T.R
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
CHEMICAL ENGINEERING SCIENCES

IMPROVEMENT OF OCTANE NUMBER OF LOCAL GASOLINE BY THE ADDITION OF SELECTIVE ORGANIC COMPOUNDS

M. Sc. THESIS

PREPARED BY: Karwan Moffaq ABDULAZIZ
SUPERVISOR: Assoc. Prof. Dr. Suha Orcun MERT

VAN-2018

T.R
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
CHEMICAL ENGINEERING SCIENCES

IMPROVEMENT OF OCTANE NUMBER OF LOCAL GASOLINE BY THE ADDITION OF SELECTIVE ORGANIC COMPOUNDS

M. Sc. THESIS

PREPARED BY: Karwan Moffaq ABDULAZIZ

VAN-2018

ACCEPTANCE and APPROVAL PAGE

This thesis entitled "IMPROVEMENT OF OCTANE NUMBER OF LOCAL GASOLINE BY THE ADDITION OF SELECTIVE ORGANIC COMPOUNDS" presented by Karwan Moffaq ABDULAZIZ under supervision of Assoc. Prof. Dr. Suha Orçun MERT in the department of Chemical Engineering has been accepted as a M. Sc. thesis according to Legislations of Graduate Higher Education on 05/04/2018 with unanimity of the members of jury.

Chair: Assoc. Dr. Zehra OZCELIK Signature:

Member: Assoc. Dr. Merve İcli OZKUT Signature:

Member: Assoc. Prof. Dr. Suha Orçun MERT Signature:

This thesis has been approved by the committee of The Institute of Natural and Applied Science on ...../...../..... with decision number .....

Signature

.....

Director of Institute

THESIS STATEMENT

All information presented in the thesis obtained in the frame of ethical behavior and academic rules. In addition all kinds of information that does not belong to me have been cited appropriately in the thesis prepared by the thesis writing rules.

Signature
Karwan Moffaq ABDULAZIZ

ABSTRACT

IMPROVEMENT OF OCTANE NUMBER OF LOCAL GASOLINE BY THE ADDITION OF SELECTIVE ORGANIC COMPOUNDS

ABDULAZIZ, Karwan Moffaq
M. Sc., Thesis Chemical Engineering Department
Supervisor: Assoc. Prof. Dr. Suha Orcun MERT
April 2018, 56 pages.

The main objectives of this work were preparing of local gasoline from KAR refinery and improving its research octane number (RON). Some organic chemical compounds were selected as additives (alcohol, aromatic, and ketone) to enhance the RON of the KAR refinery gasoline. These compounds were added to the gasoline in different volumetric ratios (0.5, 2.5, 5, and 7.5vol %) and included ethanol, methanol, isopropyl alcohol, butanol, benzol, as alcohols, benzene, toluene, xylene, and aniline as aromatics, and acetone as ketone. Zeltex 101XL device was used to measure the RON of the blends. Most of the organic compounds were succeeded to pass the RON of KAR refinery gasoline from normal gasoline to premium gasoline (according to region gasoline quality specifications-see appendix A). The best group of chemicals was the aromatics, especially Xylene then Toluene, that showed a positive effect in 2.5vol% and the best impact performed by Xylene in 7.5vol% was the increase in RON into 94.4. This is very close to pass the normal gasoline to super gasoline (RON 95), the highest allowed RON in the region. Acetone behaved like aromatics and 2.5vol% was enough to convert the gasoline from normal gasoline to premium gasoline. On the other hand ethanol showed effect in 7.5vol%, isopropyl alcohol started to affect in 5vol%, and benzol in 7.5vol%. butanol was the only additive that failed to improve the octane number. Mixtures of chemicals were used to improve RON of KAR refinery gasoline in which mixed ethanol and IPA showed a positive effect toward the premium in 7.5vol%, and it was close to IPA alone. Mixtures of toluene and xylene showed an improvement starting from 2.5vol% and this effect was intermediate between each of xylene and toluene alone.

Keywords: FT-IR, Gasoline, Octane number, Organic additives.

ÖZET

YEREL BENZİNİN OKTAN DEĞERİNİN SELEKTİF ORGANİK BİLEŞENLER KATILARAK GELİŞTİRİLMESİ

ABDULAZIZ, Karwan Moffaq
Yüksek Lisans Tezi, Kimya Mühendisliği Ana Bilim Dalı
Tez Danışmanı: Doç. Dr. Süha Orçun MERT
Nisan 2018, 56 sayfa.

Bu çalışmanın ana amaçları KAR rafinerisinde elde edilen yerel benzinin hazırlanması ve oktan değerinin (RON) iyileştirilmesidir. Bu amaçla bazı organik bileşenler (alkoller, aromatikler, ve ketonlar) KAR rafinerisinden elde edilen benzinin RON değerini geliştirmek üzere katkı malzemesi olarak seçilmiştir. Bu bileşikler farklı hacimsel oranlarda (0.5, 2.5, 5 ve 7.5 hacimsel yüzde) benzine eklenmiş olup, alkoller olarak etanol, metanol, izopropil alkol (IPA), bütanol ve benzol, aromatikler olarak benzen, tolüen, ksilen ve anilin, ve keton olarak da aseton kullanılmıştır. Karışımların RON değerlerinin ölçümünde Zeltex 101 XL cihazı kullanılmıştır. Organik bileşenlerin çoğu KAR rafinerisi benzinini normal benzinden üst kalitede benzine dönüştürmek için yeterli olmuştur (bölgesel benzin kalitesi özelliklerine göre, bkz. Ek A). En başarılı kimyasal grubunun, başta %2.5 hacimsel yüzdede bile olumlu etkiler gösteren ve %7.5 ile RON değerini 94.4'e yükselten ksileni, ve hemen ardından gelen tolüeni içeren aromatikler olduğu görülmüştür. Bu oran neredeyse normal benzini, bölgede kullanımına izin verilen en üst RON değerine sahip benzin olan süper benzine (RON 95) dönüştürmeye yeterlidir. Aseton da aromatiklere benzer etkiler göstermiş ve %2.5 hacimsel yüzde bile benzini normal benzinden üst düzey benzine dönüştürmeye yetmiştir. Diğer yandan etanol %7.5'te etki gösterirken, izopropil alkol etkisini göstermeye %5 hacimsel yüzdede başlamış, benzol ise %7.5'ta göstermiştir. Butanol, oktan değerini geliştirmede başarısız olan tek katkı maddesi olmuştur. KAR rafinerisinden elde edilen benzinin RON değerini geliştirmek için ayrıca kimyasalların karışımları da denenmiş, etanol ve IPA karışımı %7.5 hacimsel oranında üst düzey benzin etkisini elde etmiştir; bu değer tek başına IPA'nın gösterdiği performansa yakındır. Tolüen ve ksilen karışımları hacimsel olarak %2.5'ten itibaren iyileşme

göstermeye başlamıştır ve bu değer ksilen ve tolüen tek başlarına gösterdikleri performansın ortasında yer almaktadır.

Anahtar kelimeler: FT-IR, Benzin, kemometrikler, Oktan değeri, Organik katkı maddeleri.

ACKNOWLEDGEMENT

To begin with I would like to thank “Allah” (Praise be to him) for implanting the soul of endurance and faith in myself to complete this study and showing me the way to through.

My deepest gratitude and sincere thanks to my supervisors Assoc. Prof. Dr. Suha Orcun MERT for his guidance and support throughout the research. I highly appreciate his high scientific supervision and infinite patience in following up the research.

My deepest thanks and gratitude sends to Sirwan Jaf for his valuable aid in thesis writing, Rebaz Salih for his assistance in computer works and Sazan M Abdulaziz for her endless cooperation throughout the study.

Finally, words cannot express my thanks and gratitude to my great mother, my wife, my brothers and sisters for their endless assistance, kindness and pray throughout the study.

2018

ABDULAZIZ, Karwan Moffaq

TABLE OF CONTENTS

Pages

Pages

LIST OF TABLES

Tables **Pages**

LIST OF FIGURES

Figures **Pages**

SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with descriptions.

Symbols	Description
ICE	Internal Combustion Engine
ASTM D	American Standard Test Method Designation
ON	Octane Number
BTX	Benzene, Toluene, and Xylene
FCC	Fluid Catalytic Cracking
VGO	Vacuum Gas Oil
Pt	Platinum
A/F	Air To Fuel Ratio
NOx	Nitrogen Oxides
RON	Research Octane Number
MON	Motor Octane Number
RdON	Road Octane Number
AKI	Anti-Knock Index
TEL	Tertra Ethyl Lead
CFR	Cooperative Fuel Research or Committee on Fuel Research
FTIR	Fourier Transform Infra-Red
MMT	Methyl cyclopentadienyl Manganese Tricarbonyl
NIRS	Near Infra-Red Spectroscopy
MIR	Med Infra-Red
GC	Gas Chromatography
VOCs	Volatile Organic Compounds
PON	Posted Octane Number
MTBE	Methyl-Tertiary-Butyl Ether

ETBE	Ethyl-Tertiary-Butyl Ether
FFV	Flexible-Fuel Vehicle
DI	Drivability Index
IROX	Iridium Oxide
SVM	Support Vector Machines
PNN	Probabilistic Neural Networks
IRED	Infrared Emitting Diodes

1. INTRODUCTION

A petroleum-derived fluid which is utilized chiefly like a petrol in internal combustion engines (ICE), mainly spark ignition Otto Engine is called Gasoline. With several pollutants such as nitrogen, oxygen, sulfur, and certain metals, it is a combination of hydrocarbons. Furthermore, aromatics, olefins, naphthenes and paraffins are the main component set of gasoline (Demirbas et al., 2015).

In addition, in Britain gasoline is known as petrol or motor gasoline, while in Europe it is called benzene. It is a combination of flammable, volatile liquid hydrocarbon. The gasoline's boiling temperature ranged from 30°F (–1°C) to 421°F (216°C). As it is shown in Table 1.1, potentially gasoline might encompass several hundreds of isomer of different hydrocarbon. Figure. 1.1 displays that while gasoline boils below the range of kerosene, its boiling range is at alike range as naphtha (Speight, 2002).

Table 1.1. Broad summary of petroleum product kinds and the range of distillation

Product	Lower carbon limit	Upper carbon limit	Lower boiling point ^{o}C	Upper boiling point ^{o}C
Refinery gas	C_1	C_4	–161	–1
Liquefied petroleum gas	C_3	C_4	–42	–1
Naphtha	C_5	C_{17}	36	302
Gasoline	C_4	C_{12}	–1	216
Kerosene/Diesel fuel	C_8	C_{18}	126	258
Aviation tubine fuel	C_8	C_{16}	126	287
Fuel oil	C_{12}	$>C_{20}$	216	421
Lubricating oil	$>C_{20}$		>343	
Wax	C_{17}	$>C_{20}$	302	>343
Asphalt	$>C_{20}$		>343	
Coke	$>C_{20}$		>1000	

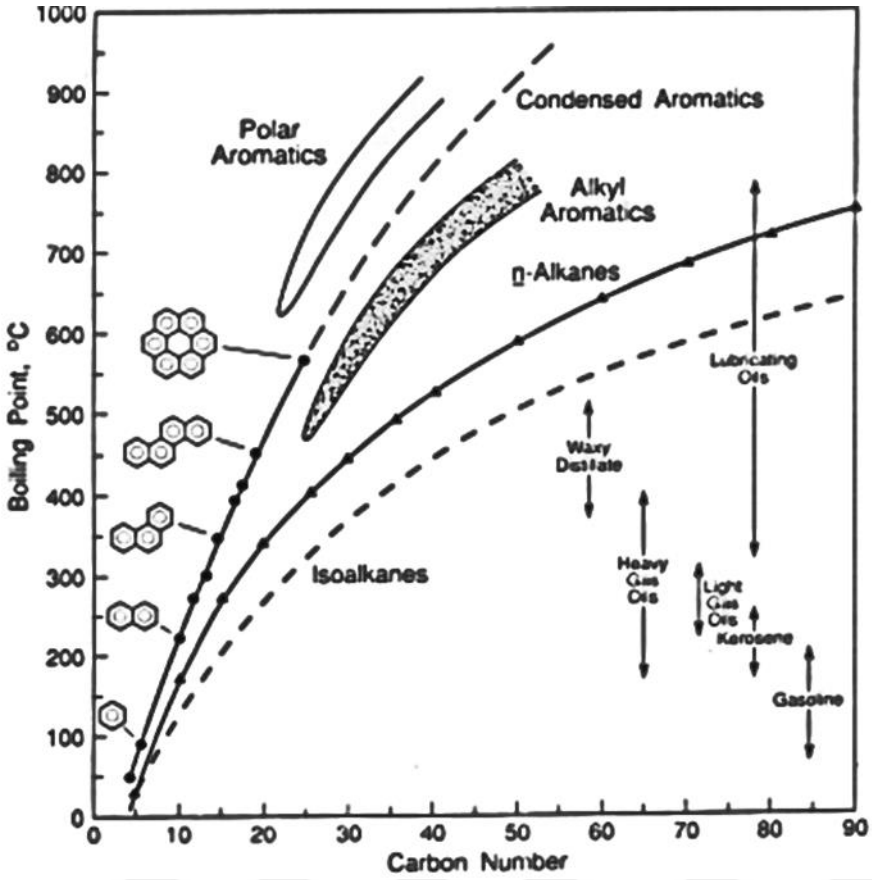

Figure 1.1. Carbon number and boiling point for different petroleum products and hydrocarbons.

1.1. Industrial Gasoline Production And Improvements

Numerous approaches have been utilized for producing and improving gasoline industrially. Currently, there are dramatic variation in the quality of gasoline on the market. They are not similar. The chemical and physical properties is differed broadly because it is a multifaceted combination of constituents. Crude oil does not comprise sufficient branched alkanes forging give it an elevated octane number (ON), Even though it comprises both straight chain and branched alkanes. The ability of gasoline for resisting knocking is referred to as Octane number. It is also known as antiknock performance of the gasoline in the combustion chamber. Fahim et al (2010) stated that gasoline attained from the fractionating column is not a highly effective gazoline. According to Demirbas et al (2015), Octane number of the straight-run gasoline is around 70.

For improving octane number, two solutions can be implemented. The first solution is the addition of chemical additives for boosting the octane number. In addition, the second approach for improving octane number is regularly conducted industrially through the subsequent chemical procedures. Although the second method might be the most famous, the desires for more efficient approaches offers the chance for new approaches in the upcoming days.

1. 1.1. The atmospheric distillation process

Fahim et al (2010) reported that in the refinery, this unit is named the skimming unit. It is the chief tower in the system and it is considered a first the gasoline producer. Figure 1.2 displays the usual products from the unit.

