ÇUKUROVA UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES

MSc THESIS

Ufuk YENİ

EFFECT OF OXYGENATE ADDITIVES INTO GASOLINE FOR IMPROVED FUEL PROPERTIES

DEPARTMENT OF MECHANICAL ENGINEERING

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ÇUKUROVA ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

BENZİNE OKSİJENAT KATKILARININ YAKIT ÖZELLİKLERİNİN İYİLEŞTİRİLMESİNE ETKİSİ

Ufuk YENİ

YÜKSEK LİSANS TEZİ

MAKİNA MÜHENDİSLİĞİ ANABİLİM DALI

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İmza:	İmza:	İmza:
Prof. Dr. Kadir AYDIN	Doç. Dr. Hüseyin AKILLI	Doç. Dr. Osman BABAARSLAN
DANIŞMAN	ÜYE	ÜYE

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Enstitü Müdürü
İmza ve Mühür

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ABSTRACT

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Supervisor : Prof. Dr. Kadir AYDIN

Year: 2005, Pages: 105

Jury : Prof. Dr. Kadir AYDIN

: Assoc. Prof. Dr. Hüseyin AKILLI

: Assoc. Prof. Dr. Osman BABAARSLAN

Automotive gasoline and gasoline-oxygenate blends are used in internal combustion spark-ignition engines. Gasoline is a complex mixture of relatively volatile hydrocarbons that vary widely in their physical and chemical properties. The gasoline may be blended, or may be required to be blended, with oxygenates to improve the octane rating, extend the fuel supply, or reduce vehicle exhaust emissions.

In this study, the effect of oxygenate additives into gasoline is researched for the improvement of physical and chemical properties of blends. Methanol, ethanol, Methyl Tert Butyl Ether (MTBE), Di-isopropyl ether (DIPE), Tert amyl alcohol (TAA), Tert butyl alcohol (TBA) have been blended into unleaded gasoline with various blended rates of 2.5%, 5%, 7.5%, 10%, 15%, and 20%. Physical and chemical properties of blends were analyzed by the standard American Society fir Testing and Materials (ASTM) methods.

Keywords: Oxygenates, Alcohols, MTBE, DIPE, TAA, TBA.

ÖZ

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Benzin ve benzin-oksijenat karışımları içten yanmalı motorlarda yaygın olarak kullanılmaktadır. Benzin, birçok farklı fiziksel ve kimyasal özelliklere sahip uçucu hidrokarbonlardan oluşan karmaşık bir karşımdır. Günümüzde birçok farklı rafineri metodu bulunan benzin, Oktan sayısını arttırmak ve zararlı egzoz emisyonlarını azaltmak amacıyla oksijenatlar ile karıştırılmaktadır.

Bu çalışmada, benzine oksijenat katkılarının karışımın fiziksel ve kimyasal özelliklerine olan etkileri araştırılmıştır. Birer oksijenat olan etil alkol, metil alkol, metil tersiyer butil eter (MTBE), di-izopropil eter (DIPE), tersiyer amil alkol (TAA), tersiyer bütil alkol (TBA), kurşunsuz benzin içerisine %2.5, %5, %7.5, %10, %15 ve %20 oranlarında karıştırılmıştır. Oluşturulan bu karışımların fiziksel ve kimyasal özellikleri, standart Amerikan Test ve Malzeme Enstitüsü (ASTM) metotlarına uygun olarak analiz edilmiş ve oksijenatların benzinin özelliklerini iyileştirmesine olan etkileri incelenmiştir.

Anahtar Kelimeler: Oksijenatlar, alkoler, MTBE, DIPE, TAA, TBA.

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NOMENCLATURE

λ	Air–Fuel Ratio
AKI	Anti Knock Index
ARCO	the Atlantic Richfield Company
ASTM	American Society for Testing and Materials
BEN	Benzene Emission Number
BSHC	Brake Specific Heat Consumption
CAA	the Clean Air Act Amendments
CAFE	Corporate Average Fuel Economy
CARB	California Air Resources Board
CEPA	Canadian Environmental Protection Act
CFRC	Co-operative Fuel Research Committee
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COC	Conventional Oxidation Catalyst
CPPI	Canadian Petroleum Products Institute
DCA	Deposit Control Additives
DI	Driveability Index
DIPE	Diisopropyl Ether
DMDEL	Dimethyl Diethyl Lead
DME	Dimethyl Ether
EDB	Ethylene Dibromide
EDC	Ethylene Dichloride
EFI	Electronic Fuel Injection
EOS	Equation of State
EPA	Environmental Protection Agency
ETBE	Ethyl Tert Butyl Ether

EtOH	Ethyl Alcohol
FBP	Final Boiling Point
GDI	Gasoline Direct Injection
GHG	Greenhouse Gas
GPA	Gas Processors Association
HC	Hydrocarbons
I&M	Inspection and Maintenance
IBP	Initial Boiling Point
ISO	International Standards Organizations
MeOH	Methyl Alcohol
MMT	Methyl Cyclopentadienyl Manganese Tricarbonyl
MON	Motor Octane Number
MTBE	Methyl Tert Butyl Ether
NAAQS	National Ambient Air Quality Standards
NAFTA	North American Free Trade Agreement
NO	Nitrogen Oxides
PM	Particulate Matter
RFG	Reformulated Gasoline
RON	Research Octane Number
rpm	Revolutions Per Minute
RVP	Reid Vapor Pressure
SI	Spark Ignition
SIDI	Spark Ignition Direct Injection
SRF	Standard Reference Fuels
SULEV	Super Ultra Low Emission Vehicle
SUV	Sport Utility Vehicles
$T0_X$	Toxic Air Pollutants
TAA	Tert Amyl Alcohol
TAEE	Tert Amyl Ethyl Ether

TAME	Tert Amyl Methyl Ether
TAME	Tert Amyl Methyl Ether
TBA	Tert Butyl Alcohol
TBA	Tert Butyl Alcohol
TEL	Tetraethyl Lead
THC	Total Hydrocarbon
TMEL	Tetra Methyl Ethyl Lead
TML	Tetra Methyl Lead
U.S.	United States
VABP	Volume Average Boiling Point
VDU	Vapor Destruction Unit
VOC	Volatile Organic Compounds
VRU	Vapor Recovery Unit
WWFC	World Wide Fuel Charter
WWI	World War I
WWII	World War II
YPA	Yearly Pool Average
ZEV	Zero Emission Vehicles

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1. INTRODUCTION

Gasoline is a complex mixture of hydrocarbons obtained from crude oil distillation and processing, as well as and other organic chemicals derived from other energy sources. Modern gasoline is a heavily processed product that can also contain various synthetic components, added to improve its performance and meet the demands of today's advanced engine technology.

Until recently, one such component was lead, which was added to gasoline to boost octane ratings and reduce engine wear. However, leaded gasoline cannot be used on cars equipped with the modern catalytic converters designed to reduce harmful exhaust emissions, as lead very rapidly and permanently annihilates the performance of the catalyst. Furthermore, the realization that lead emitted from vehicle exhausts was having serious health effects resulted in its being phased out, first in North America and then across Europe and, increasingly, the rest of the world. With the reduction or removal of lead, the octane number, the ability of petrol to avoid engine knock, must be raised by other means, such as increasing the concentration of aromatics, optimizing the use of components such as alkylates and isomerates or blending high octane oxygenates.

When Europe started to phase down lead octane additives in petrol in the 1980s, many refiners usually replaced them with aromatics, which represented the lowest-cost alternative at the time. Towards the end of the 1990s, new environmental regulations started to limit the aromatic content of gasoline. Refiners seeking alternative blending components came to rely more on fuel oxygenates: oxygen-rich, cost-effective compounds that act as octane enhancers, with the additional benefit of making gasoline burn more completely, thereby significantly reducing toxic exhaust emissions (www.efoa.org).

1.1. History of Gasoline

From about 1850 until 1900, gasoline was considered a useless by-product of kerosene production, and was disposed of by burning. However, with the invention and ensuing popularity of the automobile, the demand for gasoline increased rapidly between 1900 and 1920. Thermal cracking, a process for breaking down heavier

hydrocarbons in gasoline-range hydrocarbons, came into use in approximately 1913 to help meet the increased demand for gasoline.

The demand for gasoline increased dramatically during the World War I (WWI) years, and grew further throughout the 1920s and 1930s. Prior to the 1920s, gasoline was typically sold at general stores, grocery stores, and hardware stores. The number of gasoline stations in the United States (U.S.) increased from approximately 12,000 to 143,000 between 1921 and 1929.

In the late 1930s, the Houdry catalytic cracking process, which produced a higher octane product, replaced thermal cracking. Continued improvements in catalysts and processes occurred in the following years. Platinum catalysts were used for catalytic cracking beginning in the late 1940s. Premium gasoline, many containing proprietary additives, began to appear in the mid-1950s. U.S. gasoline demand continued to increase until approximately the mid-1970s, when demand leveled off at about 1.5 billion m^3 per year. The primary factors in the stabilization of demand were the fuel shortages of the 1970s, and the improvement in fuel economy in cars produced since that time.

Auto emissions were identified as a source of Los Angeles smog as early as the 1950s. Emissions controls, in their earliest form, were first required on U.S. cars in 1968. The Clean Air Act (CAA) of 1970 instituted numerical limits of 2.11 grams per kilometers of carbon monoxide and 0.25 grams per kilometers of hydrocarbon emissions in automotive exhaust, and set a compliance date of 1975. Nitrogen oxides emissions were to be reduced to 0.25 grams per kilometers by 1976. These requirements led to the development of the catalytic converter, which became standard equipment on automobiles beginning in the 1975 model year. In 1981, catalytic converter performance was enhanced with the addition of computer and oxygen sensors, and the development of three-point catalysts (www.chemicalhistory.com).

1.2. 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 (www.chemicalhistory.com).

1.3. Oxygenates

Oxygenates are compounds containing oxygen in a chain of carbon and hydrogen atoms. Adding oxygenates into gasoline boosts the gasoline's octane level and reduces atmospheric pollution associated with automobile emissions. Today, oxygenates are blended into gasoline in two forms:

Ethers :

ETBE (ethyl *tert*-butyl ether, 1-dimethylethyl ethyl ether, ethyl *tert*-butyl oxide, ethyl tertiary butyl ether, 2-ethoxy-2-methylpropane, *tert*-butyl ethyl ether)

DIPE (diisopropyl ether, diisopropyl oxide, isopropyl ether, 2-isopropoxypropane, 2,2'-oxybis propane)

DME (dimethyl ether, methyl ether, wood ether)

MTBE (methyl *tert*-butyl ether, 1, 1-dimethylethylether methyl, 2-methoxy-2-methyl propane, methyl *t*-butyl ether, methyl tertiary butyl ether)

TAEE (*tert*-amyl ethyl ether, 2-ethoxy-2-methylbutane)

TAME (*tert*-amyl methyl ether, methyl *tert*-pentyl ether, 2-methoxy-2-methylbutane, *tert*-pentyl methyl ether)

Alcohols :

EtOH (ethanol, alcohol, ethyl alcohol, ethyl alcohol anhydrous, ethyl hydrate, ethyl hydroxide, grain alcohol, methylcarbinol)

MeOH (methanol, carbinol, methyl alcohol, methyl hydrate, methyl hydroxide, monohydroxymethane, wood alcohol)

TAA (*tert*-amyl alcohol, amylene hydrate, dimethylethylcarbinol, ethyl dimethyl carbinol, 2-methyl-2-butanol, 3-methyl-butanol, *tert*-pental alcohol, *tert*-pentanol, tertiary amyl alcohol)

TBA (tert-butyl alcohol, 1,1-dimethylethanol, 2-methyl-2-propanol, t-butanol, t-butyl hydroxide, tert butanol, tertiary butyl alcohol, trimethylcarbinol, trimethylmethanol)

In alcohols, each oxygen atom is linked to a carbon atom and a hydrogen atom, forming a carbon-oxygen-hydrogen sequence. Ethanol is the most commonly used alcohol oxygenate. In ethers, each oxygen atom is linked to two carbon atoms, forming a carbon-oxygen-carbon sequence. MTBE is the most commonly used ether oxygenate.

MTBE is the most widely used fuel oxygenate, due to its combination of technical advantages and supply availability. As an octane enhancer, MTBE is an effective replacement for aromatics, because it delivers high octane numbers at relatively low cost. By comparison with alcohols, MTBE offers low water solubility, low reactivity and low volatility-characteristics that enable refiners to avoid the handling problems associated with alcohol oxygenates (www.eia.doe.gov).

In this study, methanol, ethanol, MTBE, DIPE, TAA, TBA have been blended into unleaded gasoline with various blended rates of 2.5%, 5%, 7.5%, 10%, 15%, and 20%. Physical and chemical properties of blends were analyzed by the standard ASTM methods using Çukurova University, Faculty of Engineering and Architecture, Department and Mechanical Engineering, Automotive Division, Fuel Quality Analyzes Laboratory (ÇÜYAL). The effects of oxygenate additives into gasoline for improved fuel quality have been concluded.

2. PREVIOUS STUDIES

Al-Hasan (2002), studied the effect of ethanol–unleaded gasoline blends on engine performance and exhaust emission. In this study, the effect of using unleaded gasoline–ethanol blends on a Spark Ignition (SI) engine performance and exhaust emission was investigated. The unleaded gasoline was blended with ethanol to get 10 test blends ranging from 0% to 25% ethanol with an increment of 2.5% and a four stroke, four cylinder SI engine (type TOYOTA, TERCEL-3A) was used for conducting this study. Performance tests were conducted for equivalence air–fuel ratio, fuel consumption, volumetric efficiency, brake thermal efficiency, brake power, engine torque and brake specific fuel consumption, while exhaust emissions were analyzed for carbon monoxide (CO), carbon dioxide (CO_2) and unburned hydrocarbons (HC), using unleaded gasoline–ethanol blends with different percentages of fuel at three-fourth throttle opening position and variable engine speed ranging from 1000 to 4000 rpm. The results showed that blending unleaded gasoline with ethanol increases the brake power, torque, volumetric and brake thermal efficiencies and fuel consumption, while it decreases the brake specific fuel consumption and equivalence air–fuel ratio. The CO and HC emissions concentrations in the engine exhaust decrease, while the CO_2 concentration increases. The 20 vol.% ethanol in fuel blend gave the best results for all measured parameters at all engine speeds.

The results of this study were summarized as follows. Using ethanol as a fuel additive to unleaded gasoline causes an improvement in engine performance and exhaust emissions. Ethanol addition results in an increase in brake power, brake thermal efficiency, volumetric efficiency and fuel consumption by about 8.3%, 9.0%, 7% and 5.7% mean average values, respectively. In addition, the brake specific fuel consumption and equivalence air–fuel ratio decrease by about 2.4% and 3.7% mean average value, respectively. Using an ethanol–unleaded gasoline blend leads to a significant reduction in exhaust emissions by about 46.5% and 24.3% of the mean average values of CO and HC emission, respectively, for all engine speeds. On the other hand, CO_2 emissions increase by about 7.5%. The 20% ethanol fuel blend gave the best results of the engine performance and exhaust emissions. The addition of

25% ethanol to the unleaded gasoline is achieved in our experiments without any problems during engine operation.

Ceviz (2004), investigated the effects of using ethanol–unleaded gasoline blends on cyclic variability and emissions in a spark-ignited engine. Results of this study showed that using ethanol–unleaded gasoline blends as a fuel decreased the coefficient of variation in indicated mean effective pressure, and CO and HC emission concentrations, while increased CO_2 concentration up to volume of 10% ethanol in fuel blend. On the other hand, after this level of blend a reverse effect was observed on the parameters aforementioned. The volume of 10% ethanol in fuel blend gave the best results.

Bayraktar (2005), studied the experimental and theoretical investigation of using gasoline-ethanol blends in spark ignition engines. In the theoretical study, a quasi-dimensional SI engine cycle model, which was firstly developed for gasoline-fueled SI engines by author, has been adapted for SI engines running on gasoline–ethanol blends. Experimental applications have been carried out with the blends containing the volume of 1.5%, 3%, 4.5%, 6%, 7.5%, 9%, 10.5% and 12% ethanol. Numerical applications have been performed up to volume of 21% ethanol. Engine was operated with each blend at 1500 rpm for compression ratios of 7.75 and 8.25 and at full throttle setting. Results obtained from both theoretical and experimental studies are compared graphically. Experimental results have shown that among the various blends, the blend of 7.5% ethanol was the most suitable one from the engine performance and CO emissions points of view. However, theoretical comparisons have shown that the blend containing 16.5% ethanol was the most suited blend for SI engines. Furthermore, it was demonstrated that the proposed SI engine cycle model has an ability of computing SI engine cycles when using ethanol and ethanol–gasoline blends and it can be used for further extensive parametric studies.

General results concluded from this study can be summarized as follows:

1. The results obtained with presented mathematical cycle model are in acceptable agreement with those measured ones. In general, an agreement of 6% was determined between theoretical and experimental results. This means

that presented model can be used for more extensive parametric studies concerning the using of gasoline–ethanol blends in SI engines.

2. Ethanol addition to gasoline leads to leaner operation and improves combustion. Consequently, cylinder pressure and temperature increase and combustion duration decreases.
3. Engine performance parameters such as effective power and effective efficiency increase with increasing ethanol amount in the blended fuel as a result of improved combustion.
4. Using the gasoline–ethanol blends in SI engines dramatically reduces the CO concentrations. However, NO concentrations are adversely affected due to rising cylinder temperature with increasing ethanol proportion in the blend.
5. In general, most suitable blend for SI engines has been specified theoretically as the blend of 16.5% ethanol and experimentally as the blend of 7.5% ethanol. This means that if some problems, which arise in SI engines when fuelling with gasoline–ethanol blends, will be removed, the blends including ethanol up to 16.5% by volume can be used in SI engines without any modification to the engine design and fuel system.

Wu (2004), investigated the influence of air–fuel ratio on engine performance and pollutant emission of an SI engine using ethanol–gasoline-blended fuels. In this study, ethanol and gasoline blended fuel was tested in a conventional engine under various air–fuel equivalence ratios (λ) for its performance and emissions. The amount of fuel injection was adjusted manually by an open-loop control system using a consult controller. It was found that without changing throttle opening and injection strategy, λ could be extended to a leaner condition as ethanol content increased. The results of engine performance tests showed that torque output would increase slightly at small throttle valve opening when ethanol–gasoline-blended fuel was used. It was also shown that CO and HC emissions were reduced with the increase of ethanol content in the blended fuel, which resulted from oxygen enrichment. At an air–fuel equivalence ratio slightly larger than one, the smallest amounts of CO and HC and the largest amounts of CO_2 resulted. It was noted that

under the lean combustion condition, CO_2 emission was controlled by air–fuel equivalence ratio; while under the rich combustion condition, CO_2 emission is offset by CO emission. It was also found that CO_2 emission per unit horse power output for blended fuel was similar or less than that for gasoline fuel. From the experimental data, the optimal ethanol content in the gasoline and air–fuel equivalence ratio in terms of engine performance and air pollution was found.

The experimental conditions were as follows: two engine speeds, 3000 and 4000 rpm six throttle valve openings, 0%, 20%, 40%, 60%, 80% and 100% (wide open throttle) were used. The fuels were E0, E5, E10, E20 and E30, indicating the content of ethanol in different volume ratios (e.g. E5 contains 5% ethanol and 95% gasoline in volume). The controllable range of injection was between +25% and -25% of original injection strategy and an increment of 5% were used for a step. The properties of different ethanol-gasoline-blended fuels were shown in table 2.1.

Table 2.1. The Properties of Different Ethanol-Gasoline Blended Fuels (Wu, 2004).

Property Item	Test Fuel					Method
	E0	E5	E10	E20	E30	
Density (kg/l at 15.5°C)	0.7575	0.7591	0.7608	0.7645	0.7682	ASTM D4052
RON	95.4	96.7	98.1	100.7	102.4	ASTM D2699
RVP (kPa at 37.8°C)	53.7	59.3	59.6	58.3	56.8	ASTM D5191
Sulfur (wt%)	0.0061	0.0059	0.0055	0.0049	0.0045	ASTM D5453
Washed Gum (mg/100ml)	0.2	0.2	0.2	0.6	0.2	ASTM D381
Unwashed Gum(mg/100ml)	18.8	18.6	17.4	15	14.4	
Lead Content (g/l)	<0.0025	<0.0025	<0.0025	<0.0025	<0.0025	ASTM D3237
Corrosivity (3h at 50°C)	1a	1a	1a	1a	1a	ASTM D130
Distillation Temperature (°C)						ASTM D86
IBP	35.5	36.5	37.8	36.7	39.5	
10 vol%	54.5	49.7	50.8	52.8	54.8	
50 vol%	94.4	88.0	71.1	70.3	72.4	
90 vol%	167.3	167.7	166.4	163.0	159.3	
End Point	197.0	202.5	197.5	198.6	198.3	
Heating Value (cal/g)	10176	9692	9511	9316	8680	
Carbon (wt%)	86.60	87.70	86.70	87.60	86.00	
Hydrogen (wt%)	13.30	12.20	13.20	12.30	13.90	
H/C ratio	1.84	1.67	1.83	1.68	1.94	
Residue (vol%)	1.7	1.5	1.5	1.5	1.5	
Color	Yellow	Yellow	Yellow	Yellow	Yellow	Visual

The results of this study were summarized as follows: when air fuel ratio is slightly smaller than one, maximum torque output and minimum brake specific heat consumption (BSHC) are available. Using ethanol-gasoline-blended fuels improve torque output. However BSHC does not change noticeably. CO emission depends on air-fuel equivalence ratio. With the increase of ethanol content, CO emission is

reduced due to oxygen enrichment coming from ethanol. CO_2 emission depends on air fuel ratio and CO emission concentration. The maximum CO_2 concentration appears at $\lambda \sim 1$. Unburned HC is the product of incomplete combustion. It is related to air-fuel equivalence ratios. When λ is slightly larger than one, HC emission is the lowest; but if λ is far from one, HC emission will rise again. It is noted that adding ethanol can reduce HC emission because of oxygen enrichment.

According to these results, Wu concluded that using E10 blend fuel at air-fuel equivalence ratio slightly larger than one can reduce pollutant emission efficiently.

Hsieh (2001), experimentally investigated the engine performance and pollutant emission of a commercial SI engine using ethanol–gasoline blended fuels with various blended rates (0%, 5%, 10%, 20%, 30%). In this study, fuel properties of ethanol–gasoline blended fuels were first examined by the standard ASTM methods and similar result was found as table 2.1. Results were showed that with increasing the ethanol content, the heating value of the blended fuels is decreased, while the octane number of the blended fuels increases. It was also found that with increasing the ethanol content, the Reid vapor pressure of the blended fuels initially increases to a maximum at 10% ethanol addition, and then decreases.

In this study, Hsieh found that using ethanol-gasoline blended fuels CO and HC emissions may be reduced 10-90% and 20-80%, respectively, while CO_2 emission increases 5-25% depending on the engine conditions. It was noted that NO_X emission is closely related to the equivalence ratio, such that NO_X emission reaches a maximum near the stoichiometric condition ($\lambda \sim 1$) and that NO_X emission depends on the engine operating condition rather than the ethanol content.

He (2002), studied on emission characteristics of an EFI engine with ethanol blended gasoline fuels. The effect of ethanol blended gasoline fuels on emissions and catalyst conversion efficiencies was investigated in a spark ignition engine with an electronic fuel injection (EFI) system. The addition of ethanol to gasoline fuel enhances the octane number of the blended fuels and changes distillation temperature. Ethanol can decrease engine-out regulated emissions. The fuel containing 30% ethanol by volume can drastically reduce engine-out total hydrocarbon emissions (THC) at operating conditions and engine-out THC, CO and

NO_X emissions at idle speed, but unburned ethanol and acetaldehyde emissions increase. Pt/Rh based three-way catalysts are effective in reducing acetaldehyde emissions, but the conversion of unburned ethanol is low. Tailpipe emissions of THC, CO and NO_X have close relation to engine-out emissions, catalyst conversion efficiency, engine's speed and load, air/fuel equivalence ratio. Moreover, the blended fuels can decrease brake specific energy consumption.

General results concluded from this study can be summarized as follows:

1. The addition of ethanol to gasoline fuel enhances octane number of the blended fuels and decreases distillation temperature except for IBP.

2. At operating conditions, ethanol blended fuels slightly decrease engine-out CO and NO_X emissions, but they can significantly reduce engine-out THC emissions. At idle, E10 has little effect on the decrease of engine-out CO, THC and NO_X emissions, but E30 can drastically reduce engine-out CO, THC and NO_X emissions.

3. At most cases, ethanol blended fuels can decrease tailpipe CO, THC and NO_X emissions. The tailpipe emissions have close relations to engine-out emissions, conversion efficiencies, engine operating conditions (speeds and loads) and ethanol content and air/fuel equivalence ratio.

4. With the increase of ethanol content, engine-out unburned ethanol and acetaldehyde emissions increase. Pt/Rh based three-way catalysts can effectively convert acetaldehyde emissions, but the conversion of unburned ethanol is low.

5. Ethanol blended fuels can decrease BSEC.

Niven (2004), investigated the use of ethanol as a gasoline (petrol) additive, at levels around 10% by volume (E10) as well as an 85% blend (E85). By detailed reviews of the peer-reviewed and technical literature, five environmental aspects of ethanol enrichment are examined: its purported reduction in air pollutant emissions; its potential impact on subsurface soils and groundwater; its purported reduction in greenhouse gas emissions; the energy efficiency of ethanol; and the overall sustainability of ethanol production. The study indicates that E10 is of debatable air pollution merit (and may in fact increase the production of photochemical smog);

offers little advantage in terms of greenhouse gas emissions, energy efficiency or environmental sustainability; and will significantly increase both the risk and severity of soil and groundwater contamination. In contrast, E85 offers significant greenhouse gas (GHG) benefits, however it will produce significant air pollution impacts, involves substantial risks to biodiversity, and its groundwater contamination impacts and overall sustainability are largely unknown.

This study examines the ethanol enrichment of unleaded gasoline, with specific attention to the following environmental impacts: air pollutant emissions; subsurface impacts; greenhouse gas emissions; energy efficiency and sustainability. Based on detailed literature reviews, it is found that:

• The claimed air pollution benefits of E10 over E0 do not match the evidence in the scientific literature. E10 causes lower tailpipe CO and particulate emissions, but higher acetaldehyde, ethanol and NO_X emissions. Without RVP control, lower hydrocarbon and air toxic tailpipe emissions are negated by higher evaporative losses; whilst all emission benefits may be negated by life cycle losses. There is some case study evidence of a connection between E10 and higher ground ozone levels.

• E10 increases the risk and severity of soil and groundwater contamination, by increasing the risk of tank corrosion, reducing the NAPL-water interfacial tension, increasing contaminant solubility and inhibiting biodegradation. Modeling and case studies indicate that dissolved benzene plumes associated with E10 are 7-150% longer than those produced by E0.

• E10 offers only a marginal (1-5%) reduction in GHG emissions over E0. As a GHG abatement measure, E10 is much less cost-effective than other methods such as a forestation.

• Ethanol has a low to negative over its life cycle (K 80 to C 40%).

• The sustainability of ethanol production is affected by generous producer and agricultural subsidies; trade barriers; oligarchic concerns; and the need for agricultural expansion (existing feedstocks) and/or genetic engineering (future feedstocks).The effects are summarized in the schematic diagram in figure 2.1.

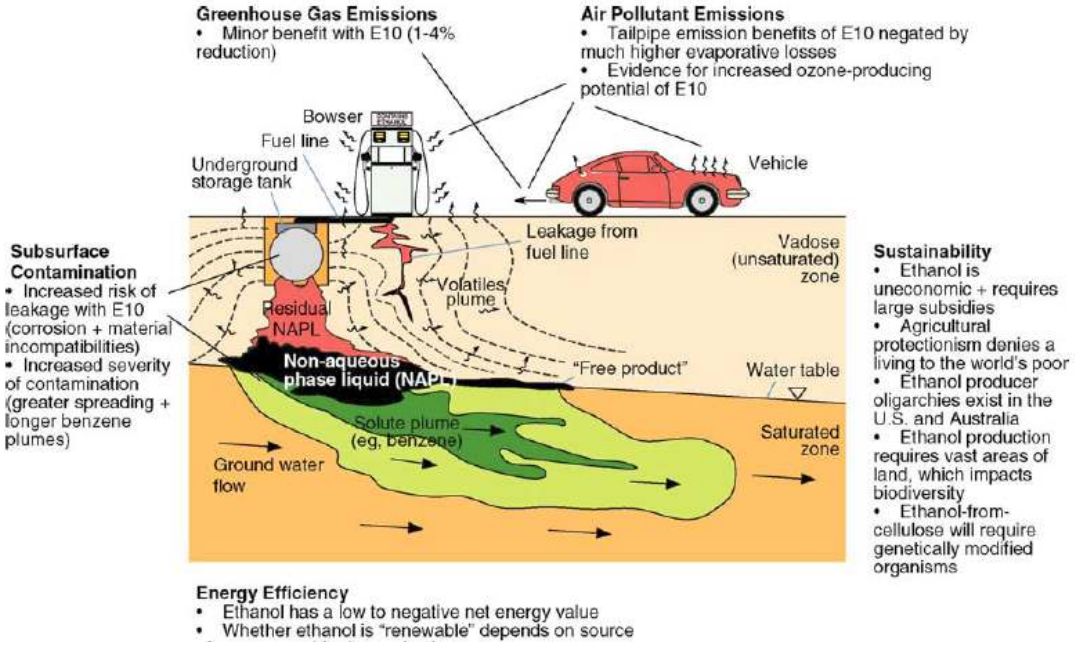

Figure 2.1. Schematic Representation of the Environmental Impacts of Ethanol in Gasoline (Niven, 2004).

Poulopoulos (2000), investigated the effect of methyl-t-butyl ether (MTBE) addition into gasoline on the exhaust emissions from internal combustion engines. A four-cylinder OPEL 1.6L engine equipped with a hydraulic brake dynamometer was used in all the experiments. Fuels containing 0.0-11.0% MTBE were used in a wide range of engine operations, and the exhaust gases were analyzed for CO, HC (total unburned hydrocarbons, methane, ethylene) and MTBE, before and after their catalytic treatment by a three-way catalytic converter. The addition of MTBE into gasoline resulted in a decrease in CO and HC emissions only at high engine loading. During cold-start up of the engine, MTBE, HC, CO emissions were significant and increased with MTBE addition into fuel. At the catalytic converter outlet MTBE was detected when its concentration in fuels was greater than 8% and only as long as the catalytic converter operates at low temperatures. Methane and ethylene emissions were comparable for all fuels tested at engine outlet, but methane emissions remained almost at the same level while ethylene emissions were significantly decreased by the catalytic converter.

