

Physical Properties Changes Accompanies Treating Gasoline Fraction of Petroleum with Synthetic Zeolite

Mutaz Mohamed Ahmed Elshiekh¹, Nazar Abdulaziz Elnasri²

¹Department of Chemistry, Faculty of Science and Technology, Ahfad University, Omdurman, Sudan

²Department of Chemistry, Faculty of Engineering, Sudan International University, Khartoum, Sudan

Email address:

elshiekhmutaz@gmail.com (M. M. A. Elshiekh), nazarelnasri@gmail.com (N. A. Elnasri)

To cite this article:

Mutaz Mohamed Ahmed Elshiekh, Nazar Abdulaziz Elnasri. Physical Properties Changes Accompanies Treating Gasoline Fraction of Petroleum with Synthetic Zeolite. *International Journal of Bioorganic Chemistry*. Vol. 2, No. 4, 2017, pp. 180-184.

doi: 10.11648/j.ijbc.20170204.14

Received: August 20, 2017; Accepted: September 7, 2017; Published: November 30, 2017

Abstract: The main aim of this work is to study the physical changes in the gasoline portion of the Sudanese petroleum upon treating with synthetic zeolite. Treating gasoline with zeolites usually performed in order to enhance the octane number of the oil. The octane number measures the degree of the gasoline resist to self-ignition prior to combustion. Gasoline with higher octane number has higher tendency to resist self-ignition. Gasoline containing branched and aromatic hydrocarbons resists self-ignition rather than gasoline containing straight chain hydrocarbons. 2,2,4 trimethyl pentane name disooctane (has octane number 100) and n-heptane (has octane number 0) are used to measure the octane number of the oil under the test. Zeolites are frame work of tetrahedral silicates (TO₄), with a net negative charge balanced by a positive cation. Zeolite/Li indicating that the Li cation is used to neutralized the frame work. Zeolite/refinery refers to an industrial zeolite brought from Sudanese Petroleum Company. The gasoline portion used before treatment with any zeolites is considered to be a standard and is called a blank. Physical properties (distillation, density, S.G@150C, Reid vapor pressure and the degree of corrosion) were carried out for the blank, the mixture of zeolite/Li with the gasoline and the mixture of zeolite/refinery with the gasoline. The density of the gasoline after treatment with zeolite/Li was found to be higher than the density of the blank. The Reid vapor pressure of the gasoline after treatment with zeolite/Li was found to be lower than the Reid vapor pressure of the blank. The distillate properties (the initial boiling point IBP and the final boiling point FBP) for the blank, gasoline after treatment with zeolite/Li and zeolite/refinery were not found to change considerably. The blank and the blank after treatment with zeolite/refinery were found to possess the same degree of corrosion (1b) which is the slightly corrosive whereas the blank after treatment with zeolite/Li has a (2c) degree which is moderate corrosive.

Keywords: Zeolite, Blank, IBP (Initial Boiling Point), FBP (Final Boiling Point), Reid Vapor Pressure, Corrosion, A. S. T. M. (American Standard Test for Materials)

1. Introduction

1.1. Gasoline

Crude oil is a mixture of hydrocarbons that exists in liquid phase in natural underground reservoirs and remains liquid at atmospheric pressure after passing through surface separating facilities. [1].

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 It has an initial boiling point at atmospheric pressure of about 35°C (95°F) and a final boiling point of about 200°C (395°F) [2].

1.2. Reforming

Reforming is a process which uses heat, pressure and a catalyst (usually containing platinum) to bring about chemical reactions which upgrade naphthas into high octane petrol and petrochemical feedstock. The naphthas are hydrocarbon mixtures containing many paraffins and

naphthenes, this naphtha feedstock comes from the crudes oil distillation or catalytic cracking processes, but it also comes from thermal cracking and hydro cracking processes. Reforming converts a portion of these compounds to isoparaffins and aromatics, which are used to blend higher octane petrol.

1. Paraffins are converted to isoparaffins.
2. Paraffins are converted to naphthenes.
3. Naphthenes are converted to aromatics.