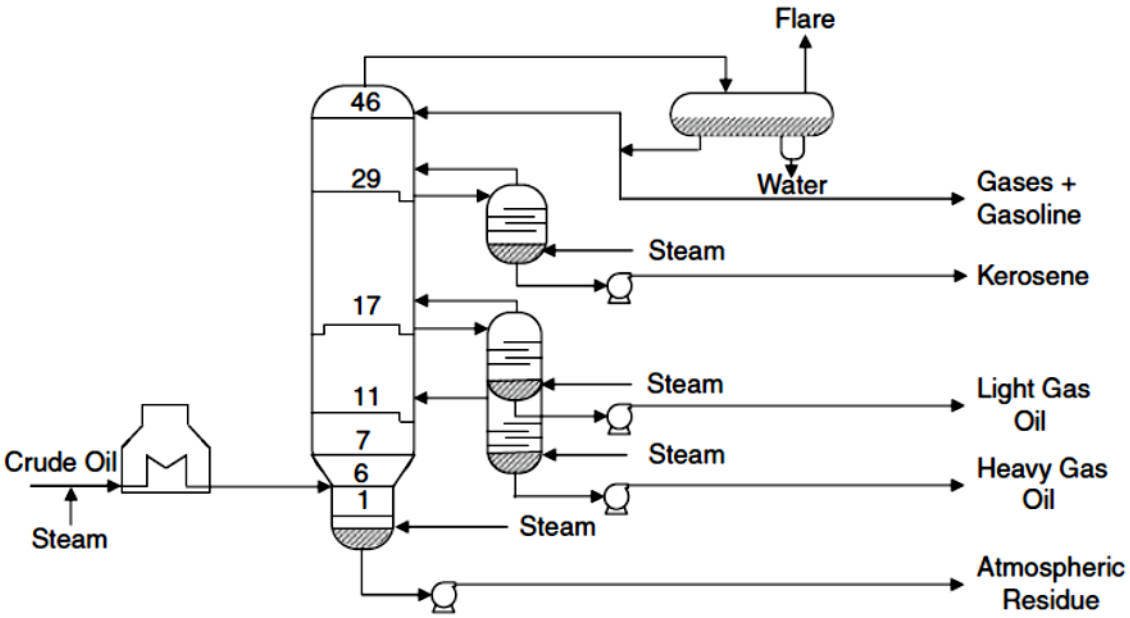

Figure 1.2. Atmospheric Distillation Diagram (Fahim et al., 2010).

1.1.2. Catalytic reforming

For restructuring naphtha fraction (C_6–C_{10}) into iso-paraffins and aromatics a distinct catalyst (silica or silica base alumina supported by platinum metal) is utilized in this procedure. In comparison to the feed, the generated naphtha reformate has greater ON.

In the formulation of gasoline and as a feedstock for production of aromatic, this reformate is utilized (benzene–toluene–xylene, BTX) (Fahim et al., 2010).

1.1.3. Catalytic cracking

The key player for gasoline production is Fluid catalytic cracking (FCC). For the cracking function, in this circumstance the catalyst is a zeolite base. The vacuum gas oil is the main feed for fluid catalytic cracking and gasoline is the product. Nevertheless, several refinery and gas oil are generated as well.

1.1.4. Alkylation

The procedure wherein isobutane responds with olefins like butylene (C_4) for producing a gasoline range alkylate is called Alkylation. In this situation, the hydrofluoric acid or sulfuric acid is catalyst. In liquid stage, the acid and hydrocarbons react. Primarily from delayed Coker and fluid catalytic cracking (FCC) isobutane olefins are gathered.

1.1.5. Isomerization

It is the procedure where low ON hydrocarbons (C_4, C_5, and C6) are converted to a divided product with similar carbon number. Products with elevated octane number are produced by this procedure. The separation of hexane (C_6) prior entering the reformer is the key benefit of this procedure. Therefore, it prevents benzene formation which generates products that cause cancer on burning with gasoline. In this circumstance, Pt-zeolite base is the key catalyst.

1.1.6. Delayed coking

Delayed Coking procedure is grounded upon the vacuum residue thermal cracking via carbon refusal creating coke and lighter products like gas oils, gasoline and gases. Needle, sponge and shot are the kinds of coke that can be generated from this procedure. In a furnace, the vacuum residue is sintered and rushed into big drums in

which the walls of these drums are covered with coke. Furthermore, through the process of distillation, the rest of the goods are alienated.

1.1.7. Flexi-coking

By utilizing air and steam, the major amount of the coke is gasified in to petroleum gas in this thermal procedure. The required heat for thermal cracking is provided by coke burning by air. Gasoline, gases and oils with tiny amount of coke are the products of this process.

1.1.8. Visbreaking

For breaking the pour points and high viscosity of vacuum deposit to the concentration that might be utilized in additional downstream processes visbreaking, which is a slight heating cracking procedure, is utilized. The remains are either dripped in a reactor for several minutes (soaker visbreaker) or destroyed in the furnace coil (coil visbreaking). Gasoline, gases and the unaltered remains are the products (David 2006, Bosch Handbook 2008 and Fahim 2010).
Figure (1.3) describes an illustration of an up to date refinery comprising the major procedures mentioned previously.

1.2.Gasoline Spark Engine

Practically, the initial four-stroke-cycle internal burning engine operated by a liquid petroleum is built by Nicolaus Otto in May 1876. Nicolaus finalized the expansion of his engine with the development of the initial magneto ignition scheme for low-voltage ignition by 1880s. The utilized fluid by Otto called gasoline. An automotive engine that powered by gasoline is an internal combustion. In the spark-ignition engine the fuel is burned in an enclosed chamber named cylinder. The quick gas expansion during burning of a compressed air-fuel mixture generates the power of the engine. The majority of automotive engines are from type of reciprocating piston. In these kind of engine, each house contain a piston that slides in to two directions. Via a linked cable to

a crankshaft that attached it to the driving wheels by a drivetrain, the power from the movement of one or more pistons is conveyed. As displayed in Figure 1.4, the majority of gasoline automotic engines work in a four-stroke cycle (Gibbs et al., 2009).

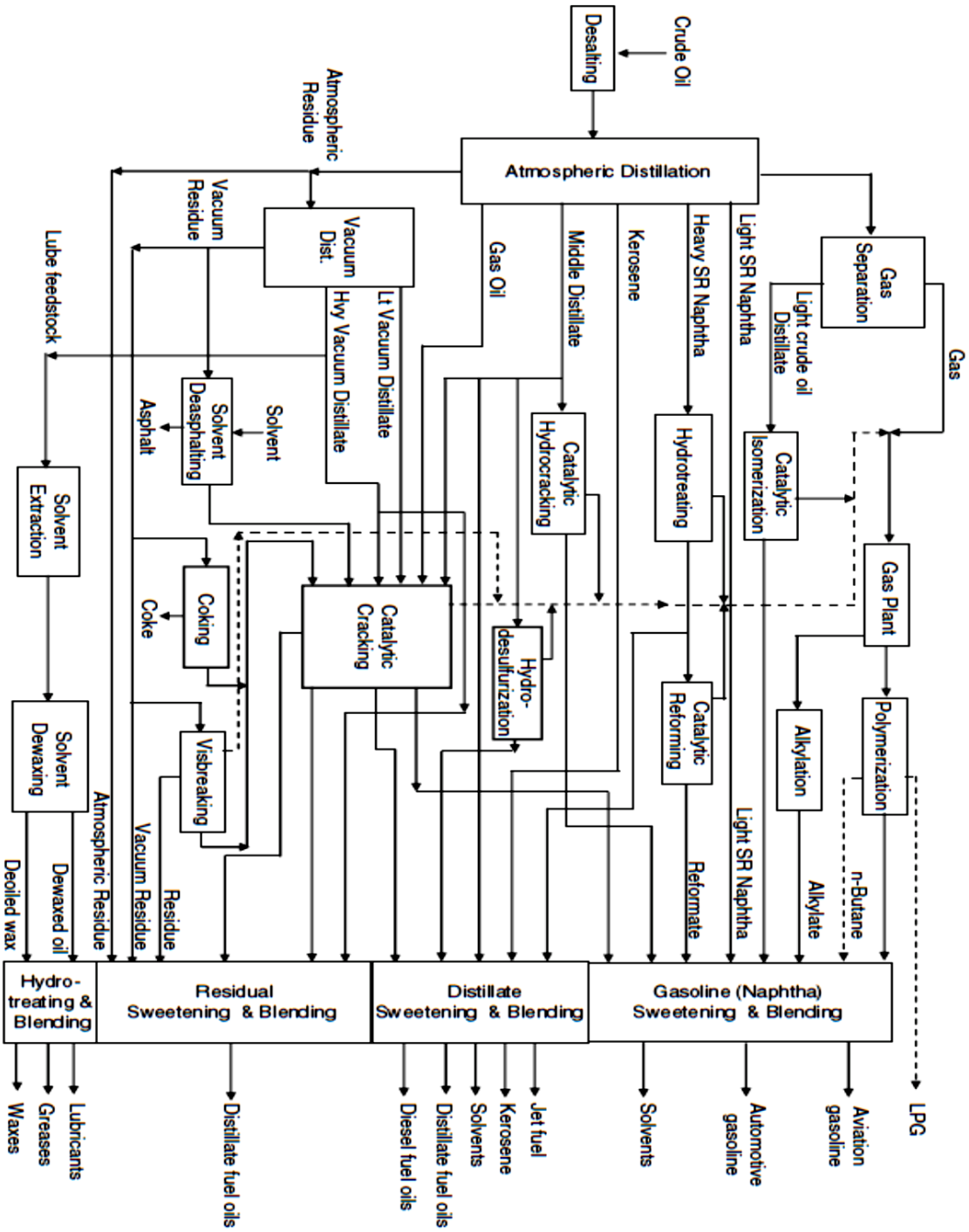

Figure 1.3. The Modern Refinery (Fahim et al., 2010).

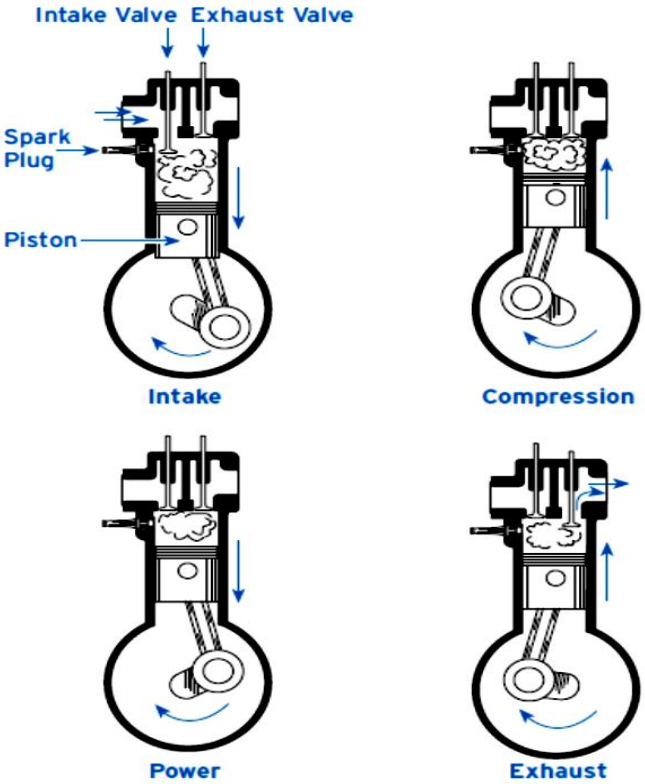

Figure 1.4. Gasoline Internal Combustion Engine with Four Strokes.

Every single stroke, up or down, is a movement of a piston. Through an open intake valves, the intake stroke which refer to the piston's first downward movement, draws a mix of fuel and air into a combustion chamber. The intake valves close when the piston begins to move back up in the reverses direction. The compression stroke is commonly referred to the piston's upward movements. The temperature and pressure of the air-fuel mixture is increased by the compression. A spark is generated by a spark plug which ignites the mixture nearby the top of the compression stroke. In third motion or power stroke, the piston moves downward and the fuel mixture expands and burns. Exhaust valves open when the piston passes bottom dead center and initiates again to transfer back up. This is the commencement of the exhaust stroke. Combusted gases are pushed outside the engine in to an exhaust manifold then ultimately outside the pipe of the exhaust by the upward movement of the piston (Gibbs et al., 2009 and Parkash, 2010).

According Bosch Handbook (2008), Chevron Corporation (2009) and Parkash (2010), the fuel have to be in the vapor state and have the right combination of fuel

vapor and air for burning to happened in a cylinder. The stoichiometric mixture is the optimum mixture which has the proportion of (14.7:1) of air mass to fuel mass in non-oxygenated gasoline. A combination with higher amount of air and fewer amount of fuel is fuel-lean while proportion with fewer amount of air and higher amount of fuel is fuel-rich. For decent engine's emissions performance, controlling the ratio of air-fuel (A/F) is crucial. The majority of present automobiles are constructed to sustain stoichiometric combination of (A/F) as carbon monoxide (CO) and volatile organic compounds (VOCs) discharge escalates under fuel-rich operation and nitrogen oxides (NO_X) discharge increases throughout fuel-lean operation.

1.3. Antiknock Performance And Octane Numbers Estimation

Via the antiknock quality characteristics of gasoline, the different grades of gasoline are classified. According to Speight (2002) detonation or knock is a kind of irregular burning in the engine. In this case the charge of the air/fuel in the cylinder ignites impulsively in a restricted zone rather than being utilized gradually via the spark-initiated flame front. When these knocking burning permitted to continue, the engine can be damaged and given severe power loss. Therefore, for guaranteeing knock-free process, different grades are designed.

The ability of gasoline for resisting knocking is referred to as Octane number. It is also known as antiknock performance of the gasoline in the combustion chamber. For measuring gasoline's octane number a two laboratory test methods are utilized. The first approach approaches the (RON) however the second brings about (MON). While MON ideally correlated with elevated temperature knocking circumstances, elevated speed (900 rpm) and with part-throttle operation, the Research octane number optimally correlated with mild-knocking circumstances and low-speed (600 rpm). MON is constantly smaller compared to RON for a given gasoline. The variations between these methods demonstrates the gasoline sensitivity to alterations in working situations. Thus it can be stated that the bigger the variations, the greater the sensitivity of gasoline. In a single-cylinder laboratory engine MON and RON are calculated thus they do not totally forecast the performance of antiknock in engines that have multi-cylinders. For measuring the gasoline's antiknock performance, the altered process includes utilizing a

real automobile. This consequent in a value named Road octane number (RdON). There have been numerous efforts for predicting RdON from MON and RON as vehicle testing is more complicated in comparison to laboratory testing. This procedure is described by the subsequent equation.

$$\mathbf{RdON = a\ (RON) + b\ (MON) + c}$$

In accordance to Gibbs (1995), Gibbs et al (2009) and Fahim et al (2010), for Road Octane Number, a decent estimation is a = b = 0.5 and c = 0, producing (RON + MON)/2, frequently inscribed as (R + M)/2. Furthermore, it is named posted octane number (PON) or the antiknock index (AKI).

1.3.1. Octane number additives and laboratory estimation

Commonly, commercially usable products are not directly produced by the refining processes. However, this procedure generates semi-finished products that have to be mixed so as to comply with the specifications of the required products. Finding the optimum approach of combining various intermediate products accessible from the refinery and several additives for adjusting the product specifications is the chief purpose of mixing products. Alcohols or oxygenated ethers are some examples of additives which could enhance the gasoline's octane number. Recently, oxygenates have substituted tetra-ethyl lead (TEL) that was utilized for the ON enhancements. Table (1.2) displays the list of oxygenates with their octane numbers (Fahim et al., 2010).

