Available online at www.elixirpublishers.com (Elixir International Journal)

Organic Chemistry

Elixir Org. Chem. 98 (2016) 42512-42517

ISSN: 2229-712X

Characterization of Physiochemical Properties of Sudanese Petrodiesel Samples Produced From Khartoum Refinery in Sudan

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ARTICLE INFO

Article history:

Received: 12 July 2016;

Received in revised form:

26 August 2016;

Accepted: 5 September 2016;

Keywords

Diesel,

Physical properties of diesel,

Chemical properties of diesel,

Khartoum Refinery.

ABSTRACT

Sudanese petrodiesel samples (S1, S2, S3 &S4) were collected from Khartoum refinery in Sudan. Samples were subjected to physicochemical investigation according to the American Society for Testing and Materials (ASTM) Tests include: density, kinematic viscosity, flash point, cloud point, colour, ash content, water content, sulfur content, carbon residue, copper strip corrosion, distillation and calculated cetane number. Results revealed that the physicochemical properties of petrodiesel samples were within the limits assigned by ASTM and Khartoum refinery except the water content for sample S1 was found to be 0.052% wlw. The cetane number was found to be 56.14, 54.72, 57.89 and 56.9 for S1, S2, S3 and S4 respectively, these values were found within recommended values to be used as fuels for diesel engines.

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1. Introduction

The physicochemical properties of diesel include: Flash point, water content, distillation, kinematic viscosity, ash content, sulfur content, copper strip corrosion, cetane number, cloud point, carbon residue, density and colour (Duncan, *et al*, 2010) (Davis, 2001). The important test of diesel is cetane number because it represent the ignition quality (Harris, *et al*, 2007) (Yamaki, *et al*, 2001).

Cetane number (CN) is a measure of the ignition quality of the diesel fuel and is determined by a standard engine test as specified by ASTM (ASTM D613).The ignition quality is quantified by measuring the ignition delay, which is the period between the time of injection and the start of combustion (ignition) of the fuel. A fuel with a high CN has a short ignition delay period and starts to combust shortly after it is injected into an engine (Duncan, *et al*, 2012). The ignition quality of the diesel fuel depends on its molecular composition. Some of the simpler molecular components such as the n-paraffins can ignite in a diesel engine with relative ease, but others like aromatics have more stable ring structures that require higher temperature and pressure to ignite (Isdale, 1976). The objectives of this paper are the empirical determination of physicochemical characteristics of four petrodiesel samples produced from Khartoum refinery and comparing the obtained results with the permissible range assigned by American Society for Testing and Materials (ASTM).

2. Materials & Methods

2.1. Materials

All chemicals used were of analytical reagent grade (AR). Samples (S1, S2, S3, S4) were collected randomly from different tanks.

2.2. Procedures

Standard Test Methods to Determine the physicochemical properties of diesel fuel (ASTM, 2005):

Density (D4052)

A small volume 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 (Ezeldin et al, 2015[a]) .

Kinematic Viscosity (D7042)

The time was measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity was the product of the measured flow time and the calibration constant of the viscometer.

Flash Point (D93)

A brass test cup of specified dimensions, filled to the inside mark with test specimen and fitted with a cover of specified dimensions, was heated and the specimen was stirred at specified rates, by either of two defined procedures (A or B). An ignition source was directed into the test cup at regular intervals with simultaneous interruption of the stirring, until a flash was detected.

Cloud Point (D5773)

The specimen was cooled by a peltier device (ASTM, 2005) until the first appearance of a cloud of wax crystal, that temperature was detected and recorded to 0.1 ^{o}C resolution. Then the recorded temperature was rounded to the next lower integer temperature. The device ensured the detection of any solid phase hydrocarbon crystals.

Colour (D1500)

Using a standard light source, a liquid sample was placed in the test container and compared with coloured glass disks ranging in value from 0.5 to 8.0. When an exact match was not found and the sample color fell between two standard colors, the higher of the two colors was reported.