Poulopoulos summarized the results of this study as follows;

(a) The addition of up to 11 w/w% MTBE into gasoline decreases HC and CO emissions only at high engine loading, compared to gasoline with no oxygenated additives. At low absorption of engine power, HC and CO concentrations increased with oxygenated fuels and the unburned MTBE constitutes a great percentage of hydrocarbons.

(b) MTBE, HC and CO emissions are significant at the engine cold start up and increased with increase of MTBE in the fuel.

(c) Concerning the catalytic treatment, the MTBE addition into gasoline resulted in a decrease of the total hydrocarbon emissions, compared to gasoline without oxygenate. MTBE is detected at the catalytic converter outlet for fuels containing 8-11 w/w% MTBE and only in conditions where the catalytic converter operates at low temperatures. Low activity of the three-way catalyst is observed in the case of methane which is the main hydrocarbon emitted at high power consumption.

Hamdan (2001), studied the effect of methyl-tertiary butyl ether (MTBE) addition to gasoline on its octane number and, hence, the performance of an engine. Also, its effect on the emitted gases was investigated. Locally produced gasoline was blended with five different percentages of MTBE, namely 0%, 5%, 10%, 15% and 20%. Then, these fuels were burned in an engine, which is coupled to a gas analyzer. It was found that the octane number of the gasoline increases continuously and linearly with MTBE percentage in the gasoline. The best performance of the engine occurs at around 10% MTBE addition, and this percentage also gives the best reduction in exhaust gases emissions.

This study concluded that MTBE is an effective compound in increasing the value of the octane number of gasoline, hence the performance of the engine. Also, the addition of MTBE causes a considerable reduction in the main pollutants emitted from the engine after burning the fuel blend. It was found that the best performance of the engine and the maximum reduction in the pollutants emission were obtained when 10% of MTBE was used in the fuel blend.

Silva (2005), studied on the effects of additives on the antiknock properties and Reid Vapor Pressure of gasoline. In this study, An evaluation was made of the effect produced by the addition of oxygenates such as ethanol, ETBE and MTBE and nonoxygenates such as isooctane and toluene on the Reid vapor pressure (RVP) and octane number of two types of gasoline with different chemical compositions. Locally produced gasoline was blended with five different percentages (v/v) of the additives, i.e. 5, 10, 15, 20 and 25%. Ethanol and MTBE increased significantly the RVP of the mixtures, but ETBE, and particularly toluene and isooctane, decreased the RVP of the original fractions when mixed with gasoline. The octane rating of gasoline was found to increase continuously and linearly with the addition of the oxygenated compounds toluene and isooctane. Moreover, the mixture octane number of the oxygenated compounds was superior to the octane number of the same compounds of high purity grade.

This study concluded that the addition of ethanol and MTBE to the gasoline compositions led to the mixtures increased RVP and octane ratings. Isooctane and toluene reduced the mixture's RVP and increased the octane number, although this increase was not as significant as that produced by the oxygenated compounds. The increase in RVP observed in the mixtures indicates the increase of evaporative emissions, mainly in ethanol-containing mixtures. The use of oxygenated additives led to improved burning in the combustion process, and reduction of the emission of carbon monoxide and of the levels of aromatic compounds.

ETBE, a partially bio-renewable additive since it is synthesized with ethanol, increased the anti-knocking properties of the formulations and reduced the vapor pressure without compromising the volatility required for cold-starting engines. It also presented lower potential evaporative losses.

3. FUEL PROPERTIES, ADDITIVES and TEST STANDARTS

3.1. Automotive Gasoline

The spark ignition engine has remained the power plant of choice for personal transport for almost a century, and the fuel specifically formulated for SI engines is called gasoline (U.S.) or petrol (U.K.) Gasoline has evolved continuously since it was first produced in quantity to meet the burgeoning demand from mass production of the automobile in the early 1900s. It was first produced from light naphtha batch distilled from crude oil and liquid condensate from natural gas production, and in the early days, had no test methods or specifications at all. It became a carefully formulated mixture of hydrocarbons and additives, seasonally blended to match local ambient conditions, providing good performance and efficiency for constantly changing vehicle fleet. More recently, gasoline has been reformulated to reduce various emissions and minimize the impact of automobiles on urban air quality.

For the first 60 years of gasoline production, formulation and manufacture were focused on optimizing desirable performance properties, cost, and yield. Increased octane allowed increased engine power and fuel efficiency. Volatility was controlled to minimize vapour lock, carburettor icing, stalls, sag, hesitation, hard starting, and other measures of driveability performance. Stability additives were developed to minimize auto-oxidation, and detergents to keep carburettors clean. Increased yield from crude oil and other sources made gasoline more available and affordable. Gasoline properties are increasingly influenced by regulatory requirements intended to reduce air and water pollution during manufacture, distribution, and use.

The current generation of North American "Tier 0" and "Tier 1" vehicles for current emissions standards have converged towards electronic fuel injected engines and 3-way catalyst emission control systems. Globally, automakers are facing increasingly stringent Tier 2 emissions limits for the 2004-2009 time periods. While it has been recognized that meeting the Tier 2 emission standards will be a challenge for gasoline vehicles, the U.S. EPA does not expect that any

major technological innovation will be required to achieve compliance. However, low sulphur gasoline must be available for these standards to be feasible. In turn, the automakers are promoting global fuel specifications based on vehicle technology levels, and have produced the "World Wide Fuel Charter" (WWFC) on this basis. The WWFC receives serious consideration when nations and economic regions are revising fuel specifications, even though it is not an accredited consensus standard, and is the subject of ongoing technical debate. ASTM Standard Practices, Test Methods and Specifications continue to be key to domestic and International Specifications and Regulations, and are used globally through affiliated ISO standard writing organizations.

3.2. History of Gasoline

3.2.1. Leaded Gasoline (Pre-control)

In the late 19th century, fuels, for the automobile were coal tar distillates and the lighter fractions from the distillation of crude oil. It's believed that a gasoline fraction was separated by Joshua Merrill in Boston, and was used for lighting. It was also used in Nicolaus Otto's first four-stroke cycle engine in 1876. By the late 1800s the early refiners were producing volatile gasoline by batch distillation from crude oil. Natural gas producers were making volatile naphtha from the hydrocarbon condensed from compressed natural gas (condensate, casing head, or natural gasoline). There were no standard test methods or national specifications, or definition of quality. Some of the earliest standard test methods were not developed until the 1920s, allowing development of the first widely accepted gasoline specifications. Some test methods developed in the 1920s are still in use today, such as the Reid Vapour Pressure (originally developed for casing head gasoline) and Distillation (the oldest currently used ASTM gasoline test method, first published in 1930). The D86 was based on tests developed for casing head or natural gasoline by the predecessor organization of the Gas Processors Association (GPA). The data triggered an intensive discussion

of the relationship between gasoline distillation profile (volatility) and engine performance, such as vapour lock, oil dilution, knock, and sooting.

Automotive engines were rapidly being improved and required a more consistent and suitable fuel. New test methods, specifications, and refining processes were developed to better separate and increase the octane of components. Compression absorption and continuous fractional distillation in pipestills replaced batch distillation with a continuous process in the 1920s. The first sweetening processes were developed to remove smelly and corrosive sulphur compounds. Thermal cracking was introduced just prior to World War I, followed by steam cracking, coking, fluid catalytic cracking, reforming, catalytic hydrogenation (hydro-treating), and many others. Gasoline specifications were developed to control the composition, properties and performance of the finished gasoline, with the three main areas of octane, volatility, and cleanliness.

Fixed bed cracking or reforming was introduced in the early 1930s, which significantly increased the octane of cat-naphtha relative to straight-run or thermally cracked naphtha, with a good alkyl lead response. Higher octane of the gasoline components allowed production of some of the first premium gasoline, called high-test at the time, a reference to their higher octane number test result. During World War II, continuous fluid cat cracking and semi-continuous reforming processes were developed, along with catalytic desulphurization, which further increased the alkyl lead response. Processes were developed to convert C_3 and C_4 olefins from cat cracking into gasoline by polymerization (polygas) and alkylation (alkylate). Highly leaded cracked naphtha, reformate, and alkylate blends were ideal for aviation gasoline for high compression and turbo or supercharged aviation engines developed during WWII, using performance number octane ratings based on the increased percent power attained above the baseline of 100% iso-octane fuel. With rare exception, all post WWII North American automotive gasoline contained TEL.

In the early 1950s changes in engine designs and driving patterns required the re-introduction of the Research Octane Rating. Automakers utilized military technology to continue to increase the engine compression ratio, requiring higher octane number fuels. The octane race occurred during the 1960s, as high performance engines

required fuels with increased octane. The octane increase was non-linear with alkyl lead concentration, with diminishing returns, so there was an economic limit to the maximum amount used. The maximum permitted concentration in gasoline was 1.14g Pb/L, which was well above the optimum alkyl lead response for most refinery streams. Highly leaded premium gasoline was produced for use in high-compression ratio big-block muscle cars with RON as high as about 105 (Owen and Coley, 1990).

3.2.2. History of Alkyl Lead in Gasoline

During the 1910s, laws prohibited the storage of gasoline on residential properties, so Charles F. Kettering modified a Spark Ignition (SI) engine to run on kerosene. However the kerosene-fuelled engine would knock and crack the cylinder head and pistons. He assigned Thomas Midgley, Jr. to confirm that the cause was the kerosene droplets vaporizing on combustion, as he presumed. Midgley demonstrated that the knock was caused by a rapid rise in pressure after ignition, not during pre-ignition as believed. The combination of TML and TEL along with alkyl bromide and chloride alkyl lead scavengers were widely used starting shortly after discovery by teams led by Thomas Midgley Jr. in 1922. Several eminent public health officials campaigned against the widespread introduction of alkyl leads but after a review, the U.S. Surgeon General decided in favour of use in 1926. The toxicity of TEL soon became apparent, as it was originally handled and added in concentrated form at the point of sale. This was changed to point of production to eliminate handling of alkyl lead concentrates outside of refineries, where it could be better controlled (Chevron, 1994).

Alkyl lead is unique among organometallic additives in that alkyl halides were effective alkyl lead scavengers to prevent build-up of alkyl lead oxides and related solids in the engine and exhaust system. This allowed lead alkyls to be used at much higher concentrations than any other organometallic. The alkyl lead chloride and bromide had a lower melting point and higher vapour pressure than the oxide, resulting in the alkyl lead being scavenged and expelled with the exhaust. About 1-1.5 times, the molar amount (theories) to make the alkyl lead tetrahalide was used to provide good scavenging. Aviation gasoline uses only one theory of alkyl bromide to protect against chloride induced corrosion of the hotter exhaust valves. Tricresyl phosphate (TCP) has

also been used as a alkyl lead scavenger (mostly in avgas), to form alkyl lead phosphate that has a lesser tendency to form glowing deposits, foul spark plugs, or accumulate deposits in aviation exhaust side turbochargers (Gibbs, 1995).

3.2.3. History of Octane Ratings

In 1921, the Co-operative Fuel Research Committee (CFRC) was formed to research fuels and engine performance. The CFR engine was developed to evaluate knock performance of fuels under controlled conditions, measuring knock intensity with a bouncing pin knockmeter. In 1927 Graham Edgar developed an octane rating scale based on high and low reference fuels, and showed that fuels had Octane Ratings between 40-60. This became the C.F.R. Research Octane Number in 1930. The RON test method was first published in 1932, became a tentative method in 1947, and was adopted as an ASTM standard in 1951 (Chevron, 1996).

Graham Edgar used two pure hydrocarbon isomers that could be produced in sufficient purity and quantity as reference fuels for rating the anti-knock ability of fuel. These were normal heptane, which was commercially available in sufficient purity from the distillation of Jeffrey pine oil, and an octane, named 2, 4, 4-trimethylpentane that he first synthesized (commonly called isooctane today, although there are 17 different isomers possible, and about five prevalent C_8 isomers from C_4 alkylation). The heptane and iso-octane were given the arbitrary octane numbers of 0 and 100, respectively. These have similar volatility properties (Table 3.1.), specifically boiling point, thus the varying ratios 0:100 to 100:0 would have consistent vaporization behaviour.

Table 3.1. Selected properties of normal heptane and iso-octane

	Melting Point, °C	Boiling Point, °C	Density, g/ml	Heat of Vapour MJ/kg
Normal Heptane	-90.7	98.4	0.684	0.365 at 25°C
Iso Octane	-107.45	99.3	0.6919	0.308 at 25°C

The volume percentage of isooctane in the binary blend that gave the same knock intensity as the fuel being tested was assigned as the Octane Number of the sample. The early work quickly identified that the highest useful compression ratio (efficiency, power) was related to the CFR Research octane number. The sulphur containing gasoline was

initially restricted because sulphur in gasoline inhibited the octane enhancing effect of the alkyl lead. In addition, different fuels had different susceptibility or octane response to the alkyl leads. Parafins have the best alkyl lead response, followed by napthenes, olefins, and aromatics, while the response of alcohols is negative. The RON of the gasoline could be increased from 60 to 75, and the highest useful compression ratio increased from 5.3 to 6.8, increasing the constant-speed fuel economy by about 30%.

The Motor Octane Number (MON) was developed in 1932, using conditions that better matched actual vehicle knock performance climbing the long constant grade hill at Union-town, Pennsylvania. This method is similar to the operating conditions of the current Motor Octane procedure. The MON test was a tentative method from 1933 to 1939, when it was adopted as an ASTM standard. During the late 1940s through the middle 1960s, the Research method became the more important rating because milder conditions more closely represented the octane requirements of the vehicle current engines and driving conditions. Most retail fuels were marketed according to their research octane rating (CRC, 1991).

3.2.4. Vehicle Emission Standards and Alkyl Lead Phase Down

During the late 1950s and 1960s, ambient air quality deteriorated, especially in densely populated urban areas. Research quickly identified the primary pollutants in raw exhaust (HC, CO, and NO_X) and sunlight driven photochemical reaction to be a major source of SMOG (SMoke + fOG). Ground level ozone and other secondary pollutants are formed by photochemical reactions driven by sunlight. The concentrations of pollutants followed a daily pattern determined by driving cycles (rush hours), daytime sunlight intensity, and local geography and wind patterns, with the most severe area in the U.S. being southern California. The original Clean Air Act was passed in 1963 to protect and enhance the quality of the Nation's air resources. The first vehicle emissions standards were imposed in California in 1966 and federally in 1968. The early attempts to reduce HC and CO with carburettor calibrations and thermal reactor (thermactor, air + time delay) type exhaust systems were only about 60% effective for HC. However, this was

still a larger drop than all of the emission reductions since, due to the high emission rates at the time. A number of attempts were made to develop lead-tolerant catalysts and alkyl lead traps that would allow continued use of leaded gasoline. However, several new potential problems with continued widespread use of leaded gasoline were found, and R&D to develop viable exhaust oxidation catalysts went into high gear.

Alkyl lead is a toxin by itself, and there was a drive to reduce exposure levels from many sources, ranging from alkyl lead solder in pipes, food cans, toothpaste tubes, alkyl lead pigment in paints, and alkyl leads in gasoline. In addition, the alkyl lead scavengers ethylene dibromide and ethylene dichloride could react with unburned hydrocarbons in the exhaust to form traces of organo-halogen compounds, including dioxins. It is unlikely that high levels of TEL use would have continued even if a lead-tolerant catalyst had been found.

Separate regulations were put in place to minimize the amount of alkyl lead (primarily TEL) used in the remaining leaded gasoline produced and sold, creating low lead in a series of reductions in 1985/86. A smaller fill nozzle diameter was adopted for non-leaded gasoline to prevent misfueling catalyst cars with leaded gasoline. In the United States, alkyl lead could not be knowingly added to non-leaded gasoline, and the maximum allowable concentration of 13 mg/L was applied as a contamination limit for incidental contact with leaded fuels during distribution. Other jurisdictions have slightly different legal definitions and contamination limits for non-leaded gasoline, but the terms non-leaded and unleaded tend to be used interchangeably, even if this is not technically or legally correct in all cases. Octane ratings of leaded gasoline decreased from the octane race levels, about 1.5-3 AKI lower.

Some predominately small engines were designed for 87 AKI non-leaded fuels, but were alkyl lead tolerant, because they could meet the emission standards of the time without a catalytic converter, so could use either leaded or non-leaded gasoline.

The last premium leaded gasoline was sold in 1981, and the last regular leaded in 1996 in the United States and in 1990 in Canada.

Alkyl lead has been credited variously with allowing rapid development of high power and efficiency SI engines, and even being a deciding factor in aviation in World War II. It is not widely appreciated that Thomas Midgley's other famous discovery, per fluorocarbon refrigerant, had the same dichotomous history as alkyl lead. It provided enormous social benefits, but was eventually banned due to stratospheric ozone depletion. It was replaced with less long-lived halocarbons that are decomposed at lower altitudes (Kettering, 1944).

3.2.5. Non-leaded Gasoline

Introduction of the first Conventional Oxidation Catalyst (COC) systems required non-leaded and low phosphorous gasoline to protect the exhaust catalyst over the useful lifetime of the car. Alkyl lead and phosphorus are potent catalyst poisons that slowly decreased catalytic activity, eventually resulting in near total deactivation of the converter. Phosphorous contents were reduced to sub-ppm levels by eliminating the use of phosphate ester based corrosion inhibitors. Alternate corrosion inhibitor additives were readily available, so phosphorus reduction did not pose a problem to fuel manufacturers. It did require the automakers to significantly reduce oil consumption, as the only remaining significant source of phosphorous was from crankcase lubricant. Replacing the octane boost from alkyl lead was a big problem for the fuel manufacturers, as there was no readily available replacement. This required significant changes to both fuel and engine design.

Gasoline manufacturers found that it was possible to produce, on average, a non-leaded regular gasoline with an 87 AKI and about 91 RON in the United States, and a premium 95 RON in Europe and elsewhere. United States automakers built engines with EGR and reduced compression ratios initially around 8:1 for use on 87 AKI non-leaded gasoline to reduce engine-out NO_X to regulated levels. Air injection reduced HC and CO by oxidation over a COC. Efficiency and fuel economy were reduced because of the compression ratio reduction. However, this was more than offset by Corporate Average Fuel Economy (CAFE) regulations in 1975 that required average fuel economy

determined in standard tests to increase over a period of years up to 27.5 mpg. This was accomplished with a variety of technologies. Vehicle size, weight, and rolling or wind resistance were dramatically reduced. The majority of the fleet converted to front wheel drive, using more efficient transverse L4 and V6 engines and transmissions, both using lower viscosity and friction modified lubricants.

3.2.6. 1970 US EPA Clean Air Act and 1977 Amendment

The 1970 U.S. Clean Air Act (CAA) established the Environmental Protection Agency and required a 90% reduction in automotive emissions by 1975 (HC/CO) and 1976 (NO_X). This resulted in the widespread introduction of conventional oxidation catalysts and non-leaded gasoline in 1975 in response to the HC and CO standards. These regulations were technology forcing especially for NO_X, and the U.S. Congress put an interim NO_X standard in place until 1978. The 1977 Clean Air Act Amendments required reduction in HC in 1980 and CO and NO_X in 1981. This resulted in the widespread introduction of sophisticated three-way catalysts computer controlled closed loop air-fuel ratio control with exhaust oxygen sensors in most 1981 model year cars. The 1977 CAA amendments contained the first provisions that controlled the properties of future gasoline. It had a general requirement that gasoline is substantially similar to fuel or fuel additives used to certify 1975 or subsequent year's vehicles. The intent was that future gasoline would not render the new catalysts or emission controls ineffective over time. The EPA subsequently promulgated the substantially similar ruling, which had a more detailed definition of the meaning. It also provided that additives containing only C, H, O, N and S (which combust to the regulated emissions) did not require a waiver at concentrations below volume of 0.25% (CPPI, 1994).

The United States EPA may grant waivers for non-leaded gasoline formulations that are shown by testing to not cause or contribute to emission device failures. A waiver request is granted if the EPA does not decline the application after 180 days. In 1978, the EPA granted the first waiver for 10% by vol-

ume of ethanol. The EPA subsequently issued waivers for gasoline containing a variety of alcohols, ethers, and mixtures, of which MTBE and ethanol (gasohol) are the most commercially important today.

In 1981 the EPA ruled that fuels with up to 2 wt% oxygen from aliphatic alcohols or ethers were substantially similar and thus did not need a waiver. In 1991 the maximum oxygen content was increased to 2.7 wt% oxygen. To ensure sufficient base gasoline was available for ethanol blending, the EPA also ruled that gasoline containing up to 2 vol% of MTBE could subsequently be blended with 10 vol% of ethanol.

3.2.7. Vapour Controls

As the tailpipe emissions were reduced by improved exhaust emission control systems, other hydrocarbon emission sources became more important. This includes hydrocarbons from evaporation or fugitive emissions of gasoline during distribution and storage, vehicle refuelling, vehicle at rest, or vehicle during use. The United States CAA required summer reductions in VP in two phases in 1989 and 1992, to reduce a number of fugitive emission sources (running loss, diurnal, refuelling) summer vapour pressure controls have virtually eliminated hot driveability problems. They tend to be design related, appearing as select model problems when they occur.

Stage 1 vapour control systems reduce truck loading vapour emissions at terminals and at service stations during loading and unloading of trucks. At the service station, the vapour space of the truck is connected to the vapour space of the underground tank, whose vapour is displaced (vapour balanced) back into the truck during fuel delivery. The truck returns to the terminal, where the hydrocarbon saturated air delivery truck are collected and sent to a Vapour Recovery Unit (VRU) or to a Vapour Destruction Unit (VDU, combustor, flare) as the truck is loaded.

Stage 2 systems reduce point of sale vehicle refuelling emissions. Vapours from the vehicle tank are vapour balanced with the underground storage tank, or

sent to an absorber or combustor. Newer systems incorporate vapour pumps to remove the exact amount of air from the fill pipe as volume of gasoline dispenses, and do not require the rubber nozzle snout to make a vapour tight seal. These systems are recognized by air slots near the nozzle tip to remove air from the fill spout via an annular tube in the delivery hose. Vehicles are also equipped with enhanced activated carbon canisters (bigger capacity than required for diurnal control) to treat the vehicle tank vapour while refuelling. These are subsequently desorbed by a small airflow and burned in the engine during normal use, once specified vehicle speeds and coolant temperatures are reached. Some activated carbons used in older vehicles do not function efficiently with oxygenates, but modern carbon canister systems can reduce evaporative emissions by more than 95% from uncontrolled levels. On-board canister systems tend to make Stage 2 balancing redundant as the on-road population equipped with enhanced canister systems increases.

3.2.8.1990 CAA Amendments

The 1990 Clean Air Act (CAA) amendments and California Air Resources Board (CARB) Phase 2 (1996) specifications required further reductions in tailpipe emissions, more stringent test procedures and vehicle on-board monitoring technology, and new clean fuels programs. These established emission limits for reformulated gasoline, compared with typical 1990 baseline gasoline. The first stage, the Simple Mode was an interim stage between 1 Jan. 1995 to 31 Dec. 1997. The second stage, the Complex Model had two phases: Phase I (1995-1998) and Phase II (2000+) (Howe-Grant, 1993).

Metropolitan regions with severe ozone air quality problems were required to use reformulated gasoline containing at least 2.0 wt%, oxygen to reduce 1990 volatile organic carbon compounds by 15% (1994), and reduce specified toxic emissions by 15% (1995) and 25% (2000). Because of a lack of data, the EPA was unable to define the required parameters for the CAA, so an advisory committee containing representatives of regulatory, petroleum industry,

environmental, and consumer interests recommended a two-stage system for implementation. The EPA also gave the refining industry a choice of standard, based on either per gallon, or averaged, based on volumetric averages over an annual or seasonal production period (Yearly Pool Average, YPA, or summer/winter). In some jurisdictions, regulations include requirements around sampling, test methods, and validation/demonstration of test proficiency, as well as certified third party testing, auditing, and field attest monitoring.

Areas in attainment with air quality objectives continued to use conventional gasoline. The anti-dumping provisions of the regulation ensured that the quality of conventional gasoline was not degraded to facilitate production of RFG. Conventional gasoline must be blended to provide equivalent emissions of the national baseline gasoline (default for domestic or import), or individual refiner's baseline based on prior production. The intent of these anti-dumping restrictions was to ensure emission improvements and non-attainment did not result in emission increases in areas currently in attainment with the National Ambient Air Quality Standards (NAAQS). Emission improvements had to be made by increased refinery processing for the manufacture of RFG (Kozole, 1996).

The Auto-Oil Air Quality Improvement Research Program (AQUIRP, Auto-Oil) provided the basis for the simple and complex models used in EPA and most other North American gasoline regulations. Measured emissions were correlated to gasoline properties in a wide variety of vehicle emission system types. These spreadsheet type correlation models predict emissions from all sources associated with using gasoline in vehicles. They take into account the time of year (winter/summer), gasoline composition as measured by eight parameters (called the model parameters), and an assumed on-road vehicle fleet with a mixture of various generations of emission control types.

For Phase I, for example, the CAA specifies no increase in NO_X emissions, reductions in VOC by 15% during the ozone season, and specified toxins by 15% all year. These criteria indirectly established vapour pressure and composition limits that refiners had to meet. The percent reductions are calculated with the complex model, which predicts volatile organic compounds (VOC), specified

toxic air pollutants ($T0_X$) and nitrogen oxides (NO_X as a function of eight composition related model inputs. Sulphur, benzene, vapour pressure, %oxygen and aromatics have the largest impact on predicted emissions. D86 evaporation volumes E200 and E300, and olefin content have lesser, but still significant impact. Federal regulations reduced vapour pressure and benzene directly; however, aromatics or other parameters could be limited to meet emissions criteria. For example, a fuel with the maximum permitted 1% benzene requires total aromatics to be limited to about 27% to meet the emissions reduction requirements (Sasol, 2001).

Federal (EPA) RFG and California Phase 2 RFG composition limits require the use of oxygenate. The California Phase 2 RFG requires the hydrocarbon composition of the RFG to be significantly more modified than the existing oxygenated gasoline to reduce unsaturated hydrocarbons, volatility, benzene, sulphur, and the reactivity of emissions. California Phase 2 does not require the use of oxygenates in the summertime if using the "Predictive Model" except for federal ozone non-compliance areas of the state where the EPA RFG limits apply as well.

Oxygenates were first added to gasoline as a high percentage level blend component (as opposed to a ppm level de-icer) to extend gasoline supply supported by some State and Provincial Governments with a reduced gasoline tax rate. In 1992, 2 wt% oxygen gasolines was mandated in cold, high altitude areas starting in 1994, as a means to lean the mixture, and reduce unburned HC and CO by over 10% in carburetted vehicles. However, some oxygenates such as methanol, ethanol, and light ethers increase the vapour pressure of the gasoline, causing increased evaporative emissions that reduced or reversed the benefit. Newer Tier 0 and later technology cars have very fast adaptive feedback loops to control the oxygen content in the exhaust to near stoichiometric using the oxygen sensor. These vehicles are much less sensitive to fuel effects, so the net benefit of oxygenates decreases with time, as the older predominately carburetted engines are retired from service. Other researchers have observed similar reductions when oxygenates are added to reformulated gasoline on older

and newer vehicles, but have also shown that NO_X levels may increase, as also may some regulated (Calingaert, 1998).

By 2000, MTBE was the preferred oxygenate in RFG, but concerns about toxicity and water pollution were mounting. MTBE has a much higher (4.3 wt %) solubility in water than hydrocarbons, a relatively low bio-degradability, and very low odour threshold. This makes MTBE objectionable in potable water at trace concentrations, and a concern for water contamination from spills, leaks and marine engines using gasoline-containing MTBE. In 1999, California applied to the Federal government for a waiver from the Federal RFG requirement concerning oxygen content to eliminate MTBE. However, that application was declined in June 2001. In March 2000, the EPA provided advance notice of its intent to initiate rulemaking pursuant to section 6 of the Toxic Substances Control Act (TSCA) to eliminate or limit the use of MTBE as a fuel blend component. Several U.S. Federal and individual state bills have proposed elimination of MTBE since then including two U.S. Federal Energy bills. At the time of this writing, use of MTBE is likely to be either banned or significantly restricted.

Canadian refiners must meet 1 wt% benzene NTE, or optionally a 0.95 wt% YPA and 1.5 wt% NTE, effective July 1, 2000. In addition, a 72/91 summer/winter Benzene Emission Number (BEN) requirement is based on the complex model, not including olefins. The BEN is the sum of exhaust and non-exhaust benzene, excluding calculation terms of the complex model using olefins. There are several measurement and reporting differences between the U.S. and Canadian RFG regulations. One Canadian province (BC) has VO_X and NO_X requirements based on the full complex model, but using a BC baseline gasoline for the calculation. Several other Canadian Provinces have standalone summer Vapour Pressure regulations. Canadian vehicle emission standards have tended to follow closely upon U.S. 49 state requirements, with some differences in phase in schedules.

3.2.9. 2004+ Vehicle and Fuel Regulation (Future RFG)

In April 2000, new Federal Tier 2 criteria for vehicle emissions and fuels were announced phased in beginning in 2004 and extending to 2007+. Officially published sources of information should always be used for regulatory compliance purposes.

Most U.S. refiners and importers must meet a corporate average gasoline sulphur standard of 120 ppm and a cap of 300 ppm beginning in 2004. In 2005 the cap remains at 300 ppm, with the corporate average reducing to 90 ppm and refinery average at 30 ppm. In 2006, the average will be 30 ppm and cap 80 ppm, with some areas and refineries having until 2006-2009 to comply. The EPA also noted that gasoline should not be advertised as "low sulphur gasoline" unless it contains 95 ppm sulphur or lower.

California has legislated faster implementation of a 30 YPA, 80 NTE sulphur standard, and others, such as North Carolina's SB 953. Part II of that law, NCGS 119-26.2, proposes the same for after January 1, 2004.