Virtually, ordinary isooctane and heptane (2, 2, 4, trimethyl pentane) are utilized for comparing the octane number of the gasoline fuel. While isooctane has elevated resistance for knocking assigned an octane number of 100, normal heptane has low resistance for knocking and allocated an (ON) of 0. The mixes of both assist as an orientation petroleum scheme. In both American Standard Testing Method (ASTM) and Cooperative Fuel Research (CFR) single-cylinder engine with an adjustable density proportion are utilized as a standard for measuring the octane number.

Table 1.2. ON of several Oxygenates (Alcohols and Ethers)

Compound	RON	MON
Methanol	125-135	100-105
Ethanol	120-130	98-103
Methyl-tertiary-butyl ether (MTBE)	113-117	95-101
Ethyl-tertiary-butyl ether (ETBE)	118-122	100-102
Tertiary-butyl alcohol (TBA)	105-110	95-100
Tertiary-amyl-methyl ether (TAME)	110-114	96-100

The engine is worked with test fuel at (900 rpm) in this test approach, and the compression ratio is escalated till knocking commencement. Then, a combination of normal heptane and isooctane substituted the test fuel with in different ratio till a combination is discovered that matches the test fuel's knocking characteristics. The fuel's octane number is proportion of isooctane in the mixture. The same test is applied for measuring the (MON) and (RON) however with various test circumstances. As per ASTM D 2699, the RON is determined, at (600 rpm) the test is conducted. Furthermore, input air at 20 to 52°C, relying upon barometric pressure, and time is stabilized at 13 degree. (Parkash, 2010).

Gary et al (2001) defined the true octane as the octane number that attained utilizing a cooperative fuel research examinations. However, in addition to requirement of enormous examination for CFR (Committee on Fuel Research) engine, this approach is also boring, time consuming and costly. In the determination of the composition and RON of naphtha, gasoline and other solvents, the hydrocarbon kind analysis is imperative. For the analysis of oxygenates concentration, olefins and aromatics in petrol and petrol-oxygenates mixes and for octane number estimation, the distribution properties and the vapor pressure, the FTIR is a beneficial approach. The distillation properties of petrol is also identified in this technique. Apparatus accessible in MID IR range measurements is grounded upon interferometry. Several companies offer automatic FTIR analyzers (Ram et al., 2011).

Via the contributions of the hydrocarbon types grounded on measurement approach the RON and MON values can easily be calculated (Riazi 2005, Fahim et al., 2010, and Ram et al., 2011).

The estimation of octane number relies upon several factors, such us the gasoline, the additives and the altitude. Some characteristics of gasoline might be lost by the evaporation. Altitude impact the octane number requirement significantly. For every (1000 ft.) of elevation for a persistent spark progress is nearly 3 units smaller. Practically, nevertheless, for improving the performance of the engine and the net impact and for reducing the PON of the marketed gasoline via nearly two numbers for a (5000 ft.), the spark is increased at greater elevations. Owing to the variations in engine deposits, tune-up as well as clearances, Octane requirements for similar engine model will differ by 7 to 12 RON. In Table (1.3), a number of typical impacts of variables on engine octane requirements are listed (Gary et al., 2001).

Table 1.3. The impacts of variables on the requirements of octanes

Variable	Effect on octane requirements
Altitude	-3 RON per 1000 ft (305 m) increase in altitude
Humidity	-0.5 RON per 10% increase in rel. humidity at 70°F (21.1°C
Engine speed	-1 RON per 300 rpm increase
Air temperature	-1 RON per 20°F (11.1°C) rise
Spark advance	+1.5 RON per 1° advance
Coolant temperature	+1 RON per 10°F (5.6°C) increase
Combustion chamber deposits	+1 to 2 RON per 1000 miles (1609 km) up to 6000 miles(9650 km)

1.3.2. Antiknock additives (octane boosters) types

Generally, by an escalation in the chain length in the hydrocarbon molecule, the octane number declines. However, the carbon chain separating resulted in an escalation in the octane numbers. Furthermore, in aromatics, with similar number of carbons, the octane numbers upsurge. For increasing the octane number of a fuel, two approaches are available. The first approach is adding distinctive additives into the fuel

which depress auto ignition. The second method is blending high-octane fuels with the normal gasoline. Heptane, nonane, and octane, which are examples of straight chain alkanes, ignite quickly and explosive. Nonetheless, a chain of branched alkanes like 2, 2, 4-trimethylpentane (iso-octane) are not easily ignited. Straight chain mixtures have lower octane number in comparison to cyclic composites.

In the early 1920s, as an original octane promoter, gasoline was combined with Tetraethyl lead (TEL; formula $(CH_3CH_2)_4Pb$). Lead oxide, which poisons catalytic exchanger, generated as a results of TEL burning. Environmental contamination is caused by the utilization of composites comprising lead. The in several aviation gasoline grades and several developing countries like Myanmar, Afghanistan, Yemen and North Korea, TEL is still utilized as additives.

For enhancing the octane number of gasoline at low levels, in the Unite States of America, methyl tertiary-butyl ether (MTBE) had been utilized since 1979. For raising the octane number of the gasoline, MTBE is utilized as oxygenate. Gasoline completely burns, decreasing harmful tailpipe discharge from motor vehicles by the assistance of oxygen. Because of the blending properties of MTBE and for economic reasons, the majority of refiners have selected to utilize MTBE rather than other oxygenates. According to Demirbas et al (2015) MTBE might be cancer-causing agent for human being and wildlife in drinking water.

For rising the gasoline's octane number, Ferrocene [Fe $(C_5H_5)_2$] is utilized as octane booster. The TEL and MMT are more expensive than Ferrocene, thus the latter is highly preferred by as an alternative by refineries. A conductive coating on the surface of the spark plugs is formed by the iron comprising deposits by ferrocene (Stratiev et al., 2009, Demirbas et al., 2015).

Both MON and RON is escalated by aromatic hydrocarbons. Nevertheless, the MON might be impacted more by alkylbenzenes compared to RON. It is carcinogenic and burns easily. For increasing the octane number greater than 10 percent, aromatic alcohols are effective. These substances are absorbed effortlessly by the skin and highly cancer-causing (Demirbas et al., 2015).

In comparison to gasoline, ethanol has higher burning speeds, a greater octane number (109) and bigger vaporization heats. According to Eyidogan et al (2010) and

Demirbas et al (2015), the characteristics of ethanol permits shorter burning period, greater compression ratio and leaner burn engine. These characteristics resulted in theoretical competence benefits above gasoline in an ICE. Low energy density, corrosiveness, miscibility with water, low flame luminosity, low vapor pressure and poisonousness to environment are several shortcomings of ethanol (Foong et al., 2014) and (Demirbas et al., 2015).

Another octane booster, which has great octane blending property and clean burning, is methanol. It is generated from unconventional nonpetroleum energy origins like natural gases, biomass and coal (Demirbas et al., 2015) and (Yue et al., 2015). It has a greater RON (129–134). Methanol might be utilized like an additive to the gasoline or straightly like a clean fuel. Aromatic composites, which usually utilized to increase the octane number of gasoline, can be replaced by mixing high-octane methanol. However, methanol also take part in poisonous releases from automobiles. Methanol has similar drawbacks that ethanol generation has. One of the disadvantage is that so as to have an effective yields, it needs sacrificing of food resources. It might be highly complicated to start a car in cold weather as gasoline is more volatile compared to methanol. The addition of oxygenates like methanol, ethanol and MTBE to gasoline might result in very small amount of contamination as they burn. Table (1.4) demonstrates the pros and cons of gasoline octane booster additives (Demirbas et al., 2015).

1.3.3. Selected chemical compound as octane number boosters

1.3.3.1. Alcoholic compounds

Methanol

It is elevated octane blending and clean burning constituent. It is generated from unconventional nonpetroleum energy origins such as natural gas, coal and biomass. Since 1980s, commercially, methanol has been mixed into gasoline at different places and periods. Methanol has also been effectively utilized to extend gasoline supplies in various gasoline marketplaces round the globe even though it has been

extensively made for using in chemical generation. Methanol and gasoline blending have been cost-effective without subsidizing from fuel blending mandates or government different from several other alcohols.

Table 1.4. Advantages and Disadvantages of Additives of Gasoline octane Boosters

Additive	Advantages	Disadvantages
Tetraethyl lead(TEL) or $Pb(C_2H_5)4$	The ON of gasoline can be improved by adding TEL is a knock inhibitor. As anti-knock agents may be added to further increase the ON.	Burning of TEL generates lead oxide, which poisons catalytic converters. The use of compounds containing lead cause environment pollution
Methyl cyclopentadienyl manganese tricarbony1	MMT raise the ON of gasoline as an alternative to TEL	It may be health risks above a certain concentration.
Short Chain length hydrocarbon	The shorter the alkane chain, the higher the ON.	The volatility of hydrocarbon increases with a decrease in the chain length.
Aromatic hydrocarbons	Aromatics increase both RON and MON, alkyl benzenes may affect MON to a greater extent than RON.	The aromatic hydrocarbons burn sooty and are carcinogenic.
Aromatic alcohols	They are effective in increasing the ON higher than %10 dosages.	They are highly carcinogenic and are easily absorbed by the skin.
Ethanol	It has a higher RON (109). It allows for a higher compression ratio, shorter burn time and leaner burn engine, It reduces harmful emissions.	Disadvantages of ethanol include its lower energy density than gasoline, its corrosiveness, and low flame luminosity snd lower vapor pressure.
Methanol	It has a higher RON (129-134). It may be directly used as a clean fuel or as an additive to the gasoline	The disadvantages of methanol are similar to ethanol, It would be more difficult to start a car in cold weather.
Methyl tertiary-butyl ether (MTBE)	MTBE is used as oxygenate to rise the ON to rise of gasoline. Oxygen optimizes the oxidation during combustion.	MTBE may be carcinogen for animals and humans in drinking waters.
Ferrocene $[Fe(C_5h_5)_2]$	Ferrocene is used as octane booster to rise the ON to rise of gasoline.	The iron containing deposits formed from ferrocence can form a conductive coating on the spark plug surfaces.

Methanol blending supplies a clean burning and elevated octane to the oil refineries in addition to providing non-petroleum alternative energy into gasoline

supplies. This compound might be utilized for reducing energy consumption in the refineries and for improving gasoline products from the crude oil. Because of the high octane and oxygen content of methanol, it generates clean burning gasoline and greatly minimizes the exhaust discharge of automobile. In comparison to gasoline, methanol has lower carbon intensity as it produced from biomass or natural gas.

The blending of methanol in gasoline was firstly commercially announced in the beginning of the 1980s subsequent the crude oil price drop of the 1970s. Commonly, methanol blends were restricted to 3% to 5% of the gasoline blend because systems of carbureted fuel were highly predominant in the automobile fleets on the road in that period, and the limited ability of those automobiles for handling elevated oxygen concentration in the fuel.

According to new researches, in the modern automobiles, methanol blends as high as 15% volume (M15) of the gasoline can effectively be utilized. The fuel characteristics of methanol make it cleaner burning in gasoline engines. In addition to the oxygen content in methanol for improving fuel combustion, it also has an elevated value of blending octane for leaner burning, the biggest hydrogen-to-carbon proportion for a smaller carbon intensity fuel, a smaller boiling temperature for better fuel vaporization in cold engines and no pollution of Sulphur which toxins catalytic exchanger operation. The oil refineries are allowed to generate cleaner burning gasoline that decline the discharge from automobile by the above blending properties. Aromatic composites that usually utilized for the addition of octane in gasoline can be replaced by blending high octane methanol. However, this take a part in poisonous release from automobiles. Furthermore, for upgrading normal gasoline generation to higher premium grade gasoline, expanding gasoline production, meeting novel environmental regulations and minimizing refinery fund investments, oil refineries allowed methanol blending.

One of the cheapest method for expanding gasoline supplies, meeting the increasing demand on gasoline and comply with the environmental specification for the oil refinery is utilizing methanol blends. Thus, declining the capital investment in refinery treating ability.

One of the fastest and cheapest approach to displace expensive fuel energy used in the present automobile fleet, and also to reduce automobile emissions that lead

to air pollution such as ozone, carbon monoxide (CO), PM and air poisons for developing economies round the world is the blending of methanol in gasoline (Pacheco et al., 1997).

Ethanol

Since the 1970s, the notion of the addition of low ethanol contents to gasoline has emerged. At that time, petroleum supplies were declined and an exploration for sources of alternative energy started for replacing diesel fuel and gasoline. Methanol was considered as a decent additives because this alcohol can be generated from natural gas economically and it is easily to blended with gasoline (Da Silva et al., 2014).

The ethanol 85 is a combination of 15 percent gasoline and 85 percent ethanol. It is commonly utilized for flexible-fuel vehicle (FFVs), which is an automobile that has an internal combustion engine able to operate on a combination of fuels, usually ethanol and gasoline. Generally, different percentages of ethanol in gasoline are utilized in different countries round the globe, for example (10 %), (25 %), (10 %), (5 %) and (10 %) in Australia Brazil, Canada, Sweden and USA respectively. The impact of ethanol in gasoline on the constituents in the automobile and resulted in extreme wear of the fuel system's parts in the engine still debatable. Nevertheless, vehicle manufacturers in the United States of America have accepted that gasoline utilization with around 10 % of ethanol will not impact the vehicles' warranties. The utilization of an alcohol comprising blend might impact the engine's power output to different degrees because ethanol has significantly minimize energy contents (21.4 MJ/l) in comparison to gasoline (roughly 35 MJ/l). The addition of ethanol to the ultimate bulk of around10 percent to a gasoline with a 32.3 MJ/liter energy content might decline that value by 3.4 percent (Eyidogan et al., 2010).

Iso propyl alcohol

Chiefly in Europe, the United States and Japan, more than 2 m tones of IPA are generated per annum. Substantial amounts of propylene and this can be produced by refineries. This might be the instant precursor to the IPA generation. For Euro-4 and

Euro-3 fuel specifications, IPA is recognized as a satisfactory additives. IPA and Ethanol at 10 percent considered as the optimum alcohols for approaching the 95 RON goal.

No relevant information about the fate of IPA in the ecosystem is accessible while IPA is assumed as having a variety of health impacts. Nevertheless, in comparison to ethanol (a primary alcohol), IPA (as secondary alcohol) is possibly damage more slowly, however quicker than a tertiarybutyl alcohol (TBA). In natural waters, IPA might have long live. When IPA discharged to this ecosystem might volatilize (projected half-life roughly 5.4 days) and biodegrade. The IPA is not anticipated to be adsorbed or remains or bio concentrate (Eyidogan et al., 2010).

Butanol

In comparison to ethanol, butanol has superior fuel characteristics such as lower vapor pressure, greater heating value, and lower heat of vaporization in addition, it might not cause any issues with water in the fuel. However, butanol production is not economically viable. Increasing customer attentiveness for accessing butanol stimulate the activity in industry and agriculture. Thus production butanol has increased at the same time the cost of production reduced. The expectation of future escalation in prices of fossil fuel and safety low emission necessities could burning impact the production volume of butanol. From the fuel properties point of view, butanol (n-Butanol) considered as decent alternative to bioethanol. It also give pure primary burning as a 100% biofuel (Hönig et al., 2014).

