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RESEARCH ARTICLE

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THE OCTANE NUMBER OF GASOLINE IMPROVED BY BLENDING GASOLINE WITH SELECTIVE COMPONENTS

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ABSTRACT

The main objective of this project was preparation of premium gasoline, by blending of different gasoline cuts produced in Mathura Refinery. Alternative additives were prepared from blending of some selective components (alcohol, aromatic) to enhancing octane number of Mathura gasoline pool. Various petroleum streams were investigated including Light Straight Run Naphtha (LSRN), Reformate, and Power Formate, and tested by ASTM standard methods, such as RVP, Distillation temperatures, Sulfur content, Water content, Gum existent, PONA content, and octane number measuring by CFR engine and ZX analyzer.

Gasoline pool was prepared by blending 30% vol LSRN, 45% vol Reformate, and 25% vol Power Formate, RON was recorded (84.5). Selective components were added to the gasoline pool (in different vol %) to improving it octane, such as Ethanol, Methanol, Toluene, Benzene, Xylene, Aniline ...etc. Octane number of blends was measured by CFR engine. .

KEY WORDS: Gasoline Pool, Premium Gasoline, Gasoline cuts ,Octane Number, LSRN, Power Formate , PONA Contents, CFR Engine.

1. INTRODUCTION

Gasoline is a volatile, flammable liquid obtained from the refinement of petroleum, or crude oil. It was originally discarded as a byproduct of kerosene production, but its ability to vaporize at low temperatures made it a useful fuel for many machines.

Gasoline or petrol is a fuel, derived from petroleum crude oil, for use in spark-ignited internal combustion engines. Conventional gasoline is mostly a blended mixture of more than 200 different hydrocarbon liquids ranging from those containing 4 carbon atoms to those containing 11 or 12 carbon atoms. Gasoline is used primarily as fuel for the internal combustion engines in automotive vehicles as well in some small airplanes. Gasoline are primarily divided between regular and premium and in many countries in three types according to the different octane number.

Gasoline come primarily from petroleum cuts with a range of boiling points from 38 to 150-205oC and they are usually blended with components to promote anti-knocking (higher octane), ease of starting, low tendency to vapour lock, etc. Many of these gasoline types are obtained through proper blending of light straight run gasoline, catalytic reformate, catalytically cracked gasoline, hydro-cracked gasoline, alkylate and n-butane. With the elimination of lead from the gasoline pool, refiners now rely on oxygenates like Methyl Tertiary Butyl Ether(MTBE), Ethyl Tertiary Butyl Ether(ETBE), Tetra Amyl Methyl Ether(TAME), Di Methyl Ether (DME), Methanol, and Ethanol, to increase octane of the gasoline pool to achieve acceptable octane levels.

2. *GASOLINE PRODUCTION FROM PETROLEUM CRUDE OIL*

Gasoline and other end-products are produced from petroleum crude oil in petroleum refineries. For a number of reasons it is very difficult to quantify the amount of gasoline produced by refining a given amount of crude oil:

There are quite literally hundreds of different crude oil sources worldwide and each crude oil has its own unique mixture of thousands of hydrocarbons and other materials.

* There are also hundreds of crude oil refineries worldwide and each of them is designed to process a specific crude oil or a specific set of crude oils. Furthermore, each refinery has its own unique configuration of petroleum refining processes that produces its own unique set of gasoline blend components. Some crude oils have a higher proportion of hydrocarbons with very high boiling points than other crude oils and therefore require more complex refinery configurations to produce lower boiling point hydrocarbons that are usable in gasolines.

* There are a great many different gasoline specifications that have been mandated by various local, state or national governmental agencies.

* In many geographical areas, the amount of gasoline produced during the summer season (i.e., the season of the greatest demand for automotive gasoline) varies significantly from the amount produced during the winter season.

3. GASOLINE BLENDING

Streams of gasoline blending are refined from petroleum, or crude oil, an extremely complex substance. The hydrocarbon molecules in crude oil may include from one to 50 or more carbon atoms. At room temperature, hydrocarbons containing one to four carbon atoms are gases, those with five to 19 carbon atoms are usually liquids, and those with 40 or more carbon atoms are typically solids.