The Tier 2 LDV standards are the same for cars and light duty trucks, whether diesel or gasoline, so include both, nonmethane organic gases (NMOG) and Particulate Matter requirements (PM essentially for diesels and NMOG essentially for gasoline). Different phase in periods apply for different size vehicles. Light duty car and truck phase-in starts in 2004 with 100% compliance by 2007. Medium duty passenger vehicles and heavy light duty trucks will be phased in beginning in 2008, with full compliance in 2009. A new class of medium-duty passenger vehicles (MDPV), <10,000GVW, includes large Sport Utility Vehicles (SUV) and vans intended to carry less than 12 passengers. These will be treated the same as HLDT and have interim emission standards that expire in 2008.

The Canadian Environmental Protection Act (CEPA) requires refiners and importers to meet either 170 ppmw sulphur NTE over a 30 month interim period ended Dec 31, 2004, or a 150 ppm average with a 300 NTE in the last half of the interim period. Gasoline is required to be 30 ppm YPA, 80 ppm NTE starting Jan

1, 2005. One Province (Sask.) has impending oxygenate (ethanol) requirements for 2005.

3.3. Gasoline Properties

3.3.1. Gasoline Composition

a) Hydrocarbons: Gasoline can contain over 500 different hydrocarbons with between 4 and 14 carbon atoms per molecule. Detailed descriptions of structures can be found in any chemical or petroleum text discussing gasoline. The C_3 and lighter hydrocarbons are too volatile to be used as a blending component of gasoline. Both methane and propane are widely used as SI engine fuel using pressurized fuel systems and various designs of gaseous carburettors or fuel injectors. Hydrocarbons larger than about C_{14} are too heavy (non-volatile), and tend to contribute inordinately to oil dilution and incomplete combustion and soot related problems. These functional limitations result in gasoline having a typical boiling range of about 25-225°C at atmospheric pressure. Vapour pressure, Driveability Index (DI) and model based emission criteria all tend to narrow this boiling range by removing the highest and lowest volatility ranges.

The type and concentration of the various hydrocarbons in any given gasoline blend can be determined by high resolution gas chromatography, typically using 50-100 meter capillary columns to obtain the high resolution required. The number of different hydrocarbons in any given blend depends upon the type and severity of processing at any given refinery. Composition surveys on non-leaded gasoline showed that gasoline blended with high percentages alkylates or low severity reformate could contain less than 175 different hydrocarbon types. Gasoline blended with catalytically cracked naphtha tended to contain more than 350 different molecules. (Westbrook and Pitz, 1991)

b) Saturated Hydrocarbons (Paraffins, Alkanes): Saturates are the most chemically stable species, and comprise 20-80% of gasoline, with 30-60% being typical. The octane ratings of these compounds depend on the branching and number of carbon atoms. The octane primary reference fuels are both saturated

hydrocarbons (0=heptane, 100=224 trimethylpentane). Additional information is presented in table 3.1. The interested reader is directed to a standard organic chemistry text for further detail on these and the other classes of hydrocarbons.

c) Unsaturated Hydrocarbons: Unsaturated hydrocarbons are less stable as compared to saturate. The upper limit of both olefins and aromatics can be limited by emissions or other specifications. Table 3.2. contains information about the various classes of unsaturated hydrocarbons.

Table 3.2. Unsaturated Hydrocarbons

Alkenes	• Olefins, contain single carbon-carbon double bonds • Usually stable, depends upon molecular type • Clean burning, reduces VOC but increases NMOG reactivity • More reactive than alkanes, higher octane ratings. • Present in gasoline 0-25% (10-15% typical)
Dienes	• Olefins containing more than one carbon-carbon double bond • Usually unstable especially if conjugated (n, n + 2 double bonds) • More be significantly higher reactivity, toxicity and air reactivity • <<1 % generally required for stability
Alkynes	• Acetylenes, contain carbon-carbon triple bonds • Considered very reactive, only present in trace amounts, and usually in some poorly-refined gasolines • <<0.1% generally required
Arenes (Aromatics)	• Very stable, high octane. 10-50 vol% (25-35 vol% typical). Tend to be limited by emission models • Benzene >>> toxicity than other aromatics, regulated separtately • Alkyl benzenes not considered smoke precursors, as they have vaporized and are not present at the end of combustion,
PNA (Polynuclear Aromatics)	• Condensed ring aromatics (naphthalenes, alkyl napthalene, trace 3 ring) • Generally controlled to <<1 vol% by boiling point or other specifications (220-225°C vs. 260°C dimethyl napthalene)
PAH (Polycyclic Aromatic Hydrocarbon)	• Di-alkyl PNA are potent smoke precursors, and are very detrimental to spark ignition engine operations. • Naphthalene and methylnaphthalene boil at 218°C and 230°C and are not considered to be potent smoke pre-cursors.Di-methylnaphthalenes boiling above allows it to ring close on de-hydrogenation to form a larger PNA. It turns it from a "chain ender" molecule to a "smoke precursor". The extra methyl group on the aromatic allows this process to continue to completion of a multi-ring smoke molecule.

3.3.2. Gasoline Additives

Additives are compounds added in trace amounts (<2500 ppm in the EPA substantially similar ruling), to enhance some property of the fuel, or

performance of the engine, vehicle, or emissions. Specifications and regulations allow for additive use, and in some cases, require additive use, for example deposit control additives (DCA), which are beneficial for in-use emissions.

Oxygenates (De-Icers, Gas Line Anti-Freeze)

Aliphatic alcohols and ethers added at 5-15 vol% are considered to be blending components and not additives. However, at lower concentrations, low molecular weight alcohols, especially methanol, ethanol, and iso-propanol, are effective de-icing additives, commonly available as gas line antifreeze. Alcohols are typically used in the 500-2500 ppm (0.05-0.25 vol%) range for this purpose, and function by preventing traces of water (typically from temperature drop and condensation) from freezing in the vehicle fuel system. A higher rate may be required for larger water contaminations, or to prevent carburettor icing, which is accumulation of ice in the carburettor throat and throttle plate. The cooling of high humidity combustion air is caused by throttling (Joule Thompson cooling) and fuel evaporation heat of vaporization (auto-refrigeration). Gasoline with higher vapour pressure, and lower T10 and T50 (high front end volatility) has a higher propensity for producing carburettor icing.

IPA is approved as aviation fuel system icing inhibitor at a treat rate of 1 vol% in aviation gasoline (ASTM D 4171). Other alcohols and glycols have also been used for carburettors or fuel line icing, including hexylene glycol, propylene glycol, dipropylene glycol, and various glycol ethers. Methanol is the most commonly used for gasoline fuel line freezing protection in fuel-injected vehicles in cold climates. De-icers are not commonly used in automotive fuels in warm/cool climates, due to the low population of carburetted engines susceptible to carburettor icing. Some carburetted utility engines may require alcohols for operation in severe icing conditions (>85% relative humidity, 0-10°C) (Totten, 2003).

Alkyl Lead Compounds

Akyl lead compounds are no longer used in North American automotive gasoline, because of the detrimental effects on exhaust catalysts and concerns for health effects of alkyl lead in the environment.

ASTM D 910 Aviation Gasoline 100LL (low lead) has been reformulated from the original 100/130 grade with the addition of aromatics (toluene) to reduce TEL to the lowest level necessary to maintain the octane number and aircraft performance. Avgas is generally handled in segregated distribution systems, so is generally not a significant source of alkyl lead contamination in automotive gasoline. With no other source of alkyl lead contamination, typical trace alkyl lead levels in North American gasoline are usually undetectable by standard test methods.

Methylcyclopentadienyl Manganese Tricarbonyl (MMT)

As the toxicity of the alkyl lead and the halogenated scavengers became of concern, alternatives were considered. The most notable of these is methylcyclopentadienyl manganese tricarbonyl (MMT), an organo-manganese compound with similar antiknock properties as TEL, but at much lower concentrations to obtain about 1-2 octane number increase. It was used in the United States in non-leaded gasoline in the mid 1970s, but an application for an EPA waiver was declined in October 1978, effectively banning it in non-leaded gasoline in the United States. In December 1995, the EPA was forced to grant the waiver in U.S. conventional gasoline (not RFG), and MMT can be used in conventional gasoline up to 8.3 mg/L in all states except California, where it is regulated separately. In a separate case, the court held that EPA's new rules that require pre-market testing of new gasoline additives did not apply to MMT. The EPA has stated it intends to monitor MMT use, but MMT was used in only 0.02% of gasoline in 1998.

MMT has a high toxicity in concentrated form, but the combination of relatively low volatility and its miscibility with aromatic hydrocarbon solvents allows it to be stored and handled with typical equipment. MMT is light unstable

with a half life of about 30 s in strong sunlight, forming a characteristic red rust colored precipitate (MnO_2). This oxide is softer than iron oxides, and is not considered to be abrasive even at much higher concentrations than typically used in gasoline (Totten, 2003).

MMT has been in continuous use in Canada since the first introduction of non-leaded gasoline in 1972 to a maximum of 18 mg/L Mn, without major incidents. Most problems attributed to MMT are associated with excessive exhaust or catalyst temperatures. These cause the manganese oxide to "ce-ram" and form a gas impermeable glass that can coat and effectively deactivate the catalyst. This is also associated with front face catalyst plugging, due to the sticky nature of the glass. Field experience indicates that this is not a serious problem in typical driving cycles, including Tier 0 and 1 vehicles equipped with OBDII emission control monitoring systems. Two provincial inspection and maintenance (I&M) programs using IM240 (dyno-driving cycle) and ASM2525 (25 mph steady state dyno) test cycles have not found or identified any emissions related problems due to MMT on model years 1982 to present.

Proponents claim benefits in NO_X reduction, protecting the catalyst from long term deactivation by sequestering catalyst poisons (Zn, P, Pb) or coke, fuel cost benefits, emissions reduction from reduced refining severity, and lack of adverse health effects. Opponents cite high exhaust temperature catalyst plugging, exhaust gas sensor rich shift for the NO_X effect, spark plug tracking, and the potential for adverse health effects.

Dozens of controlled and non-controlled tests and surveys over 35 years have failed to conclusively resolve the debate probably because the test result depends upon the specific automobile year and model being tested and how the test is done.

Iron based Organo-metallics

Other compounds that enhance octane have been suggested, but usually have significant problems such as toxicity, cost, and increased engine wear, especially if used at high concentrations.

Dicyclopentadienyl iron (ferrocene) and nickel carbonyl have been promoted as alternatives to alkyl lead and MMT. For example, the addition of 0.02-0.04 g/L ferrocene with 0.05-0.10 g/L tertiary butyl acetate is reported to increase the AKI of susceptible gasoline hydrocarbon feedstocks by 4-6. More recently, ferrocene has been promoted as an octane enhancer at lower levels of 9 mg/L Fe to avoid any significant deposition or wear problems. The benefit is reduced to about 1-1.5 octane number at this level (similar to MMT). Unlike manganese oxides, iron oxides do not cream at high temperature.

Iron pentacarbonyl ($Fe(CO_5)$) was used in Germany at levels of 0.5% or less in gasoline during the 1930s. While the cost was low, the carbonyl decomposed rapidly when the gasoline was exposed to light to form iron oxides. It also has a relatively high vapour pressure, and is extremely toxic in concentrated form, so must be handled with care. Use of the additive at high concentrations in gasoline caused excessive deposition of iron oxide (Fe_3O_4) on the spark plug insulator, causing short circuits. The precipitation of iron oxides in the lubricating oil also led to excessive wear rates.

Iron picrate (trinitro phenate) and related oil soluble iron chelates are sometimes sold as aftermarket additives with various performance claims, but are not used in commercial production (Totten, 2003).

3.4. Gasoline Combustion

3.4.1. Spark Ignition Engines

Spark ignition engines are ideally suited for light duty transportation uses. Their relatively lightweight (compared to other internal combustion engines), wide RPM range, broad torque band, and high maximum RPM/power provide good performance with a minimum number of transmission gears.

Vehicle spark ignition engines are air throttled to control power, and have inherent limitations on peak cylinder temperatures and pressures due to engine knock so are thermally less efficient than compression ignition engines. As a result, diesel engines dominate the high torque, low rpm heavy-duty truck,

marine, locomotive, and stationary power applications. Smaller high-speed diesel engines comprise only a small percentage of the light duty vehicle market in North America, but are more prevalent in Europe. This is driven mainly by their significantly higher fuel efficiency, which provides a significant market advantage, especially in regions with high fuel prices.

Electronic fuel injection has replaced carburettors on essentially all Tier 0, Tier 1, and later model automobiles. This facilitates closed loop computer control of air/fuel ratio, to maintain exhaust composition within a narrow range required for optimal operation of a 3-way catalyst. The name 3-way is a reference to effectiveness for all three regulated exhaust emissions: unburned hydrocarbons (HC), carbon monoxide (CO) by air oxidation, and oxides of nitrogen (NO_X) by chemical reduction with HC/CO. These systems require the engine to operate in a narrow air-fuel ratio band on both rich and lean side of stoichiometric, to maintain both the regulated emissions HC, CO, and NO_X and O_2 in the optimal range where they react to extinction.

Hybrid gasoline-electric vehicles couple internal combustion engines with an electric motor for peak power and transient engine operations to obtain ultra-low steady state emissions with no significant loss in performance. A smaller, generally much higher voltage battery set stores enough power for several minutes of high power electric motor operation for cold start or accelerations. This allows a number of very efficient and ultra low emission driving cycles, since the majority of SI engine emissions are due to transient operations and cold start, before the catalyst heats up. The SI engine can shut down (zero emissions) during cold start or if required for urban zero emission vehicles (ZEV) emissions. It can run at steady state (for example on the highway) letting the electric motor handle variable power requirements (hills, wind load, corners, etc.) that would otherwise cause increased emissions from transient SI operation. It can be run at a higher steady state power, using the electric motor as a generator to recharge the batteries. Elimination of transients tends to provide highway fuel efficiency in urban driving cycles, and ultra low emissions (lower than the Super Ultra Low Emission Vehicle (SULEV) level (Totten, 2003).

Other hybrid vehicle types have been proposed, such as diesel-electric or gasoline-hydraulic, or gasoline-flywheel, but only gasoline-electric are being commercialized at this time. It is anticipated that both current RFG and 30 ppm sulphur future RFG will be compatible with hybrids, but that the lower sulphur will provide slightly lower in-use emissions.

Gasoline Direct Injection (GDI) engines (Spark Ignition Direct Injection, SIDI, etc.) have thermodynamic efficiencies between SI and diesel engines, and may be commercialized in the near future. Fuel requirements for GDI have not been established. Exhaust particulate matter may be more critical for GDI than for current engine/emissions systems.

3.4.2. Engine Management Systems

Engine management systems are now an important part of the strategy to reduce automotive pollution. A typical modern engine system would monitor and control: mass airflow (or MAP/RPM calculated air flow), exhaust oxygen sensor (lambda sensor), knock (vibration/noise) sensor, EGR, throttle plate angle, manifold air temperature and pressure, crank angle, and transmission gear. These systems can compensate for altitude (MAP), ambient air temperature (MAT), fuel octane (knock sensor), humidity, and gasoline composition (oxygen sensor, adaptive map). The engine control module (ECM, computer) then sets the ignition timing and fuel injector open time (fuel flow), and fuel injection timing with crank angle that are appropriate for the current engine operating conditions.

Almost all Tier0/l engine control systems incorporate adaptive memory maps or adaptive learning strategies. The fuel map (or schedule) conceptually consists of three blocks of data organized like three sheets in a spreadsheet, with the rows and columns representing different RPM and manifold vacuum, which together define the engine load. The three sheets contain fuel injector open time for the factory baseline settings, the long-term block learns, and the short-term block learns. Conceptually, the data is a computer binary number such as 0 to 255 for an 8-bit computer. This might represent, for example, how many

milliseconds the fuel injector should be held open, since open time is proportional to fuel volume delivered at constant pressure.

The air-fuel ratio is controlled at part throttle by a closed loop system using the oxygen sensor in the exhaust and the knock sensor (if equipped). Typical engine calibrations enrich the air-fuel ratio for smoother, stall free idle when in closed loop control, and hold a faster idle after cold start when in open loop, until the catalyst becomes heated and lights off. The amount of idle enrichment used is often adjusted according to the air temperature at the time of engine start (similar to the function of a choke on a carburettor acting against a bimetal temperature spring that held the choke on longer when cold until the engine heated up).

3.4.3. Air - Fuel Ratio and Stoichiometry

Ideally, hydrocarbons and oxygenates in gasoline combust smoothly to form water, carbon dioxide, and heat energy, with no other by-products. Non-ideal combustion affects emissions, efficiency, engine durability, and vehicle operation. Severe engine knock is associated with loss of efficiency and engine damage. If there is excess fuel (rich air/fuel ratio), the combustion is not complete, and carbon monoxide (CO) will be formed, along with unburned or partially burned hydrocarbons (HC). As CO can be burned to produce CO_2, it is "unburned" fuel, so there is a drop in efficiency and increase in emissions. Nitrogen oxides are formed as a result of conversion of nitrogen (N_2) in air to various nitrogen oxides (NO_X). High peak combustion temperatures promote NO_X (lean air/fuel ratio, high intake air temperature, low humidity, high barometric pressure and high load).

The required mass or volume of air to provide sufficient oxygen to achieve this complete combustion is the "stoichiometric" mass or volume of air. Insufficient air creates rich mixtures, and excess air creates lean mixtures. The stoichiometric mass of air for a gasoline is related to the carbon: hydrogen ratio of the fuel. However, oxygen (20.9476 vol%), Nitrogen (78.084%), and Argon

(0.934%) comprise 99.966 vol% of the atmosphere. The use of nominal masses (O_2=16) versus natural abundance masses (O_2-15.994) and ideal gas assumption.

As a result, it is common to assume that the non-oxygen component of the air is nitrogen, which can be added to the equations when the exhaust compositions are required. The error is generally much smaller than the analytical uncertainly of the actual carbon hydrogen ratio of a real gasoline, by elemental analysis or cap GC. If needed, exact molecular weights can be calculated from molecular formula and standard periodic tables weight, or from ASTM GC method peak tables for individual hydrocarbons.

For normal heptane C_7H_{16} with a molecular weight =100,204:

$$C_7H_{I6} + 11O_2 \longrightarrow 7CO_2 + 8H_2O$$

The chemical stoichiometric combustion of hydrocarbons with oxygen can be written as:

$$C_XH_Y + (x + (y/4))O_2 \longrightarrow xCO_2 + (y/2)H_2O$$

Thus 1.000 kg of C_7H_{16} requires (1/100,204).11.2.16 = 3,513 kg of O_2 and using approximation,

(3,513 kg of O_2 + (3,513/32).(28.79,0524/20,9476) = 15.113 kg of air.

(Air-fuel ratio = 15.113 vs. 15.179)

3.5. Gasoline Octane Performance Properties

3.5.1. Combustion and Knock in Engines

The critical fuel property of gasoline for internal combustion engines is resistance to engine knock, expressed as the octane number of the gasoline. During a normal (no knock) combustion cycle, a flame front travels smoothly from the point of ignition at the spark plug outward toward the cylinder walls. While this is occurring, the end gas, or unburned fuel/air mixture ahead of the flame front is heated and compressed. If the end gases ignite before the flame front arrives, the resulting sudden pressure wave reverberates across the combustion chamber, causing an audible engine knock. This adversely affects output power

and dramatically increases heat transfer to the piston and other combustion chamber surfaces. While this can cause damage on its own if severe enough, knock induced preignition can cause rapid catastrophic engine failure. This tends to be a runaway condition. Once started, it gets progressively worse until eventual engine failure, unless the throttle/load is cut quickly, as failure can occur in less than a few minutes. High heat transfer during heavy knock can cause deposits or sharp edges (for example combustion chamber deposit or exposed thread of a spark plug) to overheat. This can act as a glow plug type ignition source, causing ignition of the charge before the spark on the next combustion stroke preignition. This leads to excessively high combustion chamber temperature and pressure from combustion closer-to TDC, and rapidly increasing knock intensity. Initial stages of knock damage look like pitting on the piston top, as if it had been attacked with an ice pick or awl. The increased temperature and heat transfer to the piston top eventually causes melting of the crown land down to the rings. The final stage is either catastrophic engine failure from thrown connecting rods (metal softening near the piston wrist pin, causing the piston to separate from the connecting rod), or engine seizure (expansion of the piston, excessive friction heat, and loss of lubrication). Either condition is sufficient to ruin one's day (in addition to the engine).

The octane (and autoignition temperature) of various hydrocarbons is related to their ability to withstand preflame conditions without decomposing into species that could auto-ignite before the flame-front arrives. Unburned end gases ahead of the flame front encounter 700°C temperatures due to compression and heat transfer, and commence a series of complex preflame reactions. These reactions occur at different thermal stages, with the first stage (around 400°C) commencing with the addition of molecular oxygen to alkyl radicals. The internal transfer of hydrogen atoms within the new radical forms an unsaturated, oxygen-containing species following this stage. These new species are susceptible to chain branching involving the HO_2 radical during the intermediate temperature stage (400-600°C), mainly through the production of OH radicals. Above 600°C, the most important reaction that produces chain

branching is the reaction of one hydrogen atom radical with molecular oxygen to form O and OH radicals.

Common antiknock additives work by interfering at different points in the preflame reactions. The alkyl lead antiknock compounds interfere with hydrocarbon chain branching in the intermediate temperature range, where HO_2 is the most important radical species. Alkyl lead oxide, either as solid particles, or in the gas phase, reacts with HO_2 or removes it from the available radical pool. This reduces the major chain branching reaction sequence that results in undesirable, easily auto-ignitable hydrocarbons. Oxygenates retard the progress of the low temperature or cool-flame reactions, consuming radical species, particularly OH radicals and producing unsaturated hydrocarbons like iso-butene. The iso-butene would, in turn, consume additional OH radicals and produce unreactive, resonantly-stabilized radicals, such as allyl and methyl allyl**,** as well as stable species such as allene, which resist further oxidation.

3.5.2. Anti-knock Ratings of Fuels

The Anti Knock Index (AKI) is the average of the Research Octane Number (RON, D 2699) and Motor Octane Number (MON, D 2700), sometimes expressed as (RON+MON)/2 or (R+M)/2. The on-line Comparator Engine method D2885 determines octane numbers that are equivalent to lab RON and MON values, and can be used for blend certification and release. The RON and MON methods use two primary reference fuels, n-heptane and 2, 2, 4 trimethyl pentane, assigned octane numbers of 0 and 100, respectively. The knocking intensity of the test fuel is compared to that of reference fuel blends. The volume percent of iso-octane in the blend that gives the same knock intensity as the test fuel is taken as being the octane number of the test fuel.

The same standard engine is used for both tests, but run at different test conditions. The conditions of the MON engine tend to simulate hot, highway driving, whereas the RON test is more like heavy acceleration from a traffic light. The difference between the RON and MON for a given gasoline (sensitivity)

depends upon the composition of the blend. The RON and MON of parafins and isoparafins is almost the same, so high isoparafins (low aromatic, low olefin) blends tend to have low sensitivities, sometimes below four numbers. Aromatics have intermediate sensitivities and olefins have the highest sensitivity, so gasolines that have high catalytically cracked content (high olefins) will have high sensitivity (RON-MON), as high as about.

ASTM D 4814 recommends a minimum MON of 82 for Regular grade gasoline heavy-duty engine applications, but uses AKT for all other recommended uses. Two different 87 AKI gasolines with extreme compositions could have a RON/MON of 94/80 or 89/85. For an engine operating under more MON like conditions, the 87/85 blend will provide knock free operation at more severe conditions than the 97/80 blend. In the late 1960s select European automakers experienced catastrophic engine failures on high speed Autobahn runs, even though the Research Octane of the fuel was within specification. They discovered that either the MON or the Sensitivity (the numerical difference between the RON and MON) also had to be specified to ensure adequate performance under severe high speed Autobahn condition. Similarly, many marine and utility engines run at high load and WOT, and are susceptible to knock damage from too low a MON. In the late 1970s and early 1980s several automotive and marine OEMs promoted development of an even more severe octane method, due to concerns that the high octane contribution from alcohol in the MON test did not appear under their most severe wide open throttle engine operating conditions. However, this was not pursued, and some OEMs recommended higher octane 89-91 AK1 grades or no oxygenates or methanol for severe marine, snowmobile, outboard or utility engine applications.

3.5.3. Procedure for Anti-Knock Rating Fuels

Automotive octane ratings are determined in a standardized single-cylinder engine with a variable compression ratio (CR 4:1 to 18:1), operated under standard conditions Cooperative Fuels Research (CFR) engine. The

cylinder bore is 82.5 mm; the stroke is 114.3 mm, giving a displacement of 612 cm^3. The piston has four compression rings, and one oil-control ring. The intake valve is shrouded. The single head and cylinder casting can be adjusted relative to the crankshaft using a crank handle to obtain the desired compression ratio. The engines have a special four-bowl carburettor that permits individual bowl air-fuel-ratio adjustment and provides rapid switching between reference fuels and samples. A magneto restrictive detonation sensor in the combustion chamber now measures the rapid changes in combustion chamber pressure caused by knock, and the amplified signal is measured on a knockmeter with a 0-100 scale.

For the CR procedure, a calibration curve is prepared of knock intensity versus compression ratio for a PRF blend that has an octane number within prescribed limits from the sample. The octane number of the sample is the octane number of the single PRF used to calibrate the engine, corrected for barometric pressure and difference in knock intensity using the calibration curve. The D2885 comparator method uses the CR procedure, but using a Standard Reference Fuel (SRF) instead of a PRF.

3.5.4. Motor Octane Rating ASTM D 2700

The conditions of the Motor method represent severe, sustained high engine speed, high load (but not wide-open throttle) driving. For most hydrocarbon-fuels, including those with either alkyl lead or oxygenates, the Motor Octane Number (MON) will be lower than the Research Octane Number (RON).

3.5.5. Research Octane Rating ASTM D 2699

The research method settings represent typical high load (throttle opening) and low to medium engine speeds resulting in low inlet mixture temperatures and moderate loads on the engine.

3.5.6. On-Line Analyzer Octane Rating ASTM D 2885

On-line octane rating analyzers used in refineries are described in ASTM D 2885, taking a continuously flowing slip stream of gasoline from current production, and measuring the RON and MON continuously. The same engines and conditions are used, so consequently results are equivalent to the laboratory MON or RON procedure.

Instead of bracketing the test fuel with primary reference fuels, D 2885 uses Standard Reference Fuels, commonly called protos or gold protos that are production gasoline that have been rated by about 20 different laboratories, and assigned the average value determined by the group. The SRF is required to be close in octane to the test fuels, so that the difference in octane number can be derived from the difference in knock intensity between the SRF and the test fuel.

Standard Reference Fuels are developed through cooperative exchange programs, usually administered in association with an accredited Standards Writing Organization. Examples in North America are National Exchange Group under the auspices of ASTM, the Canadian Cooperative Exchange under the auspices of the CGSB, and the Rocky Mountain Exchange, representing refiners in high altitude areas (now associated with the NEG).

3.6. Gasoline Specifications

ASTM or CGSB gasoline specifications are not legal requirements unless they are required (referenced) in a regulation by a government authority having jurisdiction.

In the United States and Canada, a mixture of Federal, State, and Provincial Government legislation and attendant regulations proscribes gasoline requirements. Some states and associations of states may also specify regional gasoline properties to achieve regional environmental objectives that are within their jurisdiction. These regulations may reference accredited ASTM consensus standards, with or without modifications. In some cases, ASTM sampling and test methods are reproduced in regulations. This can cause

update problems, such as use of the wrong procedures for regulatory purposes, when either party changes procedures. The U.S. gasoline specifications and test methods are listed in several readily available publications, including the Federal Register, and the current Annual Book of ASTM Standards.

3.6.1. ASTM D 4814, Specification for Automotive Spark-Ignition Engine Fuel

The scope of the standard states that this specification guides in establishing requirements of automotive fuels for ground vehicles equipped with spark-ignition engines. It was first published as ASTM D 439 in 1937 and significantly revised to include oxygenates including gasohol (10% ethanol) and other alcohol blends that had EPA waivers. Several test methods were developed or modified for use with oxygenated fuels, such as Dry Reid Vapour Pressure, Tv/L, and new methods added such as wate**r** tolerance and phase separation temperature requirements.

It is a complex specification with many details that are beyond the scope of this chapter. However, in all cases, the requirements and the test method for each requirement fall into one of two categories, those that measure the properties or quality at the time of sampling, and those that predict some future condition or performance. For example, a clear and bright procedure evaluates whether the fuel is suitable for use at the time of custody transfer or sale to end consumer. An oxidation stability result, on the other hand, is a predictive test, intended to predict if the fuel will be acceptable in the future, after some time in storage prior to sale or use. Many tests are rig tests that rate relative performance of the gasoline to provide a reasonable estimate of how the gasoline will perform in actual use. For example, D 130 (Test Method for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test) measures the relative degree of corrosivity under a proscribed set of conditions. It uses a static coupon of a specified copper alloy, prepared in a specified way, exposed to the product for a specified period of time at a specified temperature. In the vast majority of cases, a pass on the D 130 test means that the fuel will not cause

significant corrosion to any copper alloy parts exposed in the fuel system, and will be widely acceptable to a broad range of vehicle fuel systems. However, if the in-use conditions for any fuel system component are more severe than the D 130 test conditions, then damage could occur even with a fuel that passes D 130. This could happen if the component is heated hotter than test conditions, or the part is in a rubbing or rolling type of service that continually removes the protective oxide/sulphide layer, or the part metallurgy is more easily corroded than the D 130 copper strip.

ASTM has two publications that are highly recommended to those not familiar with details or intent of the test methods or specification are both instructive on reasons for the test and explanation of what and how the test is intended to measure. Ideally, performance or rig tests are representative of actual in-use vehicle requirements. Hopefully these two goals always coincide, but it is always possible to pass the test and fail the field as any experienced fuels chemist will agree. Passing all the tests does not guarantee that the fuel is suitable for use in all cases, especially in cases such as unusual contamination, or new car technology for which the existing standard tests don't consider, or when in-use conditions are more severe than in the standard test method. Specifications and test methods are in a continual state of being updated as technology continually advances.