1.3.3.2. Aromatic compounds

For every 5% addition of Toluene (methyl benzene), it boost around 1 octane number. Greater octane permits the utilization of a bigger compression ratio. Sooty spark plugs might be resulted from rich carbon content in toluene. Thus, the assumption that this demonstrate a highly-rich combination. Although toluene is a decent solvent, its elevated level impact plastic and rubber constituents in the fuel system (Bob Dudlley et al., 2010).

Until 2000, in the USA there were around 23 toluene producers. The overall production capacity was nearly 2.0 billion gallon in every year. This data eliminates that around ninety percent of toluene remained in the reformate stream from which it is originated and straightly mixed into the gasoline pool. In addition, as a residue of styrene production, toluene is produced.

Toluene is utilized in a variety of application. Apart from gasoline blending, the key utilization is as an HC solvent. For several derivatives such as xylenes and benzene, toluene is a feedstock. Seventy to eighty percent of separated toluene is utilized for solvents or chemicals. The rest of toluene mixed to gasoline as an octane booster. Relying upon reforming operation severity, posted octane number of catalytic reformates is usually 88.9-94.5. Blending octane number of toluene around 106. Thus, it is valuable blending constituent, mainly in unleaded premium gasoline. The toluene coproduced as benzene and xylenes are removed for utilization in chemicals, and that surpasses needs the utilization of chemicals, has an arranged market as a mixing constituent for gasoline even though reformates are not removed merely for producing a high-octane mixing stock.

Toluene, as a blending constituent in vehicle fuels, has two main benefits. Firstly, in comparison to premium and regular unleaded gasoline, toluene has an elevated octane number. Secondly, toluene is comparatively low volatile which allows incorporation into gasoline blends of other accessible and cheaper substances like *n*-butane. The annual growth of demand on toluene is around 3% (Sinor, 2000).

It is observed that the mixed or commercial xylene regularly comprises of around 20% of o-xylene, p-xylene and ethylbenzene and approximately 40-65% m-xylene. From industrial activities, exhausts of vehicle, and via volatilization from their utilization as solvents, xylenes are discharged to the air as fugitive discharges (Meador et al., 1995).

1.3.3.3. Ketone compound (acetone)

Acetone is volatile fluid, has a sweet smell and colorless. In this industry, acetone or ketone is regarded the least poisonous solvent. The occurrence of acetone might naturally. In the generation of pharmaceuticals, lubricating oils, pesticides,

chloroform, paints, varnishes and lacquers ketone is utilized. Ketone is possibly biodegrade or volatilize prior to bio accumulate or adsorb to sediments when present in water. In soil, ketone is willingly biodegrade and volatilize. It is easily accessible around the world and it is cheap. The gasoline vaporization, fuel efficiency increase, engine longevity, and performance, hydrocarbon emissions reduction resulted from the addition of small quantity of acetone in the fuel tank. The petroleum have to be totally vaporized so as to be completely combusted. Surface tension demonstrate a hindrance to vaporization. The surface tension is considerably reduced by Acetone (La Pointe, 2005).

1.3.4. Infra-red spectroscopic analysis in octane number estimation

As described previously, (MON) and (RON) demonstrate resistance of a fuel to auto ignition under particular engine working circumstances, as described by ASTM-CFR standard testing procedures D2699 and D2700. Motor Octane Numbers (MON), Research Octane Number (RON) and the other ASTM 4814 fuel regulation propose numerous essential features to be installed in fleet of automobiles. Cooperative Fuels Research (CFR) utilized to determine the RON and MON of fuels costs more than $200,000. This process takes around 20 minutes in the laboratory and necessitates skilled technicians. For reducing the burden of these testing, investigators continuously search for less expensive and quicker noninvasive visual methods to determine RON via of statistical approach. Reliable approaches for fuel vibrational spectroscopy like Raman spectroscopy infrared absorption (IR) has been verified (Balabin et al., 2008). Several investigators in this field attempted for obtaining decent outcomes comparing to ASTM-CFR tests. For instance, tests like (RON), (MON), specific gravity, Motor vapor pressure, bromine number and contents of aromatic, saturate, alkene, sulfur, and lead utilizing a short wavelength near infrared (SW-NIR) scanning spectrophotometer (660–1215 nm) and multivariate analysis were determined by Kelly et al (1989) for correlating the spectra to the performance metrics. It revealed that to a standard error within 0.4–0.5, RON of gasoline can be projected (Kelly et al., 1989, Balabin et al., 2008). This approach is better in comparison to the ASTM RON test itself at ±0.7 (Daly et al., 2016). For enhancing techniques, considering alternative fuels, predicting

the performance of other fuel metrics, the innovative study of Kelly et al (1989) has stimulated other examinations. Grounded upon optical properties, different commercial apparatuses use these principles for quickly predicting related characteristics of diesel and gasoline fuels. For instance, radiation from light releasing diodes is passed by Zeltex ZX 101C octane analyzer via optical filters and gasoline samples (14 static wavelengths varying between 893–1045 nm). A photo detector was utilized for collecting the light. After that, at the wavelengths of interest, with an overall calculation period of 20 s and precision of ±0.5 RON units, the collected lights was processed for absorbance (Merberg, 1996). The same method grounded upon FTIR spectroscopy, gathering a wide absorption spectrum and producing data at 12,900 wavelengths was taken by IROX Miniscan IRXpert gasoline/diesel analyzer and other proceeding models. By this approach, anticipating 16 overall ASTM regulations and predicting RON with a precision of ±0.5 within 80 s were allowed (Osman et al., 2015). In comparison to CFR engine, this apparatus costs 50% less. In addition, this device does not necessitate skilled worker/ technicians.

1.3.5. computational relations adopted in octane number estimation by ft-ir spectroscopy (chemometrics)

For spectral analysis, chemometrics symbolizes the most wide spread toolbox. However, simultaneously, chemometrics are computationally difficult and mathematically complex. It is regarded as a purely empirical method because it is grounded upon statistics. A big information set with a huge amount Toluene is also derived of variables (for instance, spectra relying upon temperature, pressure and composition) require an evaluated in a systematic manner. The first stage for reducing the number of variables is regularly an independent or principal component analysis (ICA or PCA, correspondingly). Thus, for converting a group of calculated information of potentially associated variables in to a group of values of linearly not correlated variable, an orthogonal transformation is utilized (Wold et al., 1987). Kiefer (2015) the variables that are not correlated are named the principal components. For example, a principal component might be a signature of characteristic spectral that imitates alterations in the level of a substance in the combination, however it must not essentially be a highest amount of this substance.

Noack et al (2013) stated that the analysis of the regression associates the parameters defined with the amount of awareness is the second step. General approach utilizes a partial linear least squares regression (PLSR), however non-linear higher-order method like support vector machines (SVM) could be applied as well.

The mixture's octane number might have a different octane number from each element when gasoline elements are mixed together although the two elements have the same octane number. The octane number of the mixture or the blend might be less, the same as or bigger compared to that measured from the volumetric mean of the octane numbers of the mixture elements. This demonstrates the mixing is nonlinear. When blend's octane number was equivalent to that anticipated via summing the octane numbers of the components in ratio to their concentrations, the blending would be linear. Practically, the variation between the linearly predicted values and the octane numbers of blends have been correlated via particular empirical equations. In addition, such equations are utilized for correcting the linear predictions. Nevertheless, it is obvious that a precise octane blending approach is required for optimizing the mixing gasoline components.

1.4. Other Gasoline Requirements

In addition to increasing the octane number and satisfying high-performance automotive engines, gasoline have to comply precise regulations or specifications. However, some of these specifications are differed in accordance to sites and temperatures or altitudes. The single most acknowledged calculation of the quality of gasoline is probably Octane. On service station distributers, the value of octane of gasoline have to be posted.

- **Volatility**

It is the capability of a fuel that regulate the evaporation which is crucial to decent operation of the automobile. The gasoline have to be in the vapor state for burning to occur in an Otto cycle engine. Reid vapor pressure (RVP) (ASTM D323), the distillation curve (D86) and the vapor/liquid ratio (V/L) (D2533) at a provided

temperature are the three ASTM tests that define vaporization or volatility properties of gasoline. The evaporation percentage at a particular temperature (E_{XXX}); or the temperature for a particular evaporation percentage (T_{YY}) are the two approaches for expressing distillation data. The E_{XXX} values are commonly desired via refineries and blenders as E_{XXX} values blend linearly. In both approaches, the performance of gasoline specifications have been stated. Generally, the T_{YY} format is preferred by ASTM specifications. The quantity of vapor shaped from a particular liquid volume at a particular temperature in the atmosphere pressure is measured by the V/L ratio tests. The temperature where the V/L proportion is 20 (TV/L=20) is a general measure for specifying gasoline. The V/L test is time wasting and complicated, and methods have been enhanced for calculating it from RVP and D86 values even though V/L can be calculated experimentally. Gasoline blenders have to strike a balance between different performances of driveability properties when designing the targets of fuel volatility. The capability of a vehicle to start effortlessly, idle and accelerate smoothly, and react to alterations in throttle position is referred to as Driveability. Insufficient volatility is as problematic as excessive. To local ambient temperature circumstances, targets have to be harmonized. Strong functions of the design of automobile are volatility requirements like octane. Different federal and state regulations restrict the permissible gasoline RVP by location and season for controlling evaporative emissions. The blending constituent that has an RVP greater than 7 psi might encounter market restrictions (Egeback et al., 2005).

- **Startability**

In an Otto cycle engine, the ratio of A/F in the combustion cavity have to be close to the stoichiometric for achieving combustion. Regrettably, the combustion chamber’s walls and the intake manifold are not hot adequately for vaporizing considerable fuel when the engine is initially started. Thus, for metering additional gasoline and fewer air to the engine on starting hence there is sufficient vapor in the engine for supporting burning, the vehicle is designed. The RVP is a measurement of the front end of the distillation curve, either E70 or T10 are correlated with the capability of a gasoline for achieving decent starting.

- **Vapor Lock**

It happens as plenty of gasoline evaporates and starves the engine or supplies excessive gasoline to the engine. This process caused by plenty of volatility. Vapor lock takes place on warmer days and if the vehicle has reached complete working temperatures.

- **Warm-up**

It denotes the time of working which starts instantly subsequent the vehicle has begun and endures till the engine has touched regular working temperatures. This is typically happen subsequent 10 minutes or so of working. In the achievement of good warm-up performance, the middle of the distillation curve has the biggest role. While the fuel's back end, or heaviest molecules, have trouble evaporating, the fuel's front end of the completely evaporates under the vehicle operating regime. Throughout warm up process, boiling of molecules at around 100º to 150ºC is vital. For regulating driveability, the driveability index (DI) is the most general expression. It is expressed as the following:

$$\mathbf{DI = 1.5T10 + 3T50 + T90}$$

When temperature (T) is in ºC, the DI of fuels usually have values of under 570 offer decent warm-up driveability performance. Through a period of load escalation, the higher quantities of the fuel's volatile constituents (the front end) will favorably vaporize and go into the engine. In a fuel, the different normal portions might have dissimilar octane scores. A satisfactory performance of the engine provided by these type of fuel which composed of natural boiling fractions, because a low RON is provided by components with fractions that have boiling point of 45º to 105ºC. The Δ (ON), which is the alteration varying from the knocking rate of the gasoline boiling under 100ºC and the knocking rate of the whole gasoline, is the valuable notion here. The gasoline's transient performance is better in evading the knocking, when the Δ ON is low.

- **Back-End Volatility**

It is the fraction of the gasoline that have a boiling point greater than 150ºC. In this zone, the molecules have elevated energy density which considerably participate in the fuel's economy. Nonetheless, several components in this boiling range might results in issues. This could be owing to the difficulty in volatilization in this condition. In addition, when the engine is in a cold temperature, these components might tend to amass on the cylinder's walls. After that, they are swept into the fuel sump and dilute the fuel. The evaporation of these materials normally heats up the engine. Nonetheless, several back ends might not boil off and the lubricant's performance might be degraded when there are a lot of back ends in the gasoline. Molecules that have 12 carbon atoms or more might participate to deposits of the combustion chamber. Predominantly active contributors of these deposits are condensed ring aromatics (Sinor, 2000).

2. LITERATURE REVIEW

2.1. History of The Octane Boosters

Since the early 1920s, when the automobile's mass production octane boosters have been part of the fuel's supply chain. Early in the manufacturing field, the lead additives' efficiency of was recognized. At that time, worldwide octane booster was lead based additives.

During the 1970s, the initiative for lead based octane boosters eradication started. It was recognized that in several cities in the United State of America air contamination was a due to automobile emissions. The catalytic converters were the major technology for reducing these discharges however lead is incompatible with catalysts.

Novel octane boosters were essential for using catalytic converters, however sustaining the level of octane in the fuel (significant for keeping efficiency - kilometers per liter). Therefore, huge investigations were conducted for finding appropriate octane boosters well-matched with catalytic converters.

The consciousness of the issue with lead in the urban atmosphere, principally in big cities in which the lead distribution associated with traffic densities was related with this. Then, for eliminating lead in gasoline on health basis, a worldwide movement started. Once more, mainly European based organizations searched for alternatives that might help replacement of lead as an octane boosters.

In the 1970s, as potential substitutes to lead, the iron additive ferrocene and alcohols, ethers and the manganese additive MMT were identified. During the same time, the MTBE was identified as being the most broadly acceptable substitute. Subsequently, the MTBE begins to be utilized as a gasoline additive in several regions on the globe at around 1 % to 2% concentration.

After 1980s, it revealed that in some cities in the USA evident that catalytic converters did not control the air contamination level. They grieved from photochemical smog, which is mainly caused by nitrogen oxides, carbon monoxide,

unburnt hydrocarbons and fugitive releases of some gasoline constituents, mentioned as volatile organic compound (VOCs).

For solving the air contamination issue, reformulated gasoline (RFG) was issued by the United State Clean Air Act Amendments (CAAA 1990) tried via instructing formulations for the constituent combination of gasoline. A definite oxygen concentrations in the gasoline was introduced. It might be provided via the octane booster MTBE at around the 10% to 15% concentration. As a results the demand for MTBE was escalated. For supplying the United State, specially the Californian, numerous plants were constructed in several location of the world, for instance the Middle East.

Colossal growth in plants generating MTBE occurred for supplying California's market because it is the world's biggest single market for gasoline and the MTBE demand. The opportunities for other alternatives were regarded owing to likely scarcities of MTBE oxygenate and expenses related to the procedure.

For the utilization as alternative fuel, octane booster and gasoline extender, ethanol has long been considered. The motivations for the utilization of ethanol was derived from easy production from a broad range of agricultural sources. Thus, it is regarded a sustainable source of energy. Subsequent the early 1970s oil shock, Brazil utilized the biggest amount of ethanol in the world, because it was utilized as an indigenous fuel supply. In Europe and USA, extensive research has been conducted on the utilization of ethanol like a fuel. The biggest advancement for the utilization of ethanol is Nebraska, the US where it is so-called the corn states. The influential manufacturing in the US has effectively safeguarded tax-breaks for the ethanol utilization that originated from corn. In the United State market, this step permits the utilization of ethanol to contest with MTBE. In the corn-belt states, it is extensively utilized as an additive.