1.3. Hydrotreating and Sulphur Plants

A number of contaminants are found in crude oil. As the fractions travel through the refinery processing units, the impurities can damage the equipment, the catalysts and the quality of the products. There are also legal limits on the contents of some impurities, like sulphur, in products. Hydrotreating is one way of removing many of the contaminants from many of the intermediate or final products. Hydrogen combines with sulphur to form hydrogen sulphide (H_2S). Nitrogen compounds are converted to ammonia. Metals contained in the oil are deposited on the catalyst. Some of the olefins, aromatics or naphthenes become saturated with hydrogen to become paraffins and some cracking takes place, causing the creation of some methane, ethane, propane and butanes. [3]

1.4. The Zeolite Group of Minerals

Zeolites are a large group of natural and synthetic hydrated aluminum silicates. The frame work of which is consisting of interlocking tetrahedrons of SiO_4 and AlO_4 . In order for aluminium silicate to be a zeolite the ratio $(Si+Al)/O$ must equal $1/2$. The aluminum-silicate ture is negatively charged and attracts the positive cations that reside with in. They are characterized by complex three-dimensional structures with large, cage like cavities that can accommodate sodium, calcium, or other cations (positively charged atoms or atomic clusters); water molecules; and even small organic molecules.

1.5. Faujasite Zeolite Y

Zeolite Y exhibits the FAU (faujasite) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes, and is made of secondary building units. The pore diameter is large at 7.4 Å. The first zeolite with a tridirectional extra-large 14-ring pore system derived using a phosponium-based organic molecule [4]

1.6. Uses of Zeolite

Because of their ability to interact with organic molecules, zeolites are important in refining and purifying natural gas and petroleum chemicals. Thezeolites are not affected by these processes, so they are acting as catalysts. Zeolites are used to help breakdown large organic molecules found in petroleum into the smaller molecules that make up gasoline, a process called catalytic cracking. [5]

1.7. The Octane Rating

Octane rating number is defined as a value used to indicate the resistance of a motor fuel to knock. Octane numbers are based on a scale on which isooctane is 100 (minimal knock) and heptanes is 0 (bad knock). A gasoline with an octane number of 92 has the same knock as a mixture of 92% isooctane and 8% heptane. Lead in the form of tetraethyl lead was once a common additive. The selection of n-heptane as zero point in the scale due to it' s availability and purity. [6]

2. Method

2.1. Zeolite/X Preparation: [7]

Clay: K Feldspar: Na_2CO_3 : X Cln were mixed well with the ratio 2:2:2:1 by weight respectively. The mixture was then crushed to affine powder and transferred to an oven and ignited at a temperature of 1200°C for 6 hours. The product was then allowed to cool gently and collected for further use.

2.2. Mixing Zeolite with Gasoline Fraction

25 grams of the zeolite was mixed with 500 ml of the blank gasoline fraction. The mixture was boiled gently and allowed to stand overnight. The product was then filtered, collected and subjected to further analysis.

2.3. Atmospheric Distillation of Petroleum Products [8]

The specimen precisely was poured to the 100-mL mark of the receiving cylinder, and the contents of the receiving cylinder was transferred as completely as practical into the distillation flask. The temperature sensor was fitted through a fitting device, centered in the neck of the inner wall of the vapor tube. The flask vapor tube, provided rubber stopper of silicone, was fitted tightly into the condenser tube. The receiving cylinder was placed.

The distillation was started with the tip of the deflector just touching the wall of the receiving cylinder. The start time was noted, and the IBP was observed and recorded to the nearest 0.5°C.

In the interval between the IBP and the end of the distillation, data (temperature readings at prescribed percentages recovered or percentages recovered at prescribed temperature readings, or both) necessary for the calculation was observed and recorded. The volume in the receiving cylinder was measured accurately, and recorded to the nearest 0.5ml as percent recovery. After the flask has cooled and no more vapor is observed, the flask was disconnected from the condenser, its contents was poured into a 5-mL graduated cylinder, and allowed to drain, until no appreciable increase in the volume of liquid in the cylinder is observed. The volume was measured in the graduated cylinder to the nearest 0.1ml, and recorded as percent residue.