Ash content (D482)

The sample contained in a suitable vessel was ignited and allowed to burn until only ash and carbon remain.

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The carbonaceous residue was reduced to an ash by heating in a muffle furnace at 775°C, cooled and weighed.

Water Content (D95)

The Petrodiesel sample to be tested was heated under reflux with a water-immiscible solvent, which co-distilled with the water in the sample. Condensed solvent and water were continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still.

Carbon Residue (D4530)

A weighed quantity of sample was placed in a glass vial and heated to 500°C under an inert (nitrogen) atmosphere in a controlled manner for two hours. The sample underwent coking reactions and volatiles formed were swept away by the nitrogen. The carbonaceous-type residue remaining was reported as a percent of the original sample as "carbon residue (micro)" **.**

Sulfur Content (D5453)

A Petrodiesel sample was directly injected in a sample boat. The sample was place into a high temperature combustion tube where the sulfur was oxidized to sulfur dioxide (SO_2) in an oxygen rich atmosphere. Water produced during the sample combustion was removed and the sample combustion gases were next exposed to ultraviolet (UV) light. The SO_2 absorbed the energy from the UV light and was converted to excited sulfur dioxide (SO_2*). The fluorescence emitted from the excited SO_2* as it returned to a stable state SO_2 was detected by a photomultiplier tube and the resulting signal was a measure of the sulfur content in the sample.

Copper Strip Corrosion (D130)

A polished copper strip was immersed in a given quantity of sample and heated for two hours at 78 ^oC. At the end of this period the copper strip was removed, washed, and compared with the ASTM Copper Strip Corrosion Standards.

Distillation (D86)

a- A 100 mL sample was placed in a round bottom flask and heated at a rate specified for samples with its vapour 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 to the 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.

b- At the end of the distillation, the observed vapor temperatures were corrected for barometric pressure and the data were examined for conformance to procedural requirements, such as distillation rates.

c- Test results were commonly expressed as percent recovered versus corresponding temperature, either in a table or graphically, as a plot of the distillation curve (Ezeldin *et al*, 2015[b]).

Calculated Cetane Number (D4737)

$$\begin{aligned} CCI = {} & 45.2 \\ & + (0.0892)(T_{10N}) \\ & + [0.131 + (0.901)(B)][T_{50N}] \\ & + [0.0523 - (0.420)(B)][T_{90N}] \\ & + [0.00049][(T_{10N})^2 - (T_{90N})^2] \\ & + (107)(B) + (60)(B)^2 \end{aligned}$$

A correlation in SI units has been established between the ASTM cetane number and the density and 10 %, 50 %, and 90 % recovery temperatures of the fuel. The relationship is given by the following equation (ASTM, 2005) (Ezeldin *et al*, 2015[c]).:

where

CCI ≡ Calculated Cetane Index by Four Variable Equation.

D ≡ Density at 15°C, determined by Test Method D 1298

DN ≡ D − 0.85.

B ≡ [e(−3.5)(DN)] – 1.

T_{10} ≡ 10% recovery temperature, °C, determined by Test Method D 86 and corrected to standard barometric pressure.

T_{10N} ≡ T10 – 215.

T_{50} ≡ 50 % recovery temperature, °C, determined by Test Method 86 and corrected to standard barometric pressure.

T_{50N} ≡ 5 T50 – 260.

T_{90} ≡ 5 90 % recovery temperature, °C, determined by Test Method D 86 and corrected to standard barometric pressure.

T_{90N} ≡ T90 − 310.

3. Results & Discussion

A physicochemical properties for petrodiesel fuel samples are tabulated in Table 1, 2, 3 and 4.

Table 1. Density, Kinematic Viscosity, Flash Point, Cloud Point and Colour of Petrodiesel Samples.