Figure below shows the typical carbon chain lengths found in the proposed HPV test plans and demonstrates the overlap that occurs.

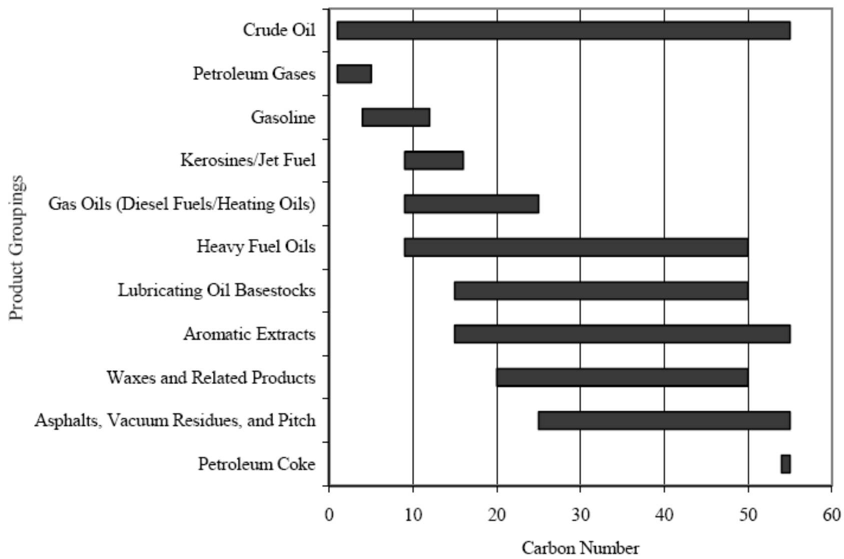


Fig. Typical carbon Chain lengths

Petroleum refining was distillation as well as chemical treatment. Catalysts and pressure are used to separate and combine the basic types of hydrocarbon molecules into petroleum streams which have the characteristics needed for blending commercial petroleum products. However streams used in the blending of gasoline must generally fall in a boiling rang -20 to 230PoPC. Gasoline are blended from several petroleum refinery process streams that are derived by the following methods:

Direct distillation of crude oil,

Catalytic and Thermal cracking,

- Hydrocracking,
- Catalytic reforming,
- Alkylation, and
- Polymerization

START UP PROCEDURE

Hydrocracking, which consists of cracking in the presence of added hydrogen, permits wide variations in yields of gasoline and furnace oils to meet seasonal demand changes and can effectively process hand to crack stocks. However since hydrocracked stocks lack the high octane olefins present in catalytically cracked stocks, they must be reformed .

Reforming process convert low octane gasoline range hydrocarbons into higher octane ones. Thermal reforming has been almost completely replaced by catalytic reforming. Most reforming catalysts are bimetallic catalysts consisting of platinum with another promoting metal, such as rhenium .

Alkylation converts refinery gases into gasoline range liquids of exceptionally high antiknock quality. However, the process is costly and is not commonly used in gasoline production.

Polymerization combines two or more low molecular weight olefin gases into higher molecular weight olefin liquids suitable for gasoline blending or for use as chemical feed stocks. However, because olefin liquids have low antiknock quality and the reactants, olefin gases, are valuable chemical feed ,the polymerization process is no longer widely used to produce gasoline blend streams

4. SCOPE OF THE PRESENT WORK

The lead additives to gasoline are no longer used in many countries around the world. Many other countries are now phasing out the lead in gasoline. Although the lead fuel is still in use in Iraq, several plans are considered to phase out the lead. The use of oxygenates to replace the lead additives in gasoline is considered now as an option in Iraqi refineries. This current experimental study is aimed to help in understanding the effect of the most popular oxygenates on enhancing octane number of Mathura Refinery gasoline.

