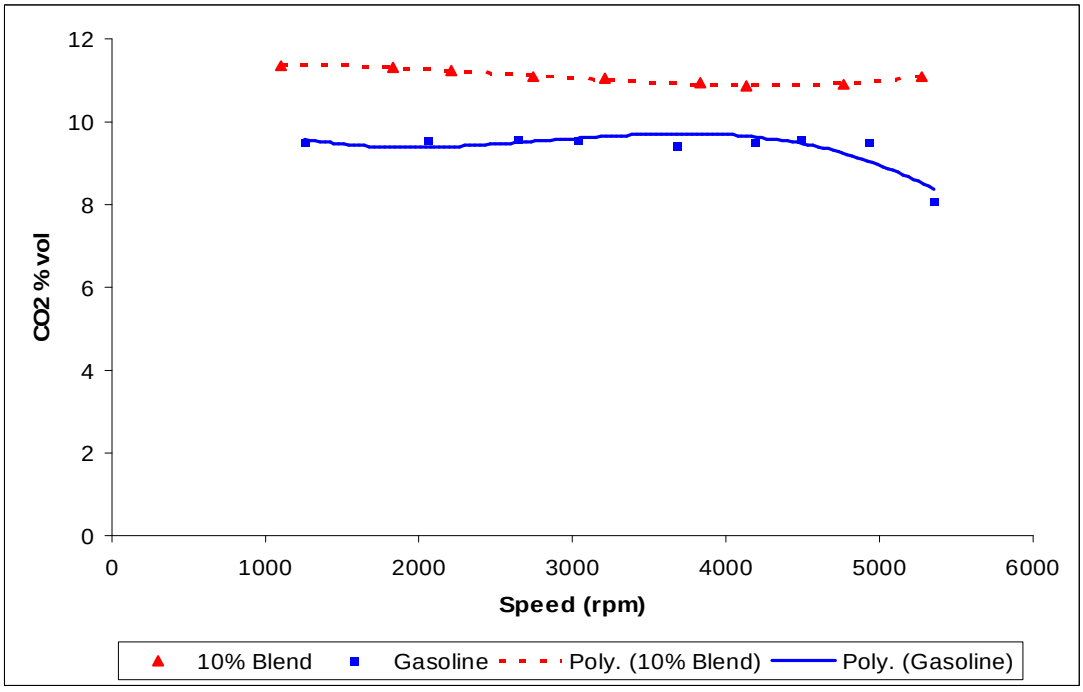


Figure 4.22. CO_2 Emission-Engine Speed Graphic for Gasoline and 10% Butanol Blend

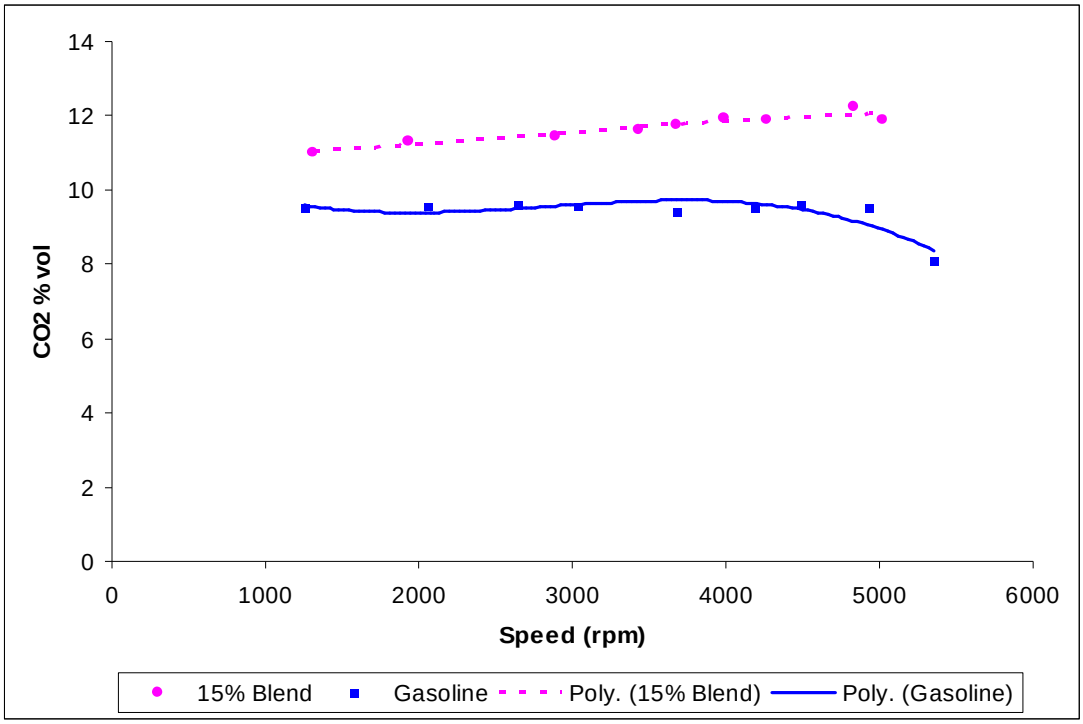


Figure 4.23. CO_2 Emission-Engine Speed Graphic for Gasoline and 15% Butanol Blend