Test	S1	S2	S3	S4	ASTM or Kh.R specifications*
Density@15°C Kg / L	0.8384	0.835.5	0.830	0.837	max 0.9 (Kh.R)
Kinematic viscosity mm^2/ S	5.15	4.694	6.1	5.6	2.2 - 8.8
Flash point °C	73	75.5	71	65.3	min 57 Kh.R)
Cloud point °C	4.9	2.8	3.6	2.1	max 12 (Kh.R)
Colour	0.1	0.2	0.05	0.2	max 3

*Kh.R ≡ Khartoum Refinery Specification

Determination of the density or relative density of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperature of 15°C (Isdale, 1976). No limits had been assigned for the density by ASTM, because they depend to a greater extent on the temperature prevailing in the country (Jadalla and Ezeldin, 2016), the results of density for four samples are shown clearly in Fig 1.

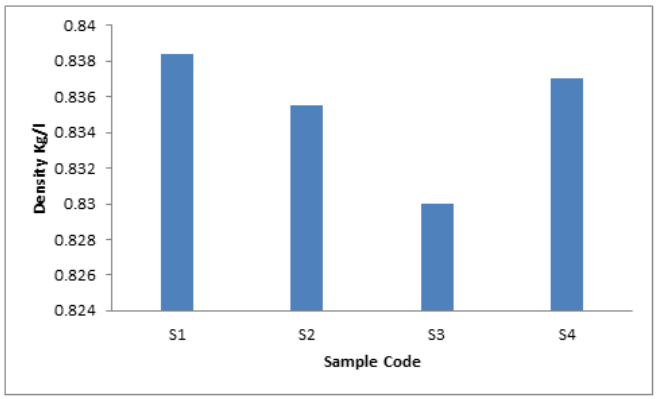

Fig 1. Comparison Between Density Results of Petrodiesel Samples.

The viscosity of petroleum fuels is important for the estimation of optimum storage, handling, and operational conditions (Lee, et al, 2002). S3 showed high viscosity but S2 represented a lowest kinematic viscosity. The results obtained from viscosity agreed with permissible limits a signed by ASTM. Kinematic viscosity for all analyzed samples are shown clearly in Fig 2.

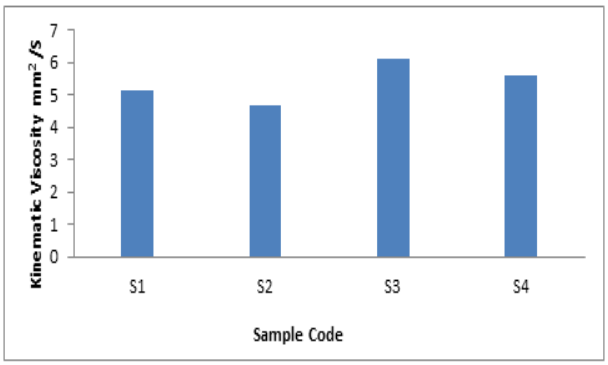

Fig 2. Comparison Between Kinematic Viscosity Results of Petrodiesel Samples.

Flash point temperature is an assessment for the overall flammability hazard of a materials (Park and Irvine, 1984). High flash point temperature lead to the delay of flammability. These revealed that the diesel is of high quality. S4 reported the lowest flash point which S2 represented a highest flash point. Flash points obtained were found within the right permissible limits assigned by ASTM , flash points for diesel fuel samples are compared in Fig 3.

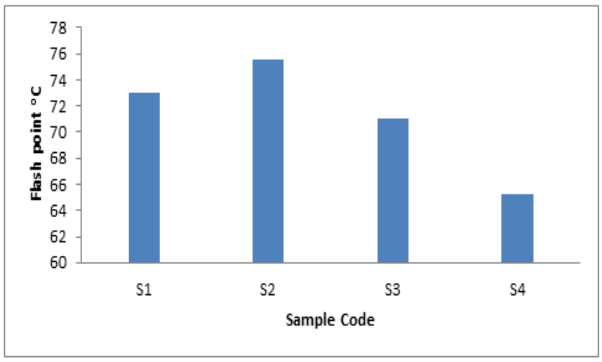

Fig 3. Comparison Between Flash Point Results of Petrodiesel Samples.

