CHARACTERIZATION OF LIBYAN CRUDE OILS AND ITS HEAVY FRACTIONS

Abdurazag A. Shebli* and Alhadi A. Elakrimi**

Abstract: Characterization of crude oil and its heavy fractions is a necessity to understand and predict their behavior. During production, transportation and processing, various problems such as solids deposition, clogging and coking can occur due to the presence of heavy components in oil. When it comes to the heavier fractions of petroleum, modern analytical methods are not able to fully isolate and characterize the molecules. Crude oils from different origins (Breaga, Sirtica and Bouri) were used in this study. Breaga and Sirtica crude oils are classified as an intermediate crude oils while Bouri crude oil is classified as a heavy one that has shown asphaltene deposition problems. The softening point for the vacuum residues of the three crudes was determined and it was found 42, 40 and 60 for Breaga, Sirtica and Bouri respectively. Compositional studies and structural characterization of the original crude oils and their asphaltenes and maltenes fractions were carried out to study a possible relationship between their properties and asphaltene deposition behavior. Structural characterization is carried out using various techniques including Fourier Transform Infrared Spectroscopy (FT-IR), Softening Point (SP) and Thermogravimetric Analysis (TGA and DTA).

Based on the FT-IR results, the asphaltenes have the highest degree of the aromaticity followed by the maltenes and parent crude oils, respectively. Among the asphaltenes materials studied, Bouri asphaltene has the highest aromatic nature as deduced from the absorption at 1600 and 700-900 cm-1.

The TGA results show that the weight loss of samples decreased with the increase of the heavy fractions. The asphaltenes sample exhibits a relatively lower weight loss comparing to the rest of samples over the whole temperature interval studied. This agrees with the fact that these samples have the highest heavy fraction, which indicates the presence of less volatile constituents than the other samples. This finding is consistent with the FT-IR analyses.

Keywords: Libyan Crudes, heavy fractions, Asphaltenes and Maltenes.

INTRODUCTION

Petroleum is a fossil fuel formed through millions of years under the earth's surface. Dead animals, plants and other microorganisms decayed and buried under sedimentary rock. When these are subjected to heat and pressure over time, petroleum is formed Petroleum is a naturally occurring, yellowish-black liquid found in geological formations beneath the Earth's surface. It is commonly refined into various types of fuels. Components of petroleum are separated using a technique called fractional distillation (www.differencebetween.com/difference-between-crude-oil-and-vs-petroleum, 2018; en.wikipedia.org/wiki/Petroleum, 2018).

The hydrocarbons in crude oil are mostly alkanes, cycloalkanes, various aromatic and a small amount of asphaltenes and resins. Its compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. Petroleum is vital to many industries and can be defined as a mixture of hydrocarbons with various molecular weights. These hydrocarbons may be aliphatic, aromatic and branched or un-branched. Hydrocarbons with a lower molecular weight (ex: methane, ethane, propane and butane) form the gases while hydrocarbons (ex: pentane, hexane and so on) form the liquids and solids. Paraffin and waxes are an example of solid hydrocarbons in petroleum. The proportion of each compound in petroleum differs from one crude to another.

Crude oil is a complex mixture of hydrocarbons and heteroatomic organic compounds of varying

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molecular weights and polarity. Crudes with high levels of sulfur are known as sour crudes, whilst those with low levels are known as sweet. Heavy fractions of crude oils at atmospheric pressure and ambient temperature can be separated into four groups: saturates (alkanes, paraffins & naphthenes), aromatics, resins, and asphaltenes (Alsaffar *et al*, 2001 and Freitag & Verkoczy, 2005).

During production, transportation, various problems such as solids deposition, clogging and coking occur due to the presence of heavy components in oil. In addition, asphaltene precipitation is a common problem in oil industry throughout the world. In many instances, these deposition phenomena render in complete clogging of flow lines and serious damage to storage vessels and processing equipment. Consequently, characterization of crude oil and heavies is necessary to be able to understand and predict their behavior. Molecules in the heaviest fractions of petroleum cannot be fully isolated and characterized by modern analytical methods. Instead, they are fractionated and classified into different categories which lead merely to definitions that are workable, but they are far away from identifying exact structures.

The number of individual components in a hydrocarbon cut increases rapidly with its boiling point and the family analysis is given by mass spectrometry, one may prefer a distribution by type of carbon. This can be done by infrared absorption spectrometry which also has other applications in the petroleum industry. While a set of structural patterns can be detected by Nuclear Magnetic Resonance (NMR) of hydrogen (or carbon); this can thus describe the average molecule in the fraction under study. Characterization can be based on single carbon number or on compound class. A compound class characterization common in industry is SARA (Saturate, Aromatic, Resin and Asphaltene) characterization (Kiefer, 2015 and Hao *et al*, 2017).

