Characterization of Sudanese reformat gasoline blended with acetone

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Abstract : Sudanese reformat gasoline (produced in Khartoum refinery located in Algily, at North of Khartoum city in Sudan) was characterized before and after the addition of acetone. Samples were tested according to the American Society for Testing and Materials (ASTM), in which the properties distillation, sulfur content, density, vapor pressure, oxidation stability, copper strip corrosion, gum existence, lead content, and octane number of the reformate gasoline (before and after addition of acetone) were characterized.

The addition of acetone (5 and 10% (v/v)) improved the properties of the Sudanese reformat gasoline to the limits assigned by (ASTM) and Khartoum refinery.

The Motor Octane Number (MON) of the reformat gasoline was determined initially by the Cooperative Fuels Research engine (CFRengine (which was found 88.5. Results showed that the addition of acetone 5 and 10 % (v/v) to the Sudanese reformat gasoline raise the value of the (MON) to 89.6 and 92 respectively.

Keywords : Sudanese reformat gasoline, Characterization, Acetone, Motor octane number.

Introduction

Additives and blending agents are added to the hydrocarbon mixture to improve the performance and stability of gasoline [1]. These compounds include anti-knock agents, anti-oxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes [2].

Environmental friendly additives which include diethylamine, di isopropyl ether,moringa oil, acetone and manyothers are gasoline soluble chemicals that mixed with reformate gasoline to enhance octane number of gasoline. Typically, they are derived from petroleum based raw materials and their fractions, chemistry are highly specialized.

Octane number (ON) is one of the most important properties of gasoline streams and is a measure of its antiknock property. It is defined as the volume percentage of iso- octane in a blend of n - heptane and iso-octane, which produces the same knock intensity as the test fuel under standard test conditions in an ASTM internal combustion engine. [3]. ON is a direct function of the molecular composition of the gasoline fuel, and any modeling effort should explicitly acknowledge it [4]. Ezeldin and Massad, found that the addition of di isopropyl ether and moringa oil improve the quality of Sudanese gasoline and increase its motor octane number (MON) [5]. Ezeldin .etal, also found that when diethylamine was added with different concentrations (5 and 10% (v/v) to the Sudanese gasoline the (MON) raised from 88.5 to 92.5and 94.9, respectively [6].

Experimental

All chemicals used were of analytical reagent grade (AR) and of highest purity degree available. All solutions were prepared according to the usual analytical procedures.

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 and 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[6].

Standard test method for distillation of petroleum products at atmospheric pressure:

1. A 100 mL sample was placed in a round bottom flask and heated at a rate specified for samples with its vapor pressure characteristics. Temperatures were recorded when the first drop was collected(initial boiling point), at recorded volumes of 5 mL, 10 mL, every subsequent 10mL interval to 90 mL, 95 mL and at the end of the test(end point). For gasoline samples, the temperatures associated with each incremental volume percentage recovered were converted to temperatures for each incremental volume percentage evaporated by correcting for any sample loss during the test.
2. At the conclusion of the distillation, the observed vapor temperatures can be corrected for barometric pressure and the data were examined for conformance to procedural requirements, such as distillation rates. The test is repeated if any specified condition has not been met.
3. Test results were commonly expressed as percent evaporated or percent recovered versus corresponding temperature, either in a table or graphically, as a plot of the distillation curve [7].Results are shown in table (1).

Standard test method for determination of the density of petroleum products:

A small volume (approximately 0.7 mL) of liquid sample was introduced into an oscillating sample tube and the change in oscillating frequency caused by the change in the mass of the tube was used in conjunction with calibration data to determine the density of the sample[7].Results are shown in table (1).

Standard test method for vapor pressure determination of petroleum products:

The chilled sample cup of the automatic vapor pressure instrument was filled with chilled sample and was coupled to the instrument inlet fitting. The sample was then automatically forced from the sample chamber to the expansion chamber where it is held until thermal equilibrium at 37.8°C (100°F) is reached. In this process the sample is expanded to five times its volume (4:1 vapour – to - liquid ratio). The vapour pressure was measured by a pressure transducer. The measured vapor pressure was automatically converted to a DVPE value by the instrument. A correction to this value is necessary to account for the observed bias between the test result and that obtained by Test Method D 4953. Where: DVPE=(0.954 X)+ A

X = measured total vapor pressure, in units consistent with A, andA = 1.94 kPa (0.281 psi),[7].Results are shown in table (1).