The main aim of this study is to provide gasoline blend which can be used without the need to modify the engine by two ways:

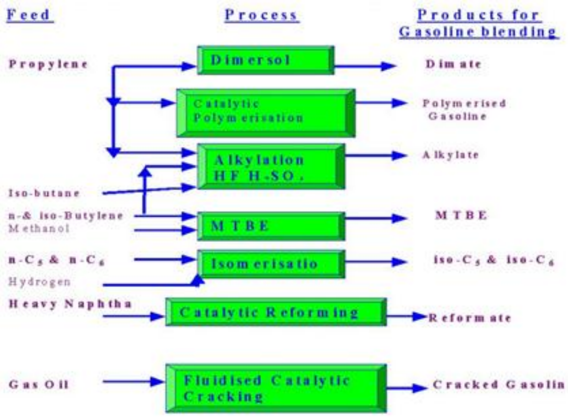
1. 1.Blending of petroleum cuts produced in Mathura Refinery to produce a desired octane rating.
2. Provide a compound or mixture of compounds which can be added to, or combined with, gasoline to produce high antiknock fuel mixture.

Another aim is measuring octane number by different methods, CFR engine and ZX analysis.

5. COMPONENTS OF GASOLINE BLENDING:

1. Catalytic Naphtha Reforming: It is Saturated ,by this low octane hydrocarbons converted into higher octane product containing about 60% aromatics.
2. Fluidized Catalytic Cracking (FCC): It breaks larger hydrocarbons into a product containing 30% aromatics and 20-30% olefins.
3. Isomerisation: By this straight chain HCs converted into branched isomers.
4. Alkylation: Due to alkylation gaseous olefins streams reacted with isobutene to produce liquid high octane iso-alkanes.

6. PRODUCTS FOR GASOLINE BLENDING:



7. GASOLINE ENGINE EMISSION

Automobiles powered by gasoline are a major source of air pollution because it contains lead alkyls, which are normally added to gasoline in order to increase its octane number and, thus, increase the performance of the engine. The intense search for an effective and economical octane boosting alternative to lead has continued. Generally, internal combustion engines produce moderately high pollution levels, due to incomplete combustion of carbonaceous fuel, leading to carbon monoxide and some soot along with oxides of nitrogen , sulfur and some unburnt hydrocarbons, depending on the operating conditions and the fuel/air ratio. The primary causes of this are the need to operate near the stoichiometric ratio for gasoline engines in order to achieve combustion (the fuel would burn more completely in excess air) and the quench of the flame by the relatively cool cylinder walls.

The major pollutants emitted include:

1- **Hydrocarbons**; this class is made up of unburned or partially burned fuel, as is a major contributor to urban smog as well as being toxic. They can cause liver damage and even cancer.

2- **Nitrogen Oxides** (NORxR); these are generated when nitrogen in the air reacts with oxygen under the high temperature and pressure conditions inside the engine. NOx emissions contribute to both smoke and acid rain.

3- **Carbon Monoxide** (CO); A product of incomplete combustion, carbon monoxide reduces the bloods ability to carry oxygen and is dangerous to people with heart disease.

4- **Carbon Dioxide** (COR2R); Emission of carbon dioxide are an increasing concern as its role in global warming as a greenhouse gas has because more apparent .

8.EXPERIMENTAL WORK

GASOLINE SPECIFICATION

Gasoline are usually defined by government regulation, where properties and test methods are clearly defined. In the US, several government and state bodies can specify gasoline properties, and they may choose to use or modify consensus minimum quality standards, such as American Society for Testing Materials (ASTM). The US gasoline specifications and test methods are listed in several readily available publications, including the Society of Automotive Engineers (SAE) , and the Annual Book of ASTM Standards.

Two units operated in Mathura Refinery to improving octane number of gasoline,

One is called Reformer unit, feed for this unit is a mixture of 30%LSRN and 70% HSRN, and the product is Reformate.

The other unit is Power Former, feed is HSRN and the product is Power Formate.

Table : Comparison between Power Former &Reformer Units in Mathura Refinery

	Reformer Unit	Power former Unit
Feed	30%LSRN+70%HSRN	HSRN
Catalyst	High purity of alumina balls impregnated by platinum and promoters	High purity of alumina balls impregnated by platinum and promoters
Catalyst bulk density kg/m3	960	752
Reactor Temprature 0C.	495-525	500-540
No. Of Reactors uses	3	5
Reactor pressure atm.	5-45	30
Catalyst Size and shape mm.	4.7*4.7	4.7*2.3

High purity of alumina balls impregnated by platinum and promoters .High purity of alumina balls impregnated by platinum and promoters.