2.4. Standard Test Method for Density, Relative Density (Specific Gravity), or API Gravity [9]

The sample was transferred to the clean, temperature stabilized hydrometer cylinder. The cylinder containing the test portion was placed in a vertical position in a location free from air currents and where the temperature of the surrounding medium does not change more than 2°C during the time taken to complete the test. The appropriate thermometer or temperature measurement device was inserted and the test portion was stirred with a stirring rod, using a combination of vertical and rotational motions to ensure uniform temperature and density throughout. The temperature of the sample was recorded to the nearest 0.1°C and the thermometer/temperature measuring device and stirring rod were removed from the hydrometer cylinder. The appropriate hydrometer was lowered into the liquid. The meniscus shape was observed when the hydrometer is pressed below the point of equilibrium about 1 to 2 mm and allowed to return to equilibrium. Experiment was repeated until the meniscus shape remains constant. Air bubbles were removed and the hydrometer scale was read to the nearest one-fifth of a full scale division.

Immediately after recording the hydrometer scale reading, carefully the hydrometer was lifted out of the liquid, the thermometer or temperature measurement device was inserted and the test portion was stirred

Vertically with the stirring rod. The temperature of the test portion was recorded to the nearest 0.1°C. The corrected hydrometer scale reading was converted to density, relative density or API gravity.

2.5. Standard Test Method for Vapor Pressure of Petroleum Products [10]

The liquid chamber of the vapor pressure apparatus was filled with the chilled sample and connected to the vapor chamber that has been heated to 37.8°C (100°F) in a bath. The assembled apparatus was immersed in a bath at 37.8°C (100°F) until a constant pressure is observed. The reading, suitably corrected, is reported as the Reid vapor pressure.

The sample was removed from the cooling bath, uncapped, and the chilled transfer tube was inserted. The liquid chamber was removed from the cooling bath and placed in an inverted position over the top of the transfer tube. The entire system was inverted rapidly so that the liquid chamber is upright with the end of the transfer tube approximately 6mm (0.25in.) from the bottom of the liquid chamber. The transfer tube was removed from the liquid chamber while allowing the sample to continue flowing up. The vapor chamber was immediately removed from the water bath and coupled with the filled liquid as quickly as possible without spillage. The assembled apparatus was turned upside down and allowed the entire sample in the liquid chamber to drain in to the vapor chamber. The apparatus was shaken vigorously eight times up and down. The assembled apparatus was immersed

in the bath, maintained at 37.8±0.1°C (100±0.2°F), in an inclined position so that the connection of the liquid and vapor chambers is below the water level. After the assembled apparatus has been in the water bath for at least 5min, the pressure gage was tapped lightly and the reading was observed. The apparatus was withdrawn from the bath and the above procedure was repeated at intervals of not less than 2min, until the last two consecutive gage readings are the same. The final gage pressure was read to the nearest 0.25kPa (0.05psi) and recorded as the uncorrected vapor pressure of the sample. Without undue delay, the pressure gage was removed from the apparatus, its reading was checked. The difference observed between the pressure measuring device and the pressure gage readings, was added to the uncorrected vapor pressure and the resulting value recorded as the Reid vapor pressure of the sample.

2.6. Standard Test Method for Corrosiveness [11]

30 ml of sample, completely clear and free of any suspended or entrained water was placed into a chemically clean and dry 25-mm by 150-mm test tube. Within 1min after completing the final preparation (polishing), the copper strip was slid into the sample tube. Immediately the strip was removed with forceps and immersed in wash solvent. The withdrawn strip was dried and compared with the copper strip corrosion standards for inspection evidence of tarnishing or corrosion (see Table below).

Table 1. Distillation properties of blank gasoline, blank gasoline treated with zeolite/refinery and the blank gasoline treated with zeolite/Li.