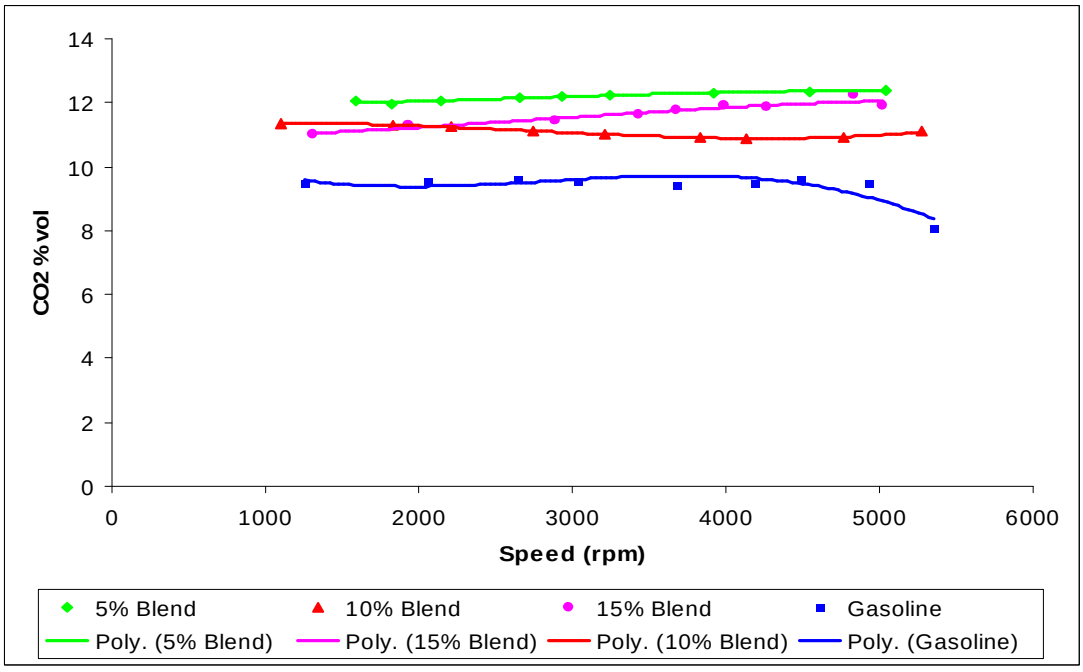


Figure 4.24. CO_2 Emission-Engine Speed Graphic for Gasoline and All Butanol Blend

4.3.3. Hydrocarbon (HC)

Variations of HC emissions with engine speed are given in the following figures. Each graphics are given with butanol blends and pure gasoline results to compare each other. Also 2nd and 3rd order polynomials are fitted to the experimental results to indicate experimental error.

As shown graphics below those HC values of 5% (Figure 4.25), 10% (Figure 4.26) and 15% (Figure 4.27) butanol blendes are quite lower than gasoline (Figure 4.28), because of nearly 15% oxygen contents of butanol. HC emissions are very high in especially high engine speed in gasoline. On the other hand, the amount of HC is stable and low for all butanol blends. The amount of HC emissions for gasoline is in between 400-450 ppm (Figure 4.28) while the amount of HC emissions for 5% butanol blend (Figure 4.25) is in between 350-400 ppm, and the amount of HC emissions for 10% (Figure 4.26) and 15% (figure 4.27) butanol blends are in between 270-325 ppm.