The ether derivative ETBE (Ethyl tert-butyl ether) could be generated from plants of MTBE for helping stimulate the ethanol utilization instead of gasoline. The supplement of the C4 olefin isobutene feedstock is one of the issues associated with MTBE production. The C5 olefins (pentenes, it was also called amylenes) can be utilized so as to supplement supplies. This generates TAME (tert-Amyl methyl ether).

The ether DIPE is generated in place of MTBE in refinery operations where there are excess of propylene. As an alternative for lead, the MMT was developed progressively in parallel to the ethers and alcohols utilization. The MMT was utilized in a tiny amounts however prevalent places. In the USA, MTBE was identified in ground water in some states such as Maine and California subsequent around five years of the reformulated gasoline utilization. Illegal drainage leaks or from underground gasoline storage tanks was the main source of pollution. Leakage from the pipeline systems considered as another source of contamination (Duncan Seddon and Eliza, 2000).

2.2. Spectroscopy Technique Types Used In Predicting The Octane Numbers

For gaining fast and precise information from the high-resolution spectra of liquid and solid samples, some techniques such as mid-infrared (MIR), Near Infra-Red Spectroscopy (NIRS) and Raman Spectroscopic techniques are utilized. Table 2.1 displays numerous benefits these techniques. These techniques are cost-effective and simplify quantitative, qualitative nondestructive and noninvasive examination. In addition, reagent- and waste-free and necessitate no extra auxiliary chemicals are some other benefits. Therefore, for industrial process monitoring and quality control, mid-infrared (MIR), Near Infra-Red Spectroscopy (NIRS) and Raman Spectroscopic techniques are utilized are perfectly appropriate. There is the right technique for almost every utilization. Nonetheless, NIRS is the most flexible technique. It has become a precious instrument for academic research and manufacturing quality control because of the accessibility of effective chemometric evaluation software and apparatuses in addition to light-fiber optics. In a single determination, multiple values are determined by NIRS. Environmentally, on-site measurements and remote sampling are applicable by utilizing NIRS.

NIRS perfectly appropriate for quality control of raw materials because it analyzes via several translucent packaging materials. Bulk material also analyzed because of its penetration depth. Alterations in present absorption bands or even the formation of novel absorption bands because intermolecular hydrogen bonding and dipole interactions changes vibrational energy. On one hand, physical parameters such as size of particle, density and moisture strongly affected spectra. Conversely, these has

made NIRS to be ideal. Furthermore, in comparison to MIR and Raman, NIRS belongs to indirect or subordinate approaches more. The spectra of these spectroscopy must be compared to primary or reference approaches for obtaining information. For establishing a NIR «predictive model» for prognosticating the composition of the investigated sample therefore mathematical means are utilized for the spectra.

Table 2.1. Comparison between Spectroscopy Techniques

	Raman	MIR	NIR
Wavenumber	50-4000 cm^{-1}	200-4000 cm^{-1}	4000-12500 cm^{-1}
Bonds	Homonuclear bonds such as C-C, C=C, S-S	Polar bonds such as C=O, C-O, C-F	H-containing bonds such as C-H, O-H N-H, S-H
Absorption bands due to	Scattered radiation	Absorbed radiation(basic vibration)	Absorbed radiation (overtones and combination)
Absorption	Strong	Weak	Weak
Absorption bands	Well-resolved, assignable to specific chemical groups	Well-resolved assignable to specific chemical groups	Series of overlapping bands
Signal Intensity	Poor	Good	Good
Quantification	Intensity(I)~concentration	Log I_0/I~ Concentration (Lambert-Beer law)	Log I_0/I~ Concentration (Lambert-Beer law)
Excitation conditions	Change of polarizability α	Change of dipole moment μ	Change of dipole moment μ
Selectivity	High	High	Low, requires calibration and chemo metrics
Interface	Broad fluorescence baseline	Water	Water, physical attributes(e.g., sample size, shape and hardness)
Particle size	Independent	Dependent	Dependent
Applicability for atline, online, inline	Good	Poor	Good
Radiation source	Monochromatic (laser VIS/NIR region)	Polychromatic by globar tungsten	Polychromatic by globar tungsten
Sample preparation	None	Reduced(except ATIR*)	None

ATR= attenuated total reflection.
Table 1 comparison between Spectroscopy Techniques.

For identifying the various components of the samples of commercial gasoline, Pasadakis and Kardamakis (2006) and Kardamakis et al (2007), utilized Chemometrics and FTIR spectroscopy. The differentiation between gasoline fractions

from processing via the cracking of fluid catalytic, alkylation, catalytic reforming, isomerization and dimerization was facilitated by the methods Pasadakis and Kardamakis (2006), Kardamakis et al (2007) and Balabin et al (2008, 2010), utilized the NIR spectroscopy for alike purpose. They carried out a comparison between a huge diversity of up-to-date Chemometrics with modern complicated data analysis approaches like support probabilistic neural networks (PNN) and vector machines (SVM). Kiefer (2015) stated that the latter two are the most operative methods. In the early 1948, to measure the concentration of olefin in various gasoline samples, Shell Oil Company advanced an IR approach (Johnston et al., 1948), and Diehl et al (1995) calculated the quantity of aromatic hydrocarbons in gasoline by GC/FTIR. For determining the fractions of saturates, aromatics, olefins, benzene and the relative density, Reboucas et al (2011) applied NIR spectroscopy.

2.3. History And Development of The Gasoline Engine

The subsequent highlights a short summary of the internal combustion engine's history:

- In 1680, an internal combustion engine, which powered with gunpowder, was devised (however had not been constructed) by Christian Huygens.
- In 1807, an internal combustion engine, which utilized a mixture of hydrogen and oxygen for fuel, was designed by Francois Isaac de Rivaz of Switzerland. Then, even though it was unsuccessful, Rivaz designed a vehicle for his engine which was the first internal combustion motorized vehicle.
- In 1824, a conventional Newcomen steam engine was adapted to be powered by gas by English engineer, Samuel Brown. After that, he utilized the engine for powering a vehicle up Shooter's Hill in London.
- In 1860, an internal combustion engine with electric spark-ignition and double-acting that powered by coal gas was invented and patented by the engineer Jean Joseph Étienne Lenoir. He attached the engine to a three-wheeled wagon that succeeded to finish a historic fifty-mile road trip in 1863 utilizing a primitive carburetor and petroleum.

- In 1862, a four-stroke engine was registered by Alphonse Beau de Rochas, a French civil engineer. However, the engine had not been constructed.
- In 1864, a one-cylinder engine with a crude carburetor was constructed by Siegfried Marc. Siegfried attached the engine to a wagon for a stony around 300m drive. After several years, an automobile that briefly ran at 10 mph was designed by Marcus. This car was regarded as the forerunner of the contemporary vehicle by several historians because it was the globe's first gasoline-fueled car.
- In 1866, the designs of Lenoir and de Rochas was enhanced by Nikolaus August Otto and Eugen Langen. They devised a highly effective gas engine.
- In 1873, unsuccessful kerosene engine with two-stroke was invented by George Brayton, an American engineer. Nevertheless, kerosene was regarded the first practical and safe oil engine.
- In 1876, a effective four stroke engine was developed by Nikolaus August Otto. Later, he patented the engine. It was recognized as the "Otto cycle".
- In 1876, Sir Dougald Clerk invented the first successful two-stroke engine.
- In 1883, a single cylinder four-stroke engine which ran on stove gas was constructed by the French engineer Edouard Delamare-Debouteville. Indeed, the construction of a car is not certain, although their design were very cutting-edge for the period in comparison to Daimler and Benz in several approaches.
- In 1885, the prototype of the modern gas engine, which consists of vertical cylinder and fuel inserted via a carburetor was invented by Gottlieb Daimler (patented in 1887). Firstly, he constructed a two-wheeled vehicle with this engine. After twelve months, Daimler constructed the first four-wheeled vehicle in the world.
- Karl Benz obtained the first patent for a gas-fueled vehicle in 1886.
- In 1889, engine with four-stroke and mushroom-molded valves and two V-slant cylinders was constructed and enhanced by Daimler.
- In 1890, the first four-stroke engine with four cylinders was constructed by Wilhelm May Bach.

2.4. Octane Boosters RON And MON Values

Numerous investigators attempted for estimating the MON and RON of chemicals that utilized as octane boosters. The MON and RON for some these chemicals are shown in table (2.2). for integrating NIR FT-IR spectroscopy task for estimating the octane numbers, the values of MON and RON are imperative (Demirbas et al., 2015).

Table 2.2. Research octane number (ron) and motor octane number (mon) values for hydrocarbon fuels

NO.	Name of fuel	RON	MON
1	Ethane	114.9	99
2	n-Propane	111	96.6
3	2-Methyl propane	102.1	97
4	2,2-Dimethyl propane	85.5	80.2
5	n-Butane	94	89.1
6	2-Methyl butane	93	89.7
7	2,2-Dimethyl butane	91.8	93.4
8	2,3-Dimethyl butane	104.3	94.2
9	2,2,3-Trimethyl butane	112.1	101.3
10	n-Pentane	61.8	63.2
11	2-Methyl pentane	73.4	73.5
12	3-Methyl pentane	74.5	73.3
13	2,3-Dimethyl pentane	91.1	88.5
14	2,4-Dimethyl pentane	83.1	83.8
15	3,3-Dimethyl pentane	80.8	86.6
16	2,3-Dimethyl pentane	92.8	95.6
17	2-Methyl-3-ethyl pentane	87.3	88.1
18	2,2,4-Trimethyl pentane	100	100
19	2,2,3-Trimethyl pentane	109.6	99.9
20	2,3,4-Trimethyl pentane	102.7	95.9
21	n-Hexane	24.8	26
22	3-Methyl hexane	52	55
23	3,4-Dimethyl hexane	76.3	81.7
24	3,3-Dimethyl hexane	75.5	83.4
25	2,2-Dimethyl hexane	72.5	77.4
26	2,2,3,3-Tetramethyl hexane	112.8	92.4
27	n-Heptane	0	0
28	2-Methyl heptane	21.7	23.8
29	3-Ethyl heptane	33.5	52.4
30	3,3,5-Trimethyl heptane	86.4	88.7
31	n-Octane	0	0
32	Cyclopentane	101.6	84.9

Table 2.2. Research octane number (ron) and motor octane number (mon) values for hydrocarbon fuels (Continued)

NO.	Name of fuel	RON	MON
33	1,1-Dimethylcyclopentane	92.3	89.3
34	1,2,4-Trimethylcyclopentane	89.2	79.5
35	1,1,2,4-Tetramethylcyclopentane	96.2	88
36	Cyclohexane	84	77.6
37	1,1-Dimethylcyclohexane	87.3	85.9
38	1,1,2-Trimethylcyclohexane	95.7	87.7
39	2-Butene	101.6	99.9
40	3,3-Dimethyl-1-butene	111.7	93.3
41	2,3,3-Trimethyl-1-butene	105.3	90.5
42	2-Pentene	87.8	87.8
43	4-Methyl-2-pentene	98.9	85.1
44	4,4-Dimethyl-1-pentene	104.4	85.4
45	2,4,4-Trimethyl-2-pentene	103.5	86.2
46	3-Hexene	94	80.1
47	2-Methyl-3-hexene	97.9	82
48	2-Heptene	73.4	68.8
49	3-Heptene	90	79.3
50	2-Methyl-3-heptene	94.6	80.6
51	4,4-Dimethyl-1-heptene	79.8	74.8
52	4-Octene	94.6	80.6
53	Benzene	90	92
54	Ethylbenzene	107	124
55	Propylbenzene	129	127
56	1,3,5-Trimethylbenzene	137	124
57	Toluene	112	124
58	o-Xylene	103	120
59	m-Xylene	124	145
60	p-Xylene	127	146

2.5. The Prediction Methods of Octane Numbers for Gasoline Blends

To predict blends' octane numbers as a sequence of binary systems grounded upon the octane rating and volumetric olefin, Schoen and Mrstik (1955) enhanced a graphical correlation. Relying on the order of calculation, the blended octane number produces dissimilar values. To be appropriate for multicomponent blends and producing more reliable outcomes, Stewart (1959) advanced this approach. The octane rating and volume of olefins of the blended constituents were required in the correlation of Stewart.

A blending index for blending octane number linearly, was developed Auckland and Charnock (1969). Extrapolating from the octane rating at a particular level to an octane rating at 100 percent level of constituent, the blending index, which is a hypothetical value, is obtained.

To estimate gasoline blends' octane number from concentrations of constituents and olefins contents, their octane ratings, aromatics and paraffins, Rusin et al (1981) demonstrated a more sophisticated transformation approach. Transformation of constituent characteristics, linear blending of these transformed characteristics and inverse transformation of the outcomes are the three stages that include in the approach. This approach is alike to the approach of blending index. This approach might also result in inconsistency in data transformation between these three stages because of the back and forth transformation (Twu et al., 1998).

The gasoline constituent blending was correlated with variations in level of octane and type of hydrocarbon among constituents by Healy et al (1959). Nonetheless, irrational mixing values might be attained, particularly when the kind of hydrocarbon or (ON) of the novel constituent is out the boundery of the constituent that examined formerly when the Healy et al (1959)'s equation is utilized for predicting the new components' blending characteristics (Morris, 1975).

For displaying nonlinear gasoline blending behavior, a fascinating equation was suggested by Morris et al. (1975). The following is the proposed equation:

$$\textit{Octane number} = x_1 a_1 + x_2 a_2 + b_{12}\, x_1\, x_2$$

at which:

ai represents the octane number of component *i*

xi demonstrate the volume fraction of component *i*

b12 represents the interaction coefficient for components 1 and 2.

To predict the octane number of gasoline mixtures, a model with five self-determining variables are projected by Zahed et al. (1993). For the model to work well for the blends utilized in the regression, the variables of the model are regressed. Nonetheless, the model might still poorly perform for other blends. The derived variables from this model are internally unreliable. The original octane numbers of the gasoline constituents are not close to the projected octane numbers from this model. The anticipated n-heptane's octane number from this equation is 108.77 against the distinct

value of zero. Likewise, the predicted iso-octane's number of this model is -108.95 against the distinct value of 100. The group of variables attained from this model might merely be utilized for this particular group of constituents inside the similar variety of configurations at which the variables were taken. The beneficial of these type of methods are restricted. It is unreliable to anticipate the blend's octane number at other circumstances utilizing this equation.

An interaction approach for anticipating the RON and MON of gasoline blends is exhibited by Twu et al (1998). The followings are several characteristics of the projected approach and correlation:

1- The blending correlation mixes precisely the octane numbers of n-heptane and isooctane.
2- When blending alike constituents, the blended octane number is not altered.
3- The behavior of blending is precisely described through the entire composition range by the blending equation.
4- In addition to working for binaries, blending correlation also works for multicomponent.
5- When a constituent is alienated into two or more alike subcomponents, the anticipated RON and MON for a particular blend from the correlation is invariant.