3.6.2. Anti-knock Index (AKI)

Anti-knock Index (AKI), also known as (RON+MON)/2, "Pump Octane," ((R+M)/2), or "Road Octane" is the average of the Research Octane Number and Motor Octane Number. Dispensing pump posting requirements are based on AKI. The only accurate method of measuring knock is to use standard knock rating engines in ASTM D 2699/D 2700 or D 2885, although several field test methods are used for screening purposes. The ASTM gasoline standard does not mandate octane levels, but lists levels appropriate for different applications. While limits are not specified, changes in engine requirements according to

season and location are discussed. Fuels with an AKI of 87, 89, 91 (non-leaded), and 88 (leaded) are listed as typical for the U.S. at sea level. However, higher altitudes may specify lower octane numbers.

3.6.3. Volatility

Volatility is measured by the ASTM D 86 distillation, the Vapour/Liquid ratio Temperature (Tv/L=20), and one of several vapour pressure test methods, most commonly ASTM D 5191, which is used for regulatory reporting. All of the volatility measurements are somewhat related thermodynamically, being various combinations of vapour pressure and cumulative boiling volumes. However the relationships are not exact, because the standard tests are not ideal thermodynamic processes.

3.6.4. Distillation, Evaporation Temperatures and Driveability Index

The distillation volatility of a finished gasoline can be expressed in several ways. One set uses the temperature at fixed distillation points, such as the T10, T50, and T90, related indices such as Volume Average Boiling Point (VABP) or ASTM Driveability Index (DI);

Driveability Index = DI - 1.5xT10 + 3xT50 + 1.0xT90

Maximum DI limits are specified in ASTM D 4814 for each Volatility Class, ranging from 569-597°C. Note that the conversion of DI from Centigrade to Farenheit units is DI (F) = DI(C)x9/5 + 176, where 176 is the sum of the coefficients (1.5 + 3.0 + 1.0)x32. Many companies use volume percent evaporated (%Evap, or D+L) at fixed temperatures, which have an advantage over Txx controls, because they blend more linearly, and are more easily adapted to linear programming (LP) optimization controls. Both are in common use at the operational level, because ASTM requires Txx type controls while the complex model requires E200 and E300. The complex model spreadsheet has a conversion from Txx to Exxx built into the model.

3.6.5. Vapour Pressure and Tv/L

ASTM vapour pressure specifications are based on VP measured under standard conditions of 4:1 vapour liquid ratio at 37.8 °C and Tv/1 20 to control gasoline front-end volatility. The Tv/120 is the temperature at which 20 volumes of vapour are formed from one volume of the original liquid, measured by ASTM D 2533 or D 5188. The intent is to produce an isobaric flash prediction, something that is well within the capabilities of modern thermodynamic equation of state (EOS) calculations.

A Tv/120 corresponds to about 10% of the gasoline vaporized under conditions of the test (a fully vaporized gasoline would have a V/L of about 220-280 depending upon the blend). As a result, there is a good correlation between measured Tv/1 and linear sums of the VP and T10, T20 up to T50, so it is much more common to calculate Tv/1 than to measure it. Some companies use an index based on VP and %Evaporation at lower temperatures, historically 70°C. These are often called Vapour Lock Indices or "Hot Fuel Handling," a reference to the original purpose of these specifications. A v/1 of 20 was originally chosen because, on average, a carbureted engine diaphragm type fuel pump could handle about 20 volumes of vapour along with the 0.9 volume of the remaining liquid (Tv/1 = 20). Any higher temperature (more vapour) would cause the pump to become vapour-locked, and not be able to satisfy engine fuel demand, causing stalls or rough engine operation. The temperature when this occurs is called the Vapour Lock Temperature. The ASTM specification has vapour-lock protection temperatures based on a regional database of ambient temperature and elevation (barometric pressure).

Fuel injected vehicles generally have submerged in-tank fuel pumps, and operate at much higher liquid fuel line (fuel rail) pressures, so are much less prone to vapour lock problems. However, certain forms of vapour lock can occur, but are usually due to other mechanical factors and not high ambient temperature. For example, a worn out fuel pump may not put out enough

pressure to prevent vapour formation in the fuel rail during a hot shutdown. The vehicle could experience a hard hot starting or no-start condition, because much lower mass vapour flow through the injector would cause an over lean air-fuel ratio. Similarly, a partially blocked primary filter (pick-up sock) can cause vapour lock on the suction side of the submerged pump at high temperatures. Routing fuel lines in areas that have high shutdown heat soak temperatures can also cause a hot restart problem.

3.6.6. Gasoline and Gasohol Blending

The distillation volatility is controlled within specification limits by varying the relative ratios of blend components to make a finished gasoline. These range from butane (normal boiling point 0°C) to the highest boiling components with Final Boiling Points slightly higher than the 225°C FBP specification for the finished gasoline. The vapour pressure is controlled below specification maximums by limiting the amount of butane in winter and northern summer grades, and butane plus some pentanes in the lowest vapour pressure summer grades.

3.6.7. ASTM Volatility Class Specifications

ASTM D 4814 gasoline specification defines six volatility classes of increasing vapour pressure, Tv/1 and Driveability Index (DI). The T10, T50 min/max and T90, FBP max limits define the allowable range of individual parameters within each volatility class. VP and Dl are generally the key blending parameters for both regulatory and specification compliance.

Insufficient volatility may result in difficult starting in cold weather, poor cold start and warm-up driveability, engine deposits and crankcase oil dilution, and increased tailpipe emissions. Excessive front-end volatility can produce poor fuel economy; poor hot driveability in fuel injected engines, vapour lock and carburettor icing in older engines, and increased running loss and evaporative emissions. The higher boiling fractions of the gasoline have

significant effects on the emission levels of undesirable hydrocarbons and aldehydes. A reduction of 40°C in the final boiling point will reduce the levels of benzene, butadiene, formaldehyde, and acetaldehyde by 25%, and will reduce HC emissions by 20%. Similar emission effects were found in the auto-oil program, and as a result, there are three volatility model parameters in the complex model,VP, E200, E300 (Vapour pressure, percent evaporated at 200°F (94°C) and 300°F (150°C), respectively) that influence predicted evaporative, tailpipe, and toxics emissions. The E200 and E300 model parameters have the least influence of all the model inputs on the predictive model emissions, and are often set at worst case values for the purpose of blend planning (although actual values must be used for reporting).

3.6.8. Maximum Alkyl Lead Content

The alkyl lead limits remain to cover fuels for off-road vehicles. Leaded fuels can contain up to 0.029 g Pb/L but none are made commercially. Non-leaded gasoline can contain up to 0.013 g Pb per liter in the U.S. (contamination limit with no deliberate addition) and 0.005 g Pb/L in Canada to protect catalytic converters.

3.6.9. Copper Corrosion

Copper, silver, brass, and other soft metal alloys are susceptible to corrosion from reactive sulphur molecules. The ASTM D 130 copper corrosion test is intended to ensure that fuels are not corrosive to these traces components under normal use conditions. More severe conditions could require even lower levels of corrosive sulphur. The total sulphur content is not correlated with D 130 test performance, and in fact, some additives that are effective at mitigating copper corrosion themselves contain sulphur. Only the most reactive types of sulphur molecules cause or contribute to D 130 copper corrosion. The copper strip test

responds to reactive sulphur, whereas the sulphur content reports the total sulphur content.

The D 130 test is a static coupon test, and may over predict durability for more easily corroded alloys such as silver, or for rubbing, rolling, or heated soft alloy fuel system components. Field problems have been experienced with some copper fuel pump commutators, silver alloy fuel sender unit resister arrays and silver plated crankcase bearing cages with gasoline that passes D 130. In general, silver alloys should not be used in gasoline fuel systems without provisions for protection from sulphating. Copper alloy components that are exposed to heat or rolling/rubbing action that removes the protective oxide layer should be tested for long-term durability with a gasoline containing traces of corrosive sulphur (H_2S, elemental sulphur).

3.6.10. Maximum Sulphur Content

Current ASTM and CGSB standards allow 0.10% mass maximum sulphur content for non-leaded gasoline, but lower levels are required by various sulphur regulations (California or Canadian Sulphur in Gasoline regulation). Sulphur is oxidized to SO_2 over the catalyst, so essentially competes for reactive sites that could otherwise be effective for HC, CO or NO_X conversion. This appears as a temporary decrease in catalyst activity at high fuel sulphur levels, and leads to the requirement for ultra low sulphur fuels to attain ultra low emissions.

Sulphur can be indirectly limited by RFG composition controls based on emission models (U.S. EPA complex model, BC TO_X/NO_X and Canadian CEPA Benzene in Gasoline regulation Benzene Emission Number (BEN) requirements. Both Canada and the United States have regulations in place that will reduce sulphur to 30 ppm YPA phased in between 2002 and 2010, coincident with introduction of low emission Tier 2 vehicles.

3.6.11. Maximum Phosphorus Content

The EPA limits phosphorus in all gasoline to 1.3 mg/L Pb, because phosphorus is a potent catalyst poison, and this limit is reflected in the ASTM specification. Typical levels of phosphorus in non-leaded gasoline are undetectable by the standard test methods.

3.6.12. Oxidation Stability

Like all organic material, hydrocarbons are susceptible to air oxidation over long periods of time. The peroxides formed from hydrocarbon oxidation are auto-catalytic, leading to runaway reaction if not controlled. Reaction rates are generally higher with unsaturated hydrocarbons, and are catalyzed by parts per billion levels of soluble metals such as copper. Motor gasoline may be stored up to six months, or more. They must not form soluble gum that collects at the point of vaporization, or precipitated insoluble gum (varnish), or form soluble peroxides that will attack rubber/elastomers in the fuel system.

Antioxidants are added to most gasolines to slow down the rate of oxidation and prevent the oxidation from becoming autocatalytic, by forming a stable radical oxidation product that does not react further. The antioxidant is sacrificial, and is gradually consumed during this process. Once depleted, the reactions will become autocatalytic, and the gasoline will eventually break and form peroxide gums as fast as oxygen can diffuse into the liquid (mass transfer controlled oxidation). Some gasolines also require metal deactivators to mitigate catalysis from 10-100 ppb traces of copper.

Oxidation stability tests generally expose a heated sample of gasoline to oxygen for a prescribed period of time to accelerate the rate of oxidation and predict on a relative basis how long the fuel will be stable under more typical conditions. In the ASTM D 525 Oxidation Stability test, the fuel sample is heated with oxygen inside a pressure vessel, and the time until significant oxygen uptake (pressure drop, break point) occurs is a relative measure of stability. The criteria

are where the pressure drop exceeds 14 kPa per 15 min. The autocatalytic reaction rate increases exponentially, becoming mass transfer controlled, and consuming all of the remaining oxygen in only 15-30 min. ASTM D 4814 requires a minimum of 240 min (4h) breakpoint, which is sufficient for most storage and distribution systems. This may require a higher level at the point of manufacture, since the measured oxidation stability will decrease over time as the sacrificial anti-oxidant is consumed. Other procedures not used in D 4814 are to weigh the oxidative gum formed after a breakpoint test, (commonly termed a 4 hour gum), or longer term storage time tests at milder conditions to better simulate field storage conditions.

It is common practice to add sufficient antioxidant to meet 360-600 min oxidation stability at the point of production, so that 240 min is obtained at the point of sale. Factory fill gasoline generally requires a much-fortified gasoline for this purpose, as storage times of automobiles prior to sale can be several months. This is especially true for some specialty fleet applications, such as police fleets, that may be made in large production runs, with the cars stored for six months or more before going into service. Hydrocarbons air oxidation has been extensively studied, and is well documented in the literature (Totten, 2003).

3.6.13. Soluble Gum (Unwashed and Solvent Washed Existent Gum)

ASTM D 4814 limits unwashed gum to 5 mg/100 mL, and has no washed (Existent Gum) requirement (used for aviation gasoline). D 381 measures the amount of fuel soluble oxidative gums and non-volatile additives remaining after evaporation in the air (i.e., total nonvolatile materials in solution). Solvent washed "Existent Gum" measures the amount of gums remaining in fuel evaporated under air and then washed with heptane to remove additives and heavier hydrocarbons. Heptane is a poor solvent for highly oxidized, high molecular weight gums. The heptane soluble portion is relatively low molecular weight material that can accumulate at any point of gasoline vaporization (intake system deposits) and react further to form insoluble gums. The heptane insoluble

portion is representative of the more fuel-insoluble gum that can contribute to gum/varnish residue problems, for example filter plugging, sticking carburettor float bowl pintle needles where there is no vaporization, as well as intake system deposits where there is vaporization.

Washed and unwashed gums measure the amount of gum formed in the fuel up to the time of the test, as no significant additional gum is formed under the relatively mild conditions of the test procedure. It is not predictive of future quality. It can identify help identify stale "peroxidized" fuels in the marketplace; Washed Existent gum is often reported to verify that a high unwashed gum is due to the presence of Deposit Control Additives that contribute to unwashed gum.

3.6.14. Water Tolerance

D 6422 Water Tolerance (phase separation) method measures the highest temperature at which phase separation of gasoline - alcohol blends occur. It is not applicable to hydrocarbon or ether oxygenated fuels. Water tolerance is particularly critical for gasoline containing alcohol. The separated lower phase alcohol-water-hydrocarbon phase settles to the bottom of the tank where the pump suctions are, and tends to get moved down the distribution system and into cars if not found and removed. The remaining gasoline layer is often off-spec after phase separation due to loss of octane from alcohol and aromatics extracted into the alcohol layer. If dispensed into a vehicle tank, it will not burn in engines, and so it causes immediate stalls, and requires a complete fuel system draining and cleaning. Like water, aqueous alcohol separated phases contribute to corrosion and pickup of rust/dirt, etc., and are also associated with accelerated filter plugging (Totten, 2003).

4. MATERIAL and METHODS

4.1. Materials

4.1.1. Gasoline

In this study, 98 octane unleaded gasoline was used to prepare mixture and obtain improvements of additives. Before preparing the mixtures gasoline was analyzed the Çukurova University Fuel Quality Analyzes Laboratory (ÇÜYAL). And the results of these analyzes are shown in table 4.1.

Table 4.1. Properties of Gasoline

Tests	Results	Methods
Density(16ºC; g/cm3)	0,7682	ASTM D4052
MON	85,3049	
RON	98,6462	
RVP (37.8ºC, kPa)	64,2	ASTM D323
Sulphur (wt%)	0,067	ASTM D4294
Calorific Value(cal/g)	10352	ASTM D240
Distillation Temp. (ºC)		ASTM D86
IBP	44,4	
10 vol%	68,4	
50 vol%	124,6	
90 vol%	174,3	
End Point	206,6	

4.1.2. Oxygenates

Oxygenates are chemicals containing oxygen that are added to fuels, especially gasoline, to make them burn more efficiently. Adding oxygenates to gasoline boosts the gasoline's octane level and reduces atmospheric pollution associated with automobile emissions. In this study six different oxygenates were used. Basically these oxygenates are classed as alcohol oxygenates and ether oxygenates. Alcohol oxygenates are ethanol, methanol, tert amyl alcohol (TAA), tert butyl alcohol (TBA) and ether oxygenates are methyl tert butyl ether (MTBE) and di isopropyl ether (DIPE). These oxygenates have been blended into the gasoline with blend rates of 2.5%, 5%, 7.5%, 10%, 15% and 20%. After preparing the blends, these blends have been analyzed in the ÇÜYAL.

4.1.2.1. Ethanol

Ethanol is an alcohol-based alternative fuel produced by fermenting and distilling starch crops that have been converted into simple sugars. Feedstocks for this fuel include corn, barley, and wheat. Ethanol can also be produced from "cellulosic biomass" such as trees and grasses and is called bio-ethanol. Ethanol is most commonly used to increase octane and improve the emissions quality of gasoline. Ethanol can be blended with gasoline to create E85, a blend of 85% ethanol and 15% gasoline. Vehicles that run on E85 are called flexible fuel vehicles (FFV) and are offered by several vehicle manufacturers. The properties of ethanol, which was used in this study, are show in table 4.2.

Table 4.2. Properties of Ethanol

Chemical Formula	C_2H_5OH
Purity (%)	99.5
Oxygen (wt%)	34.7
Molecular Weight(g/mol)	46.07
Density (16ºC; g/cm3)	0.796
Boiling Temperature (ºC)	78
RVP(37.8ºC, kPa)	16
MON	92
RON	108
Freezing Point(ºC)	-114
Flash Point, closed cup (ºC)	12.8

4.1.2.2. Methanol

Methanol is international chemical name of wood alcohol, or methylated spirits. It is a widely used solvent and raw material in the chemical and plastics industries. It is the low priced antifreeze poisonous, like gasoline, but more often hazardous because it may be confused with ethanol, or grain alcohol, and drunk. It is practically odorless. It can be made from coal, wood, waste, or any material containing carbon, but, like many other commodities, it is presently made from the most economical source, natural gas. It should be handled like gasoline, although it is somewhat less hazardous. In an engine it burns cleanly, without depositing carbon. It is the only fuel that a wise yachtsman will use in his galley range, as its exhaust is only water vapor and carbon dioxide, identical with the yachtsman’s own exhalation.

If there is a small fire, a pan of water will extinguish it, not spread it, as occurs with a kerosene or gasoline fire.

Up to 15 percent methanol can be added to gasoline in current cars, without adjustment of the engine, and with noticeable improvement in exhaust quality, economy and performance. Methanol has an octane rating of 106, compared to typical gasolines of 85 to 100. It prevents knocking or pinging common with unleaded fuels, and it alleviates running on or dieseling when the ignition is switched off. Methanol can be used to make methyl tertiary-butyl ether (MTBE), oxygenate which is blended with gasoline to enhance octane and create cleaner burning fuel. MTBE production and use has declined because it has been found to contaminate ground water. In the future, methanol could possibly be the fuel of choice for providing the hydrogen necessary to power fuel cell vehicles. The properties of methanol are shown in table 4.3.

Table 4.3. Properties of Methanol

Chemical Formula	CH_3OH
Purity (%)	99.5
Oxygen (wt%)	49.9
Molecular Weight (g/mol)	32.04
Density (16ºC; g/cm3)	0.796
Boiling Temperature (ºC)	65
RVP(37.8ºC, kPa)	31.7
MON	92
RON	107
Freezing Point(ºC)	-97.5
Flash Point, closed cup (ºC)	11.2

4.1.2.3. MTBE

MTBE (methyl tertiary-butyl ether) is a volatile organic compound (VOC) manufactured by the chemical reaction of methanol and isobutylene. MTBE is used almost exclusively as a gasoline additive used to reduce smog (ground-level ozone) in the US. It is one of a group of chemicals commonly known as oxygenates because they raise the oxygen content of gasoline. At room temperature, MTBE is a volatile, flammable and colorless liquid that dissolves rather easily in water.

MTBE has been used as an octane enhancer (helps prevent the engine from knocking) in gasoline since 1979, after the US phased out lead additives. Since 1992, MTBE has been used at higher concentrations in some gasoline to fulfill the oxygenate requirements set by Congress in the 1990 Clean Air Act Amendments. The properties of MTBE are shown in table 4.4.

Table 4.4. Properties of MTBE

Chemical Formula	$C_5H_{12}O$
Purity (%)	99.5
Oxygen (wt%)	18.2
Molecular Weight (g/mol)	88.15
Density (16ºC; g/cm3)	0.744
Boiling Temperature (ºC)	55
RVP(37.8ºC, kPa)	53.8
MON	101
RON	116
Freezing Point(ºC)	-108.8
Flash Point, closed cup (ºC)	-25.6

4.1.2.4. TBA

Tertiary-Butyl Alcohol (TBA) is a fuel oxygenate and is also an impurity in, and a breakdown problem of Methyl-Butyl Ether (MTBE). TBA is a significant potential groundwater contaminant due to its mobility, recalcitrant nature, and potential toxicity. Exposure to TBA can lead to irritation of mucous membranes, nausea, defeating of the skin, and intoxication. Metabolism of TBA leads to the formation of 2-methyl-1,2-propanediol which is oxidized to 1-hydroxybutyrate or to formaldehyde and acetone. TBA is not a substrate for alcohol dehydrogenase and appears to be more slowly metabolized than MTBE. There is currently no federal drinking water standard for TBA, although two states have drinking water action levels for TBA ranging from 100 mg/L down to 12 mg/L.

TBA is used as a denaturant for ethanol, in the manufacturing of floatation agents, flavors, and perfumes (especially in the preparation of artificial musks); as a solvent, in paint removers; and, as an octane booster in gasoline. TBA is also used as a solvent for pharmaceuticals, as a dehydrating agent, and in the manufacture of methyl methacrylate. TBA is raw material in the production of isobutylene, which

may be used to produce MTBE, a common gasoline additive, or to produce butyl elastomers used in the production of automobile tires. TBA is used in the purification of polyoelfins, for the separation of solids from coal liquids and as a blowing agent for the manufacture of iomide group-containing foams from copolymers of methacreylonitrile and methacrylic acid. TBA may be formed in the environment through oxidation of MTBE in the atmosphere followed by hydrolysis or through microbial oxidation of MTBE in impacted aquifer materials. The properties of TBA are shown in table 4.5.

Table 4.5. Properties of TBA

Chemical Formula	$C_4H_{10}O$
Purity (%)	99
Oxygen (wt%)	21.6
Molecular Weight (g/mol)	74.12
Density (16ºC; g/cm3)	0.788
Boiling Temperature (ºC)	82
RVP(37.8ºC, kPa)	5.5
MON	100
RON	130
Freezing Point(ºC)	26
Flash Point, closed cup (ºC)	11.2

4.1.2.5. TAA

Tert amyl alcohol (TAA) is not used a common oxygenates yet. In this study, possibility of usage TAA as an oxygenate was investigated. The properties of TAA are shown in table 4.6.

Table 4.6. Properties of TAA

Chemical Formula	$C_5H_{12}O$
Purity (%)	98
Oxygen (wt%)	22.4
Molecular Weight (g/mol)	88.15
Density (16ºC; g/cm3)	0.805
Boiling Temperature (ºC)	102
RVP(37.8ºC, kPa)	1.6
MON	100
RON	130
Freezing Point(ºC)	-11
Flash Point, closed cup (ºC)	21

4.1.2.6. DIPE

Di isopropyl ether (DIPE) is not used as a common oxygenate yet. In this study, possibility of usage DIPE as an oxygenate was investigated. The properties of DIPE are shown in table 4.7.

Table 4.7. Properties of TAA

Chemical Formula	$C_6H_{14}O$
Purity (%)	98+
Oxygen (wt%)	15.7
Molecular Weight (g/mol)	102.17
Density (16ºC; g/cm3)	0.725
Boiling Temperature (ºC)	83
RVP(37.8ºC, kPa)	20
MON	96
RON	124
Freezing Point(ºC)	-
Flash Point, closed cup (ºC)	-

4.2. Methods

Physical and chemical properties of blends are measured in the Ç.Ü. Fuel Quality Analyzing Laboratory (ÇÜYAL) which is belongs to Çukurova University Faculty of Engineering and Architecture, Department of Mechanical Engineering, Automotive Division. Measured values, measurement methods and equipments are given below.

4.2.1. 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 4.8. and a picture of density meter has been shown in figure 4.1.

Table 4.8. Properties of Density-meter.

Range	Density: 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
Storage temperature	-20 to 70°C
Display content	Density, temperature compensated density, specific gravity, temperature compensated specific gravity, Brix %, alcohol concentration, sulfuric acid concentration, API degree, Baume degree, Plato and Proof degree, etc.
Temperature Compensation	10 kinds of coefficients per sample plus temperature to be corrected can be entered.

Figure 4.1. A Picture of Density-meter

4.2.2. 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 which is shown in figure 4.2.

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 4.3. and some properties of equipment are outlined in table 4.9.

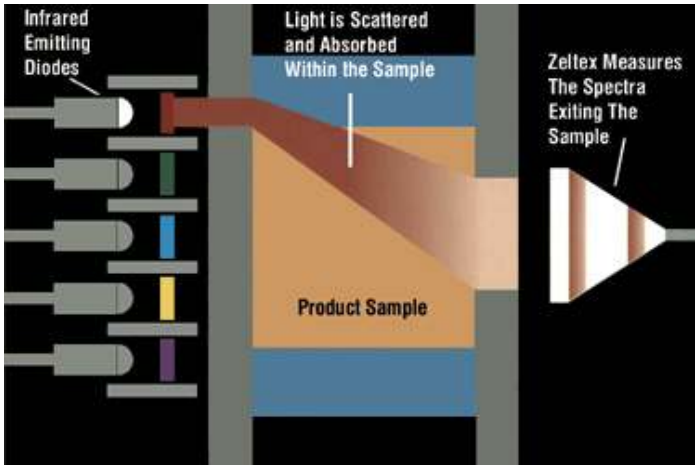

Figure 4.2. The principle of NIR technology

Figure 4.3. Octane Numbers Analyzer

Table 4.9. Properties of Octane Analyzer

Optical Capabilities	
Spectrum Range…….	37 Filters covering wavelengths from 604 to 1045 nm
Scan Speed…….	Up to 10 scans per seconds
Optical Range……..	0 to 5 AU
Resolution……	0.00001 AU
Stability…….....	0.02 mili-AU
Measurement Modes..	Diffuse transmittance
Measurement Time….	Up to 30 seconds
Measurement Data….	Log 1/T values, 1 to 37 primary wavelengths, 442 usable wavelengths
Sample Information	
Sample Size…….	200 ml with 75 mm wavelength
Sample Holder…….	Reusable glass with chemical seal cover
Measurement Range..	from 0.05 to 99%

4.2.3. Measuring of Reid Vapor Pressure (RVP)

Reid vapor pressures are measured by Tanaka AVP 30D automatic RVP analyzer. Tanaka AVP 30D RVP analyzer is shown in figure 4.4 and some properties of equipment are outlined in table 4.10.

Figure 4.4.Reid Vapor Pressure (RVP) Analyzer

Table 4.10. Properties of Reid Vapor Pressure Analyzer

Related standards	ISO 3077, ASTM D323, IP69 etc.
Type	Bench-top with 2,3, or 4 Demi-size bombs. Automated continuous shaking of test bomb by "see-saw" motion.
Measuring Range	0to196kPa(2kgf/cm^2)
Test Bombs	Small size stainless steel bombs with 66% in length and 31% in volume compared to the regular full size bombs. The V/L ratio of 4 is the same as full size bomb. A "Quick Coupler" is equipped at the center of the vapor chamber for connecting to external pressure sensor located inside of the tester.
Pressure Sensor	Semiconductor type pressure sensor. Range: 0 to 196kPa (2kgf/cm^2) Linearity: <0.3% of the range Hysteresis: <0.3% of the range
Display	LCD with back light Pressure display range: 0 to 200kPa or 0 to 2gf/cm^2
Shaking	By "see-saw" movement with angular movement of +/-15 degrees and interval of 6 sec. Temperature control: Digital controller/display with PT-100 sensor Precision: +/-0.1°C Stirring: By propeller driven by motor Heater: Stainless sheathed heater 1.15kW.

4.2.4. 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. To provide the calorimeter with cooling water, it needs to be connected to a thermostat or a firmly installed water connection. The C 2000 basic is equipped with a very convenient console to operate the unit. A picture of calorimeter analyzer is shown in figure 4.5 and some properties of equipment are outlined in table 4.11.

Figure 4.5. A picture of calorimeter

Table 4.11. 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
Analysis according to DIN 51900 (1977/84)	yes	Analysis according to ASTM D240 (2002)	yes
Analysis according to ASTM D4809 (2000)	yes	Analysis according to ASTM D1989 (1992)	yes
Analysis according to ASTM D5468 (2002)	yes	Analysis according to ASTM D5865 (2001)	yes
Analysis according to ASTM E711	yes	Protection class according to DIN EN 60529	IP 21

4.2.5. Measuring of Sulfur Contents

Sulfur contents of blends were measured by Oxford Lab-X 3500 XRF sulfur analyzer. The XRF Sulfur analyzer is shown in Figure 4.6.

Figure 4.6. XRF Sulfur Analyzer

The measuring of this analyzer based on ASTM D 4294 and the technology of this analyze called energy dispersive X-ray fluorescence technology (EDXRF) is especially reliable and suitable for solid, liquid and powdered samples and requires nearly no sample preparation. Chemical composition can be measured over a wide range of elements from sodium (11) to uranium (92) in concentration ranges of low level ppm up to 100 weight% simultaneously. A benchtop XRF analyser measuring Sulfur in Oil with detection limits down to 2.5 ppm conforming to IP336, ISO 8754 and the ISO/CD 20847. The system also complies with ASTM D4294. There are various packages available (sulfur, nickel, vanadium and iron in fuel oils; potassium, manganese and lead in gasoline) with different performances and sulfur detection limits.

4.2.6. Measuring of Distillation Characteristics

Distillation characteristics were measured by Tanaka AD-6 automatic distillation analyzer. The Tanaka AD-6 distillation analyzer is shown in figure 4.7 and some properties of equipment are outlined in table 4.12.

Table 4.12. Properties of Distillation Analyzer

Conforming standards	ISO 3405, ASTM D86, IP123 for distillation test of petroleum products (groups 0,1,2,3,4), ASTM D850 for distillation test of industrial aromatic hydrocarbons, ASTM D1078 for distillation test of volatile organic liquids.
Temperature Range	Selectable from RT to 300°C/400 °C (fuel oil) or RT to 200°C/400°C (ASTM D850, D1078)
Temperature Meas.	Pt100 Probe
Meniscus Detection	By photoelectric devices with pulse motor
Distillation Rate	Selectable form 2.0 to 9.0ml/min with 0.5 increment
Display	Monochrome LCD (120mm x 90mm) Distillation curve and other test parameters, status, and trouble message displayed
Condenser Tube	Brass tube(std) or stainless steel tube(opt) Controlled at 0 to 70 °C by Peltier elements
Receiver Room	Controlled at 0 to 70 °C by Peltier elements
Safety Features	Heater shuts down at the upper end of the scale (200/300/400°C). Upon detecting fire by thermofuse, warning buzzer beeps, heater shuts down, and fire containment system activates. The fire containment system consists of a mechanical shutter and N_2gas injector.

Figure 4.7. Tanaka AD-6 distillation analyzer

5. RESULTS and DISCUSSIONS

5.1. Properties of Ethanol-Gasoline Blended Fuels

Ethanol has been blended into unleaded gasoline with various blended rates (2.5%, 5%, 7.5%, 10%, 15% and 20%). The blends have been analyzed by the standard ASTM test methods and results are shown in table 5.1. The "E" designates ethanol and the number of next to E designates the percentage volume of ethanol. The E5 means, 5% ethanol (%99.5 purity) was blended with 95% unleaded gasoline by volume.

