American Journal of Science and Technology
2015; 2(2): 74-78
Published online March 20, 2015 (http://www.aascit.org/journal/ajst)
ISSN: 2375-3846

American Association for Science and Technology

A Comparative Elemental Analysis of the Different Kurdistan Crude Oil Fields

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Citation

Abdulsalam R. Karim, Luqman O. Hamasalih, Diary I. Tofiq, Dler M. Salih. A Comparative Elemental Analysis of the Different Kurdistan Crude Oil Fields. *American Journal of Science and Technology*. Vol. 2, No. 2, 2015, pp. 74-78.

Keywords

Crude Oil,
Fuel Oil,
Sulfur Content,
Distillation and Metal Analysis

Received: February 13, 2015
Revised: March 6, 2015
Accepted: March 7, 2015

Abstract

Five different Kurdistan crude oils produced in various fields (namely Swara tuka, Miran, Khurmala, shiwashok and Tawki) were analyzed and evaluated. From each crude oil two types of different boiling ranges (300ºC+ and 350ºC+) fuel oils were produced. All crude oil samples and fuel oils were evaluated using ASTM standard methods of testing, and compared to Iraqi specification of fuel oils. The results showed that all fuel oils are within the Iraqi specification except that produced from Tawki crude oil, which are higher in sulfur content (4.28%w/w for 300ºC+ and 5.0 %w/w for 350ºC+ fuel oils). Elemental analysis done for all crude oil samples and fuel oils, showed the highest Vanadium content in Tawki crude oil with (10 ppm) and also the highest Vanadium content in fuel oils produced from Tawki crude oil with (36 ppm for 300ºC+ and 40 ppm for 350ºC+ fuel oils), other metal content of all crude oils and fuel oils are below these value.

1. Introduction

Petroleum provides fuels and lubricants for most transportation vehicles and essential precursors for the world's petrochemical industries. The fuels that are derived from petroleum are a main energy source for more than one half of the world's total energy. Gasoline, kerosene, diesel oil and fuel oil provide fuel for automobiles, tractors, trucks, aircrafts, and ships [1, 2]. Fuel oil is a complex mixture of highly heterogeneous compounds of aliphatic (saturated), olefinic (unsaturated), aromatic and asphaltene hydrocarbons with significant amounts of additional elements, such as sulfur, oxygen, nitrogen and compounds containing metallic constituents, particularly; Vanadium, Nickel, Iron and Copper [3-7]. Fuel oil is primarily composed of high molecular weight hydrocarbons with a high carbon to hydrogen ratio including aromatics and asphaltene, resulting in high density and viscosity[5,8 and 9], because the main components of fuel oils are the heavy residues from distillation and cracking operations which consist mainly of atmospheric distillates, the content of three- to seven-ring polycyclic aromatic hydrocarbons is generally less than 5% or fuel oils that contain high proportions of heavy atmospheric, vacuum and cracked distillates or atmospheric and vacuum residues, the content of three- to seven-ring polycyclic aromatic hydrocarbons may be as high as 10%[1 and 8]. The low cost of fuel oils [10] is the reason for primarily used in industrial boilers and other direct source heating applications (e.g., blast furnaces) as well as in the production of steam and electricity in power plants, also used as a principal fuel in marine diesel applications [1 and 5]. The metals present in the crude oils are mostly Ni

(II) and V (II) porphyrins and non-porphyrins. Other metal ions reported from crude oils; include Copper, Lead, Iron, Magnesium, Sodium, Molybdenum, Zinc, Cadmium, Titanium, Manganese, Chromium, Cobalt, Antimony, Uranium, Aluminum, Tin, Barium, Gallium Silver and Arsenic. Metelloporphyrins are among the first compounds identified belonging to the biological origin [11]. Metelloporphyrins in crude oils are of fundamental interest from geochemical context for better understanding geochemical origin of petroleum source. Vanadium and Nickel Metelloporphyrins are present in large quantity in heavy crude oils. Their presence cause many problems because such metals have a deleterious effect on the hydrogenation catalysts used in upgrading process [12].