The binary interaction parameter is generalized while the correlation is in a modest formula. For the interaction correlation, a worldwide group of binary interaction parameters are developed. The RON and MON are the merely input data for the developed correlation in this research for gasoline cut. The standard laboratory examination for gasoline cuts such as aromatics, olefins and saturates contents are also inspected. The octane number of gasoline blends is predicted precisely by component type-oriented interaction approach (Twu et al., 1998).

3. MATERIALS AND METHODS

3.1. Introduction

All sample collection and examinations were conducted in KAR refinery petroleum products laboratory according to ASTMD (American Standard Test Method Designation) routines.

3.2. Materials

In this research, the gasoline samples were taken from KAR refinery nearby Erbil city in north of Iraq. It is considered as the main local supplier of market of the region. Any changes done for this gasoline octane number might positively affect the economy and environment of the region.

3.2.1. Chemicals

Nominated organic constituents that used in this research as octane number booster were added to the KAR refinery gasoline at four volumetric ratios (0.5, 2.5, 5, and 7.5 vol %). The followings are the utilized compound:

1. Alcoholic chemical compounds (oxygenates)
   - Methanol,
   - Ethanol,
   - Isopropyl alcohol,
   - Benzol(Phenol) ,
   - Butanol.
2. Aromatic chemical compounds.
   - Toluene,
   - Xylene,
   - Aniline,
   - Benzene,

3. Ketone chemical compound.

- Acetone

3.2.2. Tools used in experiments

1. 500ml graduated glass flasks.
2. Normal Refrigerator.
3. Glass bottles with fitting cover.
4. Digital Type K Thermometer with wired sensors(Figure 3.1).
5. Mercury Thermometer.
6. Rubber tape.

Figure 3.1. K-type Thermometer.

3.3. Experimental Procedure

All required chemicals and gasoline were collected in cold and dry location in appropriate containers. The Digital Type K Thermometer was calibrated by the mercury thermometer before the examinations. Because it required an open refrigerator door, measuring the temperature of sample was difficult by utilizing for the process. However, utilizing Digital Type K Thermometer with the wired sensors made the process easier without opining refrigerator door.

3.3.1. Preparation of gasoline samples

The subsequent procedure were repeated every test point:

1- In a glass container with fitting cover, 300ml of the gasoline sample was cooled in a refrigerator under 15^{o}C.

2- The Zeltex101XL device(Figure 3.2) was utilized for testing the octane number of the gasoline as the following:

- ZX-101XL was turned on. Then the sample was put in the device and covered.
- After that, the octane number was measured by the device

3- Chemical additive was added to the gasoline in the refrigerator according to selected volumetric ratio of the octane number.

4- For every test, 300ml of gasoline sample was added to four glass containers in different concentrations, then one of selected chemical additives was added to these containers using a pipette with shaking.

Figure 3.2. Zeltex 101XL device.

3.4. The ZX101™ Device

This apparatus is a portable, powered by battery and utilized for analyzing octane number in gasoline. The analyzer, a sample container and a light shield are the primary components of the device. It weighs around 5 kilograms with all its components in a carrying case. The ZX101™ device determines the octane number in less than 60 second, without requiring standard samples. This instrument applies near-infrared transmission spectroscopy approach for measuring octane number. This device includes a patented solid-state optical system, containing fourteen near-infrared emitting diodes (IREDs) with thin band pass filters, a system of silicon detector and a completely integrated microprocessor. A schematic illustration of the ZX101™ is shown in figure 3.3. The container of the sample is a closed, flat-sided, reusable glass container with an optical path length of 75 mm. The volume of the sample container is around 225 ml, for making determination of an octane number, the operator obtains a background signal from the empty sample chamber, measures the sample's absorption spectrum two times, after that obtains a second background signal. The whole procedure necessitates less than a 60 seconds (Merberg, 1996)

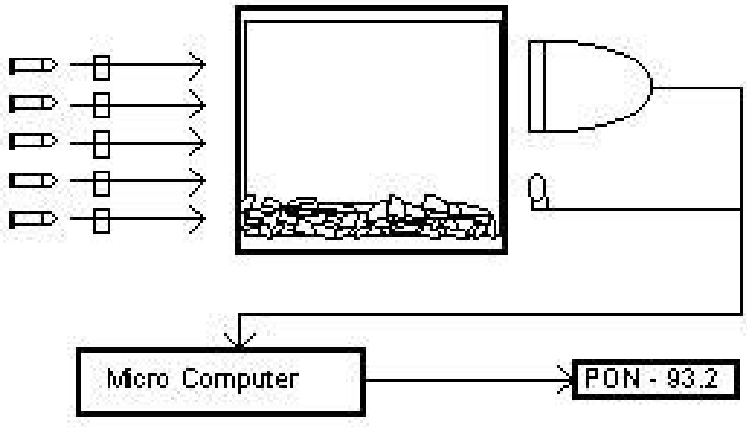

Figure 3.3. Schematic Diagram of ZX101optical system.

4. RESULTS AND DISCUSSION

4.1. Introduction

In this research, the gasoline of KAR refinery was utilized. The main specifications of this gasoline are displayed in table 4.1:

Table 4.1. KAR refinery gasoline specification (for guided purposes only)

No.	Specification	Value
1	Density(Kg/m^3)	740
2	RON	91
3	Vapor Pressure at 37.8^oC(Kpa)	54
4	Aromatics content (vol%)	29
5	Saturated components (vol%)	64
6	Initial boiling point ^oC	37
7	Final boiling point ^oC	195

In accordance to local regulations, this gasoline is considered as a normal gasoline. The objective of this research was to upgrade this gasoline to premium class without invoking high cost refinery procedures. Therefore, three chemical groups are utilized as followings:

1- Alcohols. 2- Aromatics. 3- Ketones

Table 4.2 displays the utilized chemical additives and their main specification.

Table 4.2. Main physical properties of used chemical additives

No.	Octane number additive/the type	Chemical formula	Density (Kg/m^3)	Boiling point ^oC	Vapor Pressure Kpa(at 20^oC)
2	Ethanol/Alcohol	C_2H_6O	789.3	78.3	5.95
3	Isopropyl alcohol	C_3H_8O	786	82.6	4.62
4	Benzol/Alcohol	C_6H_6O	1070	181.7	0.0533
5	Butanol/Alcohol	$C_4H_{10}O$	810	117.7	0.8
6	Toluene/Aromatics	C_7H_8	870	111	2.8
7	Xylene/Aromatics	$(CH_3)_2C_6H_4$	864	138.5	0.879
8	Aniline/Aromatics	C_6H_7N	1021.7	184.13	0.08
9	Benzene/Aromatics	C_6H_6	876.5	80.1	~12.5
10	Acetone/Ketones	C_3H_6O	784.5	56.05	~30

4.2. Effect of Alcoholic Components on RON of KAR Refinery Gasoline

In this research, five alcoholic components and four volumetric ratios (0.5, 2.5, 5, and 7.5%) were utilized. Table 4.3 listed the impacts of these components on research octane number (RON) of the samples of KAR refinery gasoline.

Table 4.3. Effect of alcoholic components on the RON of KAR refinery gasoline

No.	Alcohol name Vol%	RON at 0%	RON at 0.5%	RON at 2.5%	RON at 5%	RON at 7.5%
2	Methanol	91.2	91.1	91.4	91.8	92.2
3	Isopropyl alcohol	91.2	91.2	91.6	92.1	92.6
4	Benzol(Phenol)	91.2	91.1	91.4	91.9	92.3
5	Butanol	90.8	90.5	90.3	90	89.7

It is obvious from the previous table that Ethanol, Methanol, Isopropyl alcohol and Benzol(Phenol) demonstrated positive effects on the enhancement of RON of the gasoline especially in large volumetric ratios. However, only Butanol indicated negative impact at all volumes. Furthermore, Isopropyl alcohol had the optimum impact in higher volumetric ratio, slight alterations was monitored in lower volumetric ratios (Figure 4.1A and 4.1B).

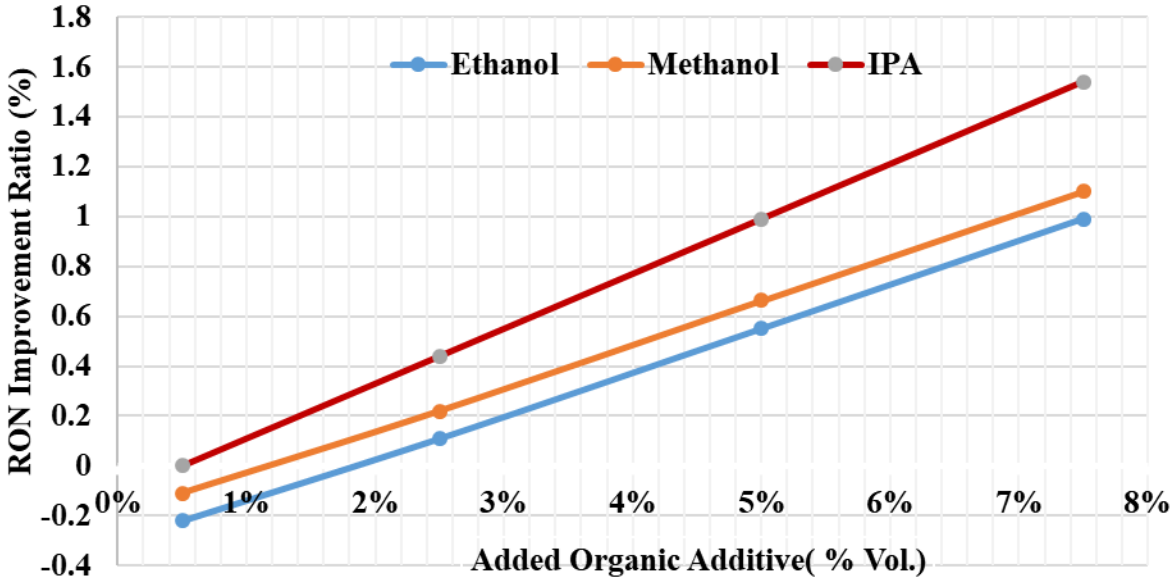

Figure 4.1A. Alcoholic components effects on RON of KAR refinery gasoline.

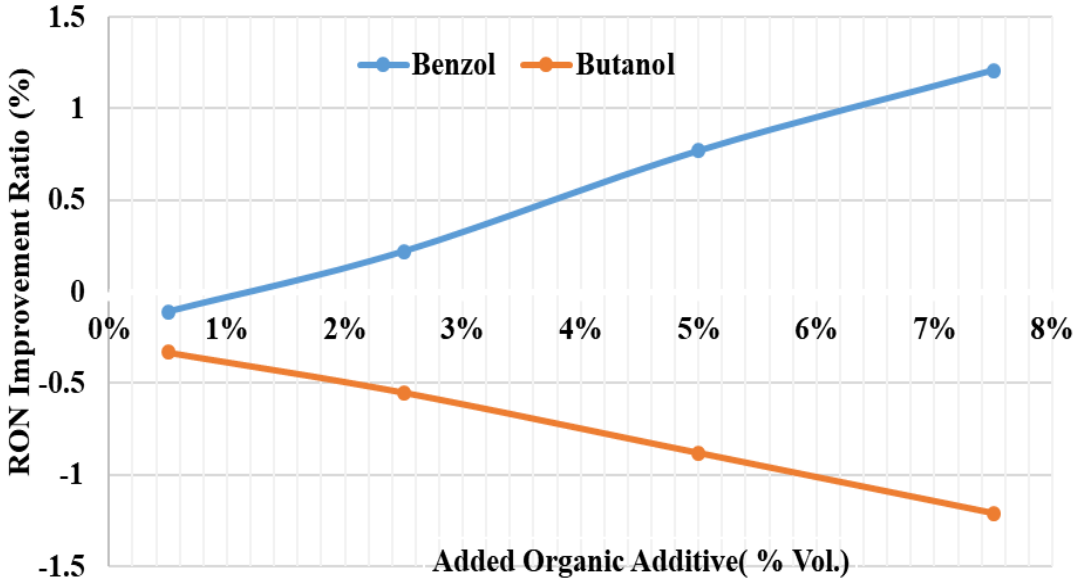

Figure 4.1B. Alcoholic components effects on RON of KAR refinery gasoline.

4.3. Effect of Aromatic Components on RON of The KAR Refinery Gasoline

In this research, four aromatic constituents are utilized. Table 4.4 demonstrates the effects of these four aromatics. The results indicated that aromatics had greater impacts on RON compared to alcohols. This is particularly true with Toluene and Xylene as they convert the gasoline from normal gasoline to premium gasoline at 5% vol (figure 4.2).

Table 4.4. Effects of Aromatic components on the RON of KAR refinery gasoline

No.	Vol% Aromatics name	RON at 0%	RON at 0.5%	RON at 2.5%	RON at 5%	RON at 7.5%
2	Xylene	91.9	91.9	92.6	93.5	94.4
3	Aniline	90.8	90	90.5	91.1	91.8
4	Benzene	90.8	90.8	91.1	91.5	91.9

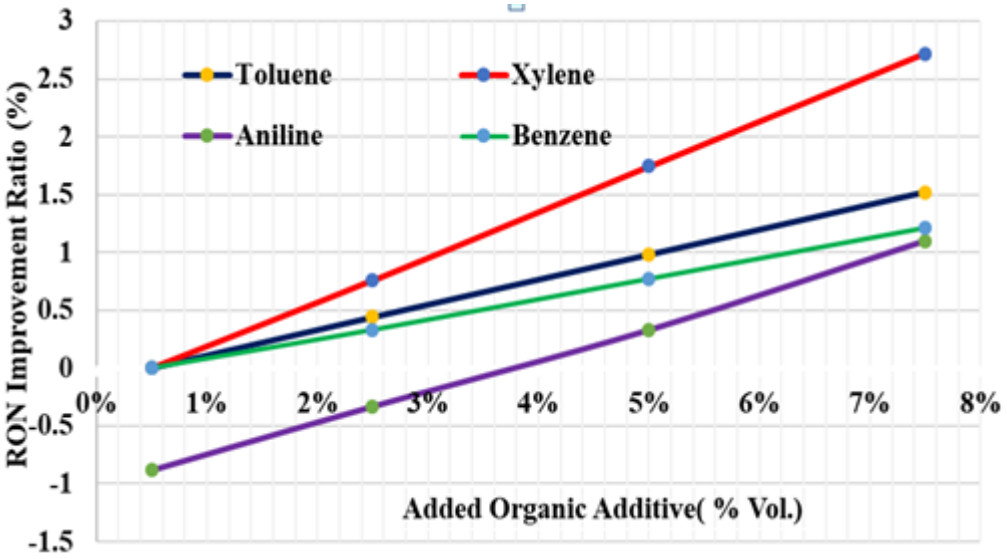

Figure 4.2. Aromatic components effects on RON of KAR refinery gasoline.

4.4. Effect of Ketone Components on RON of The KAR Refinery Gasoline

Acetone was the only ketone utilized in this work. It exhibits that acetone had a positive impact on research octane number of the gasoline. In addition, as it is seen in Table 4.5 and Figure 4.3 that the greatest impacts was monitored in 7.5% volume that is succeeded to reach 93 RON value. The impacts of acetone was intermediate between the aromatics and alcohols.