Gasoline production in Mathura Refinery included many streams they are:-

• LSRN (RON =69.2).

• Reformate (RON= 90.5) (from Reforming a mixture of 30%LSRN and 70%HSRN).

• Power Formate (RON=89.3) (from Reforming HSRN).

All feeds and products of Reformer and Power Former units were tested by ASTM standard and IROX analyzer. ASTM standard methods which used for testing petroleum cuts in this project are:-

Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method) (D323)

Summary of Test Method

1. The liquid chamber of the vapor pressure apparatus is filled with the chilled sample and connected to the vapor chamber that has been heated to 37.8°C in a bath.

   The assembled apparatus is immersed in a bath at 37.8°C until a constant pressure is observed. The reading, suitably corrected, is reported as the Reid vapor pressure.
2. All procedures utilize liquid and vapor chambers of the same internal volume. Utilizes a semiautomatic apparatus immersed in a horizontal bath and rotated while attaining equilibrium. Either a Bourdon gauge or pressure transducer may be used with this procedure.

Fig : Vapor Pressure Apparatus in Mathura Refinery

9.PREPARATION GASOLINE POOL

Gasoline pool included 30%vol LSRN and 70%vol Reformate blend which content 45%vol Reformate and 25%vol Power Formate, the procedure to prepared 10L gasoline pool are as follow:

1- 3L of LSRN with 4.5L Reformate and 2.5L Power Former were blended in a container with stirring at refrigerator temperature, to reducing vaporize of volatile components.

2- Prepared gasoline pool was tested by ASTM stander and IROX analyzer, and then measured octane number by using CFR engine and ZX measurement.

10.ANTIKNOCK AGENTS

Antiknock additives are gasoline soluble chemicals mixed with gasoline to enhance octane number of gasoline. Typically, they are derived from petroleum based raw materials and their fractions, chemistry are highly specialized. Antiknock compounds increase the antiknock quality of gasoline, because the amount of additive needed is small, they are the lowest cost method for increasing octane number compared with changing gasoline chemistry P[25]P.

Selective components were used as antiknock agent to improve octane number of unleaded gasoline divided to many groups:-

1- Metallic.

2- Alcohols.

3- Aromatics. 4- Others.

The chemical and physical properties of selective components are listed in given table.

All selective components are added to the Mathura gasoline pool at different vol% as follow:

1- 300ml pool was prepared at refrigerator temp. in glass container had fitting cover.

2- Octane number of pool was measured by CFR engine.

3- Four glass container were filled with 300ml of pool and added one of selective components to these containers with shaking by using pipette in different concentrations.

4- Octane number of these blend were measured by CFR engine.

5- Repeat the 3 and 4 with another selective component.

Table : Physical and Chemical Properties of Selective Components

Components	Chemical Structure	Molecular weight	Density gm/cm3	**Boiling point oc**	Melting point oc	RON
TEL	$(CH_3CH_2)4Pb$	323.44	1.653	85	-136	
MMT	$C_9H_7MnO_3$	218.09	1.38	2.33	-1	
Tert-Butanol	(CH3)3COH	74.12	O.789	82.3	25.5	107
2_Methyl, 2_Butanol	$C_5H_{12}O$	88.15	0.806	102	-8.1	
3_Methyl, 1_Butanol	$C_5H_{12}O$	88.15	0.809	128.5	-----	
1_Butanol	C_4H_9-OH	74.12	0.810	117.2	-89.5	96
2_Butanol	C_4H_9-OH	74.12	0.807	99.5	-------	
Methanol	CH_3OH	32.04	0.791	65	-93.9	113
Ethanol	C_2H_5OH	46.07	0.789	78.5	-117.3	116
Iso-propanol	C_3H_7OH	60.11	0.804	97.4	-126.5	118
Xylene	$C_6H_4(OH_3)_2$	106.17	0.861	138.3	13.3	117
Benzene	C_6H_6	78.12	0.877	80.1	5.5	101
Toluene	$C_6H_5CH_3$	92.15	0.867	110.6	-95	114
Aniline	$C_3H_5NH_2$	93.13	1.022	184	-6.3	
Acetone	C_3H_60	58.08	0.790	56.2	-95.4	
N_N_Dimethyl Aniline	$C_2H_{11}N$	121.18	0.956	194.8	2.5	
Ethyl Methyl Ketone	$(CH_3)_2CH_2O$	72.12	0.805	79.6	-86	
2_2_4 Trimethyl pentane	C_8H_{18}	98.19	0.695	83.4	-127.7	100
Isopropyl Ether	$(CH_3)_4(CH)_2OH$	102.18	0.724	68	-85.9	
Diethyl Ether	$(C_2H_5)_2O$	74.12	0.714	34.3	-116.2	