There is a need to determine the trace metals in the crude oils quantitatively because of their importance in the geochemical characterization of the source and origin. Trace metals have been used as a tool to understand the depositional environments and source rock [13]. The metal ions and their ratios have been observed as a valuable tool in oil-oil correction and oil-source rock correlation studies [14]. The trace metals are also indicated as biomarkers of the source rocks [15]. The determination of metal ions in crude oils has environmental and industrial importance. The metal ions like V, Ni, Cu and Fe, behave as a catalyst poisons during catalytic cracking process in refining of crude oil. It is therefore considered necessary to know the concentration of metals in the oils for meaningful impact assessment. Molecular absorption spectroscopy [16], atomic absorption spectroscopy [17], inductively coupled plasma optical emission spectroscopy (ICP-OES)[18], inductively coupled plasma mass spectroscopy (ICP-MS)[19], high performance liquid chromatography (HPLC)[20], gas chromatography (GC)[21], capillary electrophoreses [22], and X-ray fluorescence spectroscopy [23] methods have been repeated for determination of metals in crude oil. The aim of this study is trying to produce fuel oils from Kurdistan crude oil of different fields and make a comparison between them to show which one has a good quality when compared with Iraqi specifications, as it is a trial to determine metal contents of these crude oils and the fuel oils produced from them.

2. Experimental Part

2.1. Material and Reagents

Crude oil samples: all provided from Kurdistan production fields Shiwashok, Khurmala, Tawki, Swara tuka and Miran

2.2. Procedures

2.2.1. Sample Preparation

This was done by drug ashing for complete elimination of organic matter, before analytical determination and it was based on the ignition of the organic matters in air, followed by burning in a furnace at 750±25 °C, then dissolution of the residue in an acidic medium.

2.2.2. Crude Oil Distillation to Produce Fuel Oil

Two type of fuel oils of different thermal cuts were prepared by fractional distillation method, one within the range of (150-300°C) and the other within the range of (150-350°C)

2.2.3. Distillation of Crude Oil According to IP 24 (Preliminary Distillation)

A100 ml of crude oil sample was distilled in specified glass apparatus under prescribed condition of heat and rate of distillation. The volume of distillate obtained at each multiple of 25 °C was recorded, up to a maximum of 300°C, or 350°C when the distillation was stopped.

2.2.4. Evaluation Tests for Fuel Oils

1. Flash point according to ASTM D-92 (Cleveland open cup-The test cup was filled to a specified level with the sample [non-volatile petroleum fractions]. The temperature of the sample increased rapidly at first and then at a slow constant rate as the flash point is approached. At specified interval a small test flam was passed across the cup. The lowest temperature at which application of the test flame caused the vapor above the surface of the liquid to ignite was taken as the flash point.)
2. Pour point according to ASTM D-97 (After a preliminary heating, the sample –fuel oil- was cooled at a specified rate and examined at interval of 3°C for flow characteristics, The lowest temperature at which movement was observed recorded as the pour point.)
3. Specific gravity and API gravity according to ASTM D-1298 (Hydrometer test-The sample [crude oil or fuel oil] was brought to the prescribed temperature an transferred to a cylinder at approximately the same temperature. The appropriate hydrometer was lowered into the sample and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale was read and the temperature of the sample was noted. If necessary the cylinder and its contents were placed in a constant temperature-bath to avoid excessive temperature variation during the test.)

2.2.5. Determination of Total Sulfur Content by XRF-Technique

A 5g sample of crude oil or petroleum products were introduced into the sample cell of XRF instrument which was calibrated before sample measuring by standards from (0.0 – 1.0% and 1.0 – 6.0 %) sulfur .The sample was put in a sample holder of the instrument and the total sulfur content in the sample was measured and recorded.

3. Result and Discussion

3.1. Evaluation of Crude Oils

Evaluation of crude petroleum according to IP-methods (Appendix D) requires preliminary distillation to determine the distillation characteristics of small quantities of crude petroleum by IP-24 method, in which the volume of distilled fractions obtained at each multiple of 25 ºC were recorded, up to maximum of 300ºC (or 350ºC), at which the distillation was stopped. The results of all crude oils according to the IP-24 are shown in table (1).

Another type of information necessary for the refiner are operating and design data such as fractionating or true-boiling distillation to produce various fractions like naphtha (I.B.P.-170ºC), kerosene (171-240ºC), gas oil (241-300 or 350 ºC) and fuel oil (+300 or +350ºC). Table (2) show such information from all five crude oil samples, in which it is clear that the maximum production of lightest fraction (naphtha) is from shiwashok (37%) and the maximum production of heaviest fraction (fuel oil) is from khormala field (41%). Table (3) shows important information for the refiner, (API or specific gravity) for each fraction distilled, this is necessary for construction of curves of temperature and gravity verses percent distilled.