Standard test method for determination of gum content in fuels by jet evaporation:

A measured quantity of fuel was evaporated under controlled conditions of temperature and flow of air or steam. For aviation gasoline and aviation turbine fuel, the resulting residue was weighed and reported as milligrams per 100 mL. For motor gasoline, the residue was weighed before and after extracting with heptane and the results reported as milligrams per 100 mL.according to the following equation:

Wight of Gum = weight of (beaker gum) - (beaker plank) $\div$ 2000where 2000 = factor, [7].

Standard test method for copper strip corrosion:

A polished copper strip was immersed in a given quantity of sample and heated at a temperature (200°C) and for a time(2 hours) characteristic of the material being tested. At the end of this period the copper strip is removed, washed, and compared with the ASTM copper strip corrosion standards shown in the figure below[7].Results are shown in table (1).

1a	1b	2a	2b	2c	2d	2e	3a	3b	4a	4b	4c
Slight tarnish		Moderate tarnish					Dark tarnish		Corrosion		

Standard test method for determination of the motor octane number (MON):

The Motor ON of a spark-ignition engine fuel was determined using a standard test engine and operating conditions to compare its knock characteristic with those of PRF blends of known octane number. Compression ratio and fuel-air ratio were adjusted to produce standard knock intensity for the sample fuel, as measured by a specific electronic detonation meter instrument system. A standard knock intensity guide table relates engine compression ratio to octane number level for this specific method. The fuel-air ratio for the sample fuel and each of the primary reference fuel blends was adjusted to maximize knock intensity for each fuel.

The fuel-air ratio for maximum knock intensity may be obtained (1) by making incremental step changes in mixture strength, observing the equilibrium K.I. value for each step, and then selecting the condition which maximizes the reading or (2) by picking the maximum knock intensity as the mixture strength is changed from either rich-to-lean or lean-to-rich at a constant rate.

Bracketing Procedures—the engine is calibrated to operate at standard knock intensity in accordance with the guide table. The fuel-air ratio of the sample fuel is adjusted to maximize the knock intensity, and then the cylinder height is adjusted so that standard knock intensity is achieved. Without changing cylinder height, two primary reference fuels are selected such that, at their fuel-air ratio for maximum knock intensity, one knocks harder (higher K.I.) and the other softer (lower K.I.) than the sample fuel. A second set of K.I. measurements for sample fuel and reference fuels is required, and the sample fuel octane number is calculated by interpolation in proportion to the differences in average knock intensity readings, a final condition requires that the cylinder height used shall be within prescribed limits around the guide table value for the calculated octane number. Bracketing procedure ratings may be determined using either the equilibrium fuel level or dynamic fuel level approach. Compression Ratio Procedure—A calibration is performed to establish standard knock intensity using the cylinder height specified by the guide table for the octane number of the selected primary reference fuel. The fuel-air ratio of the sample fuel is adjusted to maximize the knock intensity under equilibrium conditions; the cylinder height is adjusted so that standard knock intensity is achieved. The calibration is reconfirmed and the sample fuel rating is repeated to establish the proper conditions a second time. The average cylinder height reading for the sample fuel, compensated for barometric pressure, is converted directly to octane number using the guide table.

A final condition for the rating requires that the sample fuel octane number be within prescribed limits around that of the octane number of the single primary reference blend used to calibrate the engine to the guide table standard knock intensity condition[7].Results are shown in table (1).

Determination of lead concentration in gasoline by atomic absorption spectrophotometer method:

a:Preparation of sample

In a 100 mL volumetric flask 30 mL of methyl Isoketone and 5 mL of a buffer solution were taken ,then 0.1g of iodine and 5 mL of gasoline were transferred to the solution , finely the solution was completed to the mark with iso butyl ketone [7].

b:Preparation of the standard lead (II) solution

0.5, 1.0 and 2.0 ppm of lead(II) solutions were prepared by dissolving known weight of Pb (II) in known volume of deionized water.

C: Blank of the instrument

The device was blanked with deionized water and then the sample was injected into the device where a process of atomization of lead in gasoline takes place(in the path of the light from the bulb short)and the device read the amount of lead directly[8].Results are shown in table (1).