11.RESULT AND DISCUSSION

PREPARED GASOLINE POOL

Gasoline pool was obtained from the following petroleum cuts:-

- LSRN (716m3
- Reformate (1224m/D).
- Power Formate (670m/D).

The percentage of each cut was determined:- /D).

716+1224+670=2610 m^3

LSRN= (716/2610)*100=27.4% /D total

Reformate= (1224/2610)*100=46.9%

Power Formate= (670/2610)*100=25.7 %

Prepared pool was included mixing of 30%LSRN with 70%Reformate blend, RON measuring (84.5) and expected RON (84.8) as shown in table (4-1). Reformate blend was formed from 25%Power Formate (Reforming of HSRN) and 45%Reformate (Reforming of (30%LSRN and 70% HSRN)).

Expected RON was calculated by equation (4-1).

Bt (RON)t=Σ Bi(RON)i............................ (4-1)

Where:

Bt; total gasoline blended.

(RON)t: desired octane number of blend.

(RON)i: blending octane number of component i.

Bi: vol% of component i.

100(RON)t=30*69.2+45*90.5+25*89.3

(RON)t = 8480/100 =84.8

Table :Preparation Gasoline Pool Formulation

Component	RON	Vol%	Expected RON
LSRN	69.2	30	20.8
Reformer	90.5	45	40.7

Power Formate	89.3	25	23.3
Total		100	84.8

Octane Number Measurement

Octane number was measured for petroleum cuts, prepared pool (unleaded gasoline), leaded gasoline, and commercial gasoline (Irani gasoline) by CFR engine and ZX measurement.

Octane number increased with increasing aromatics and paraffins branches, for this octane number of Reformate and Power Formate was larger than for LSRN and HSRN, because in the catalytic reforming of HSRN many chemical reactions occur, such as convertion of naphthenes to aromatics and paraffins to naphthenes and isoparaffins, or in other words catalytic reforming increase aromatics and isoparaffins content.

The ZX octane analyzer provides CFR engine accuracy with the new vital features of speed and portability.

CONCLUSIONS

Based on the previously discussed analyses, the following conclusions may be drawn.

- Preparation gasoline pool (RON=84.5) include 30%vol LSRN,45%vol Reformate, and 25%vol Power Formate.
- The experimental results of this project for three RON measuring methods showed that ZX was fast, acuurecy, and reliable analysis of gasoline.
- All selective chemical components act positively to improved octane number of Al Doura Refinery pool, except Diethyl Ether had negative effect.
- The Octane Booster of this project was Aniline, which was recorded the largest RON.
- Eleven preparation component mixtures were prepared from active selective components; include alcohol, and aromatic group.
- The best four preparation component mixtures (E10, E11, E9, and E6) are better act with high octane gasoline than less (LSRN).
- (E10) is the best prepared component mixtures, and act better with preparation pool than two sample used. However, there is still a need to generate data and experience by running tests and analyzing the environmental effects of blending gasoline.
- Thus the need to apply the precautionary principle to any gasoline blending component, and insist on a thorough evaluation of implications of such a decision. We must be much more certain of the toxicity, persistence and bioaccumulation of gasoline blending components, since it is given that these chemicals will be used in large amounts throughout the world[61] .

SUGGESTIONS

Following suggestion are put forward for future work:

- Measuring evaporative emissions from the combustion of different blends of preparation gasoline pool with prepared component mixtures and without.
- Blended distillation fractions of Mathura Refinery petroleum cuts to producing premium gasoline.
- Study analysis of all Mathura petroleum cuts and their fractions via GC analyzer to enhancement gasoline.

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