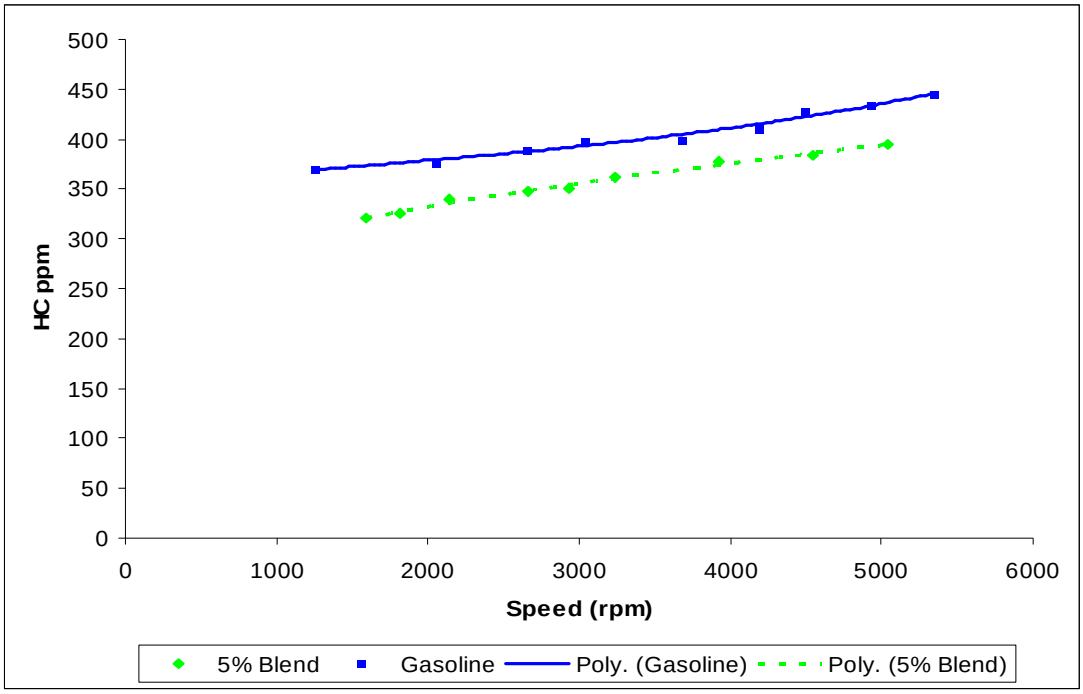


Figure 4.25. HC Emission-Engine Speed Graphic for Gasoline and 5% Butanol Blend

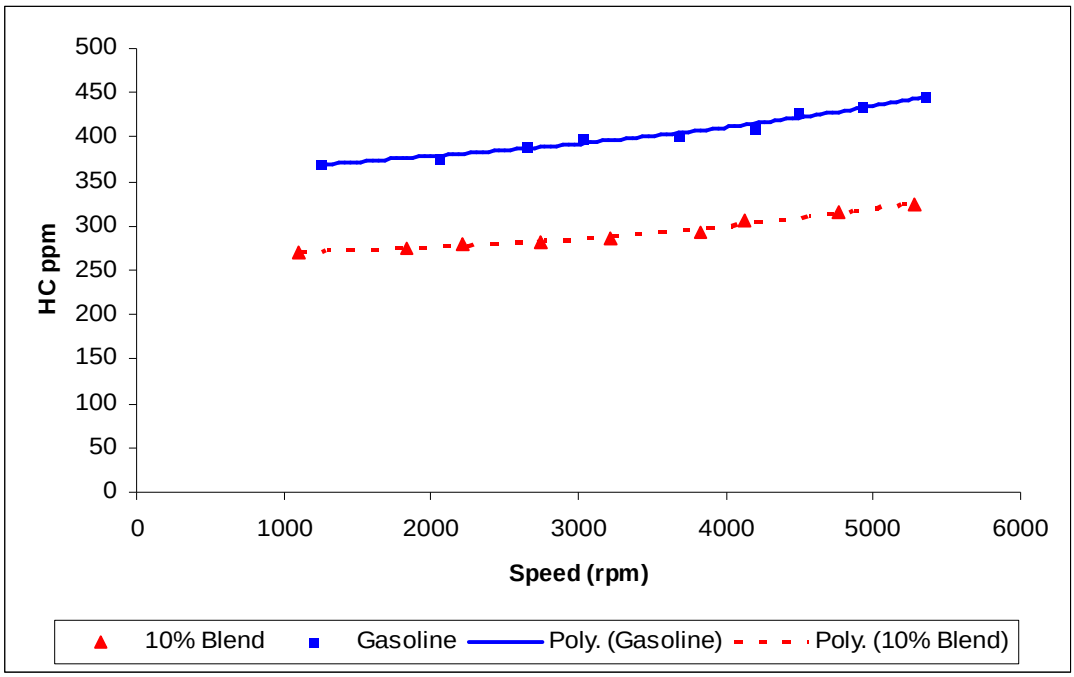


Figure 4.26. HC Emission-Engine Speed Graphic for Gasoline and 10% Butanol Blend

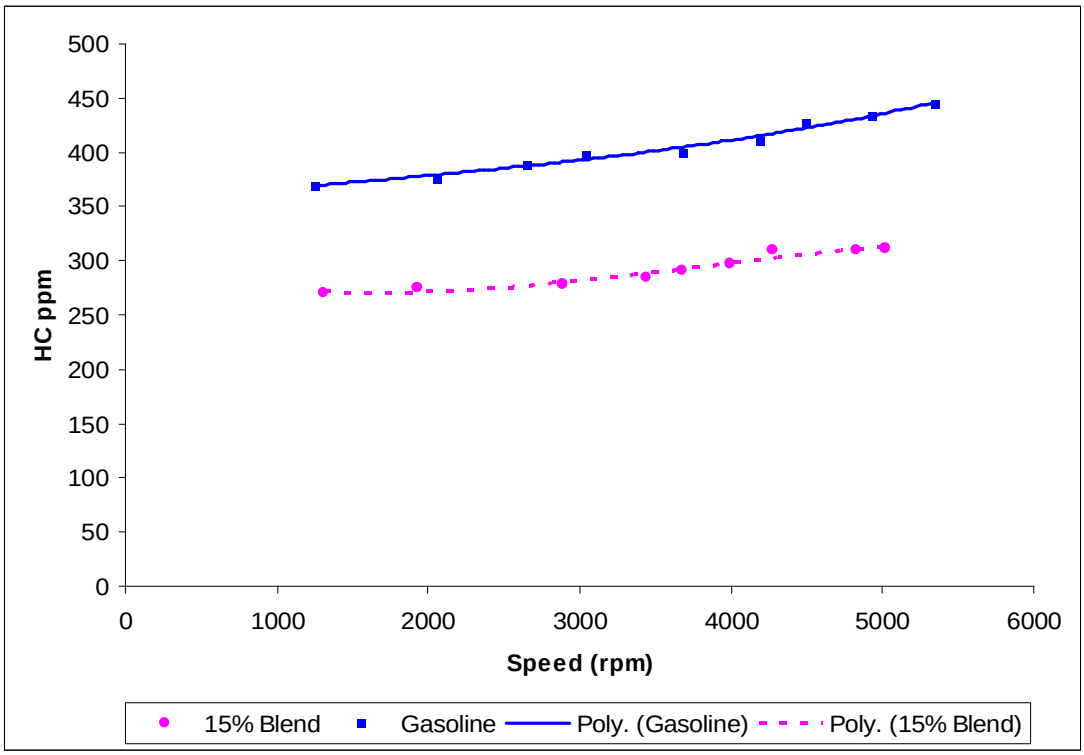


Figure 4.27. HC Emission-Engine Speed Graphic for Gasoline and 15% Butanol Blend

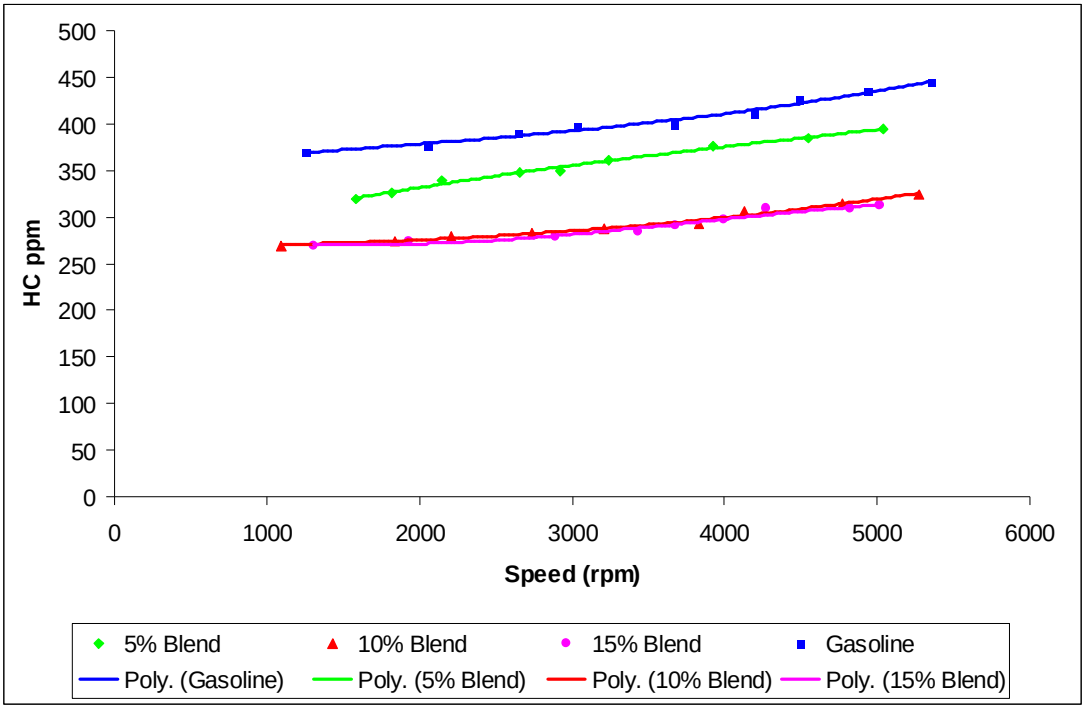


Figure 4.28. HC Emission-Engine Speed Graphic for Gasoline and All Butanol Blend

4.3.4. Air Fuel Ratio (AFR)

Variations of AFR values with engine speed are given in the following figures. Each graphics are given with butanol blends and pure gasoline results to compare each other. Also 2nd and 3rd order polynomials are fitted to the experimental results to indicate experimental error.

Air-fuel ratio (AFR) is the mass ratio of air to fuel present during combustion. When all fuel is combined with all free oxygen, this is chemically balanced and this AFR is called the stoichiometric mixture. AFR is an important measure for anti-pollution and performance of engines. Lambda (λ) is an alternative way to represent AFR. For gasoline fuel, the stoichiometric air/fuel mixture is approximately 14.7 times the mass of air to fuel. Any mixture less than 14.7 is considered to be a rich mixture; any mixture more than 14.7 is a lean. As shown below graphics, AFR for all butanol blends (Figure 4.29-Figure 4.31) are higher and near to stoichiometric

air/fuel mixture compared to gasoline (Figure 4.32). AFR of gasoline is in between 12-13.9 which is rich mixture.