Table 5.1. Properties of Ethanol-Gasoline Blended Fuels.

Ethanol-Gasoline	E0	E2.5	E5	E7.5	E10	E15	E20
Density(16ºC; g/cm^3)	0,7682	0,7686	0,769	0,7701	0,7711	0,7726	0,7754
MON	85,3049	85,9823	86,2058	86,9911	87,4726	88,6054	88,7598
RON	98,6462	99,4344	99,4634	99,9504	100,4521	100,7383	100,989
RVP (37.8ºC, kPa)	64,2	66,8	68,2	67,8	67,3	67	66,8
Sulphur (wt %)	0,067	0,0651	0,0645	0,0636	0,0613	0,0603	0,0591
Calorific Value(cal/g)	10352	10207	10121	10053	9974	9844	9712
Distillation (ºC)							
IBP	44,4	34,2	33,2	38,5	49,4	34,9	37,4
10 vol%	68,4	53,4	55,9	56,3	65,7	57,6	59
50 vol%	124,6	111,9	110,2	109,4	132,3	79,4	74,1
90 vol%	174,3	168,9	167,9	169,2	174	164,5	168,2
End Point	206,6	194,2	194	196	204,3	194,5	188,1

The result of the ASTM analysis, some of the combustion related properties have been summarized in table 5.1. The table shows the variations of density, Motor Octane Number (MON), Research Octane Number (RON), Reid Vapor Pressure (RVP), sulfur content, calorific value as different blend rates of ethanol-gasoline blends.

Table 5.1. also presents the variations on distillation temperatures of different ethanol- gasoline blended fuels, including the initial boiling point (IBP), 10%, 50%, 90% distillation temperatures and final distillation temperature. It can be observed that the IBP, 10%, 90% and final distillation point are almost independent of the ethanol content except 50% distillation temperature.

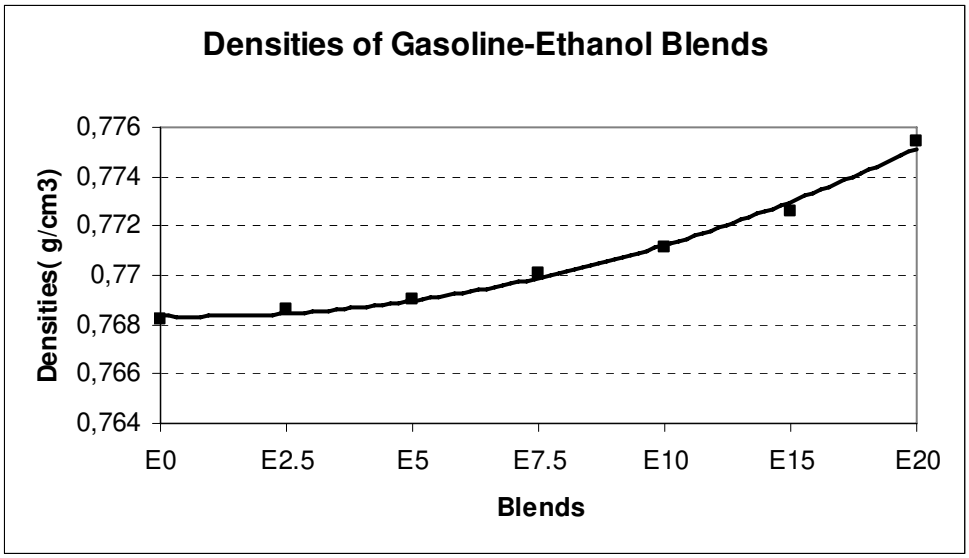

Figure 5.1. Densities of Gasoline-Ethanol Blends.

As it seen in figure 5.1. the densities of the blends is increasing by the percentage of ethanol. This increase can be explained the densities of the components. The density of ethanol is 0.80 g/cm^3, in spite of this the density of gasoline 0.76 g/cm^3. Therefore, densities of the blends are dependent of the ethanol content directly.

The quality of gasoline is constantly based on its octane number (or rating), which indicates its antiknocking strength. To this end, isooctane is given an octane number equal to 100, while the octane number of n-heptane is zero. The octane number is an indicator of the gasoline's antiknocking strength. This number is determined experimentally in an engine with a variable compression rate. According to the operating conditions of this test engine, the octane number is determined with the help of an engine (Motor Octane Number, MON or Research Octane Number, RON). The average of the octane numbers MON and RON is known as the Antiknock Index, AKI = [(RON+MON)/2].

The MON evaluates the gasoline's antiknocking strength when the engine is operating under more severe conditions, high rotation and full load, as is the case when driving uphill in low gear and high rotation simulating a driving condition in a city. The RON evaluates the gasoline's antiknocking strength when the engine operates under milder conditions, low rotation, simulating a driving condition on a

highway. MON and RON numbers of gasoline-ethanol blends are shown in figure 5.2. and figure 5.3.

The antiknocking strength is an extremely important property of gasoline, since it should not autoignition by compression, but by sparking. Gasoline having a high octane index produces a milder and more effective combustion. The octane number is simply a numerical description of its resistance to autoignition without entering into a knocking process (spontaneous burning of the mixture).

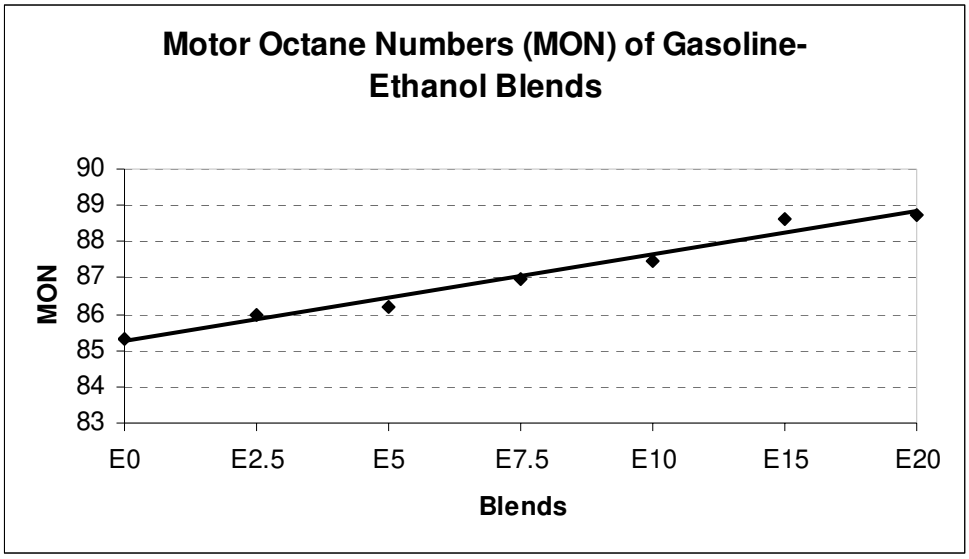

Figure 5.2. Motor Octane Numbers of Gasoline Ethanol Blends.

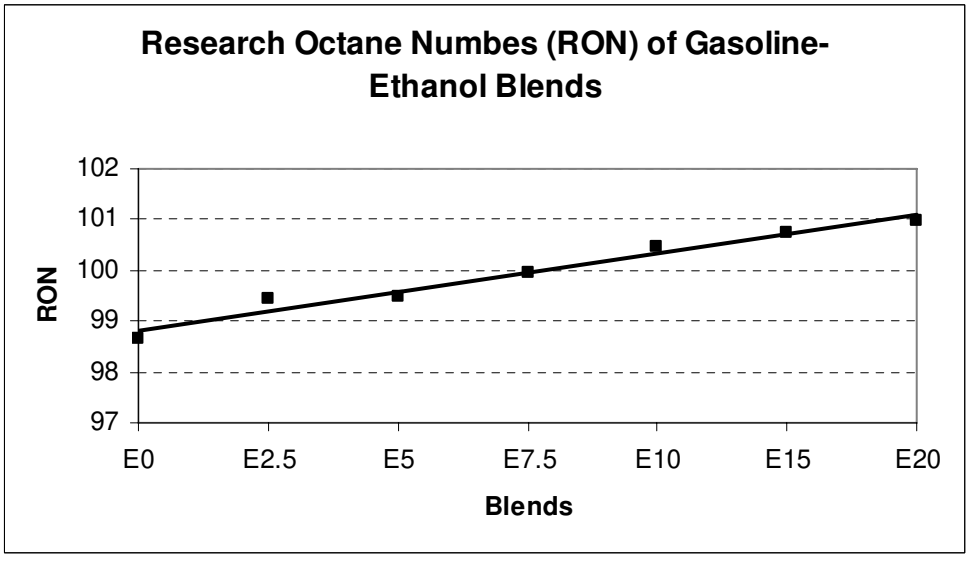

Figure 5.3. Research Octane Numbers of Gasoline Ethanol Blends.

The results of the vapor pressure in kPa measured at 37.8 8C (RVP) of the original gasoline compositions and of the ones formulated with different percentages of ethanol are shown in figure 5.4.

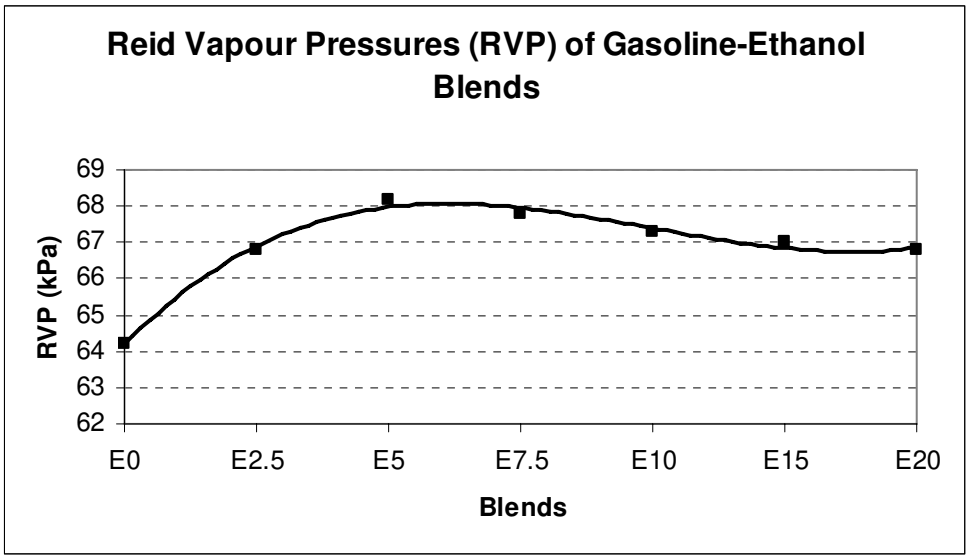

Figure 5.4. Reid Vapor Pressures of Gasoline Ethanol Blends.

As can be seen from figure 5.4., the addition of ethanol led to a significant increase with the first 5% of alcohol volume added. With percentages of over 10%, the vapor pressure tended to decrease.

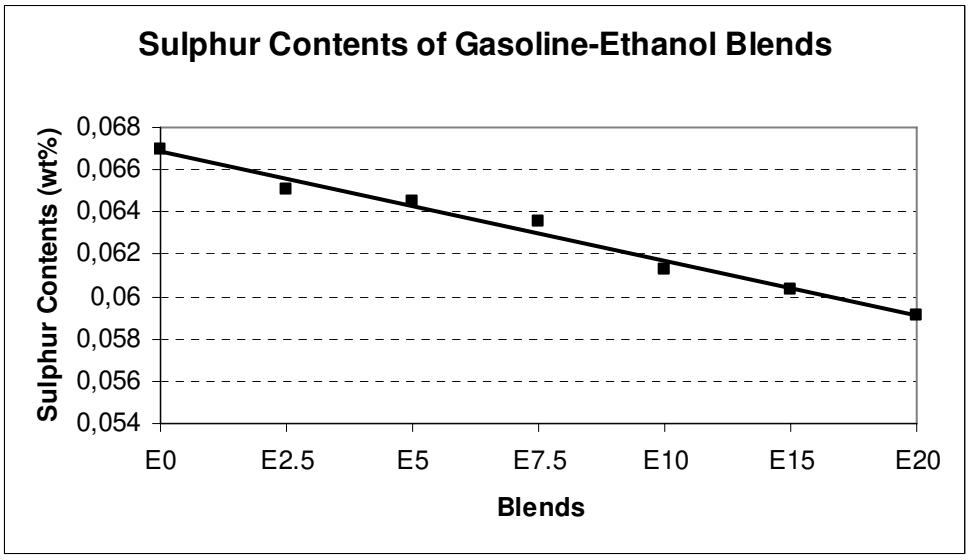

Figure 5.5. Sulphur Contents of Gasoline Ethanol Blends.

Sulphur contents and calorific values of ethanol-gasoline blends are shown in figure 5.5. and figure 5.6., respectively. Distillation graphics of the ethanol-gasoline blends are shown in figure 5.7. and as seen in this graph distillation temperatures of blends are decreasing with increasing EtOH contents.

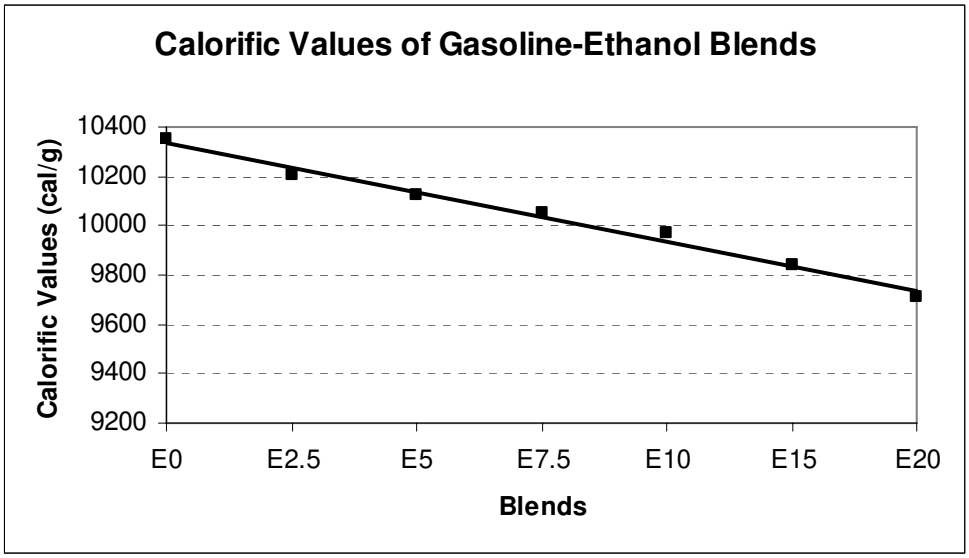

Figure 5.6. Calorific Values of Gasoline-Ethanol Blends

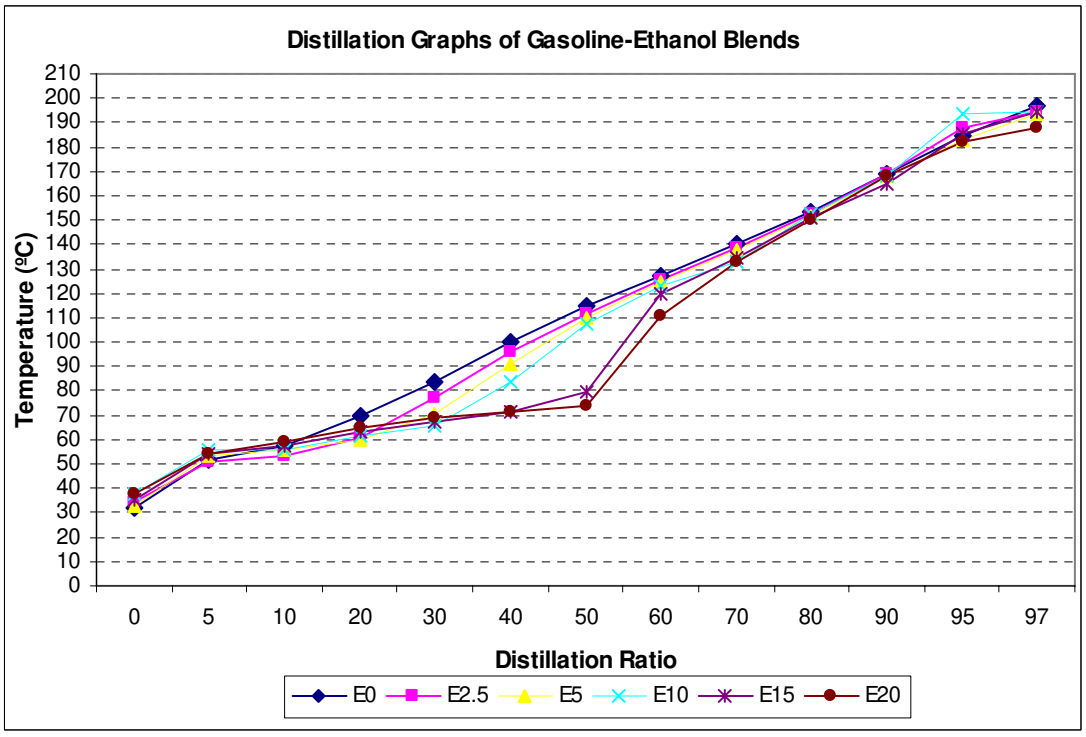

Figure 5.7. Distillation Graphs of Gasoline Ethanol Blends

5.2. Properties of Methanol-Gasoline Blended Fuels

Methanol has been blended into unleaded gasoline with various blended rates (2.5%, 5%, 7.5%, 10%, 15% and 20%). The blends have been analyzed by the standard ASTM test methods and results are shown in table 5.2. The "M" designates methanol and the number of next to M designates the percentage volume of methanol. The M5 means, 5% methanol (%99.5 purity) was blended with 95% unleaded gasoline by volume.

Table 5.2. Properties of Methanol-Gasoline Blended Fuels.

Methanol-Gasoline	M0	M2.5	M5	M7.5	M10	M15	M20
Density(16ºC; g/cm^3)	0,7682	0,7736	0,774	0,7743	0,7747	0,775	0,7755
MON	85,3049	86,3079	87,2249	88,0641	88,0379	88,3559	90,2303
RON	98,6462	99,8166	100,3542	100,8741	100,915	101,296	103,2597
RVP (37.8ºC, kPa)	64,2	74,3	76,9	77,3	77,1	76,8	76,2
Sulphur (wt %)	0,067	0,065	0,0648	0,0645	0,0643	0,0639	0,0634
Calorific Value(cal/g)	10352	10271	10184	10097	9994	9942	9873
Distillation Temp. (ºC)							
IBP	44,4	41,7	34,2	35,4	32,9	34,3	36,5
10 vol%	68,4	51,5	51,7	52,4	51,3	52,3	53,5
50 vol%	124,6	115,4	113,2	112,6	109,5	105,3	103,2
90 vol%	174,3	170	170,9	169	167,7	169,7	168
End Point	206,6	196,7	196,2	191,8	194	191,6	190,4

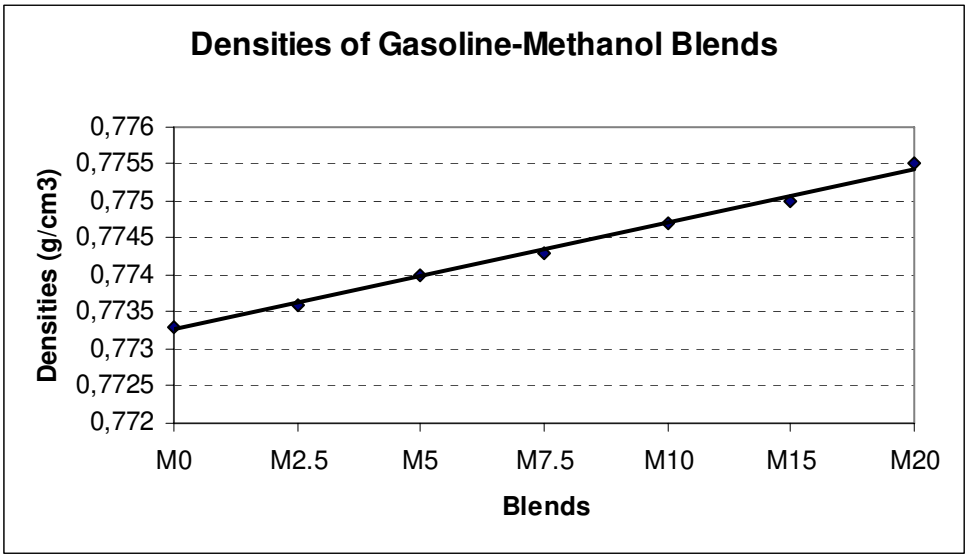

Figure 5.8. Densities of Gasoline-Methanol Blends

Densities of gasoline-methanol blends are increasing related to methanol contents clearly because of its higher density and this can be seen in figure 5.8. The density of methanol which was used in this study 0.7915 °C at 16°C.

Motor octane numbers of gasoline-methanol blends are shown in figure 5.9. and as it seen this figure, MON is getting higher with addition to methanol significantly. Research octane numbers of gasoline-methanol blends are shown in figure 5.10. and as it seen this figure, RON is increasing up to 104 with methanol addition.

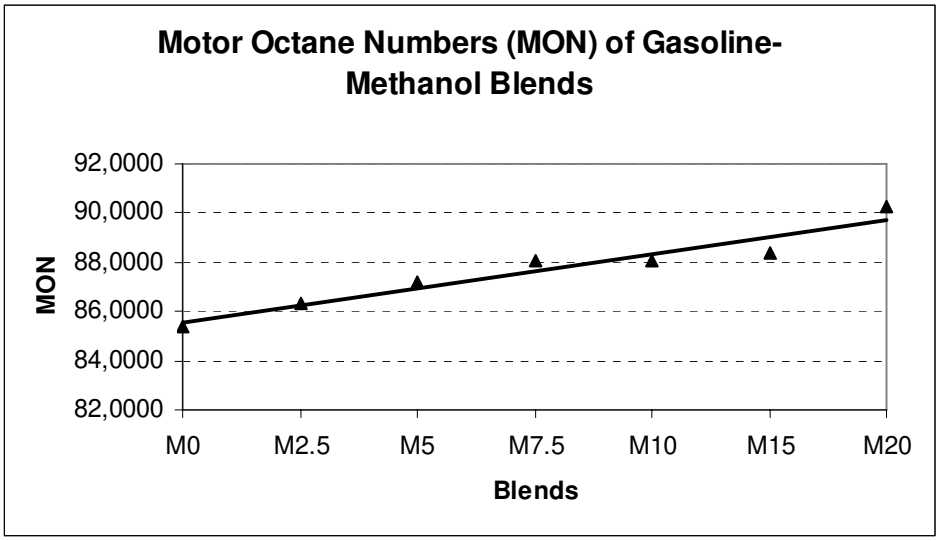

Figure 5.9. Motor Octane Numbers of Gasoline-Methanol Blends.

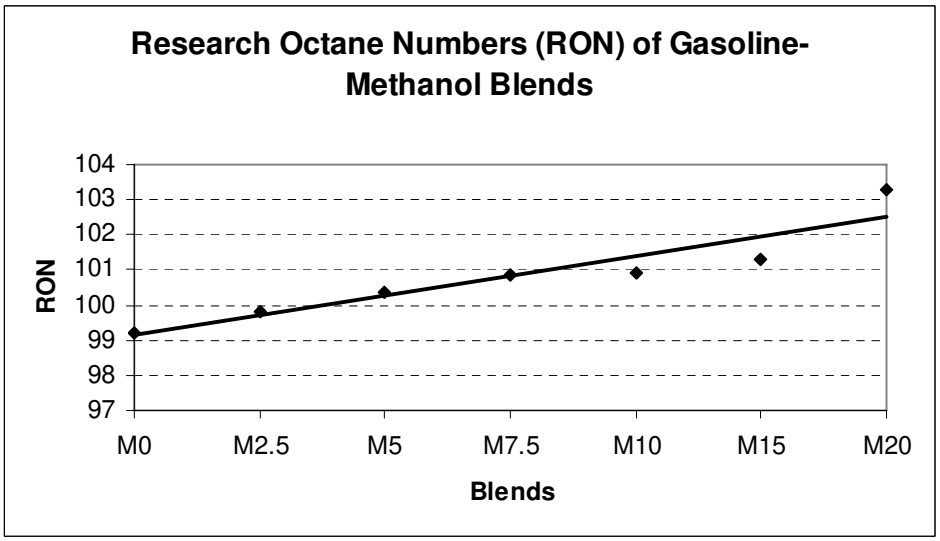

Figure 5.10. Research Octane Numbers of Gasoline-Methanol Blends.

Reid vapour pressures and sulphur contents of gasoline-methanol blends are shown in figure 5.11. and figure 5.12., below.

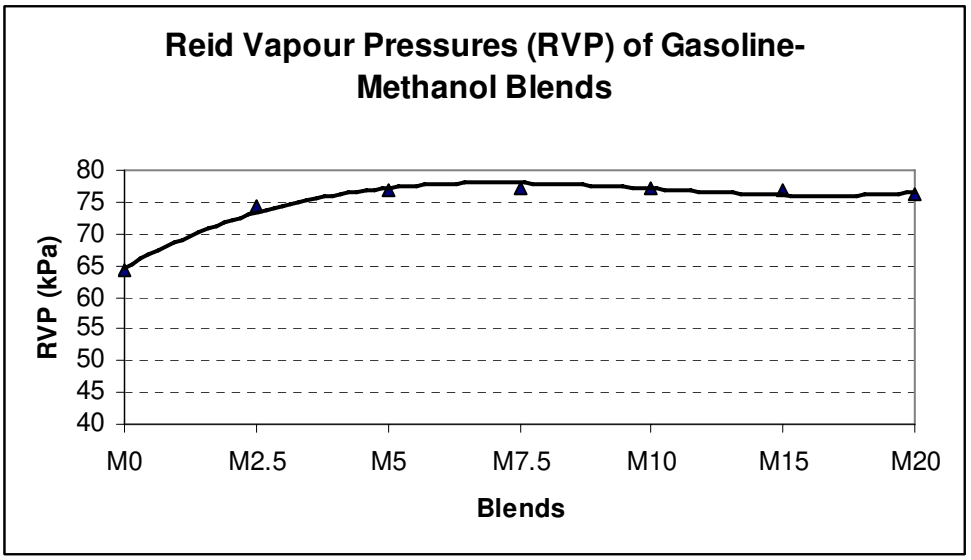

Figure 5.11. Reid Vapour Pressures of Gasoline-Methanol Blends.

As seen in figure 5.12., the sulphur contents of gasoline-methanol blends is dramatically decreasing by percentage volume of methanol. The reducing the sulphur contents provide low harmful exhausts emissions such as SO_2.

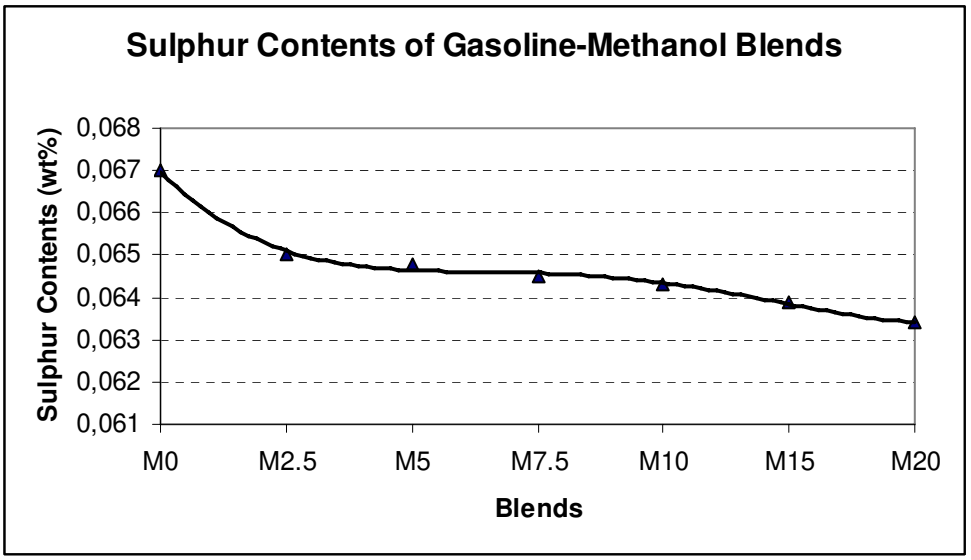

Figure 5.12. Sulphur Contents of Gasoline Methanol Blends.

Figure 5.13. shows effects of the methanol addition into gasoline on calorific values and distillation graphics of gasoline-methanol blends are shown in figure 5.14.

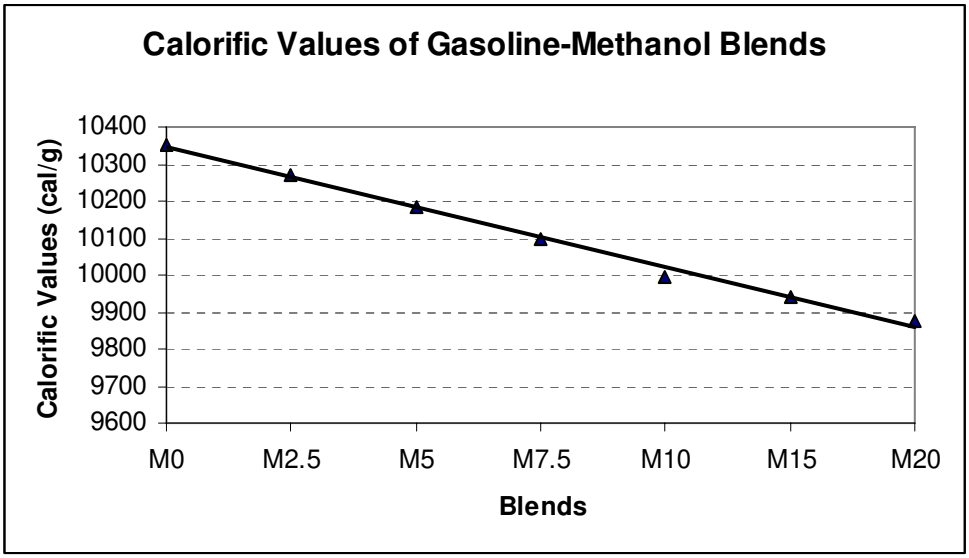

Figure 5.13. Calorific Values of Gasoline Methanol Blends.