Table 4.5. Effect of Acetone on the RON of KAR refinery gasoline

No.	Vol% Ketone name	RON at 0%	RON at 0.5%	RON at 2.5%	RON at 5%	RON at 7.5%
1	Acetone	91.9	91.9	92.2	92.7	93.1

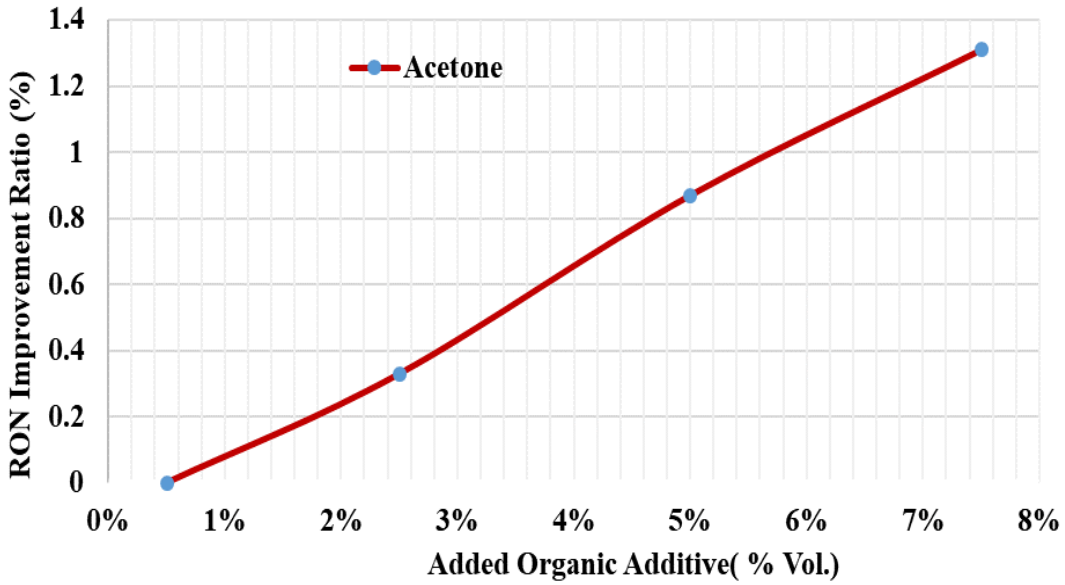

Figure 4.3. Effect of Acetone on the RON of KAR refinery gasoline.

4.5. Effect of Mixtures of Chemical Additives on RON of The KAR Refinery Gasoline

For determining the potential impacts of combining of two constituents from every groups of aromatics and alcohols. In this stage, the equal-volumetric ratio of ethanol with IPA and Toluene with Xylene were utilized. The results indicate that the combination of IPA and ethanol had a greater impact on RON in comparison to each of ethanol and IPA. However, the effect of the combination of Xylene and Toluene was near the average impact between each of Toluene and Xylene individually (Table 4.6 and Figure 4.3).

Table 4.6. Effects of mixed chemical additives on the RON of KAR refinery gasoline

No.	Vol% Aromatics name	RON at 0%	RON at 0.5%	RON at 2.5%	RON at 5%	RON at 7.5%
1	Toluene+ Xylene	91.9	91.9	92.5	93.2	94
2	Ethanol +IPA	90.8	91.1	91.4	91.9	92.3

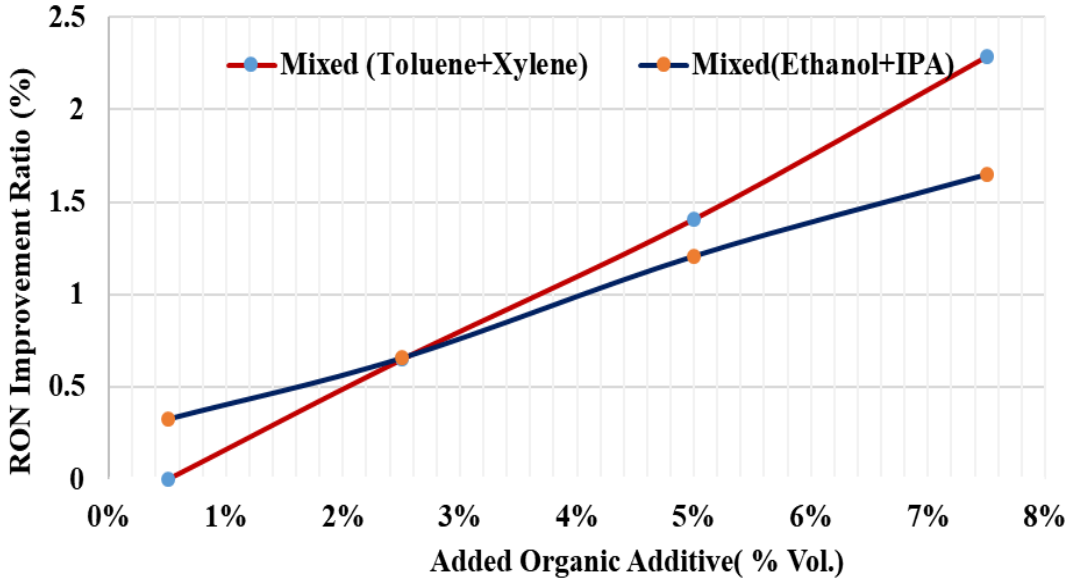

Figure 4.4. Mixed alcohol and mixed aromatics effects on RON of KAR refinery gasoline.

The following table was constructed for demonstrating the entire results attained from this research. It also comprises of the overall impact of the chosen chemical additives on the research octane number of KAR refinery gasoline. Table 4.7 demonstrates that the Xylene had greatest positive impacts on the research octane number of KAR refinery gasoline. It might be because of high research octane number of the Xylene itself.

Improvement ratio=[(RONvol% − RONsample)÷RONsample] × 100

Table 4.7. Improvement ratio of the chemical additives on the RON of KAR refinery gasoline

No.	Chemical Additive	0.5% Vol	2.5% Vol	5%Vol	7.5%Vol
2	Methanol	-0.11	0.22	0.66	1.10
3	Isopropyl alcohol(IPA)	0.00	0.44	0.99	1.54
4	Benzol(Phenol)	-0.11	0.22	0.77	1.21
5	Butanol	-0.33	-0.55	-0.88	-1.21
6	Toluene	0.00	0.44	0.98	1.52
7	Xylene	0.00	0.76	1.74	2.72
8	Aniline	-0.88	-0.33	0.33	1.10
9	Benzene	0.00	0.33	0.77	1.21
10	Acetone	0.00	0.33	0.87	1.31
11	Toluene+ Xylene	0.00	0.65	1.41	2.29
12	Ethanol +IPA	0.33	0.66	1.21	1.65

5. CONCLUSION

The objectives of this research were preparation of local gasoline (KAR refinery gasoline) and enhancing its research octane number via adding several chemical composites such as alcohol, aromatic and Ketone. They were supplied to the gasoline in various volumetric ratio (0.5, 2.5, 5, and 7.5vol %). The Zeltex 101XL device was utilized for measuring the Research Octane number (RON) of blends. The majority of utilized additives positively enhanced the octane number of KAR refinery gasoline. Furthermore, this improvement correlated positively with the volume of the additives:

1- In comparison to other chemical additives in this research Xylene had the greatest RON gain while Butanol presented the lowest negative effects.
2- It revealed that the aromaticity and the aromatics affected the octane number of KAR refinery gasoline more positively compared to the other additives in this research. The effect of the aromatic escalated positively with higher branches of these Aromatics. For example, Toluene with one branched Alkyl had less positive impact on octane number compared to Xylene which has two Alkyl. In addition, Benzene with no branched alkyl presented less impact.
3- Acetone, the only utilized ketone, had a valuable impact on the RON value of KAR refinery gasoline and this effect could be because of the C=O group.
4- Among the alcohol additives, IPA exhibited the highest effect on the RON, followed by ethanol and methanol that demonstrated nearly similar results.
5- Mixture ratio of (50:50vol %) of Ethanol and IPA had RON boosts higher than Ethanol alone and lower than or close to IPA alone.
6- Mixture of (50:50vol %) of Xylene and Toluene had RON boosts higher than Toluene alone and lower than Xylene alone.

For the future investigation, the following suggestions ought to consider:

- Investigating the environmental consequences of these additives and selecting the best volume of each of the chemical additives that have the least negative effects on pollution and health.

Studying the other characteristics of KAR refinery gasoline that directly impact machine performance such as motor octane number (MON), sulfur content, vapor pressure and specific gravity.

REFERENCES

Balabin, R. M., Safieva, R. Z., 2008. Gasoline classification by source and type based on near infrared (NIR) spectroscopy data. ***Fuel,* 87**(7): 1096-1101.

Balabin, R. M., Safieva, R. Z., Lomakina, E. I. 2010. Gasoline classification using near infrared (NIR) spectroscopy data: Comparison of multivariate techniques. ***Analytica Chimica Acta,* 671**(1-2): 27-35.

Dudley. B., Tony. H., 2010. BP Australia. ***Fuel News***: fuel, octane & power. Available in: ***https://www.bp.com***

Bosch, R., 2008. ***Bosch Handbook For Automotive Electrics And Automotive Electronic***. 5th edition. Robert Bosch GmbH, Stuttgart.

Silva, G., Foong, T. M., Morganti, K. J., Michael, J. B., Yang, Y., 2014. The octane numbers of ethanol blended with gasoline and its surrogates. ***Fuel***, **115**: 727-739.

Daly, S. R., Niemeyer, K. E., Cannella, W. J., Hagen, C. L., 2016. Predicting fuel research octane number using Fourier-transform infrared absorption spectra of neat hydrocarbons. ***Fuel,* 183**: 359-365.

Demirbas, A., Balubaid, M. A., Basahel, A. M., Ahmad W., Sheikh, M. H., 2015. Octane rating of gasoline and octane booster additives. ***Petroleum Science And Technology***, **33**(11): 1190-1197.

Diehl, J. W., Finkbeiner, J. W., DiSanzo, F. P., 1995. Determination of aromatic hydrocarbons in gasolines by gas chromatography/fourier transform infrared spectroscopy. ***Analytical Chemistry,* 67**(13): 2015-2019.

Seddon. D., 2000. ***Setting National Fuel Quality Standards:*** Proposed management of petrol octane enhancing additives/products. Available in: ***http://www.environment.gov.au***.

Egebäck, K., Henke, M., Rehnlund, B., Wallin, M., Westerholm, R., 2005. Blending of ethanol in gasoline for spark ignition engines–Problem inventory and evaporative measurements. ***Rapport MTC***, *5407*.

Eliza, M., 2000. Octane enhancing petrol additives/products literature review and analysis. ***Duncan Seddon Associates Pty Ltd. Available In***: ***http://www.environment.gov.au***.

Eyidogan, M., Ozsezenm, A. N., Canakci, M., Turkcan, A., 2010. Impact of alcohol–gasoline fuel blends on the performance and combustion characteristics of an SI engine. ***Fuel,* 89**: 2713–2720.

Fahim M., Al-Sahaaf, T., Elkilani., A. 2010. ***Fundamentals of Petroleum Refining***. 1st edition. Elsevier B.V.

Gary, G. J. and G. E. Handwerk., 2001. ***Petroleum Refining Technology And Economics***. 5th edition. Marcel Dekker, Inc.

Georgiev, R. P., 2011. Design a four-cylinder internal combustion engine: project and engineering department, final project. ***Navarra University Publications***. Available in: ***http://mechanic.zanjansadra.ir***.

Gibbs, L. M., 1995. Automotive fuels–gasoline: encyclopedia of energy, technology and the environment. ***John Wiley & Sons***.

Gibbs, L., Anderson, B., Barnes, K., Engeler, G., Freel, J., Horn, J., Ingham, M., Kohler, D., Lesnini, D., MacArthur, R., Mortier, M., 2009. Motor gasolines

technical review. ***Chevron Products Company, San Ramon, CA***. available at: ***http://www.chevron.com***.

Hönig, V., Kotek, M., Mařík, J., 2014. Use of butanol as a fuel for internal combustion engines. ***Agronomy Research,*** **12**(2): 333-340.

Johnston, R. W. B., Appleby, W. G, Baker, M. O., 1948. Determination of Olefins in Gasoline. ***Analytical Chemistry,*** **20**(9): 805-812.

Jones, D. S. J., Pujado, P. R., 2006. ***Handbook of Petroleum Processing***. 1st edition, Springer Publications.

Kardamakis, A. A., Mouchtaris, A., Pasadakis, N., 2007. Linear predictive spectral coding and independent component analysis in identifying gasoline constituents using infrared spectroscopy. ***Chemometrics And Intelligent Laboratory Systems,*** **89**(1): 51-58.

Kelly, J.J., Barlow, C.H., Jinguji, T.M., Callis, J.B., 1989. Prediction of gasoline octane numbers from near-infrared spectral features in the range 660-1215 nm. ***Analytical Chemistry,*** **61**(4): 313-320.

Kiefer, J., 2015. Recent advances in the characterization of gaseous and liquid fuels by vibrational spectroscopy. ***Energies,*** **8**(4): 3165-3197.

LaPointe, L., 2005. Acetone in fuel said to increase mileage, ***LaPointe's Permission forPure Energy Systems News.*** Availble in: ***http://www.thebirdman.org/Index***.

Meador, J. P., Stein, J. E., Reichert, W. L., Varanasi, U., 1995. Bioaccumulation of polycyclic aromatic hydrocarbons by marine organisms. In ***Reviews of Environmental Contamination And Toxicology*** (pp. 79-165). Springer, New York, NY.

Merberg, G.N. 1996., Evaluation of an octane analyzer. ***American Laboratory,*** **28**(13): 68-69.

Noack, K., Eskofier, B., Kiefer, J., Dilk, C., Bilow, G., Schirmer, M., Buchholz, R., Leipertz, A., 2013. Combined shifted-excitation Raman difference spectroscopy and support vector regression for monitoring the algal production of complex polysaccharides. ***Analyst,*** **138**(19): 5639-5646.

Osman, S., Duaij, O.K. and Taha, K.K., 2015. Enhancement the octane number of sudanese gasoline (Nile Blend). ***International Letters of Chemistry, Physics And Astronomy,*** **9**(2), p.184.

Pacheco, M.A., Marshall, C. L., 1997. Methanol gasoline blends: Alternative fuel for today's automobiles and cleaner burning octane for today's oil refinery. ***Energy Fuels,*** **11**, pp.2-29.

Parkash, S., 2010***.*** ***Petroliumm Fuels Manufacturing Handbook***. 1st edition. John Wiley & Sons, Inc.

Pasadakis, N., Kardamakis, A. A., 2006. Identifying constituents in commercial gasoline using Fourier transform-infrared spectroscopy and independent component analysis. ***Analytica Chimica Acta,*** **578**(2): 250-255.

Ram, S.M.J. and Jaiswal, A.K., 2011. A complete analysis of postmortem materials received in forensic toxicology laboratory. ***Journal of Forensic Medicine And Toxicology***, **28**(1): 22.

Reboucas, M. V., Santos, J. B., Pimentel, M. F., Teixeira, L. S., 2011. A novel approach for development of a multivariate calibration model using a Doehlert experimental design: Application for prediction of key gasoline properties by Near-infrared Spectroscopy. ***Chemometrics And Intelligent Laboratory Systems,*** **107**(1): 185-193.