Classification	Designation	Description	
1	Slight tarnish	a. Light orange b. dark orange	
2	Moderate tarnish	a. Claretred b. Lavender c. Multicolored d. Silvery e. Brassy or gold	
3	Darktarnish	a. Magentaonbrassystrip. b. Multicolored with red and green.	
4	Corrosion	a. Transparent black. b. Graphite c. jet black	
Property	Blank gasoline	Blank gasoline after treatment with Zeolite/ref	Blank gasoline after treatment with Zeolite/Li
IBP	43°C	48°C	47°C
10% Recovered	61°C	62°C	67°C
50% Recovered	102°C	104°C	107°C
90% Recovered	165°C	161°C	167°C
FBP	196°C	195°C	197°C
20% - 10%	0.9	10.00°C	0.9°C
Residue	1.2 ml	1.5 ml	1.4 ml
Recovery	97 ml	196.5 ml	197 ml

3. Results

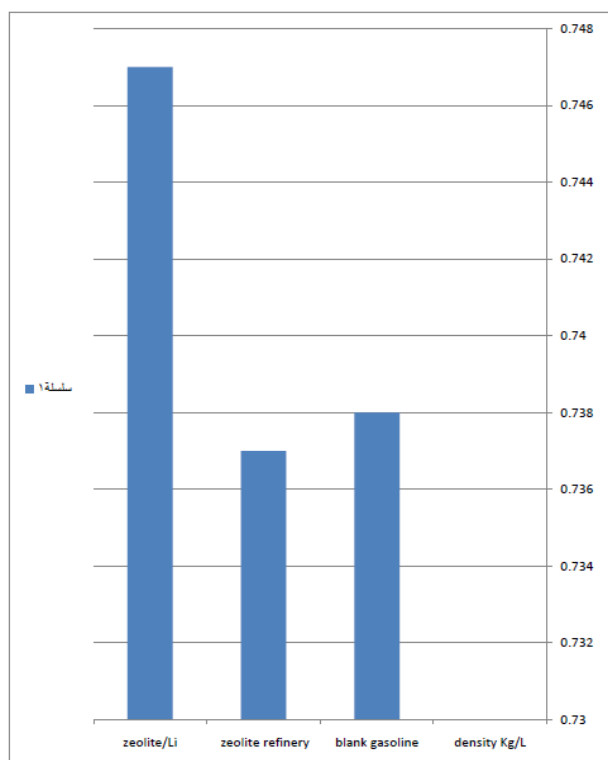


Figure 1. Density variation of blank gasoline, blank gasoline treated with zeolite/Li and blank gasoline treated with zeolite/refinery.

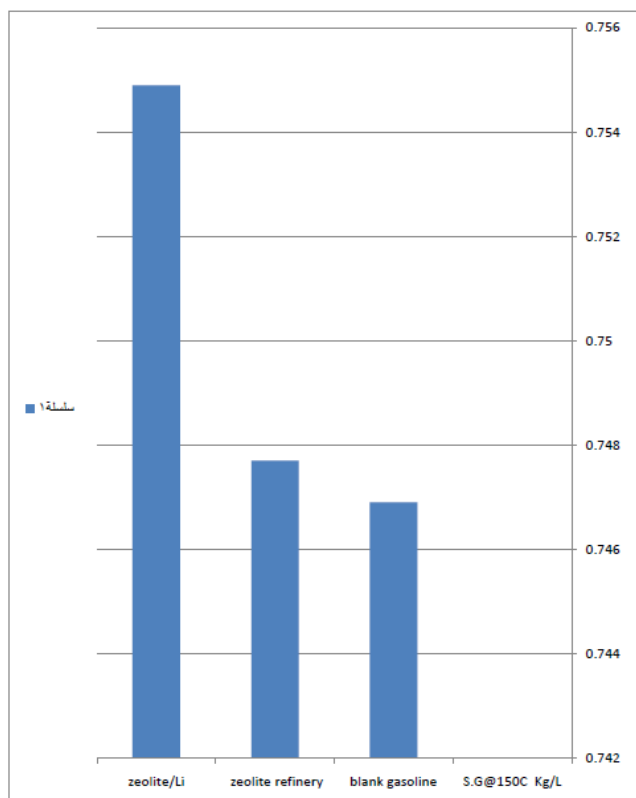


Figure 2. S.G.@15°C blank gasoline, blank gasoline after treatment with and zeolite/Li and blank gasoline after treatment with and zeolite/refinery.