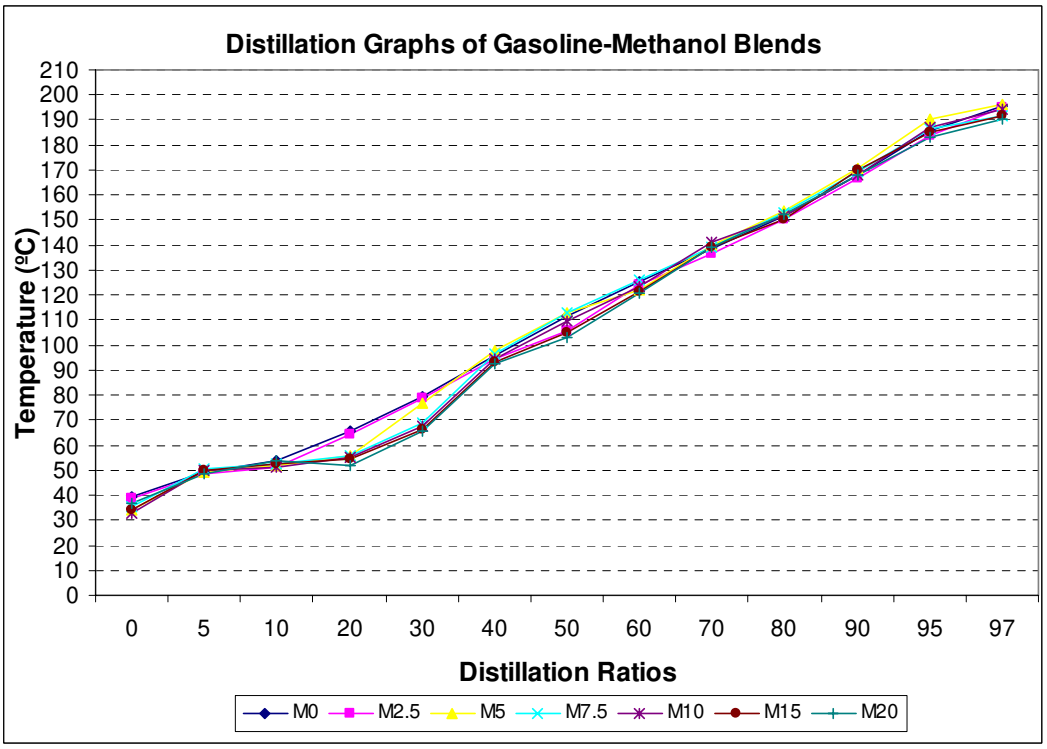

Figure 5.14. Distillation Graphs of Gasoline Methanol Blends.

5.3. Properties of TBA-Gasoline Blended Fuels

The blends have been analyzed by the standard ASTM test methods and results are shown in table 5.3. The "TB" designates Tert-butyl alcohol or tert-butanol (TBA) and the number of next to TB designates the percentage volume of TBA. The TB5 means, 5% TBA (%99 purity) was blended with 95% unleaded gasoline by volume.

Table 5.3. Properties of TBA-Gasoline Blended Fuels.

TBA-Gasoline	TBA0	TBA2.5	TBA5	TBA7.5	TBA10	TBA15	TBA20
Density(16ºC; g/cm^3)	0,7682	0,7726	0,7732	0,775	0,7765	0,7789	0,7806
MON	85,3049	86,6094	88,8175	89,7572	90,9958	92,7711	94,5379
RON	98,6462	97,8255	101,383	102,563	103,354	104,754	107,928
RVP (37.8ºC, kPa)	64,2	50,4	51,6	47,9	49,9	53,7	52,2
Sulphur (wt %)	0,067	0,0608	0,0583	0,0575	0,0556	0,0532	0,0516
Calorific Value(cal/g)	10352	10273	10017	9797	9729	9701	9680
Distillation Temp. (ºC)							
IBP	44,4	41,4	43,7	44,6	44,6	45,2	48,7
10 vol%	68,4	59,3	62,2	60,5	60,1	61,8	63,7
50 vol%	124,6	117,7	119,9	114,9	111,1	98,5	93,3
90 vol%	174,3	176,5	175,6	175,3	175,9	173,2	174,8
End Point	206,6	203,2	205	205,2	201,4	203,1	196,6

Densities of gasoline-TBA blends are increasing related to TBA contents clearly and this can be seen in figure 5.15.

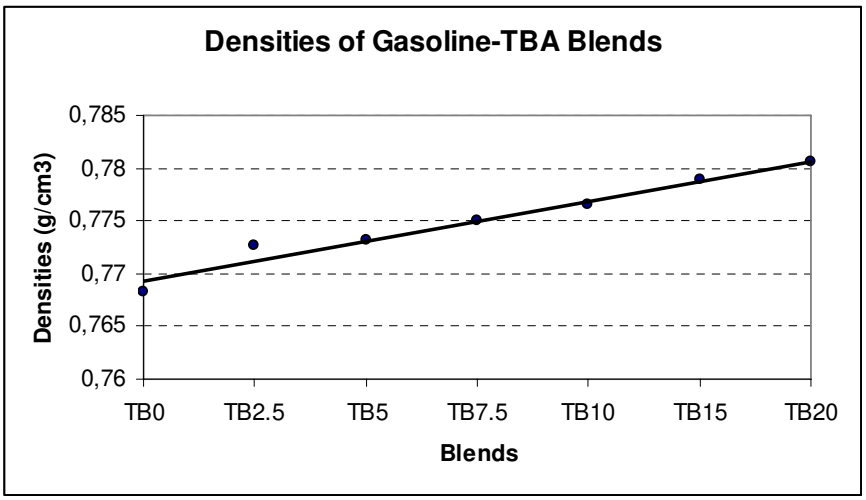

Figure 5.15. Densities of Gasoline-TBA Blends.

Motor octane numbers of gasoline-TBA blends are shown in figure 5.16. and as it seen this figure, MON is getting higher with addition to TBA significantly.

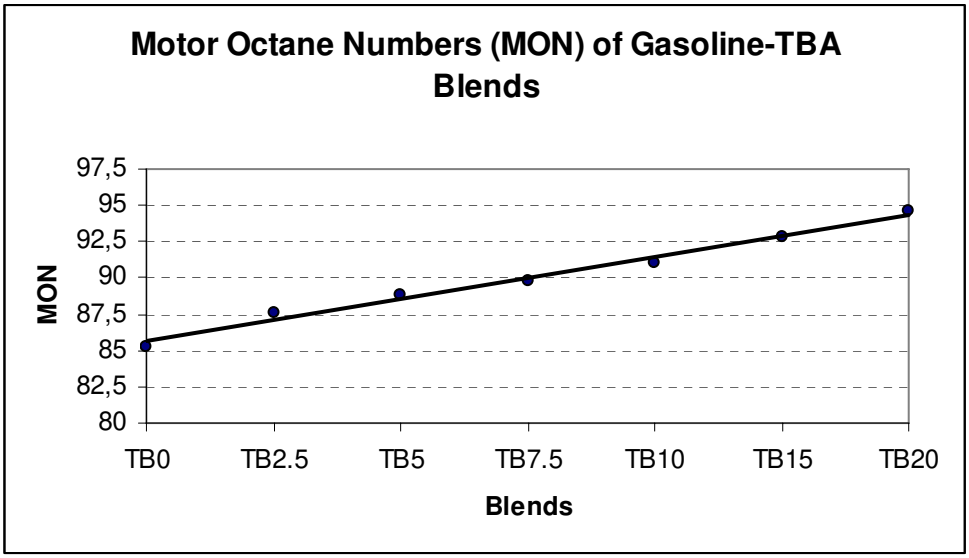

Figure 5.16. Motor Octane Numbers of Gasoline-TBA Blends.

Research octane numbers of gasoline-TBA blends are shown in figure 5.17. and as it seen this figure, RON is increasing up to 108 with TBA addition.

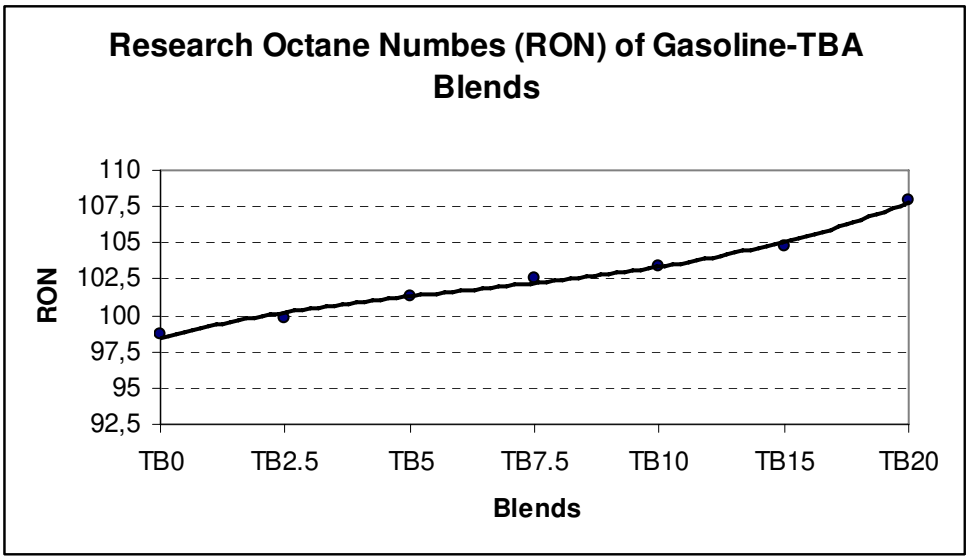

Figure 5.17. Research Octane Numbers of Gasoline-TBA Blends.

Reid vapour pressures and sulphur contents of gasoline-TBA blends are shown in figure 5.18. and figure 5.19., below.

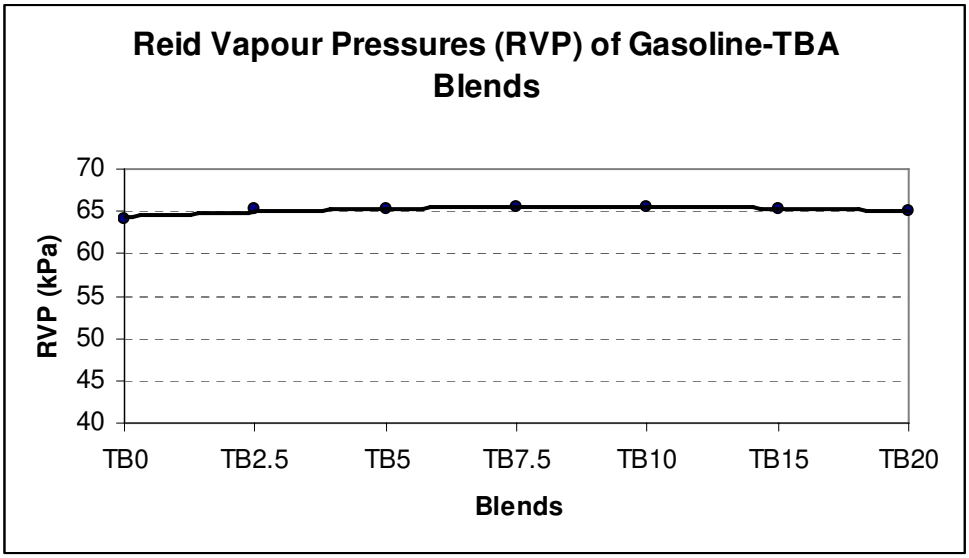

Figure 5.18. Research Octane Numbers of Gasoline-TBA Blends.

As seen in figure 5.19., the sulphur contents of gasoline-TBA blends is dramatically decreasing by percentage volume of TBA. The reducing the sulphur contents provide low harmful exhausts emissions such as SO_2.

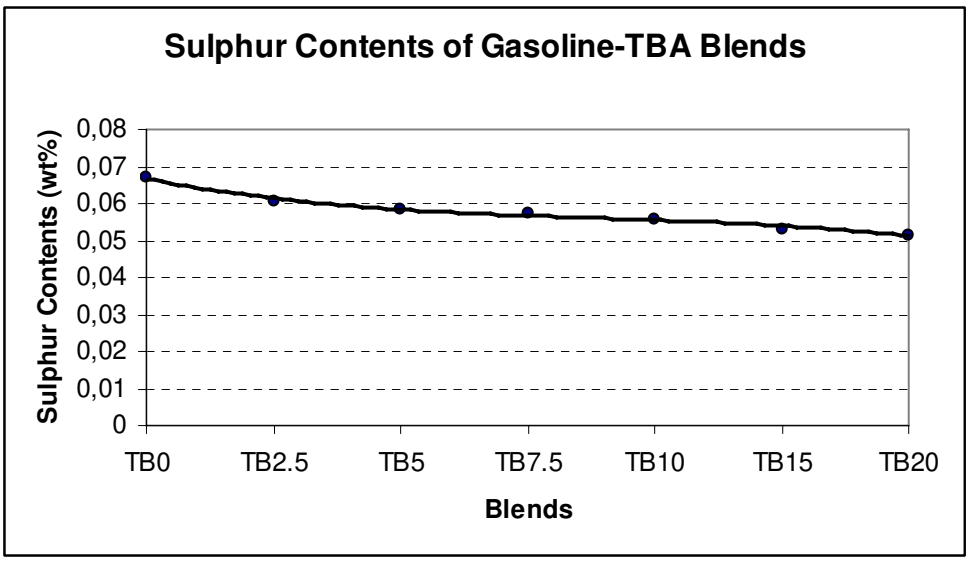

Figure 5.19. Sulphur Contents of Gasoline-TBA Blends.

Figure 5.20. shows effects of the TBA addition into gasoline on calorific values and distillation graphics of gasoline-TBA blends are shown in figure 5.21.

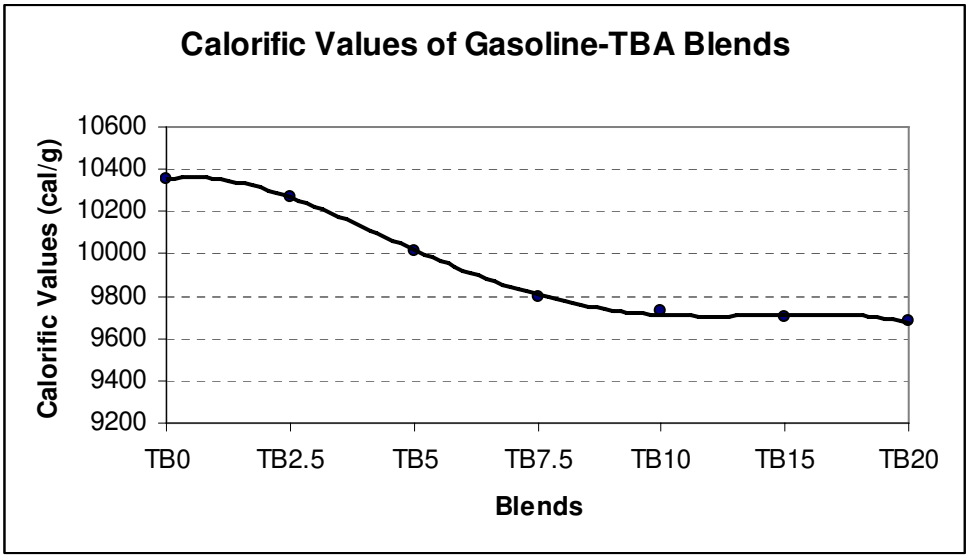

Figure 5.20. Calorific Values of Gasoline-TBA Blends.

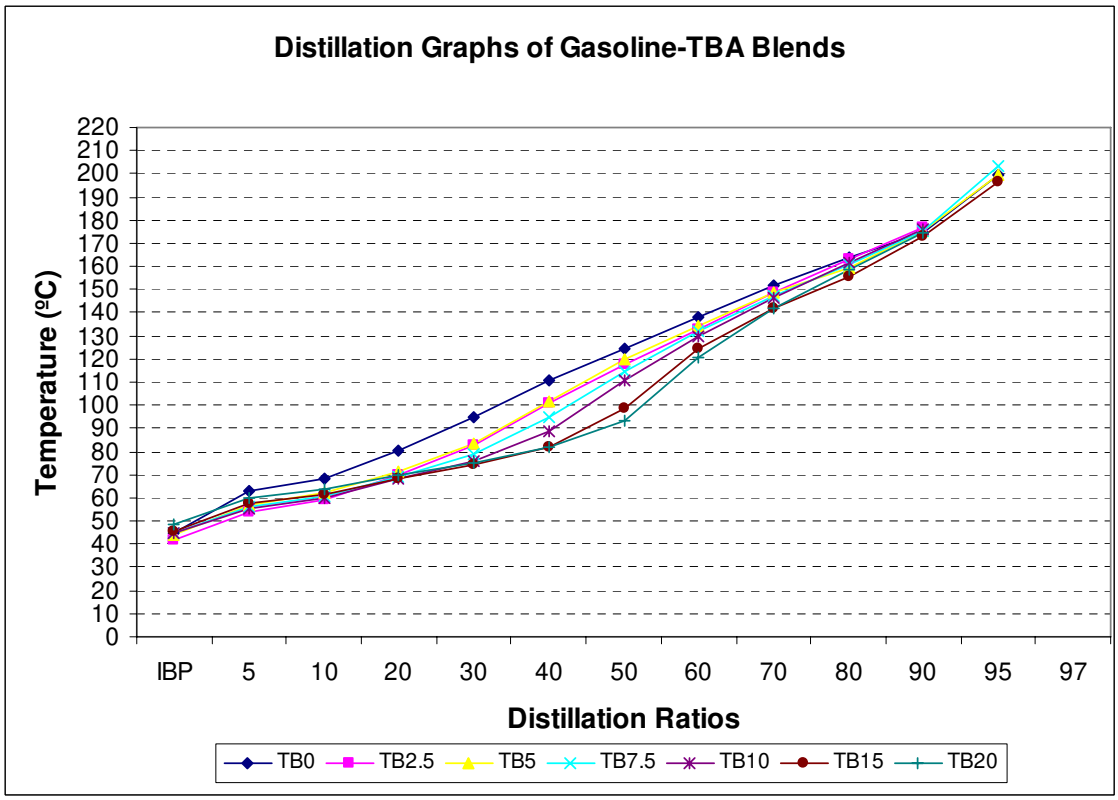

Figure 5.21. Distillation Graphs of Gasoline-TBA Blends.

5.4. Properties of TAA-Gasoline Blended Fuels

Tert-amyl alcohol (TAA)-gasoline blends have been analyzed by the standard ASTM test methods and results are shown in table 5.4. The "TA" designates TAA and the number of next to TA designates the percentage volume of TAA. The TA5 means, 5% TAA (%99 purity) was blended with 95% unleaded gasoline by volume.

Table 5.4. Properties of TAA-Gasoline Blended Fuels.

TAA-Gasoline	TAA0	TAA2.5	TAA5	TAA7.5	TAA10	TAA15	TAA20
Density(16ºC; g/cm^3)	0,7682	0,767	0,7678	0,7689	0,7698	0,7718	0,774
MON	85,3049	85,657	87,403	89,038	90,353	91,478	93,833
RON	98,6462	99,936	101,08	102,69	103,67	105,36	107,54
RVP (37.8ºC, kPa)	64,2	64,7	62	60,3	54,4	51,8	51
Sulphur (wt %)	0,067	0,0628	0,0623	0,062	0,0611	0,0608	0,0588
Calorific Value(cal/g)	10352	10138	10090	10064	10034	9928	9834
Distillation Temp. (ºC)							
IBP	44,4	39,3	38,5	42,4	43,1	42,2	43,1
10 vol%	68,4	57,4	58,3	62,5	72,6	64,8	65,9
50 vol%	124,6	110,4	108,9	106,6	110,8	102,5	101
90 vol%	174,3	168,5	167,9	168,3	168,2	167,7	166,2
End Point	206,6	197,4	193,9	193,1	193,8	193,1	191

Densities of gasoline-TAA blends are increasing related to TAA contents clearly and this can be seen in figure 5.22.

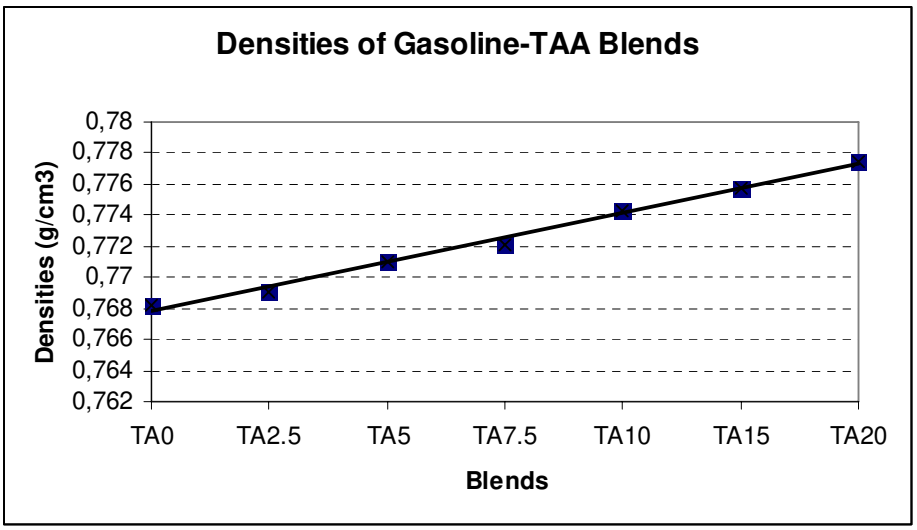

Figure 5.22. Densities of Gasoline-TAA Blends.

Motor octane numbers of gasoline-TAA blends are shown in figure 5.23. and as it seen this figure, MON is getting higher with addition to TAA significantly.

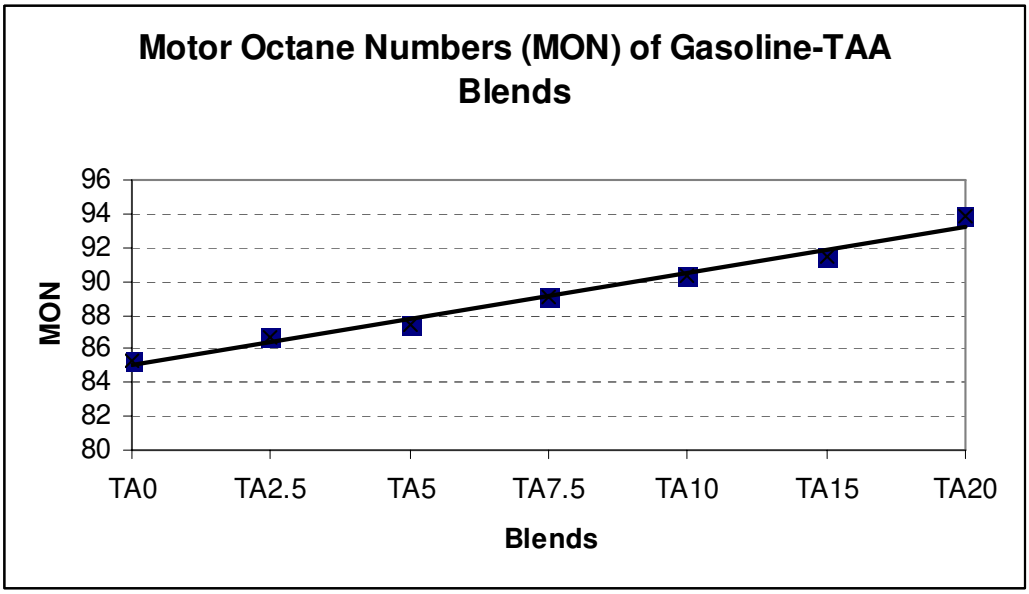

Figure 5.23. Motor Octane Numbers of Gasoline-TAA Blends.

Research octane numbers of gasoline-TAA blends are shown in figure 5.24. and as it seen this figure, RON is increasing up to 107.5 with TAA addition.

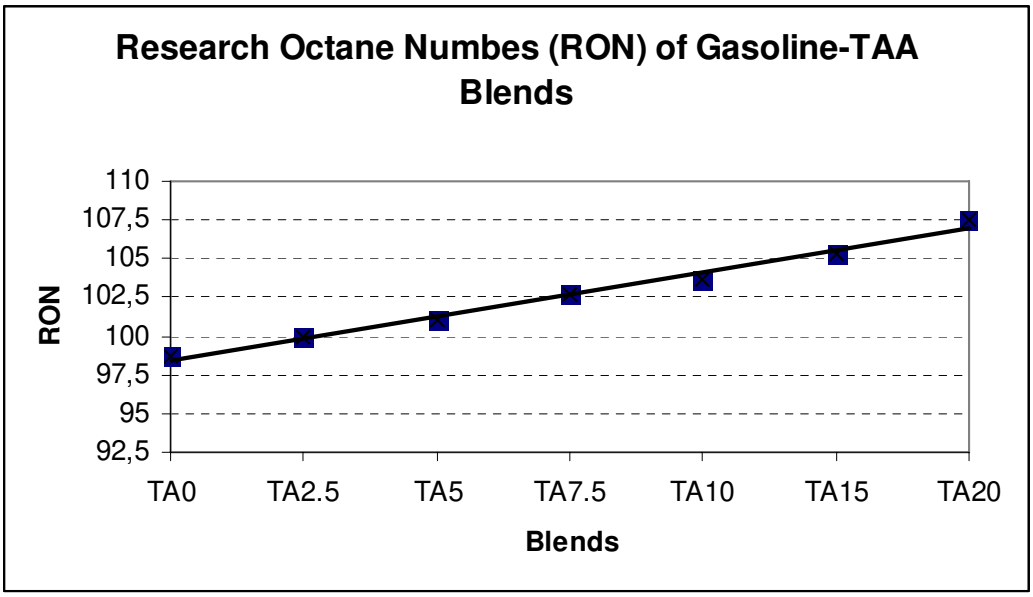

Figure 5.24. Research Octane Numbers of Gasoline-TAA Blends.

Reid vapour pressures and sulphur contents of gasoline-TAA blends are shown in figure 5.25. and figure 5.26., below.

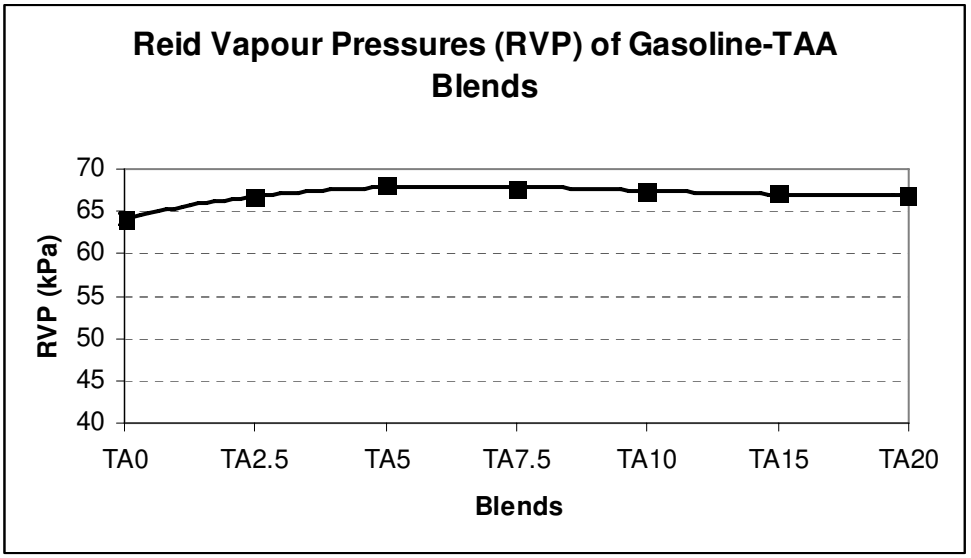

Figure 5.25. Reid Vapour Pressures of Gasoline-TAA Blends.

As seen in Figure 5.25., the sulphur contents of gasoline-TAA blends is dramatically decreasing by percentage volume of TAA. The reducing the sulphur contents provide low harmful exhausts emissions such as SO_2.

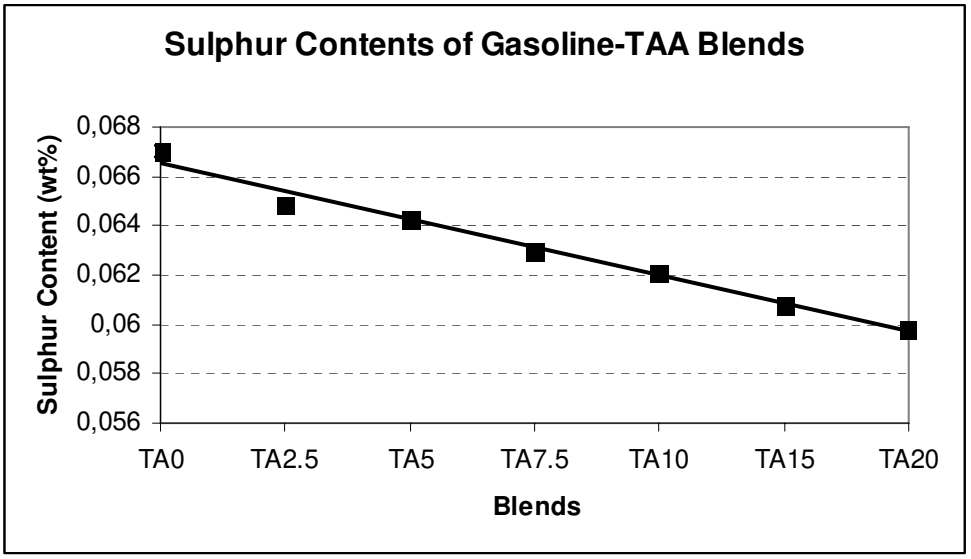

Figure 5.26. Sulphur Contents of Gasoline-TAA Blends.

Figure 5.27. shows effects of the TAA addition into gasoline on calorific values and distillation graphics of gasoline-TAA blends are shown in figure 5.28.