Standard test method for oxidation stability of fuels:

The sample was oxidized in a pressure vessel initially filled at 15 to 25°C with oxygen pressure at 690 to 705 KPa and then heated at a temperature between 98 and 102°C. The pressure was recorded continuously or read at stated intervals until the breakpoint was reached. The time required for the sample to reach this point is the observed induction period at the temperature of test, from which the induction period at 100°C can be calculated by one of the following equations:

1. When the test temperature is above 100°C: Induction period at 100°C, min = (IPt) (1 + 0.10) (t a − 100)
2. When the test temperature is below 100°C: Induction period at 100°C, min =(IP t)/(1 + 0.101)(100 − tb)

Where:

IPt = induction period, min, at the temperature of the test,

t_a = test temperature when above 100°C, °C, and

t_b = test temperature when below 100°C[7].

Results are shown in table (1).

Standard test method for determination of sulfur content in gasoline by energy dispersive X-ray fluorescence spectrometry:

The sample was placed in the beam emitted from an X-ray source. The resultant excited characteristic X radiation was measured, and the accumulated count was compared with counts from previously prepared calibration standards to obtain the sulfur concentration in mg/kg. One group of calibration standards was required to span the concentration 5 to 1000 mg/kg sulfur [7].Results are shown in table (1).

The effect of adding different concentrations of acetone to Sudanese reformat gasoline:

Acetone as additive is gasoline soluble chemicals which mixed with reformat gasoline to enhance its octane number. Acetone was added to the reformat gasoline at different concentrations 5% and 10% (v/v) as follow:

a. A 1000 ml of reformat gasoline was prepared at refrigerator temp. and transferred to glass container had fitting cover.
b. The octane number of gasoline was measured by CFR engine, and all physicochemical properties of gasoline were also detected before the addition of acetone.
c. Two glass container were filled with 1000ml of reformat gasoline and by using a pipette acetone was added in different concentrations 5% and 10% (v/v) with shaking .
d. The octane number of these blends was measured by CFR engine, and all physicochemical properties were also detected after the addition of acetone.

Results are shown in table (1).

Results and discussion

Some physicochemical properties of Sudanese reformate gasoline were checked by applying many tests according to American Society for Testing and Materials (ASTM), which included distillation, density, vapor pressure, stability, copper strip corrosion, lead content, gum content, sulfur content and octane number.

The numerical values of these properties are outlined in table (1).

Table (1): Some physicochemical properties of Sudanese reformate gasoline before and after addition of acetone

1000 ml .R.G +100ml acetone		1000 ml .R.G + 50ml acetone		Reformate Gasoline (R.G) before addition of acetone		Test name
35.5^{O}C	Initial Boiling Point (IBP)	35.9^{O}C	Initial Boiling Point (IBP)	37.9^{O}C	Initial Boiling Point (IBP)	Distillation
52°C	10%	54.1^{O}C	10%	58.5^{O}C	10%	
89°C	50%	94.9^{O}C	50%	97.2^{O}C	50%	
155.3^{O}C	90%	158.3^{O}C	90%	159.0^{O}C	90%	
184°C	Final Boiling Point (FBP)	188.4^{O}C	Final Boiling Point (FBP)	190.5^{O}C	Final Boiling Point (FBP)	
687.6 k/m^3 (150°C)		701.1 k/m^3 (150°C)		736.4 k/m^3 (150°C)		Density
49.2KPa(37.8^{O}C)		51 KPa(37.8^{O}C)		52.5 KPa(37.8^{O}C)		Vapor pressure
0.95 mg/100ml		0.8 mg/100ml		0.8 mg/100ml		Gum content
1a		1a		1a		Copper corrosion
0.001 mg/L		0.001 mg/L		0.001 mg/L		Lead percentage
300 min		302 min		504 min		Oxidation stability
40 mg/L		49.3 mg/L		58.49 mg/L		Sulphur percentage
0.532KPa		0.567KPa		0.583KPa		Pressure reading in CFR engine
92		89.6		88.5		Motor octane number

From the table it is obvious that, the distillation test of reformat gasoline before and after treatment showed a decrease in the final boiling points (FBP),which give a strong evidence, that the quality of the reformat gasoline has improved after two additions of (5, 10% v/v) of acetone . Also, the initial boiling points (IBP) of the same reformat gasoline sample after treatment were decreased, this may be attributed to the conversion of some liquid petroleum gas (LPG) into fuel[9].The decrease in the initial boiling points (IBP) after all additions also indicated that, the quality of gasoline was improved.