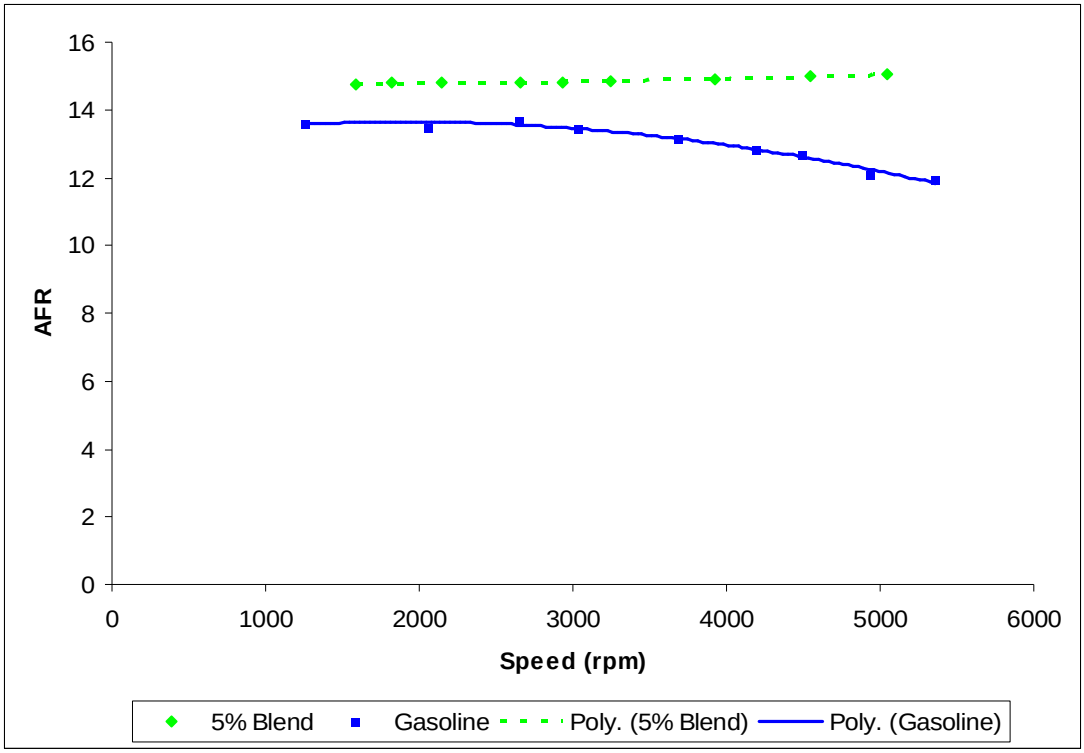


Figure 4.29. AFR-Engine Speed Graphic for Gasoline and 5% Butanol Blend

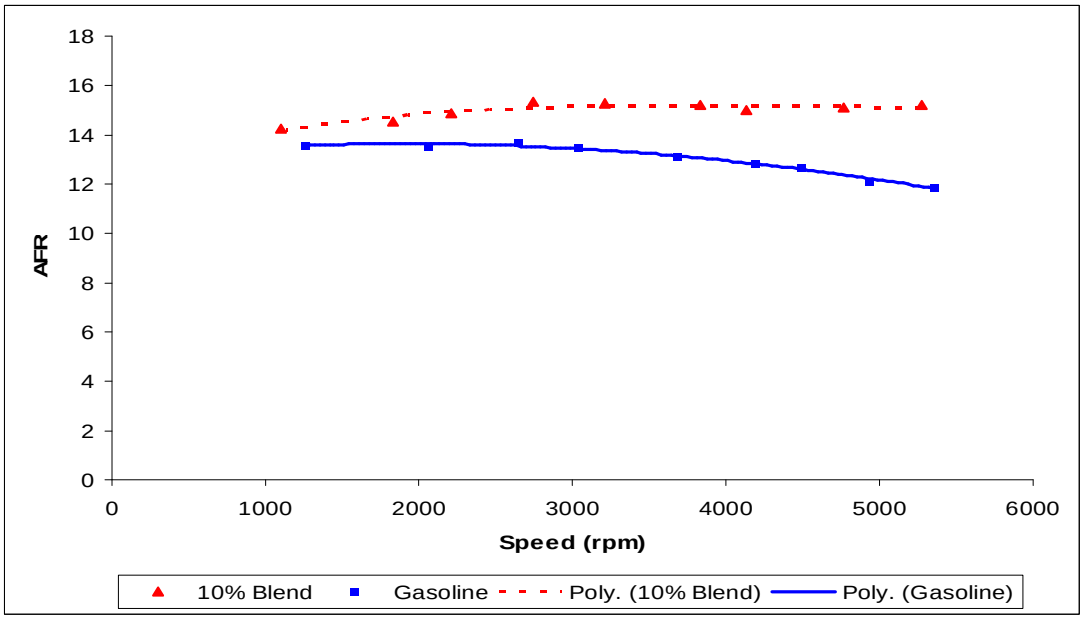


Figure 4.30. AFR-Engine Speed Graphic for Gasoline and 10% Butanol Blend

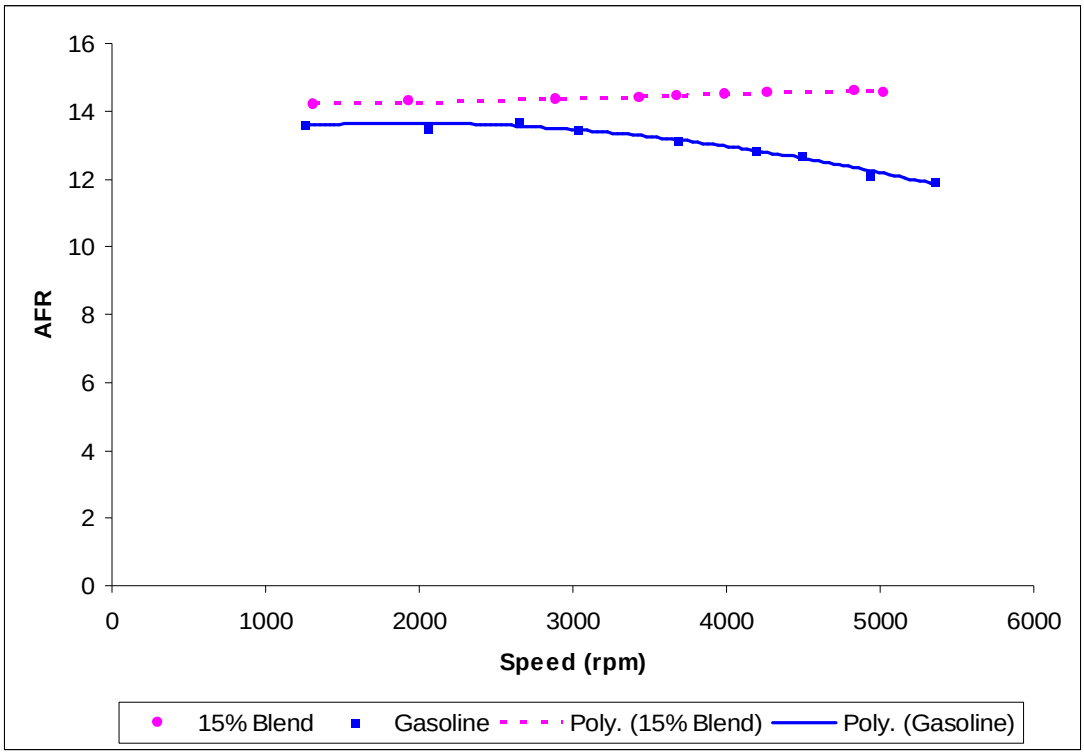


Figure 4.31. AFR-Engine Speed Graphic for Gasoline and 15% Butanol Blend