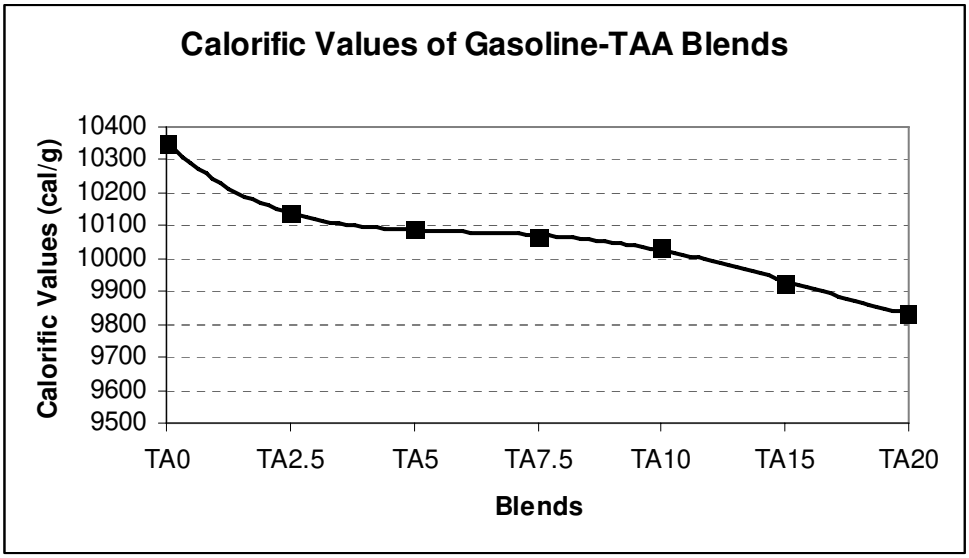

Figure 5.27. Calorific Values of Gasoline-TAA Blends.

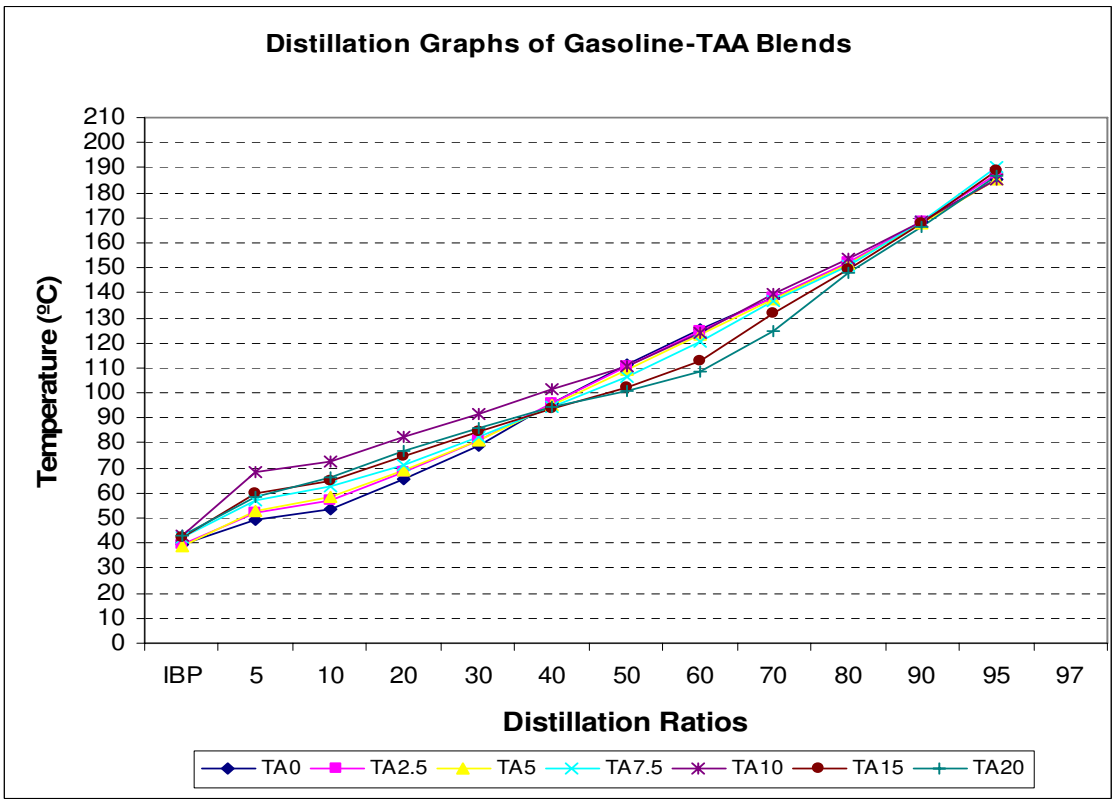

Figure 5.28. Distillation Graphs Values of Gasoline-TAA Blends.

5.5. Properties of MTBE-Gasoline Blended Fuels

Methyl tert butyl ether (MTBE)-gasoline blends have been analyzed by the standard ASTM test methods and results are shown in table 5.5. The "MT" designates MTBE and the number of next to MT designates the percentage volume of MTBE. The MT5 means, 5% MTBE (%99.5 purity) was blended with 95% unleaded gasoline by volume.

Table 5.5. Properties of MTBE-Gasoline Blended Fuels.

MTBE-Gasoline	MT0	MT2.5	MT5	MT7.5	MT10	MT15	MT20
Density(16ºC; g/cm^3)	0,7682	0,7689	0,7683	0,7676	0,767	0,7663	0,7636
MON	85,3049	84,5361	85,2387	85,4315	85,8324	86,5014	87,3358
RON	98,6462	97,0673	97,7389	98,1469	98,3679	99,1566	100,254
RVP (37.8ºC, kPa)	64,2	64,1	56,45	59,4	61,05	52,4	54,6
Sulphur (wt %)	0,067	0,0781	0,0774	0,0757	0,0729	0,071	0,0685
Calorific Value(cal/g)	10352	10322	10311	10284	10069	9924	9746
Distillation Temp. (ºC)							
IBP	44,4	37,6ºC	31,7	42,1	39,2	38,3	32,7
10 vol%	68,4	60,5ºC	61,4	60,1	61	58,3	55,5
50 vol%	124,6	116,8ºC	111,1	119,6	111,7	103	92,5
90 vol%	174,3	177,1	175,4	193,7	175,5	175,2	171,6
End Point	206,6	203,9	198,6	200,9	196,1	196,2	198,9

Densities of gasoline-MTBE blends are increasing related to MTBE contents clearly and this can be seen in figure 5.29.

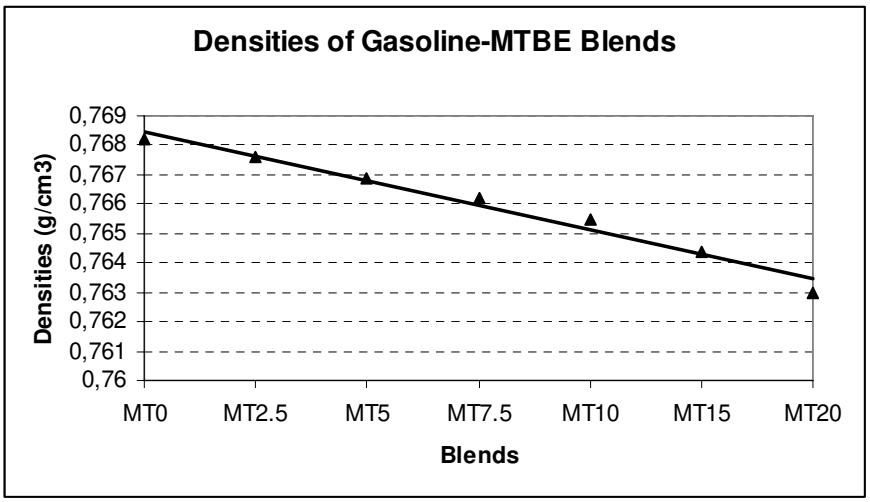

Figure 5.29. Densities of Gasoline-MTBE Blends.

Motor octane numbers of gasoline-MTBE blends are shown in figure 5.30. and as it seen this figure, MON is getting higher with addition to MTBE significantly.

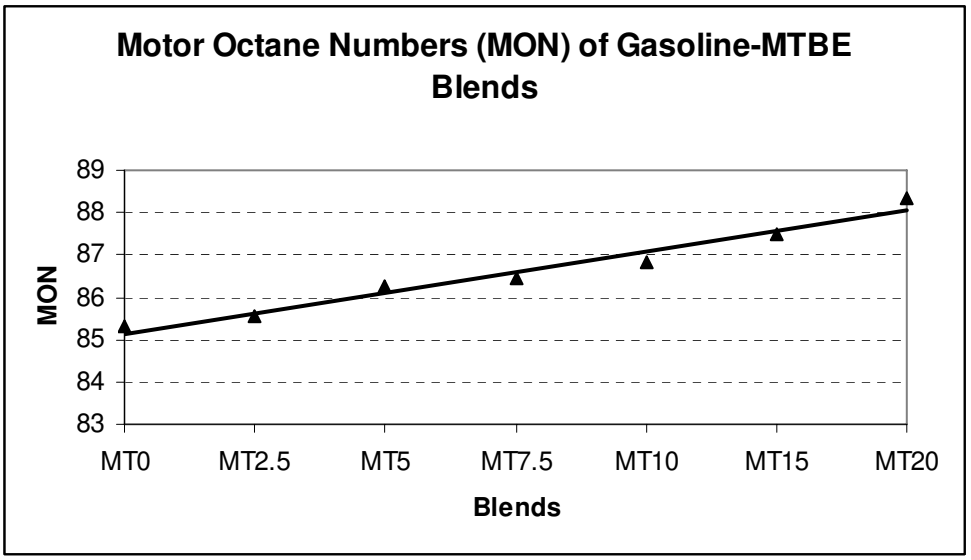

Figure 5.30. Motor Octane Numbers of Gasoline-MTBE Blends.

Research octane numbers of gasoline-MTBE blends are shown in figure 5.31. and as it seen this figure, RON is increasing up to 101 with MTBE addition.

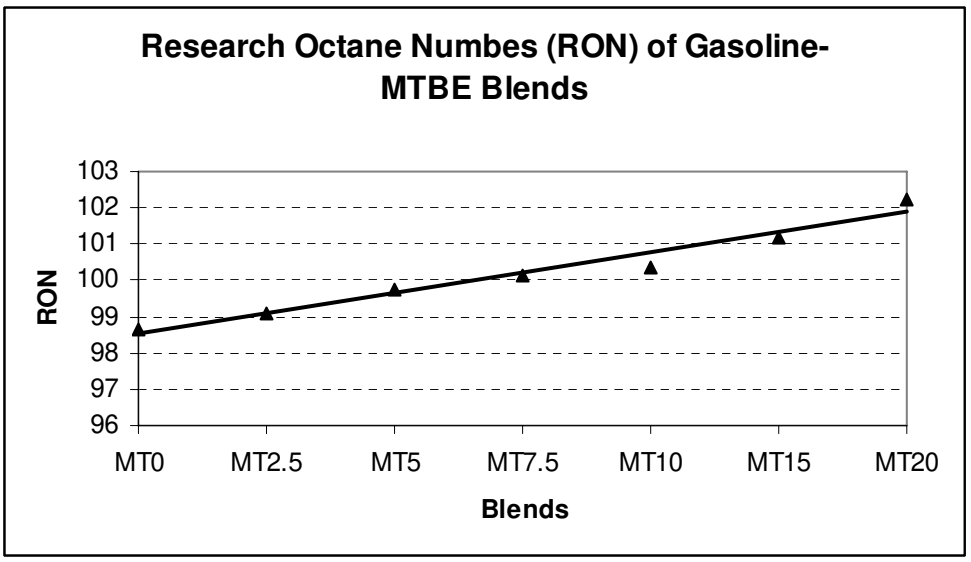

Figure 5.31. Research Octane Numbers of Gasoline-MTBE Blends.

Reid vapour pressures and sulphur contents of gasoline-MTBE blends are shown in figure 5.32. and figure 5.33., below.

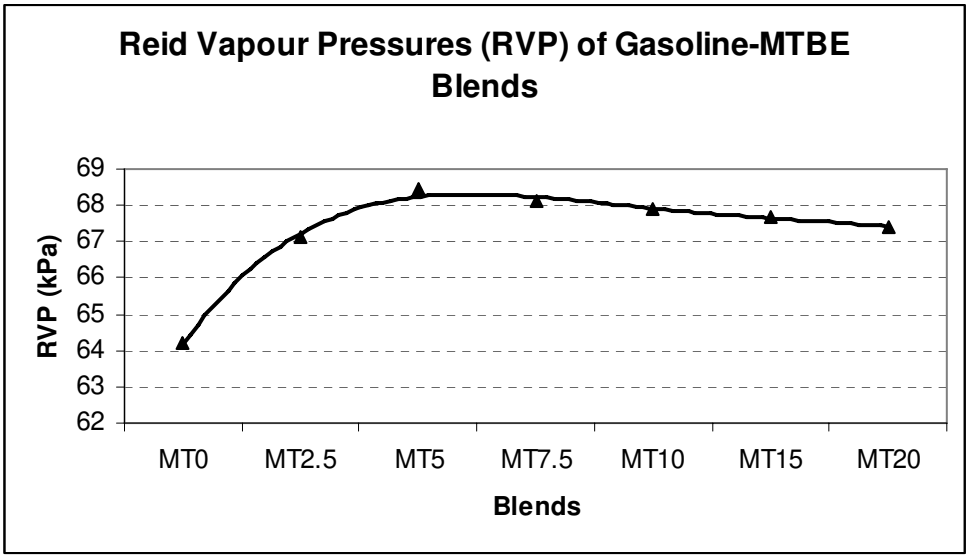

Figure 5.32. Reid Vapour Pressures of Gasoline-MTBE Blends.

As seen in Figure 5.31., the sulphur contents of gasoline-MTBE blends is dramatically decreasing by percentage volume of MTBE. The reducing the sulphur contents provide low harmful exhausts emissions such as SO_2.

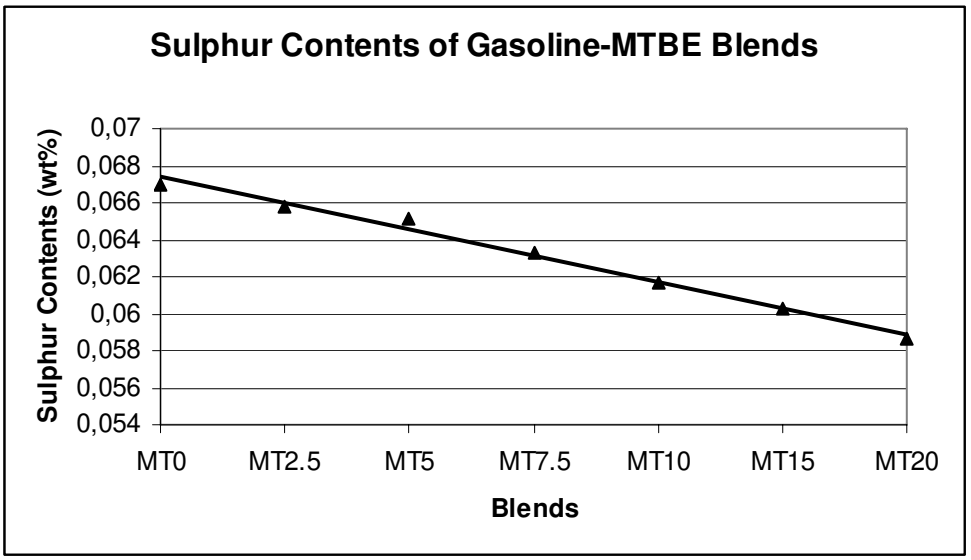

Figure 5.33. Sulphur Contents of Gasoline-MTBE Blends.

Figure 5.34. shows effects of the MTBE addition into gasoline on calorific values and distillation graphics of gasoline-MTBE blends are shown in figure 5.35.

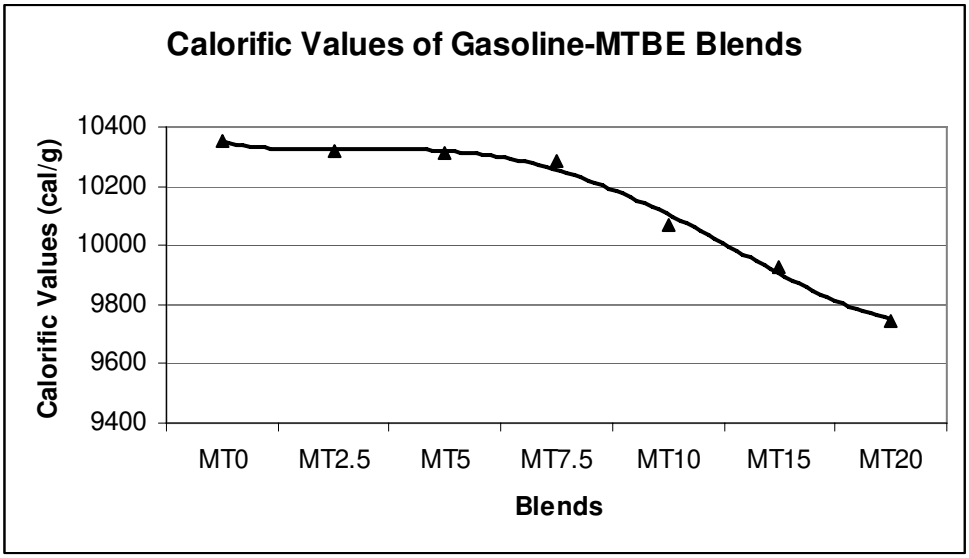

Figure 5.34. Calorific Values of Gasoline-MTBE Blends.

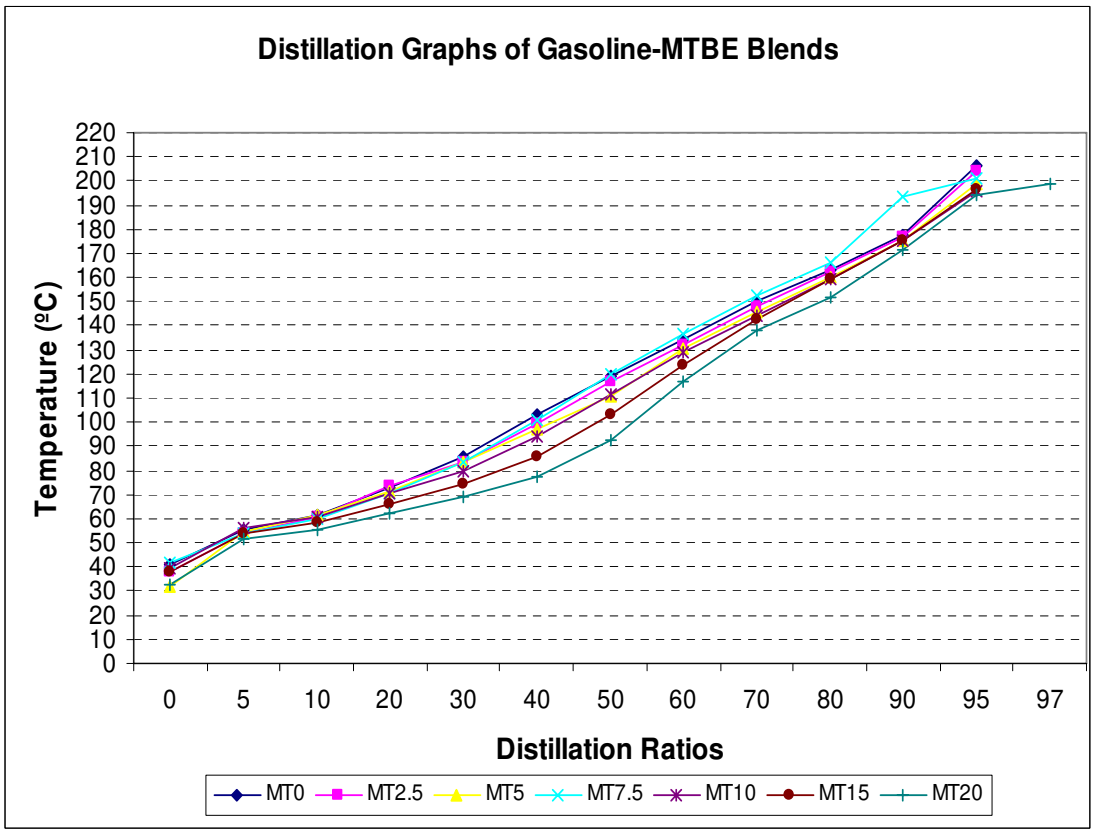

Figure 5.35. Distillation Graphs of Gasoline-MTBE Blends.

5.6. Properties of DIPE-Gasoline Blended Fuels

Di isopropyl ether (DIPE)-gasoline blends have been analyzed by the standard ASTM test methods and results are shown in table 5.6. The "D" designates DIPE and the number of next to D designates the percentage volume of DIPE. The D5 means, 5% DIPE (%98+ purity) was blended with 95% unleaded gasoline by volume.

Table 5.6. Properties of DIPE-Gasoline Blended Fuels.

DIPE-Gasoline	D0	D2.5	D5	D7.5	D10	D15	D20
Density(16ºC; g/cm^3)	0,7682	0,7712	0,7702	0,7692	0,7682	0,766	0,7636
MON	85,3049	85,1382	85,655	85,8723	86,6069	87,1885	87,9733
RON	98,6462	97,8298	98,206	98,5175	99,4357	99,9543	101,083
RVP (37.8ºC, kPa)	64,2	54	54,4	58,3	60,7	61,5	63
Sulphur (wt %)	0,067	0,051	0,0493	0,0477	0,0475	0,0465	0,0458
Calorific Value(cal/g)	10352	10150	10134	10044	9988	9853	9597
Distillation Temp. (ºC)							
IBP	44,4	43,6	43,3	42,3	32	32	41,5
10 vol%	68,4	62,9	63,7	61,3	61	62	61,4
50 vol%	124,6	119,6	115,8	113,2	110,1	104,5	97,4
90 vol%	174,3	175,5	174,9	175,4	174,7	173,8	173,2
End Point	206,6	202,2	204,4	197,4	200,1	202,5	200

Densities of gasoline-DIPE blends are decreasing related to DIPE contents clearly and this can be seen in figure 5.36.

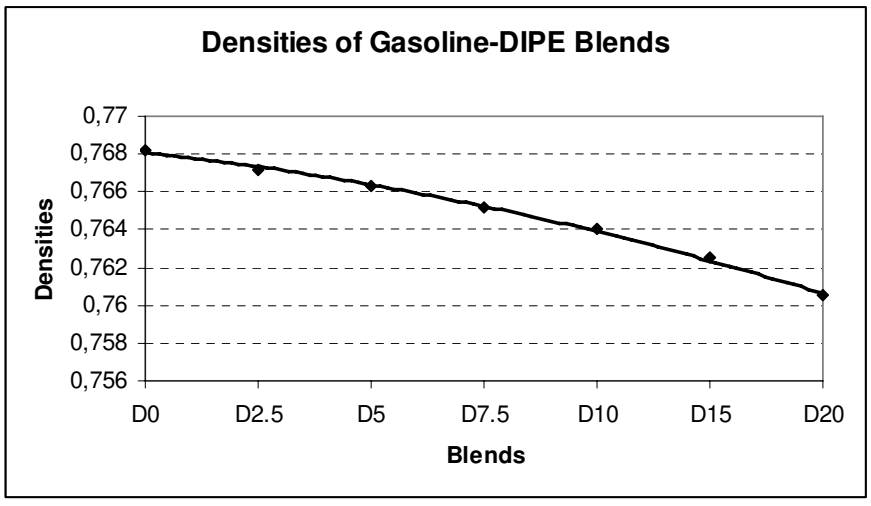

Figure 5.36. Densities of Gasoline-DIPE Blends.

Motor octane numbers of gasoline-DIPE blends are shown in Figure 5.37. and as it seen this figure, MON is getting higher with addition to DIPE significantly.

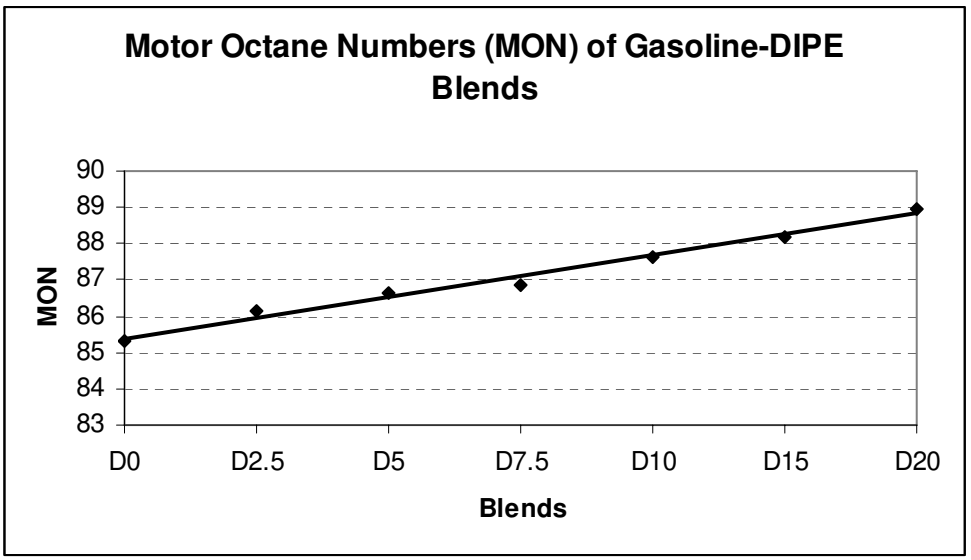

Figure 5.37. Motor Octane Numbers of Gasoline-DIPE Blends.

Research octane numbers of gasoline-DIPE blends are shown in figure 5.38. and as it seen this figure, RON is increasing up to 101 with DIPE addition.

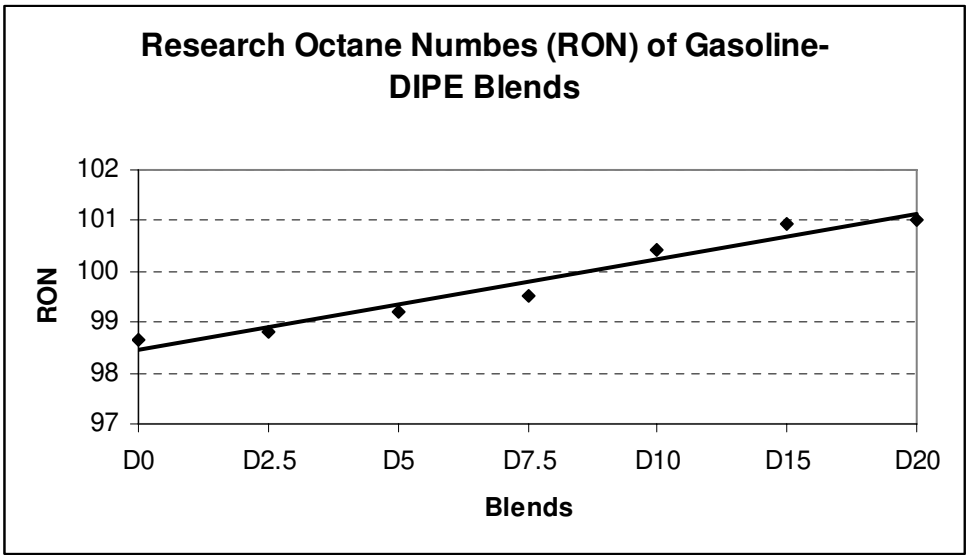

Figure 5.38. Research Octane Numbers of Gasoline-DIPE Blends.

Reid vapour pressures and sulphur contents of gasoline-DIPE blends are shown in figure 5.39. and figure 5.40., below.

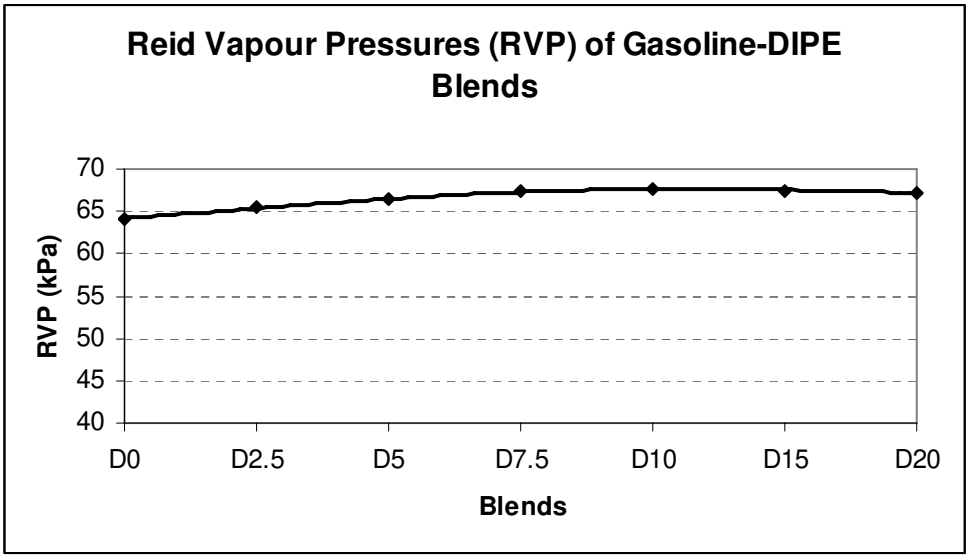

Figure 5.39. Reid Vapour Pressures of Gasoline-DIPE Blends.

As seen in figure 5.38., the sulphur contents of gasoline-DIPE blends is dramatically decreasing by percentage volume of DIPE. The reducing the sulphur contents provide low harmful exhausts emissions such as SO_2.