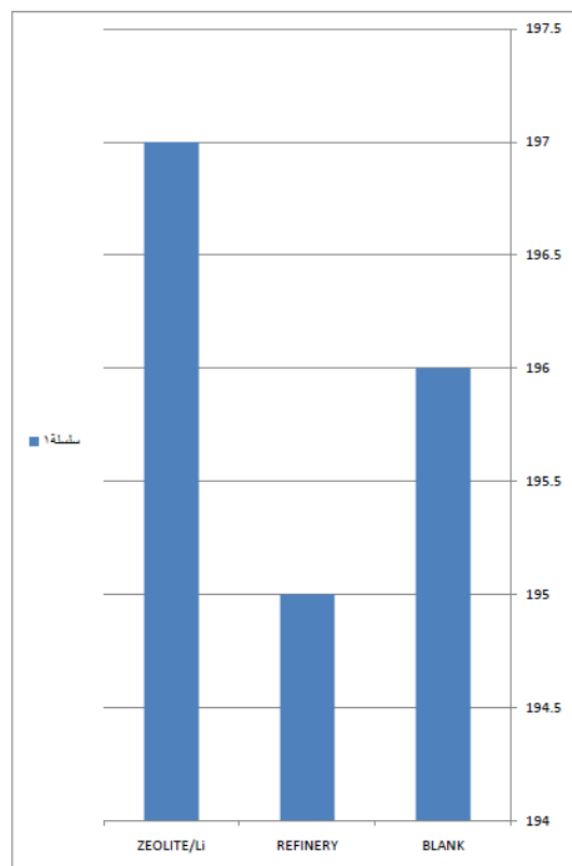


Figure 3. EP blank gasoline, blank gasoline after treatment with and zeolite/Li and blank gasoline after treatment with and zeolite/refinery.

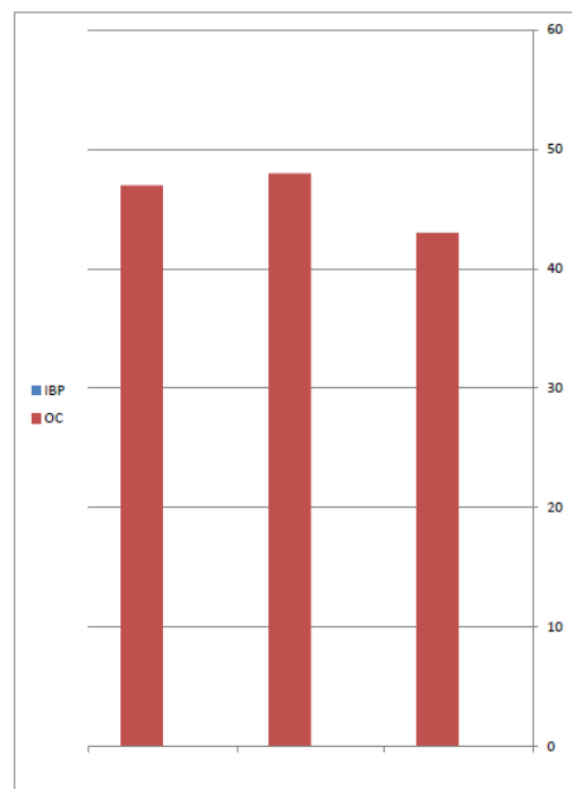


Figure 4. IBP blank gasoline, blank gasoline after treatment with and zeolite/Li and blank gasoline after treatment with and zeolite/refinery.