The cloud point of a petroleum products is an index of the lowest temperature of its utility for cretin applications. Wax crystals of the sufficient quantity can plug filters used some in fuel systems (Park and Irvine, 1984). The cloud point of petrodiesel samples agreed with the limits assigned by ASTM. The comparison between cloud points of analyzed samples are shown in Fig 4.

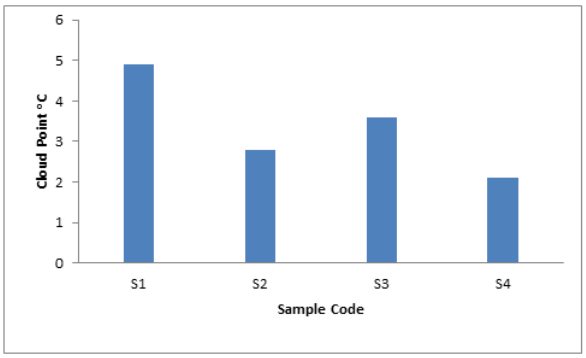

Fig 4. Comparison Between Cloud Point Results of Petrodiesel Samples.

Determination of the colour of petroleum products is used mainly for manufacturing control purposes and is an important quality characteristic since color is readily observed by the user of the product (Park and Irvine, 1984). In some cases the color may serve as an indication of the degree of refinement of the material (Park and Irvine, 1984). When the color range of a particular product is known, a variation outside the established range may indicate possible contamination with another product. However, color is not always a reliable guide to product quality and should not be used indiscriminately in product specifications. From Table 5 ASTM assigned max limit for colour of diesel fuel (0.3), the four samples exhibited results that the lower than maximum limit. The comparison between colour of S1, S2, S3& S4 are represented in Fig 5.

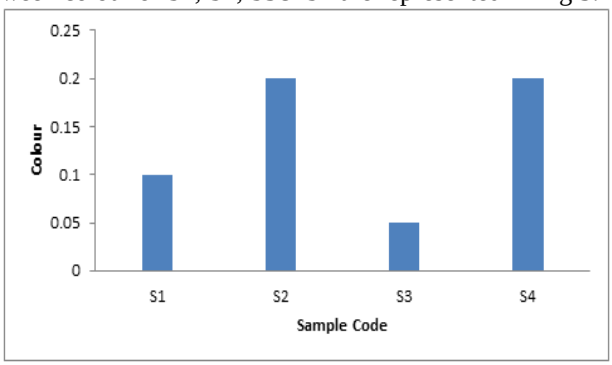

Fig 5. Comparison Between Colour Results of Petrodiesel Samples.

Table 2. Ash content, water content, sulfur content, carbon residue and copper strip corrosion of used petrodiesel sample.

Test	S1	S2	S3	S4	ASTM Specifications
Ash content (w/w%)	0.002	0.009	0.006	0.001	Max 0.01
Water content (w/w%)	0.03	0.02	0.052	0.01	Max 0.05
Sulfur content (w/w%)	0.0084	0.0089	0.0089	0.0047	Max 0.05
Carbon residue (w/w%)	0.02	0.02	0.03	0.01	Max 0.3
Copper strip corrosion	1a	1a	1a	1a	1a and 1b

Increased ash content in diesel my lead to a decrease its quality because ash my precipitate in engine tank (Riazi and Al-Otaibi, 2000). The obtained results from ash test for all samples were found to be within right permissible assigned by ASTM. The comparison between ash content for S1, S2, S3 and S4 are represented in Fig 6.

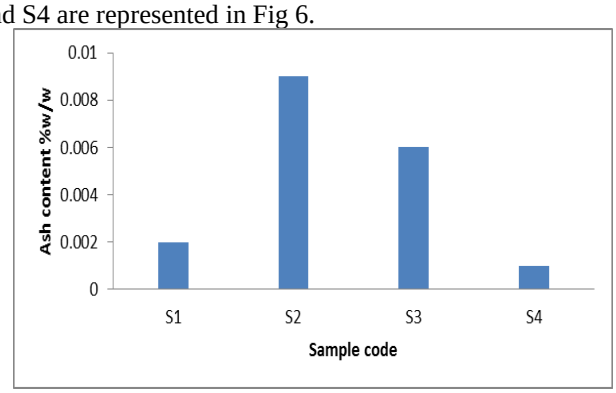

Fig 6. Comparison between ash content for S1, S2, S3 and S4.