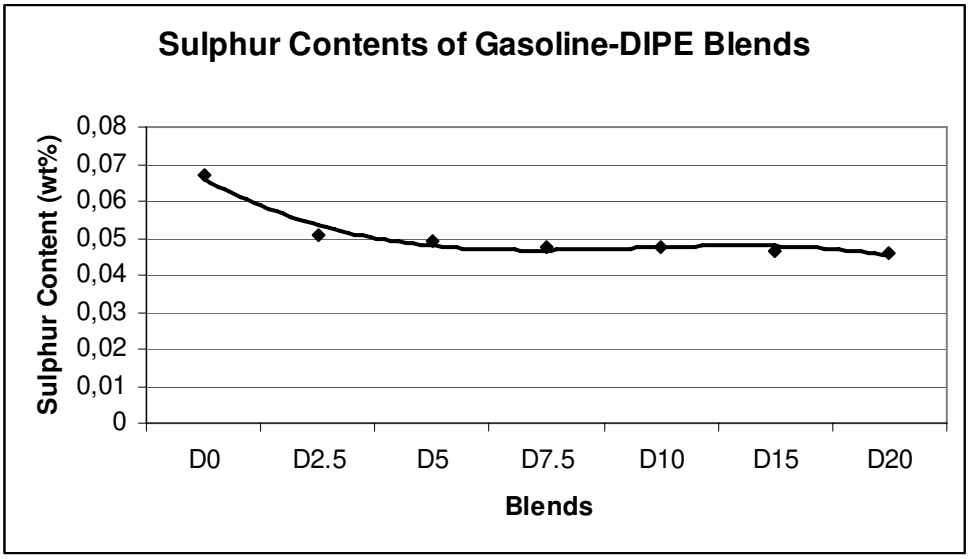

Figure 5.40. Sulphur Contents of Gasoline-DIPE Blends.

Figure 5.41. shows effects of the DIPE addition into gasoline on calorific values and distillation graphics of gasoline-DIPE blends are shown in figure 5.42.

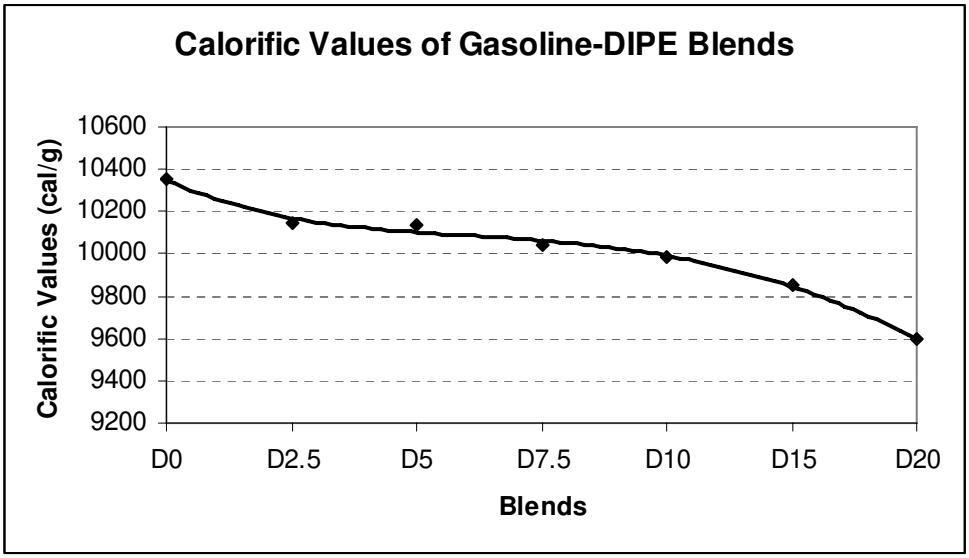

Figure 5.41. Calorific Values of Gasoline-DIPE Blends.

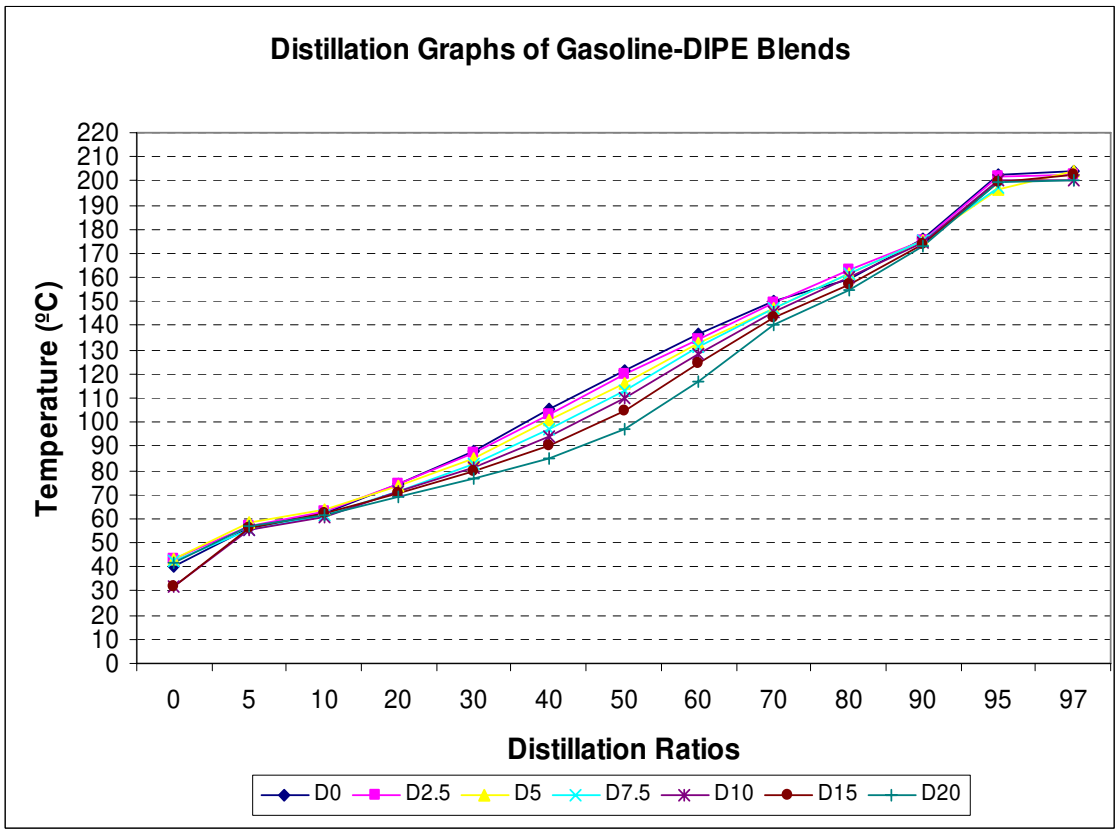

Figure 5.42. Distillation Graphs of Gasoline-DIPE Blends.

6. CONCLUSION

In this study, ethanol, methanol, TBA, TAA, MTBE and DIPE blend with the gasoline different ratios (2.5%, 5%, 7.5%, 10%, 15% and 20%) and the effects of the each blend on the gasoline were investigated. The effects of the blends on the densities are shown in figure 6.1.

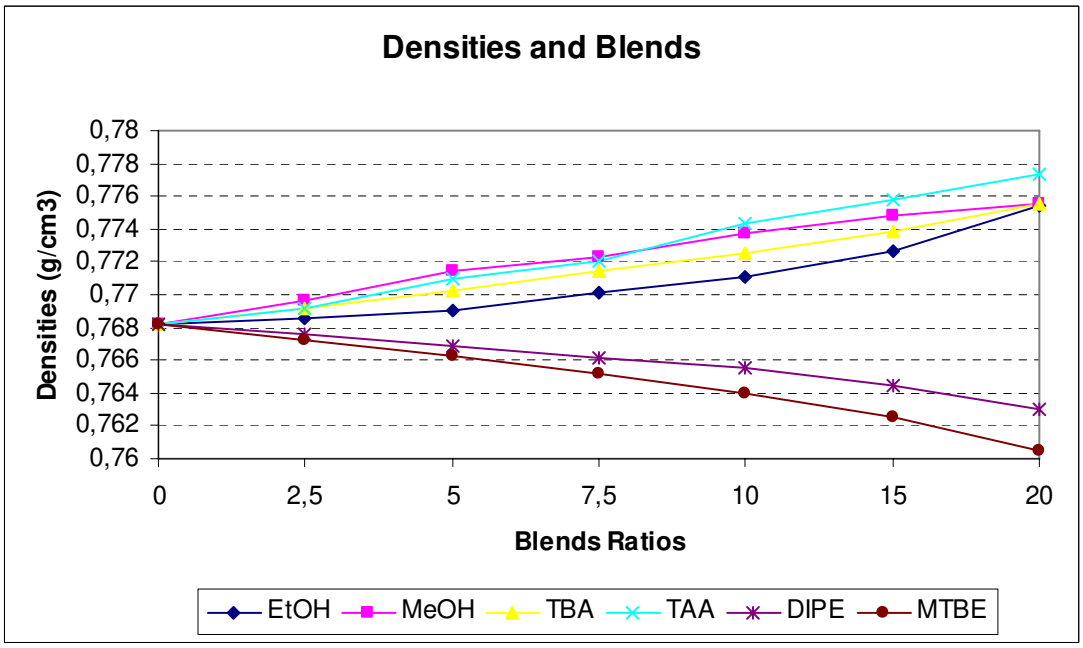

Figure 6.1. Densities and Blends

As can be seen from figure 6.1., densities of the alcohol oxygenates-gasoline blends increases because of their high densities, on the other hand the densities of the ether oxygenates-gasoline blends decreases because of their low densities.

Research and motor octane numbers of all blends clearly increase with both alcohol and ether oxygenates. These increases are shown in figure 6.2 and 6.3. respectively. As it seen in these figures, maximum increases have been found TBA and TAA blends. For research octane numbers, best octane booster is TAA and for motor octane numbers, best octane booster is TBA. In addition to these results, alcohol oxygenates have better results versus the ether oxygenates for both research and motor octane numbers.

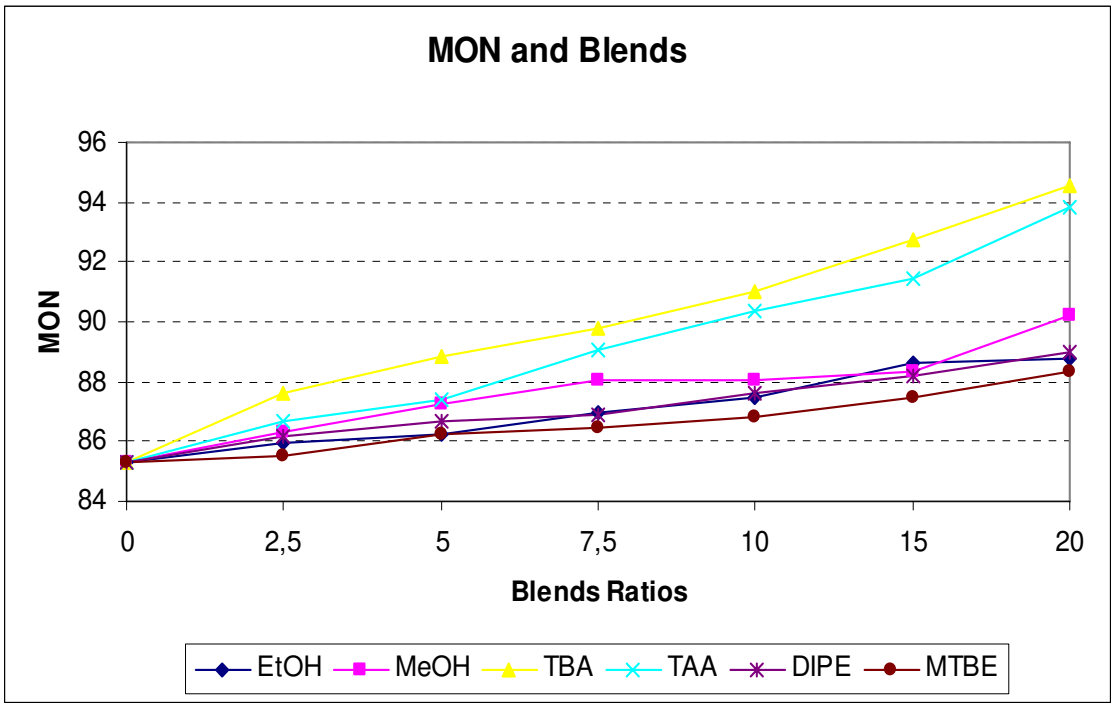

Figure 6.2. MON and Blends.

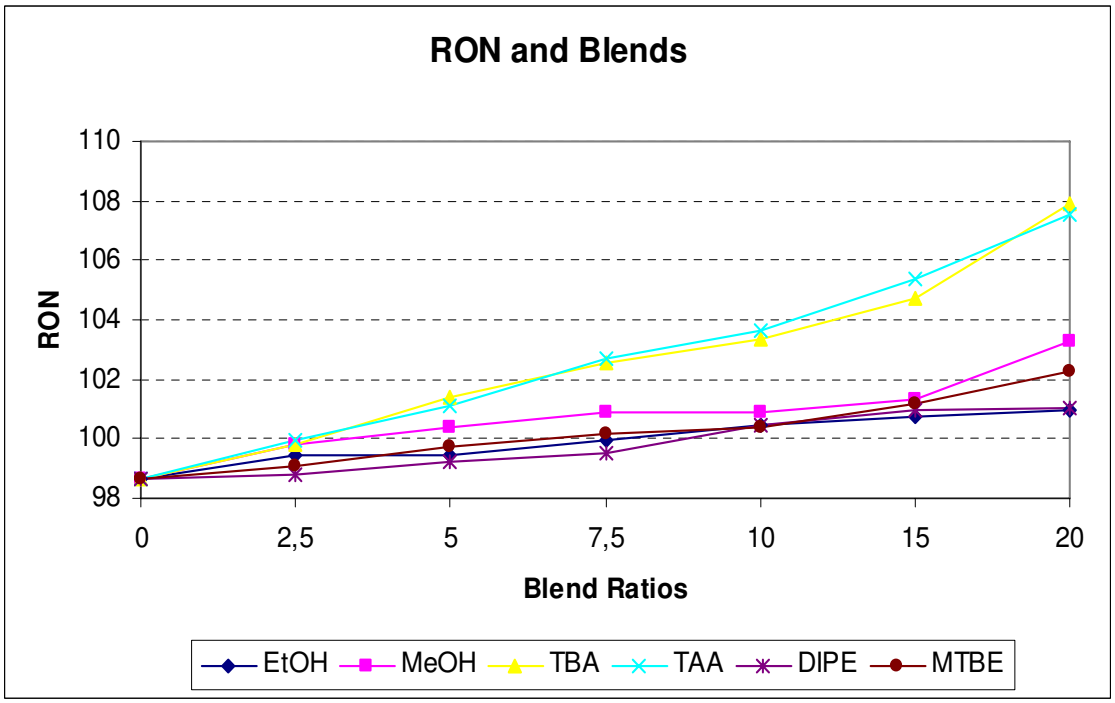

Figure 6.3.RON and Blends.

RVP is the most important indicator both volatility and emissions because of the relation of the existing volatile organic compounds in fuels. Also, RVP is very important the driveability of the fuels in year around. Figure 6.4. shows the effects of the all oxygenates on the RVP.

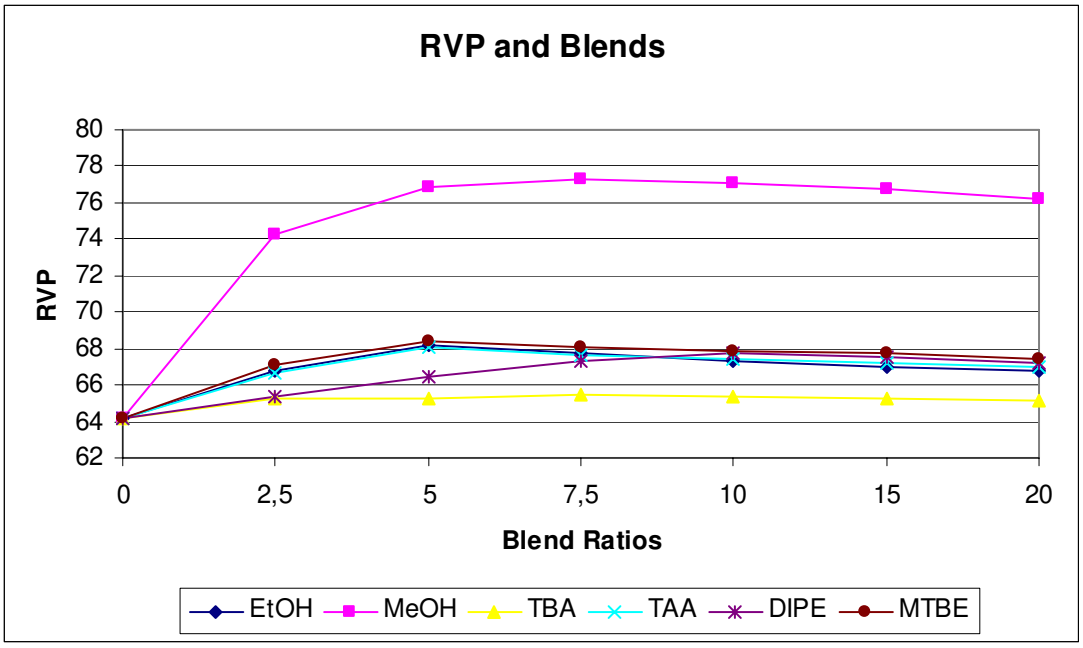

Figure 6.4. RVP and Blends.

As it seen in the Figure 6.4., alcohol oxygenates-gasoline blends has higher RVP. This means, alcohol oxygenates-gasoline blends more volatile than the ether oxygenates. Adding alcohols into gasoline causes an increase in vapour pressure and depresses the boiling temperature. Also, higher RVP values can be cause of the vapour lock and higher evaporative harmful emissions. That's why, RVP was limited more countries with federal legislations. Maximum increase of RVP values has methanol-gasoline blends. In addition to these, maximum increase of RVP occurs with 5-10% addition of all oxygenates.

The lowest effects of oxygenates on sulphur contents have been found with to adding methanol and the highest effect have been found by the by the addition of DIPE. It can be related their chemical properties. These effects are shown in figure 6.5.

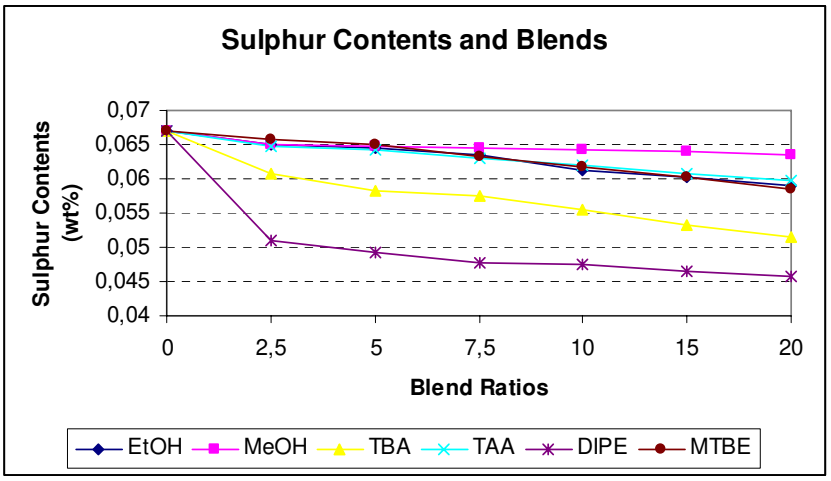

Figure 6.5.Sulphur Contents and Blends

The lowest calorific values of the blends have been found DIPE and the highest have been found methanol. These result are shown in Figure 6.6.

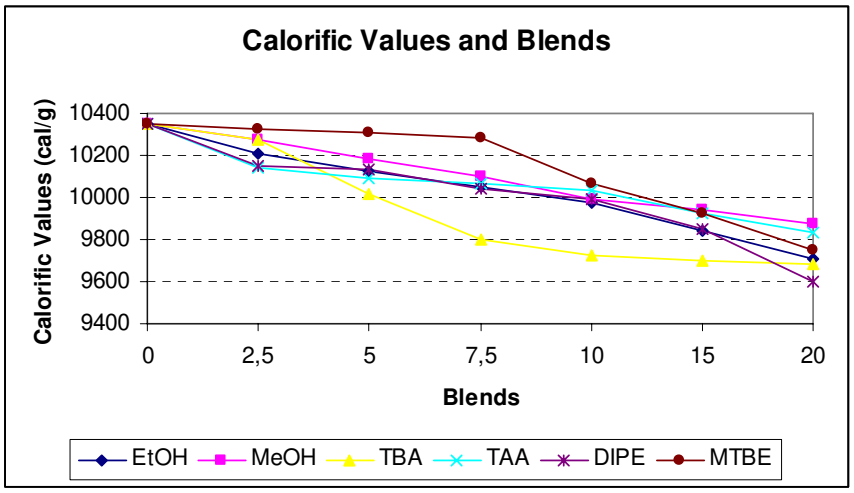

Figure 6.6.Calorific Values and Blends

In addition to these, all oxygenates decrease the distillation temperatures significantly. Figure 6.7 shows the effect of adding more than 10% by volume of ethanol into the base gasoline. Clearly, this results in the front end to the mid region of the curve being heavily distorted in terms of significantly increasing the volatility of the fuel in these regions. Adding more than 10% volume of ethanol into gasoline continues to increase the volatility of the blend as evidenced by further reductions of both the T50 and T90 distillation temperatures. The T50 term is used to denote the temperature at which 50% by volume of the fuel will evaporate, and therefore T90 is

the temperature at which 90% of the fuel will evaporate. The reductions seen in T50 and T90 between 10 and 20% ethanol are greater than the reductions from neat gasoline to the 10% ethanol blend, demonstrating a non-linear trend.

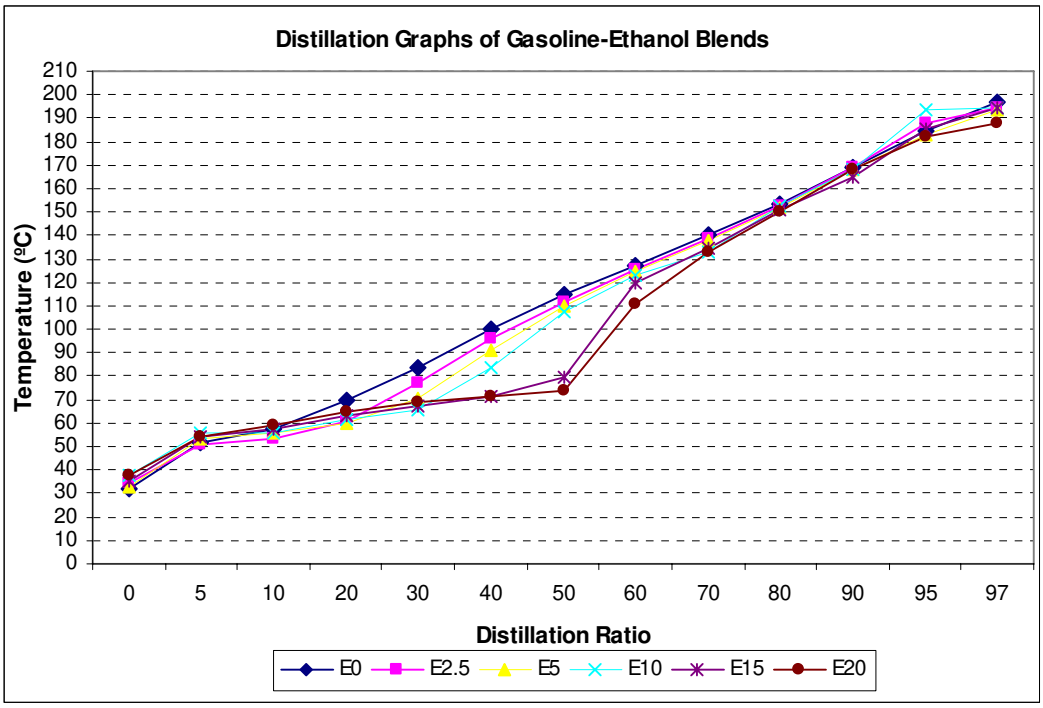

Figure 6.7. Distillation Curve of Ethanol-Gasoline Blends.

From the experiments of this study the results can be summarized below;

- Alcohol oxygenates increases the density because of their higher densities.
- Ether oxygenates decreases the density because of their lower densities.
- All oxygenates improve both motor and research octane numbers.
- The highest MON improvement has been found by the addition TBA.
- The lowest MON improvement has been found by the addition of MTBE.
- The highest RON improvement has been found by the addition of TAA.
- The lowest RON improvement has been found by the addition of DIPE.
- The highest effect on the RVP has been obtained the addition of methanol.
- The lowest effect on the RVP has been obtained the addition of TBA.
- The highest effect on the sulphur content has been obtained the addition of DIPE.

- The lowest effect on the sulphur content has been obtained the addition of methanol.
- The highest lost of calorific value has been found by the addition of DIPE.
- The lowest lost of calorific value has been found by the addition of ethanol.

All over the world, petroleum based energy sources are decreasing and their harmful effects are getting dangerous for both human health and nature day by day. At the end of the 1970s there was one common additive to improve octane numbers, was lead. But those years, scientist realized that its harmful effects and informed governments and companies which were related the petroleum products and then lead had been started to ban first in North America and then Europe but nowadays in the most of countries lead is still using, unfortunately. This example is a simple explanation to change dependency of the additives. That's why, gasoline additives really important because of their usage and economics. In our country, we are still using the leaded gasoline, we haven't stopped the using the lead yet. But our government has been studying on alternative energy sources and their production potential in Turkey. At the end of the year, to decrease the imports of the petroleum products, using renewable or bio-fuels will be an obligation with new regulations.

These regulations will have been reduced our dependency of import petrol. This study may have been a start point of using oxygenates. When oxygenates have been compared, which is used in this study, the most available oxygenate is ethanol for our country because of their properties and easily producible current technologies. Ethanol can be produced from every agricultural product which contains cellulose or fermentable sugar. In this way, our farmers will have been support by our government indirectly. Moreover, our economy will have been developed and our country will have being healthy.

REFERENCES

AL-HASAN, M., 2003. Effect of Ethanol-Unleaded Gasoline Blends on Engine Performance and Exhaust Emission. Energy Conversion and Management,44: 1547-1561.

BAYRAKTAR, H., 2005. Experimental and Theoretical Investigation of Using Gasoline-Ethanol Blends In Spark Ignition Engines. Renewable Energy: 1-15.

CALINGAERT, G., 1998. Section 11: Anti-knock Compounds. The Science of Petroleum, Oxford University Press, Vol. 4: 3024-3029

CEVIZ, M.A., YUKSEL, F., 2005. Effects of Ethanol-Unleaded Gasoline Blends on Cyclic Variability and Emissions in an SI Engine. Applied Thermal Engineering, 25: 917-925.

CPPI, 1994. Composition of Canadian Unleaded Gasoline, available from Canadian Petroleum Products Institute, Canada.

"Federal Reformulated Gasoline," Chevron Technical Bulletin FTB 4, Chevron, San Ramon, CA, 1994.

"Gasoline and Other Motor Fuels," 1993.Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., Vol. 12, M. Howe-Grant, Ed., Wiley, NY,.

GIBBS, L. M, 1995. Transportation Fuels; Automotive Gasoline. Encyclopedia of Energy Technology and the Environment: 2675-2698

HAMDAN, M.A., AL-SUBAIH, T.A., 2002. Improvement of Locally Produced Gasoline and Studying Its Effects on Both the Performance of the Engine and the Environment. Energy Conversion and Management, 43: 1811-1820.

HE, B., WANG, J., HAO, J., YAN, X., XIAO, J., 2003. A study on Emission Characteristics of an EFI Engine with Ethanol Blended Gasoline Fuels. Atmospheric Environment, 37: 949-957.

HSIEH, W., CHEN, R., WU, T., LİN, T., 2002. Engine Performance and Pollutant Emission of SI Engine Using Ethanol–Gasoline Blended Fuels. Atmospheric Environment, 36: 403-410.

KETTERING, C. F., 1944. The Effect of the Molecular Structure of Fuels on the Power and Efficiency of Internal Combustion Engines. Industrial Engineering and Chemistry Research, 36: 1079-1085.

KOZOLE, K. H., 1996. In-Use Vehicle Emission Survey Program. CPPI Report No.E12-B005248-Final, Canadian Petroleum Products Institute.

"Mass Exhaust Emissions Results from Reformulated Gasolines", May 1991.Technical Bulletin No. 4, Auto/Oil Air Quality Improvement Research Program, Coordinating Research Council, Atlanta.

"Motor Gasolines Technical Review (FTR-1)", 1996.Chevron Products Company. San Ramon, CA,

NIVEN, R.K., 2004. Ethanol in Gasoline Environmental Impacts and Sustainability Review Article. Renewable and Sustainable Energy: 1-21.

OWEN, K. and COLEY, T., 1990. Automotive Fuels Reference Book, First ed., Society of Automotive Engineers, Inc.

POULOPOULOS, S., PHILIPPOPOULOS, C., 2000. Influence of MTBE addition Into Gasoline on Automotive Exhaust Emission. Atmospheric Environment, 34: 4781-4786.

"Response to the Sasol report of 23 May 01 and the Ethyl report of July 2001," Presented at the IPIECA, September 2001, Delta Motor Corporation, Shannon, Ireland, Aug. 24, 2001.

SILVA, R., CATALUNA, R., MENEZES, E.W., SAMIOS, D. CLARISSE, M., PIATNICKI, C.M.S., 2005. Effects of Additives on the Antiknock Properties and Reid Vapor Pressure of Gasoline. Fuel, 84: 951-959.

TOTTEN, G.T., 2003. Fuels and Lubricant Handbook. ASTM International, 1087.

WESTBROOK, C. K. and PITZ, W. J., 1991. The Chemical Kinetics of Engine Knock, Energy and Technology Review: 1-13.

WU, C., CHEN, R., PU, J., LIN, T., 2004. Influence of Air–Fuel Ratio on Engine Performance and Pollutant Emission Of An SI Engine Using Ethanol–Gasoline Blended Fuels. Atmospheric Environment, 38: 7093-7100.

www.efoa.org : The European Fuel Oxygenates Association web site.

www.chemicalhistory.com : Petroleum Distillates website.

www.eia.doe.gov : U.S. Energy Information Administration Official website.

CURRICULUM VITAE

Ufuk YENİ was born in Adana, 1980. After being graduated from Adana Cagri Bey Lisesi, he enrolled in Mechanical Engineering Department of Cukurova University. He graduated from Cukurova University as a Mechanical Engineer in June 2002. He started his Master of Science education in Mechanical Engineering Department of Çukurova University in 2002.