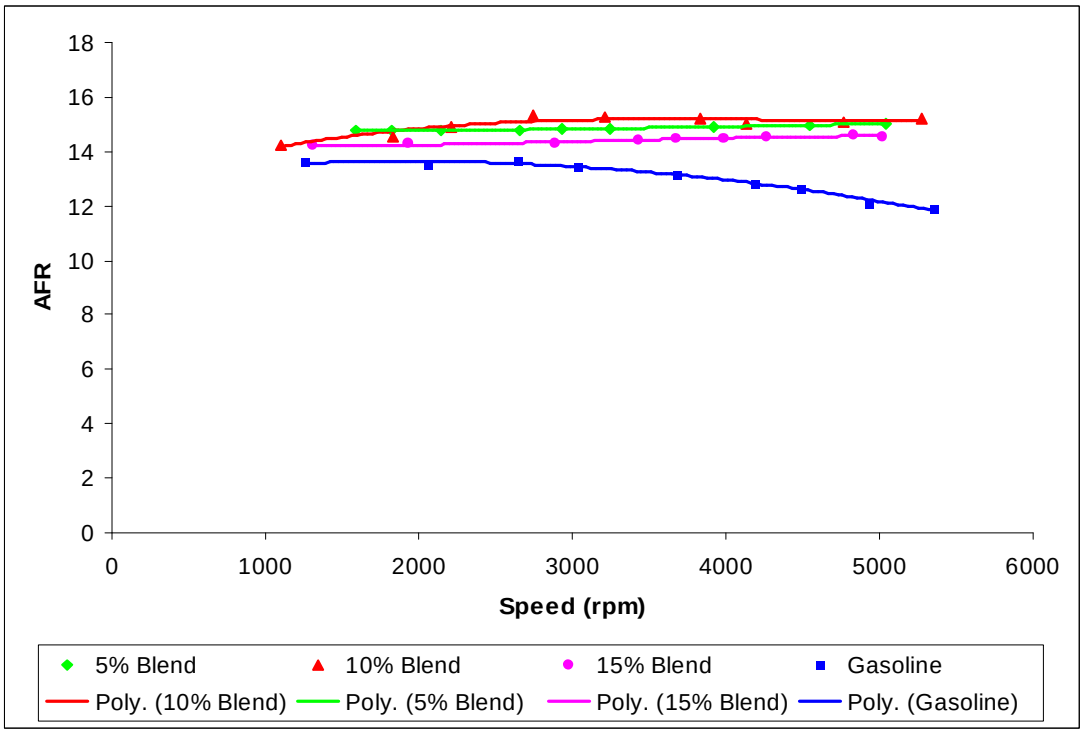


Figure 4.32. AFR-Engine Speed Graphic for Gasoline and All Butanol Blends

5. CONCLUSION

Butanol is an alcohol which can be used as a fuel in spark ignition engines without engine modification. It is typically a product of the fermentation of biomass by the bacterium. The advantages of butanol as known:

- It has got high octane rating and high energy content, only about 10% lower than gasoline, and subsequently about 50% more energy dense than ethanol, 100% more so than methanol.
- Due to its low vapor pressure it can be easily blended with gasoline.
- It is less corrosive; it is also expected to be more suitable for use in existing oil pipelines.
- Butanol when consumed in an internal combustion engine yields no SO_X, NO_X or carbon monoxide all environmentally harmful by products of combustion. CO_2 is the combustion by product of butanol.
- While ethanol and methanol have lower energy densities than butanol, their higher octane number allows for greater compression ratio and efficiency. Higher combustion engine efficiency allows for lesser greenhouse gas emissions per unit motive energy extracted.

On the other hand, the disadvantages of butanol are:

- Butanol is much more expensive than ethanol (approx. 6 TL per liter) and ethanol and methanol.
- It has got high flashpoint (35 °C), toxicity (note that toxicity levels exist but are not precisely confirmed), and the fact that the fermentation process for renewable butanol emits a foul odor.
- To match the combustion characteristics of gasoline, the utilization of butanol fuel as a substitute for gasoline requires fuel-flow increases (though butanol has only slightly less energy than gasoline, so the fuel-flow increase required is only minimal, around 10%).
- Alcohol-based fuels are not compatible with some fuel system components.
- Alcohol fuels may cause erroneous gas gauge readings in vehicles with capacitance fuel level gauging

In this experimental study, affects of fuel blends that are prepared by mixing butanol with gasoline at volumetric rate of 5%, 10% and 15% to performance and exhaust emissions of a petrol engine were investigated. According to experimental results it was determined that addition of butanol to gasoline decreased engine performance values due to its lower heating value; however, since butanol contains oxygen, it increased combustion efficiency and as a result caused reduction of exhaust emission values at important rates. Based on the experimental study, the following results were obtained:

- The density of gasoline is 0.749 g/cm^3. Therefore, densities of the blends are dependent of the butanol content in the blend directly.
- MON of pure butanol is very low compared to gasoline (76.3 instead of 87.54). However, butanol blends with gasoline have given better results; therefore pure butanol used in this study is not suitable for spark ignition engines.
- RON of butanol is 82.13 compared to gasoline of 98.76. RON of butanol used in this study is low and it has to be blended with gasoline at the ratio of maximum of 25%.
- The calorific value shows that butanol used in this study contains water (purity 96%) and butanol has to be dehydrated before any usage in spark ignition engines.
- Torque-speed curves of the butanol fuel blends are similar to the torque-speed curve of pure gasoline. Only, torque values of 15% blend is lesser than the others. 5% butanol blend achieved the maximum of 101.62 Nm torque value at 2142 rpm compared to the 10% butanol blend achieved the maximum of 102.29 Nm torque value at 2206 rpm and 15% butanol blend achieved the maximum of 82 Nm torque value at 3435 rpm. Pure gasoline achieved the maximum of 101.94 Nm torque value at 2050 rpm. Calorific value of butanol is lesser than the calorific value of gasoline therefore it is expected that any butanol addition to the gasoline reduces the torque output of the engine. However oxygen content of butanol improves the combustion in the cylinder

and with the 5% and %10 butanol blends similar value are achieved with gasoline.

- The engine torque increases up to the maximum torque point. And then, torque curve begins to go down. Viscous friction effects increase quadratically with engine speed. So, the torque curve decrease at high engine speeds. Since, the torque will depend on the product of air-fuel ratio and delivery ratio. When the two variables are increased simultaneously there will be large change in the torque.
- Butanol addition to the gasoline does not affect engine power significantly, but especially at high engine speed (over 4500 rpm) there is a sharp reduction the power curves compared to pure gasoline. The reason of this reduction can be affected by the low calorific value of butanol. Higher purity butanol (99.8% purity) has to be used for fuel blend instead of technical butanol (96% purity) used in this study or dehydration process has to be applied to the technical butanol before any use in spark ignition engines.
- CO values of 5%, 10% and 15% butanol blendes are quite lower than gasoline, because of nearly 15% oxygen contents of butanol. CO emissions are very high in especially high engine speed in gasoline. On the other hand, the amount of CO is stable and low for all butanol blends. The amount of CO emissions for gasoline is in between 7-10 % volume while amount of CO emissions for butanol blends are in between 4-5 % volume. There is almost 80% reduction of CO emission with adding butanol to the gasoline.
- CO_2 emissions are more in all butanol blends (Figure 4.21-Figure 4.23) compared to the gasoline because of oxygen contents of butanol results complete combustion. The amount of CO_2 emissions for gasoline is in between 8-10 % volume while amount of CO_2 emissions for butanol blends are in between 11-12 % volume.

- HC values of 5%, 10% and 15% butanol blendes are quite lower than gasoline, because of nearly 15% oxygen contents of butanol. HC emissions are very high in especially high engine speed in gasoline. On the other hand, the amount of HC is stable and low for all butanol blends. The amount of HC emissions for gasoline is in

between 400-450 ppm while the amount of HC emissions for 5% butanol blend is in between 350-400 ppm, and the amount of HC emissions for 10% and 15% butanol blends are in between 270-325 ppm.