Riazi, M. R., 2005. ***Characterization And Properties of Petroleum Fractions***. 1st edition. ASTM, USA.

Sinor, J.E., 2000. Review of market for octane enhancers, final report. ***National Renewable Energy Laboratory***. Available in: ***https://www.nrel.gov***.

Speight, J. G., 2002. ***Handbook of Petroleum Roduct Analysis***. 1st edition . John Wiley & Sons, Inc.

Stratiev, D., Kirilov, K., 2009. Opportunities for gasoline octane increase by use of iron containing octane booster. ***Pet. Coal,*** **51**: 244-248.

Twu, C., Coon, J., 1998. A generalized interaction method for the prediction of octane numbers for gasoline blends**.** ***Simulation Science Inc***, pp.1-18.,

Wold, S., Esbensen, K., Geladi, P., 1987. Principal component analysis. ***Chemometrics And Intelligent Laboratory Systems,*** **2(**1-3): 37-52.

Yue, L., Wu, C., Zhang, M., 2015. Natural resources efficiency and green growth: a unified analysis framework. Energy Ed. ***Sci. Technol. B,*** 7:291–300.

EXTENDED TURKISH SUMMARY
(GENİŞLETİLMİŞ TÜRKÇE ÖZET)

IMPROVEMENT OF OCTANE NUMBER OF LOCAL GASOLINE BY THE ADDITION OF SELECTIVE ORGANIC COMPOUNDS

YEREL BENZİNİN OKTAN DEĞERİNİN SELEKTİF ORGANİK BİLEŞENLER KATILARAK GELİŞTİRİLMESİ

ABDULAZIZ, Karwan Moffaq
Yüksek Lisans Tezi, Kimya Mühendisliği Ana Bilim Dalı
Tez Danışmanı: Doç. Dr. Süha Orçun MERT
Nisan 2018, 56 sayfa

ÖZET

Bu çalışmanın ana amaçları KAR rafinerisinde elde edilen yerel benzinin hazırlanması ve oktan değerinin (RON) geliştirilmesidir. Bu amaçla bazı organik bileşenler (alkoller, aromatikler, ve ketonlar) KAR rafinerisinden elde edilen benzinin RON değerini geliştirmek üzere katkı malzemesi olarak seçilmiştir. Bu bileşikler farklı hacimsel oranlarda (0.5, 2.5, 5 ve 7.5 hacimsel yüzde) benzine eklenmiş olup, alkoller olarak etanol, metanol, izopropil alkol (IPA), bütanol ve benzol, aromatikler olarak benzen, tolüen, ksilen ve anilin, ve keton olarak da aseton kullanılmıştır. Karışımların RON değerlerinin ölçümünde Zeltex 101 XL cihazı kullanılmıştır.

Organik bileşenlerin çoğu KAR rafinerisi benzinini normal benzinden üst kalitede benzine dönüştürmek için yeterli olmuştur (bölgesel benzin kalitesi özelliklerine göre, bkz. Ek A). En başarılı kimyasal grubunun, başta %2.5 hacimsel yüzdede bile olumlu etkiler gösteren ve %7.5 ile RON değerini 94.4'e yükselten ksileni, ve hemen ardından gelen tolüeni içeren aromatikler olduğu görülmüştür. Bu oran neredeyse normal benzini, bölgede kullanımına izin verilen en üst RON değerine sahip benzin olan süper benzine (RON 95) dönüştürmeye yeterlidir.

Aseton da aromatiklere benzer etkiler göstermiş ve %2.5 hacimsel yüzde bile benzini normal benzinden üst düzey benzine dönüştürmeye yetmiştir. Diğer yandan etanol %7.5'te etki gösterirken, izopropil alkol etkisini göstermeye %5 hacimsel

yüzdede başlamış, benzol ise %7.5'ta göstermiştir. Butanol, oktan değerini geliştirmede başarısız olan tek katkı maddesi olmuştur.

KAR rafinerisinden elde edilen benzinin RON değerini geliştirmek için ayrıca kimyasalların karışımları da denenmiş, etanol ve IPA karışımı %7.5 hacimsel oranında üst düzey benzin etkisini elde etmiştir; bu değer tek başına IPA'nın gösterdiği performansa yakındır. Tolüen ve ksilen karışımları hacimsel olarak %2.5'ten itibaren geliştirme göstermeye başlamıştır ve bu değer ksilen ve tolüen tek başlarına gösterdikleri performansın ortasında yer almaktadır.

Anahtar kelimeler: benzin, oktan değeri, organik katkı maddeleri, FT-IR, ve kemometrikler

1. GİRİŞ

Ön Bilgiler:

Benzin, özellikle kıvılcım buji ateşlemeli Otto motoru başta olmak üzere içten yanmalı motorlarda yakıt olarak kullanılan ve petrolden elde edilen bir sıvıdır. Benzin hidrokarbonların bir karışımı olup sülfür, nitrojen, oksijen ve bir takım metaller dâhil bazı kirleticiler de içermektedir. Benzinin yapısında bulunan dört ana grup olefinler, aromatikler, parafinler ve naftenlerdir. Benzinin oktan değerinin geliştirilmesi benzin üretiminin en önemli aşamalarından biridir. Bu işlem genellikle benzine katkı maddesi olarak bilinen bazı kimyasalların eklenmesi ile yapılır.

2. KAYNAK BİLDİRİŞLERİ

2.1. Oktan geliştiricilerin tarihçesi

1920'li yılların başlarından itibaren otomobillerin seri üretimine geçilmesiyle, oktan geliştiriciler yakıt tedarik zincirinin önemli bir parçası haline gelmiştir. Kurşun içerikli katkı maddelerinin etkinliği bu endüstri alanının erken yıllarında keşfedilmiş ve kurşun içerikli katkı maddeleri evrensel oktan geliştiriciler haline gelmiştir.

2.2. Oktan değerlerinin tespitinde kullanılan spektroskopi teknikleri

NIRS, MIR ve Raman Spektroskopi teknikleri, bir ön (NIRS) veya redüklenmiş (Raman) numune hazırlığı işlemine ihtiyaç duymaksızın katı ve sıvı numunelerdem yüksek çözünürlüklü spektralar elde ederek hızlı ve doğru bilgi ortaya koyabilme kabiliyetleri nedeniyle kusursuz iş görmektedir.

2.3. Benzin motorunun ortaya çıkışı ve tarihçesi

İçten yanmalı motorların kısa tarihçesi aşağıdaki ana maddelerden oluşmaktadır:

- 1680 - Hollandalı fizikçi Christian Huygens barutla çalışacak bir içten yanmalı motor tasarlamıştır (ancak bu motoru üretmemiştir).
- 1858 - Belçika doğumlu mühendis Jean Joseph Étienne Lenoir, içten yanmalı motoru geliştirdi. Bu tür motorlar için önceki tasarımlar 1807'nin başlarında patentlendi (De Rivaz motoru), fakat hiçbiri ticari açıdan başarılı olamamıştı. Lenoir'un motoru, içten yanmalı motorlar için bir ilk olarak, başarı olarak düşünülmesi için yeterli miktarda ticarileştirildi.
- 1980 – Wilhelm Maybach ilk dört silindir, dört zamanlı motoru üretmiştir.

2.4. Oktan geliştiriciler RON ve MON değerleri

Çoğu araştırmacı oktan geliştirici olarak kullanılan kimyasalların RON ve MON değerlerini tespit etmeye çalışmıştır.

3. MATERYAL ve YÖNTEM

3.1. Giriş

Tüm testler ve numune işlemleri KAR rafinerisi petrol ürünleri laboratuvarında ve ASTM D rutinleri uyarınca gerçekleştirilmiştir.

3.2. Malzemeler

Bu çalışmada kullanılan benzin numuneleri Kuzey Irak'ta Erbil şehri yakınlarında bulunan KAR rafinerisinden alınmıştır, bu rafineri bölgenin ana tedarikçisi olarak kabul edilmektedir. Bu benzinin oktan değerinde gerçekleştirilecek herhangi bir iyileştirmenin bölge ekonomisine ve çevresine olumlu katkıları olacaktır.

3.3. Deneysel Yöntem

İhtiyaç duyulan tüm benzin numuneleri ve kimyasallar soğuk ve kuru ortamlarda uygun kaplara toplanmıştır. Testlerden önce, Dijital Tip K termometresi cıva termometresi ile kalibre edilmiştir. Numunelerin sıcaklıklarının cıva termometresi ile ölçülmesi, dolap kapağının açılmasını gerektirmesi nedeniyle sorunlu olmaktadır, oysa Dijital Tip K termometresi kablolu alıcıları sayesinde kapak açılmadan sıcaklıklar ölçülebilmiştir.

3.4. ZX101^{TM} cihazı

ZX101^{TM} taşınabilir, pille çalışan bir benzin oktan analiz cihazıdır. Üç ana bileşenden oluşmaktadır: analiz ünitesi, numune kabı ve ışık kalkanı. Bir çanta içindeki tüm test kiti 5 kg'dan daha hafif gelmektedir. Cihaz, oktan ölçümünü 1 dakikadan kısa sürede yapmaktadır ve standart numunelerin kullanılmasını gerektirmemektedir.

4. BULGULAR ve TARTIŞMA

Numunesi alınan benzin, bölgesel değerlendirmelere göre normal benzin olarak kabul edilmektedir; bu çalışmada yüksek masraflı rafineri işlemlerine gerek duyulmaksızın bu benzinin sınıfını üst düzey benzin sınıfına getirmek amaçlanmıştır. Bu amaçla üç grup kimyasal kullanılmıştır:

1- Alkoller 2- Aromatikler 3- Ketonlar

Bulgular aşağıdaki sonuçları göstermektedir:

- Alkol katkıları içinden en iyi etkiyi IPA göstermiştir, ancak yine de özellikle düşük hacimsel oranlarda etki oranı düşük kalmaktadır.

- Aromatikler, özellikle tolüen ve ksilen, RON değerini geliştirmede genel anlamda alkollerden daha başarılıdır.
- Keton bileşiklerinden yalnızca aseton kullanılmıştır, ve RON değerini geliştirmede alkoller ve aromatikler arasında kalan ortalama bir başarı göstermiştir.

5. SONUÇLAR

Bu çalışmanın amaçları yerel benzinin hazırlanması (KAR rafinerisi benzini) ve buna organik kimyasal bileşikler katılarak (alkoller, aromatikler ve ketonlar) RON değerinin (araştırma oktan değeri, research octane number) geliştirilmesidir. Bu bileşikler farklı hacimsel oranlarda benzine katılmıştır (0.5, 2.5, 5 ve 7.5 hacimsel yüzde). Karışımların RON değeri Zeltex 101XL cihazı ile ölçülmüştür. Seçilen çoğu katkı maddesi olumlu etki göstermiş ve KAR rafinerisinden alınan benzinin oktan değerini geliştirmiştir, katkı maddelerinin miktarının artışı ile birlikte gelişim oranı da artmaktadır:

1- Ksilen, bu çalışmada kullanılan diğer kimyasallara oranla en yüksek RON kazanımını sağlarken, Butanol en düşük etkiyi göstermiştir.
2- Genel olarak aromatiklerin bu çalışmadaki diğer kimyasal gruplarına göre KAR rafinerisi benzini RON değeri üzerinde daha büyük olumlu etkisi olmuştur. Bu olumlu etki aromatiklerin dallarının sayısı arttıkça daha da yükselmektedir. Dallı iki alkile sahip olan ksilen, tek dallı tolüenden daha yüksek etki göstermiştir. Hiç dallı alkili olmayan benzen en düşük etkiyi göstermiştir.
3- Kullanılan tek keton olan aseton, KAR rafinerisi benzini RON değeri üzerinde hatırı sayılır bir etki göstermiştir, bu etkinin kaynağı olarak C=O grubu gösterilebilir.
4- Alkol katkı maddeleri arasından RON değeri üzerinde en büyük etkiyi IPA göstermiştir, bunu yakın değerler gösteren etanol ve metanol takip etmektedir.
5- Etanol ve IPA'nın karışımı (hacimsel %50:50) tek başına etanolün performansından daha iyi, ancak tek başına IPA'nın performansından daha düşük performans göstermiştir.

6- Ksilen ve Tolüen'in karışımı (hacimsel %50:50) tek başına tolüen'in performansından daha iyi ancak tek başına ksilen'in performansından daha kötü performans göstermiştir.

Gelecek çalışmalar için aşağıdakiler önerilmektedir:

- Bu çalışmada kullanılan katkı maddelerinin en uygun hacimlerinin belirlenmesinde çevre temizliği ve sağlık üzerinde asgari olumsuz etkileri belirleyecek çevresel çalışmalar ziyadesiyle önemlidir.
- KAR rafinerisi benzinin, makine performansına etki eden motor oktan değeri (MON), sülfür içeriği, buhar basıncı ve özgül ağırlığı gibi diğer özelliklerinin incelenmesi ve geliştirilmesi gerekmektedir.

CURRICULUM VITAE

He was born in Erbil/Iraq, 1989. He has completed his primary and secondary education in Erbil. He graduated in 2011-2012 at the University of Salahaddin, the College of Science, Department of Chemistry. At the February of 2014 He started his master study in Van Yuzuncu Yıl University.

Address: Iraq/Erbil
Phone number: 009647504289293
Email: karwanmabdulaziz@gmail.com

UNIVERSITY OF VAN YUZUNCU YIL
THE ISTITUTE OF NATURAL AND APPLIED SCIENCES
THESIS ORIGINALITY REPORT

Date:15/05/2018

Thesis Title: IMPROVEMENT OF OCTANE NUMBER OF LOCAL GASOLINE BY THE ADDITION OF SELECTIVE ORGANIC COMPOUNDS.

The title of the mentioned thesis,above having total 56 pages with cover page, introduction, main parts and conclusion,has been checked for originality by ithenticate computer program on the date of 01/03/2018 and its detected similar rate was 1%according to the following specified filtering

Originality report rules:

- Excluding the Cover page,
- Excluding the Thanks,
-Excluding the Contents,
- Excluding the Symbols and Abbreviations,
- Excluding the Materials and Methods
- Excluding the Bibliography,
- Excluding the Citations,
- Excluding the publications obtained from the thesis,
- Excluding the text parts less than 7 words (Limit match size to 7 words)

I read the Thesis Originality Report Guidelines University of Van YuzuncuYilfor Obtaining and Using Similarity Rate for the thesis, and I declarethe accuracy of the information I have given above and my thesisdoes not contain any plagiarism; otherwise I accept legal responsibility for any dispute arising in situations which are likely to be detected.

Sincerely yours,

01/03/2018

Name and Surname: Karwan Moffaq ABDULAZIZ

Student ID#:149101249

Science:Chemical Engineering

Program: Chemical Engineering

Statute:M. Sc.☒ Ph.D.☐

APPROVAL OF SUPERVISOR
SUITABLE

Assoc. Prof. Dr. Suna Orcun MERT

APPROVAL OF THE INSTITUTE
SUITABLE

PROF. DR. ŞENSOY
Enstitü Müdürü