A knowledge of the water content of petrodiesel is important in the refining, purchase, sale, and transfer of products The amount of water as determined by this test method (to the nearest 0.05 volume %) may be used to correct the volume involved in the custody transfer of petrodiesel

(Riazi and Al-Otaibi, 2000). water content of S1, S2 and S4 were found to be within ASTM specification, the water percentage of S3 was found to be 0.052 % this result out of limit assigned by ASTM. the comparison between water content for S1, S2, S3 and S4 are shown clearly in Fig 7.

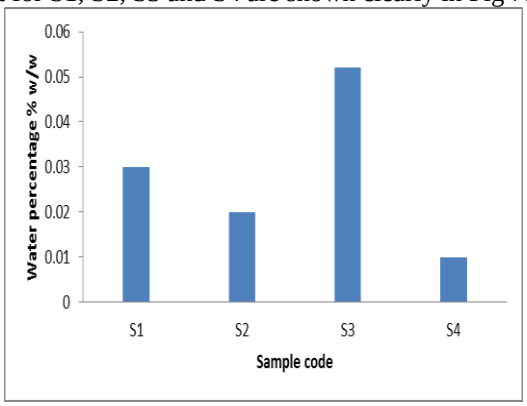

Fig 7. Comparison between water content for S1, S2, S3 and S4.

The Sulfur content of petrodiesel can be used to determine sulfur in process feeds and can also be used to control sulfur in finished products. some process catalysts used in petroleum and chemical refining can be poisoned when trace amounts of sulfur bearing materials are contained in the feedstock (Riazi and Al-Otaibi, 2000). The obtained results from sulfur percentage agree with right permissible range assigned by ASTM. The Comparison between sulfur percentage for S1, S2, S3 and S4 are represented in Fig 8.

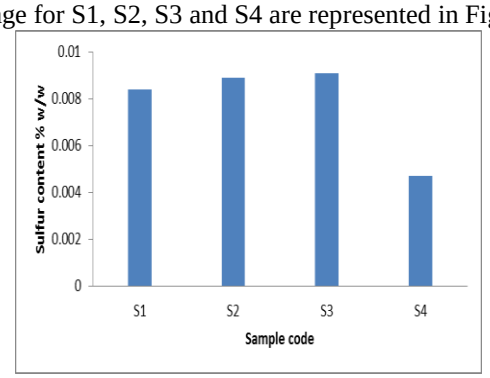

Fig 8. Comparison between water content for S1, S2, S3 and S4

The carbon residue value of petrodiesel serves as an approximation of the tendency of the material to form carbonaceous type deposits under degradation conditions similar to those used in the test method (Yamaki, *et al*, 2001*)* and can be useful as a guide in manufacture of certain stocks. However, care needs to be exercised in interpreting the results. The obtained results from carbon residue test were found within right ASTM limits. The comparison between carbon residue percentage for S1, S2, S3 and S4 were shown in Fig 9.

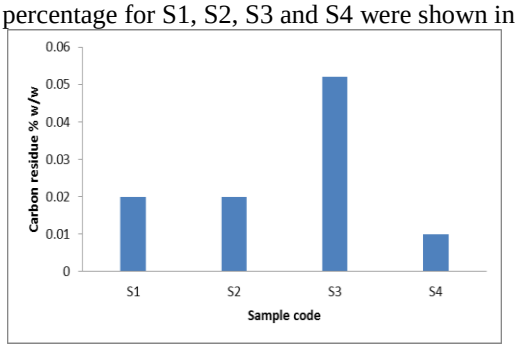

Fig 9. Comparison between Carbon Residue Percentage for S1, S2, S3 and S4.