Heavy oil is about 70% of the total crude oils (James, 1996). Asphaltenes are possibly the most studied fraction and yet it is the least understood materials in the petroleum industry. Everything about asphaltenes appears to be non-conclusive, elusive, and complex. However, asphaltenes have attracted numerous researchers with varied views and research approaches, varying from practical modelling approach to ivory tower study of asphaltenes molecular structures. It is considered the least valuable component of the crude oils. The presence of asphaltene cause a marked increase in crude oil viscosity, making it difficult to transport and process. Characterization of crude oil and heavies is necessary to be able to understand and predict their behavior, some analysis of typical asphaltenes samples from various sources illustrate significant and characteristic difference between the compositions of asphaltenes derived from several different sources. Maltenes remained after the precipitation of asphaltenes by n-alkanes are subjected to liquid chromatography the components eluted by the more polar solvents are called resins.

The aim of this work is to characterize some of Libyan crude oils (Brega, Sirtica and Bouri) and their heavies in terms of chemical structure by various characterization techniques such as thermogravimetric (TGA), Fourier transform infrared spectroscopy (FTIR) spectroscopy and general crude oil tests (API gravity, pour point, asphaltene contents and n-Heptane insoluble, etc.).

The characterization data obtained for the heavy components of crude oils and residues namely asphaltenes and maltenes can be used to improve thermodynamic model being developed for wax precipitation. Its applicability to other predictive models is also possible.

EXPERIMENTAL WORK

Bouri, Brega, and Sirtica crude oils and their vacuum residues are used in this study. They are selected as part of a program oriented to evaluate the feasibility of producing carbon fiber precursors from Libyan oil residues. Some properties of those crude oils and their vacuum residues are compiled in Tables 1 and 2, respectively (Petroleum Research Centre, Internal Report, 1994).

Vacuum Residues Preparation

25 liters of each crude oil were distilled in the Kontes Martin (ASTM D2892) apparatus under atmospheric pressure to 175^{o}C and then under vacuum at a pressure of 10 mm Hg to 400^{o}C. The vacuum is distilled on the Sarina High Vac (ASTM P196) still at 0.3mm Hg to 565^{o}C. The vacuum residues obtained from these three crude oils (Bouri, Breaga and Sirtica) were coded as (BVR, BrVR and SVR).

Asphaltene Precipitation

Separation of asphaltene content from the samples, the vacuum residue of Bouri (BVR), Brega (BrVR) and Sirtica (SVR) was carried out as follows:

Table 1. General characteristic of BCO, BrCO and ACO

Property	*Bouri Co.*	*Sirtica Co.*	*Briga Co.*
API	25.86	41.11	42.44
Asphaltene	3.3	0.46	0.16
Total Sulfur	1.86	0.42	0.22
Pour Point °C (°F)	+9 (+48)	-9 (+16)	-9 (+16)
kinematic viscosity (υ) At 100°F	18.62	2.935	2.696
n.-Heptane Insoluble	21.3	0.84	0.41

Table 2. General characteristic of BrVR, SVR and AVRTable.3A Bouri Crude Oil General Tests

Property	*Bouri VR*	*Sirtica VR*	*Briga VR*
API	4.30	9.39	11.78
S	3.36	1.38	0.74
PP °C	+69	+51	+51
V & N (ppm)	60 & 69	11.3 & 28.4	7.8&4.7
HI	81.8	1.7	0.64
Aspaltenes	14.4	3.2	2.7
Yield %	25.1	12.6	10.1

***Keys** VR Vacuum Residue,* PP Pour: Point (°C), S: total Sulfur, HI: n Heptane Insoluble, V: Vanadium, N: Nickle

n- heptane is used as a solvent for the precipitation of the asphaltenes from the crude oil sample. A 40: 1 ratio of n- heptane to sample is used then digested in an ultrasonic path for 24 hours, until the precipitation occurs.

It is important to remember that asphaltenes are a solubility class. Initial sample weight of up to 35 grams. Precipitated asphaltenes are separated by vacuum filtration, dried in an oven and weighed. Maltenes are isolated from the filtrate by rotary evaporation. Figure 1 shows schematic of apparatus used for Separation of Asphaltene.