Table 1. *Distillation of crude oils according to IP 24*

Tests	Swara tuka	miran	Khurmala	shiwashok	Tawki
ASTM Dist.	v/v%	v/v%	v/v%	v/v%	v/v%
I.B.P.	46	178	70	35	60
25	-	-	-	-	-
50	Few dps.	-	-	2	-
75	2	-	0.3	8.1	1
100	5	-	2	16	4.5
125	11	-	4	23	9
150	16	-	11	33	14
175	23	-	16	42	19
200	28	0.5	21	50	24
225	35	0.8	26	56	30
250	41	1.2	33	62	36
275	49	10	39	67	43
300	56	20	47	74	50

Table 2. *ASTM distillation for production the amount of light products*

Tests	Swara tuka	miran	Khurmala	shiwashok	Tawki
Dist.	v/v%	v/v%	v/v%	v/v%	v/v%
I.B.P.-170	22	Few drops	16	37	18
171-240	17	1	15	20	16
241-350	23	39	41	24	31
I.B.P-150.	16	Few drops	11	33	14
151-300	40	20	36	41	36

Table 3. *The specific gravity for all light products produced from crude oils*

Tests	Swara tuka	miran	Khurmala	shiwashok	Tawki
Specific gravity@15.6°C					
I,B.P.-170	0.7210	-	0.7035	0.7026	0.7034
171-240	0.7791	-	0.7798	0.7701	0.7964
241-350	0.8317	0.8900	0.8505	0.8251	0.8575
I.B.P.-150	0.7101	-	0.7024	0.7013	0.7016
151-300	0.8031	0.8780	0.7981	0.7785	0.8053

3.2. Evaluation of Fuel Oils Produced According to the ASTM Standards

Fuel oils are complex mixture of hydrocarbon; they cannot be rigidly-classified or defined precisely by chemical formation or definite physical properties. Classification of fuel oils is based on their application than on their chemical or physical properties, however, two brand classifications are generally recognized (1) distillate fuel oil (2) residual fuel oil. The conventional description of fuel oil is generally associated with the black, viscose residual material remaining as the result of refinery distillation of crude oil.

Detailed analysis of residual fuel oil is more complex than the analysis of lower-molecular weight liquid products, because several tests that are usually applied to the lower molecular weight colorless products are not applied to residual fuel oil (e.g. aniline point and cloud point) because of suffering from visibility effects of the color of the fuel oil.

Fuel oil, therefore, in its various categories has an extensive range of applications, and the choice of a standard procedure to be used for assessing or controlling product quality depend on both the type of fuel and its ultimate use, but more precise specifications of quality requirements such as: density (specific gravity), flash point, pour point, metal content, calorific value, water content and sulfur content may be required for any given application. Table (4) shows these properties and specification in comparison to Iraqi requirements for marketing specification for fuel oil.

Density or specific gravity is used whenever conversion must be made between mass and volume measurements, and it is used also in combination with other test results to predict oil quality. Flash point, as for all petroleum products, considerations of safety in storage and transportation and contamination by more volatile products are required. The pour point is indication of the lowest temperature at which the oil can be transferred from one place to another. The calorific value of residual fuel oil is lower than that of lower-boiling fuel oil, because of the lower atomic hydrogen to carbon ratio and the incidence of greater amounts of less combustible material, such as water and sediment, and higher levels of sulfur.