The copper strip corrosion property is designed to assess the relative degree of corrosivity of a petroleum products., crude petroleum contains sulfur compounds, most of which are removed during refining. However, of the sulfur compounds remaining in the petrodiesel, some can have a corroding action on various metals and this corrosivity is not necessarily related directly to the total sulfur content Yamaki, et al, 2001). The effect can vary according to the chemical types of sulfur compounds present. All analyzed sample showed result 1a from copper strip corrosion and these results within the permissible range assigned by ASTM .

Table 3. Distillation Percentages Without their Boiling Points for analyzed Sudanese Petrodiesel Sample

Distillation	S1	S2	S3	S4	ASTM specifications
10 %	231.1 °C	216 °C	221 °C	214 °C	max 250
50 %	274.9 °C	276.4 °C	282.1 °C	278 °C	max 300
90 %	338.2 °C	338.9 °C	344 °C	340 °C	max 350
95 %	353.2 °C	353.8 °C	363 °C	360 °C	max 370

The distillation (volatility) characteristics of petrodiesel have an important effect on their safety and performance, especially in the case of fuels. The distillation characteristics are critically important for both automotive and since it affects starting, warm-up, and tendency to vapor lock at high operating temperature or at high altitude, or both. The presence of high boiling point components in these and other fuels can significantly affect the degree of formation of solid combustion deposits Yamaki, *et al*, 2001*)*. The Results obtained results from distillation test were found to be within the ASTM specification. The results of distillation points for S1, S2, S3 and S4 are shown clearly in Figures 10, 11, 12 and 13, respectively.

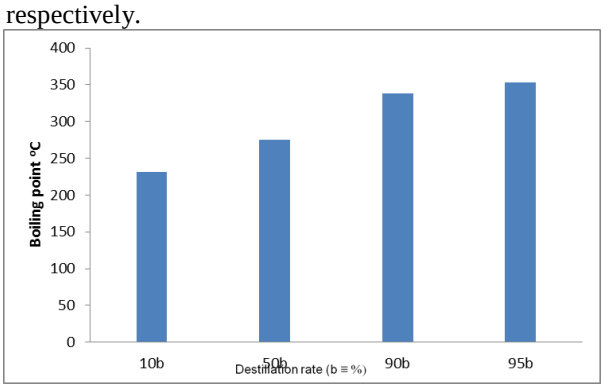

Fig 10. Comparison between distillation rates and their boiling points for S1 sample.

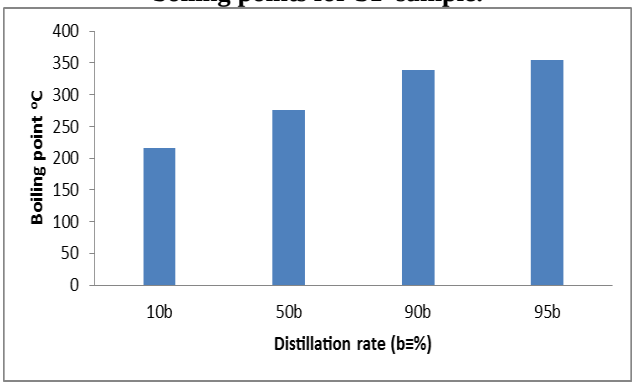

Fig 11. Comparison between distillation rates and their boiling points for S2 sample.

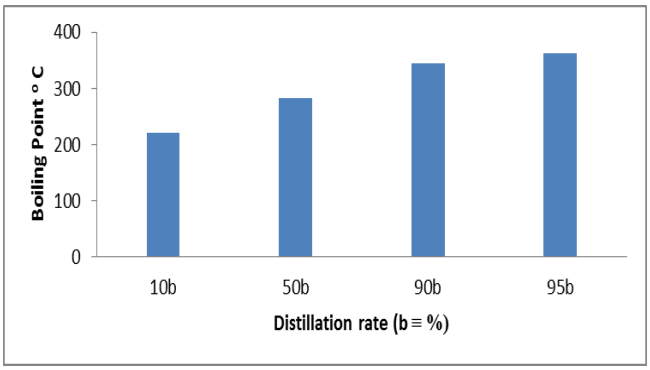

Fig 12. Comparison between distillation rates and their boiling points for S3 sample.