In conclusion, although butanol blends were not very good in performance of torque and power in engine against to gasoline, but, provided regular working in engine. Especially, 5% and 10% butanol blends can be used in engine for providing lesser fuel consumption and lesser air pollutions by providing enough engine performance.

REFERENCES

ALASFOUR, F.N., June 1997, Butanol a Single Cylinder Engine Study, Applied Thermal Engineering, Vol.17, Number 6, pp. 537-549.

COONEY, C., WALLNER, T., MCCONNELL, S., May 2009, Effects of Blending Gasoline with Ethanol and Butanol on Engine Efficiency and Emissions using a Direct-Injection Spark-Ignition Engine, Proceedings of the ASME Internal Combustion Engine Division 2009 Spring Technical Conference ICES2009-76155, Milwaukee, Wisconsin, USA.

COLLINS, C.D., 2007, Implementing Phytoremediation of Petroleum Hydrocarbons, Methods in Biotechnology, Vol. 23, pp. 99-108.

DAGAUT, P., TOGBE, C., November 2008, Oxidation Kinetics of Butanol–Gasoline Surrogate Mixtures in a Jet-Stirred Reactor: Experimental and Modeling Study, Fuel, Vol. 87, Issues 15-16, pp. 3313–3321.

MINTER, S., 2006, Alcoholic Fuels, Taylor&Francis Group, 270 pages.

RAMEY, D., YANG, S.T., 2004, Production of Butyric Acid and Butanol from Biomass, Final Report, U.S. Department of Energy, DE-F-G02-00ER86106, 103 pages.

RAKOPOULOS, C.D., MICHOS, C.N., May 2009, Generation of Combustion Irreversibility in a Spark Ignition Engine under Biogas–Hydrogen Mixtures Fueling, International Journal of Hydrogen Energy, Vol. 34, Issue 10, pp. 4422-4437.

RAKOPOULOS, D.C., RAKOPOULOS, C.D., GIAKOUMIS, E.G., DIMARATOS, A.M., KYRITSIS, D.C., 2010, Effects of Butanol–Diesel Fuel Blends on the Performance and Emissions of a High-Speed DI Diesel Engine, Energy Conversion and Management, Vol.51, Issue 10, pp. 1989-1997.

SARATHY, S.M., THOMSON, M.J., TOGBE, C., DAGAUT, P., HALTER, F., MOUNAIM-ROUSSELLE, C., 2009, An Experimental and Kinetic Modeling Study of *n*-butanol Combustion, Combustion and Flame, Vol. 156, pp. 852-864.

SMITH, J.L., WORKMAN, J.P., December 2007, Alcohol for Motor Fuels, Fact Sheet, Colorado State University, No. 5.010.

SZWAJA, S., NABER, J.D., 2010, Combustion of n-Butanol in a Spark Ignition IC Engine, Fuel, Vol. 89, Isuse 7, pp.1573-1582.

TOPGÜL, T., YÜCESU, H., ÇINAR, C., 8-9 September 2004, The Experimental Investigation of the Effect of Ethanol–Gasoline Blends on Engine Performance in Different Compression Ratios on a Spark Ignition Engine, Eighth International Combustion Symposium, Ankara, Turkey.

YACOUP, Y., BATA, R., GAUTAM, M., 1998, The Performance and Emission Characteristics of C1–C5 Alcohol–Gasoline Blends with Matched Oxygen Content in a Single Cylinder Spark Ignition Engine, Proceedings of Institution of Mechanical Engineers, Part A. Journal of Power and Energy, Vol. 212, No: 5, pp. 363–379.

YAO, M., WANG, H., ZHENG, Z., YUE, Y., 2010, Experimental Study of *n*-butanol Additive and Multi-Injection on HD Diesel Engine Performance and Emissions, Fuel, Vol. 89, Issue 9, pp. 2191, 2201.

YENİ, U., 2005, Effect of Oxygenate Additives into Gasoline for Improved Fuel Properties, M.Sc. Thesis, Adana, Turkey, 105 pages.

http://en.wikipedia.org/wiki/Butanol_fuel, May 2010.

http://www.afdc.energy.gov/afdc/fuels/emerging_biobutanol_distribution, May 2010.

http://www.bioenergywiki.net/index.php/Butanol, May 2010.

http://www.butanol.com/, May 2010.

http://www.lightparty.com/Energy/Butanol.html, May 2010.

CURRICULUM VITAE

Cumali ÇELİKTEN was born in Adana, 1973. After being graduated from Adana Erkek Lisesi (Adana Male College), he enrolled in Mechanical Engineering Department of Çukurova University. He graduated from Çukurova University as a Mechanical Engineer in June 1998. He started working as a service engineer in a different trade mark of automotive industry, became service manager and general manager in the automotive industry. He is still working a as service manager in Otokoç-Adana. He is married and has two children. He is Master of Science student in Mechanical Engineering Department of Çukurova University more than 10 years.