Table 4. *The properties of fuel oils produced*

Boiling range above 300 °C						**Iraqi specification**	
Tests	**Swara tuka**	**miran**	**Khurmala**	**shiwashok**	**Tawki**	**Fuel oil**	**Blend fuel oil**
Specific gravity@15.6 ºC	0.8933	0.9711	0.9555	0.8839	0.9619	(0.950)	(0.980)
API. gravity	26.9	14.2	16.59	28.58	15.6	17.44	12.88
Flash point (C.O.C)	161	180	158	154	158	60 (min.)	65 (min.)
Pour point ºC	+6	+ 9	+ 6	+ 3	+ 9	+21 (max.)	+27 (max.)
Water content v/v %	0.0	0.0	0.0	0.0	0.0	0.5 (max.)	0.5(max.)
Sulfur content w/w%	1.1	2.06	2.8	1.05	4.28	4.0 (max.)	4.5(max.)
Boiling range above 350 °C						Iraqi specification	
Tests	Swara tuka	miran	Khurmala	shiwashok	Tawki	Fuel oil	Blend fuel oil
Specific gravity@15.6 ºC	0.9123	0.9821	0.9733	0.9104	0.9821	(0.950)	(0.980)
API. gravity	23.6	12.57	13.88	23.92	12.57	17.44	12.88
Flash point (C.O.C)	192	204	194	192	190	60 (min.)	65 (min.)
Pour point ºC	+9	+ 18	+ 12	+ 6	+ 15	+ 21 (max.)	+27 (max.)
Water content v/v %	0.0	0.0	0.0	0.0	0.0	0.5 (max.)	0.5(max.)
Sulfur content w/w%	1.3	2.49	3.0	1.3	5.0	4.0 (max.)	4.5(max.)

3.3. Metal Analysis in Crudes and Fuel Oil Produced

During the last year, gas turbines have been modified so they may be fueled by all types of liquid fuels, from distillates to residual and crude oil. Ash forming contaminants often present in various fuels lead to corrosion and deposit problems. Ash-forming materials may be in a fuel as oil soluble organo-metallic compounds, as water soluble salts or as solid foreign contamination. Their presence and concentration vary with the geographical source of a crude oil. They are concentrated in the residual fractions during the refining process. Table (5) shows the metallic analysis namely (Co, Cu, Fe, Ni, Pb, V) of five crude oil samples and fuel oil produced from them.

Results show highest (V) content in Tawki crude (10 ppm) and Tawki fuel oils (36ppm and 40 ppm) and lowest values in swara tuka crude (0.22ppm) and swara tuka fuel oils (1.2 ppm and 1.7 ppm). In heavy fuel oil the vanadium concentration is used to calculate the amount of magnesium treatment compound to be added to the fuel. Pre-conditioning of the fuel before it reaches the gas turbine or diesel engine has become a prerequisite for installations that use heavy petroleum fuels, so on-site fuel analysis to determine the extent of contamination is an integral part of a fuel quality management program.

Table 5. *The metallic analysis of Crude oils and fuel oils*

Metallic analysis for Crude oils					
Metals	**Swara tuka**	**miran**	**Khurmala**	**shiwashok**	**Tawki**
Co	Nil	Nil	Nil	Nil	Nil
Cu	Nil	Nil	0.05	Nil	Nil
Fe	0.4	0.98	1.2	0.3	9
Ni	Nil	2.1	1.6	0.38	5
Pb	0.01	0.12	0.05	0.08	0.04
V	0.22	4.8	6.2	2.8	10
Metallic analysis for Fuel oils produced above 300°C					
Metals	Swara tuka	miran	Khurmala	shiwashok	Tawki
Co	Nil	Nil	Nil	Nil	Nil
Cu	Nil	Nil	0.11	Nil	Nil
Fe	3.1	2.5	2.8	1.8	32
Ni	Nil	6	4.6	2	19
Pb	0.029	0.41	0.13	1.5	0.13
V	1.2	15	20	5.6	36
Metallic analysis for Fuel oils produced above 350°C					
Metals	Swara tuka	miran	Khurmala	shiwashok	Tawki
Co	Nil	Nil	Nil	Nil	Nil
Cu	Nil	Nil	0.14	Nil	Nil
Fe	3.86	3	3	2	34
Ni	Nil	7	5.1	2.3	22
Pb	0.036	0.5	0.16	1.7	0.14
V	1.7	18	22	6	40

4. Conclusions

It was concluded that shiwashok crude oil gives highest yield of lightest fractions (37%v/v) and lowest yield of fuel oils at (+350°C) which is (19%v/v) while miran crude oil gives the lowest yield of lightest fractions (less than 1%) and highest yield of fuel oil at (+300°C) which is (80%v/v).\

Fuel oils produced from tawki crude oil gives higher sulfur content (4.28%w) and (5.0%w) for fuel oil at (+300°C and 350°C) respectively.

Tawki crude oil and fuel oils produced from it gives higher Vanadium content (10ppm, 36ppm and 40ppm) for crude oil, fuel oil at 300°C and fuel oil at 350°C respectively.

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