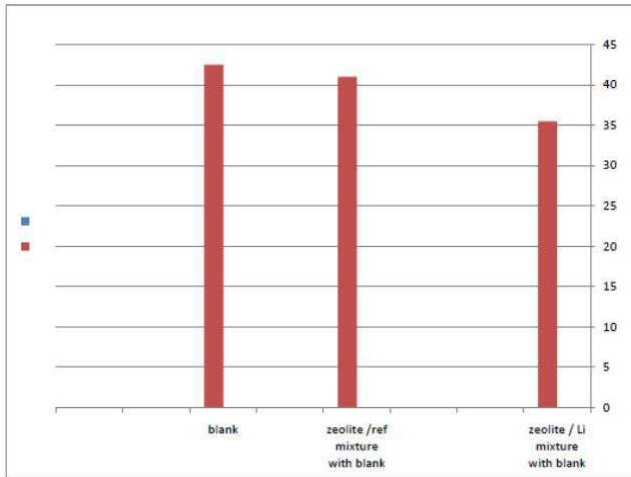


Figure 5. Reid vapor blank gasoline, blank gasoline after treatment with and zeolite/Li and blank gasoline after treatment with and zeolite/refinery.

4. Discussion

Concerning The density, it was found that the density of the blank gasoline treated with zeolite/Li increased considerably comparing with the blank and gasoline treated with zeolite/refinery mixture (Figure 1) and this is expected since the zeolites added to the gasoline act as a catalyst enhancing trans formation of the branched and aromatic hydrocarbons with higher masses and/or low volumes and consequently increasing the density. Increasing the density of the gasoline portion will lead to increase the combustion ratio of the oil which is a factor for enhancing the octane rating. The specific gravity $S.G@15^{\circ}C$, showed the same observation above that the blank gasoline treated with zeolite/Li has the highest value compared to that of the blank and blank gasoline treated with zeolite/refinery (Figure 2), and this could also be explained in terms of the alkylation and aromatization rearrangements mentioned above.

The distillate properties for blank gasoline treated with zeolite/Li and the blank gasoline treated with zeolite/refinery were not found to change considerably compared with the blank gasoline that is the initial boiling points (IBP) for the blank, blank gasoline treated with zeolite/Li and the blank gasoline treated with zeolite/refinery were $43^{\circ}C$, $47^{\circ}C$ and $48^{\circ}C$ respectively where as the final boiling points (FBP) were $195^{\circ}C$, $197^{\circ}C$ and $196^{\circ}C$ respectively (Table 1, Figure 4 and Figure 3), and this is also expected and good since changing the distillates properties will lead to change the worm up time (initiating time) of the machine, which is a character affecting the gasoline/mixture compression step leading to change in the performance of the machine.

The vapor pressure of a gasoline is a measure of its propensity to evaporate. The reid vapor pressure of the blank gasoline treated with zeolite/Li decreased compared to the blank and blank gasoline treated with zeolite/refinery (Figure

5), and also this a good result since high vapor pressure is undesirable concerning vapor lock the machine.

The corrosion of the machine caused by the gasoline is detected by copper strip corrosion test. The blank and the zeolite/refinery have the same degree of corrosion (1b) which is the slightly corrosive. Zeolite/Li has a (2c) degree which is the moderate corrosive, and this is expected since the zeolite/Li gasoline mixture is made in our laboratories without addition of any other additives to suppress the content of the sulphur.

5. Conclusion

Mixing zeolite with certain elements and cations and treating the gasoline oil petroleum fraction with the mixture leads to better oil quality concerning the octane number enhancement. Comparing the physical properties, the blank gasoline, the gasoline fraction treated with zeolite/Li and the gasoline fraction treated with zeolite/refinery showed a considerable variations in terms of ignition properties and the degree of corrosiveness. Treatment of the gasoline fraction with zeolite/Li was found to be the best choice among the other available cations in order to produce gasoline fraction with better ignition properties.

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