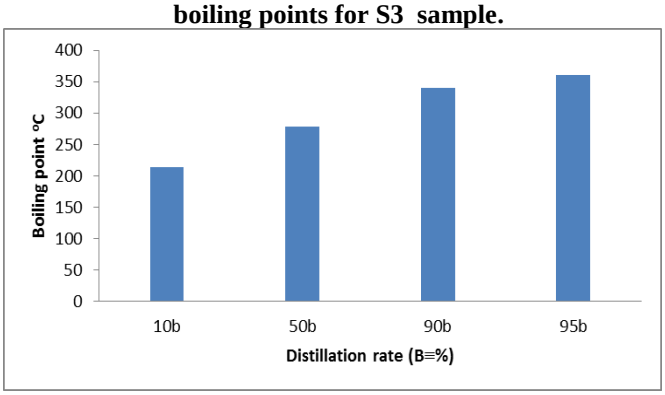

Fig 13. Comparison between distillation rates and their boiling points for S3 sample.

Table 4. Calculated Cetane Number of Sudanese Petrodiesel Samples (S1, S2, S3 and S4).

Sample code	Cetane Number	ASTM specification
S1	56.14	min 45
S2	54.72	
S3	57.89	
S4	56.9	

The Calculated cetane number by four variable equation is useful for estimating ASTM cetane number when a test engine is not available for determining this property directly. It may be conveniently employed for estimating cetane number when the quantity of sample available is too small for an engine rating. In cases where the ASTM cetane number of a fuel has been previously established, the calculated cetane number by four variable equation is useful as a cetane number check on subsequent samples of that fuel, provided the fuel's source and mode of manufacture remain unchanged (Elamin *et al*, 2015). Within the range from 32.5 to 56.5 cetane number, the expected error of prediction of the Calculated Cetane Index by Four Variable Equation will be less than 62 cetane numbers for 65 % of the distillate fuels evaluated (Gruse and Stevens, 1960). Errors may be greater for fuels whose properties fall outside the recommended range of application. The obtained results in above table revealed that the decreasing of density led to increase in a cetane number and all results from cetane number high than 45 (ASTM recommended value (see Table 5)). S1 showed the highest cetane number but S2 reported the least value that attributed to their densities. The comparison between calculated cetane number for S1, S2, S3 and S4 are shown in Fig 14.

4. Conclusion

In conclusion results of the four samples were found to be within the recommended range assigned by ASTM and Khartoum Refinery except the water content of S2 sample was found to be out of range, the cetane number of S1, S2, S3 and S4 were found to be 56.14, 54.72, 57.89 and 56.9, respectively.

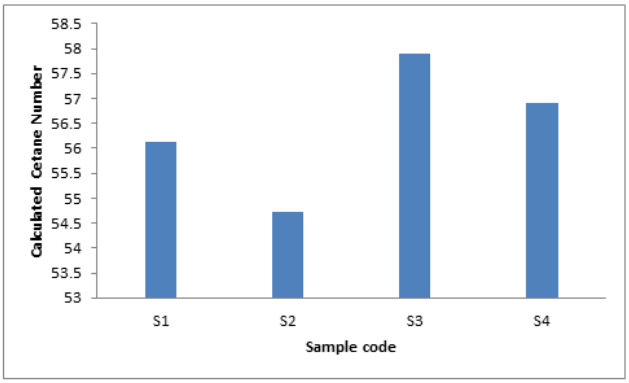

Fig 14. comparison between calculated cetane number for S1, S2, S3 and S4

Acknowledgment

We would like to express our special thanks to Prof. Hatel H. Alkamali, Dean Faculty of Science and Technology, Omdurman Islamic University. We wish also acknowledge the management of the Khartoum Refinery Company for they availed us the opportunity to use their laboratory facilities.

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