The addition of acetone with different concentrations raises the value of the octane number after the distillation and refining processes. Therefore, the distillation test gives an interpretation about the raising or lowering of the octane number only [5]. No limits had been assigned for the density and vapor pressure by ASTM, because they depend to a greater extent on the temperature of the country, but the refineries has assigned limits to these physical parameters as shown in table (2).

Table (2): Limits of physical parameters gasoline assigned by Khartoum refinery

Winter	Summer	Test
>740 kg/m^3	>740 kg/m^3	Density
40 – 85KPa	40- 67 KPa	Vapour pressure

According to the limits assigned for the density and vapor pressure, the results obtained in table (1)., appears to be in permissible range.

The percent of gum in gasoline affect its stability, which can be a (+ve) or (–ve) effect on the octane number and the quality of the gasoline. the gum existence after first addition being stable at (0.8 mg/100ml) and after the second addition increased to 0.95 mg/100ml and these results appears to be in permissible range assigned by ASTM as shown in table (3).

Table (3): The permissible range assigned by ASTM

Test name	Permissible range	ASTM
Distillation	FBP ≤250◦c	D86-99a
Gum content	0.5-2mg/100ml	D381-99
Copper strip corrosion	1a or 1b	D183-91
Oxidation stability	>240mints	D525-99a
Sulfur content	≯250 ppm	D4294-89
Lead content	≯ 0.001 ppm	D3341-91

Copper strip corrosion may take place in the gasoline tank or the engine that use gasoline ,so the test of the copper strip is very important to be carried out[10]

ASTM stablished a color table from which it is possible to determine if corrosion of a copper plate when immersed in a gasoline sample takes place or not by comparison with ASTM copper strip corrosion standard. It is obvious that the result (1a) obtained after both additions is with in permissible limits which indicates good quality of the Sudanese reformate gasoline.

The lead content of the reformat gasoline before any addition of acetone was found (0.001mg/L) which it is within the permissible assigned by ASTM, this value was not altered after both additions of acetone. Oxidation stability considered as one of the most important property that used to assess the quality of gasoline, since it give clue on the circumstances of the product storing, and also the heat required to start the combustion of gasoline inside the engine [11].Results obtained from the oxidation stability test also lies within the permissible range of ASTM as shown in table (3).

When adding acetone 5 and 10% (v/v) respectively it was observed that the Sulphur percentage was lowered appreciably from 58.49 before addition to 49.3 and 40 mg/l respectively, and this means a high improvement in quality was occurred because high Sulphur content causes corrosion and lowers the octane number.

Figure (1) shows the effect of adding acetone at different concentrations to the Sudanese reformat gasoline. The increase in the value of the motor octane number of the Sudanese reformate gasoline from 88.5 initially to 89.6 and 92 by the addition of 5 and 10% (v/v) acetone respectively, indicates that acetone improve the quality of the Sudanese reformat gasoline , this improvement is attributed to the ability of the material to convert the linear chains hydrocarbon chains into cyclic compounds or increasing the branched chains in gasoline.
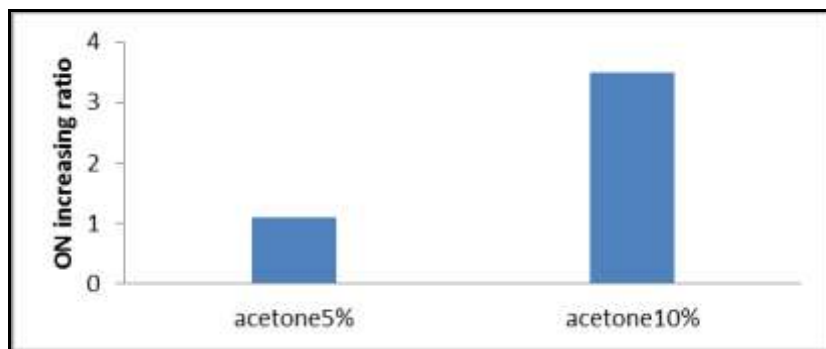
Figure (1): Effect of acetone concentration on the value of MON

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