Infrared spectroscopy

The IR spectra were used for characterization of the molecular nature of the samples; Bouri Crude Oil (BCO), Breaga Crude Oil (BrCO) and Sirtica Crude Oil (SCO) together with their asphaltenes and maltenes, where obtained with IFS-25IR spectrophotometer. The solid and viscose samples are measured and placed uniformly on pre-weighed KBr windows. While the liquid ones are measured in IR cuvettes. IR spectra where used for a qualitative comparison of molecular nature of the samples.

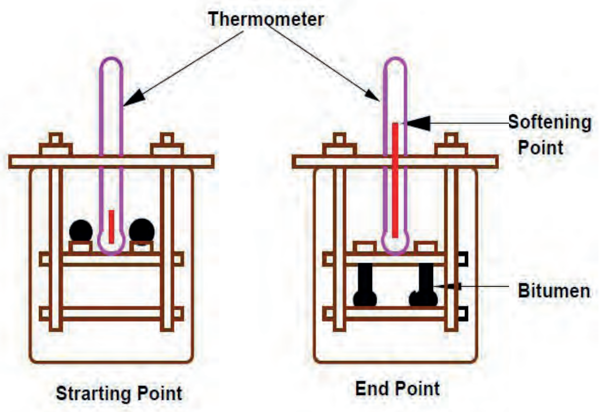

Fig. 1. Schematic of apparatus used for separation of asphaltene.

Thermogravimetric analysis

To gain a better knowledge of the chemical composition of the samples above stated in IR spectroscopy, the samples were characterized with thermogravimetric analysis. TGA/DTG measurement was conducted in DTG50. At the samples were deposited on Aluminium cell, using samples mass of ~ 10mg, with heating rate of 10c/min over the 293-873k° (20-600°C) temperature intervals.

Softening point

Generally, there are several methods such as Mettler Softening Point, Hot Stage Microscopy and Ring-and-Ball method for determining the softening temperature and the temperatures measured by these different methods vary to some extent from each other. In this study, the softening point of pitches was determined by a ring-and-ball method according to a standard ASTM procedure (D36-86). Two horizontal disks of pitches (2gr.), cast in shouldered brass rings, are heated at controlled rate in a liquid bath (glycerin) while each supports a steel ball. The softening temperature is reported as the mean of the temperatures at which the two disks soften enough to allow each ball, enveloped in pitch sample, to fall a distance of 25mm. Figure 2 shows assembly of the apparatus of softening point measurements used in this study.

RESULTS AND DISCUSION

Materials

The parent crude oils (Bouri, Brega and Sirtica) and their vacuum residues were subjected to different characterization analysis, the results of which are compiled in Tables 3 and 4 (Petroleum Research Centre, Internal Report, 1994).

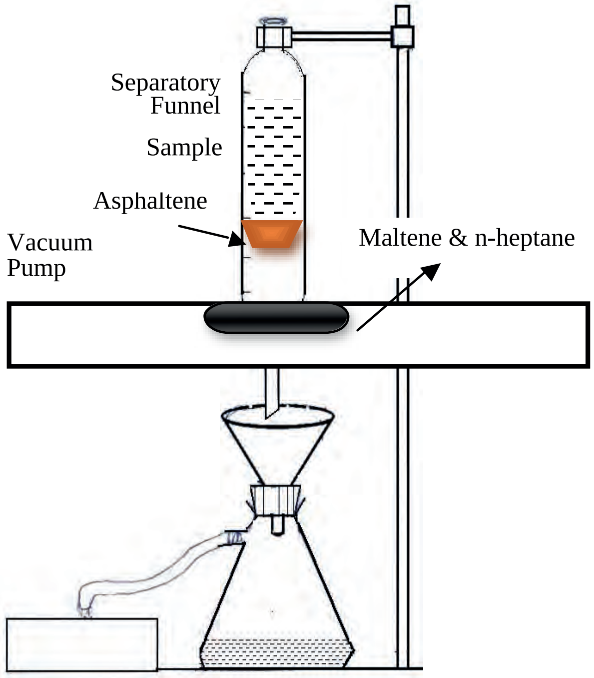

Fig. 2. Assembly of the apparatus used for softening point measurements.

Bouri Crude Oil

Bouri is close to Middle-East than N. African crude. It is classified as an intermediate crude oil having a gravity of 25.9°API and a total sulphur content of 1.86wt%.

Bouri crude has a pour point of 9°C and a kinematic viscosity of 57.4cSt at 21.1°C. For a heavy crude, both vanadium, nickel and conradson carbon content are moderate at 28ppm and 2.3wt% respectively. However, compared to other heavy crudes, Bouri has an unusually high n-heptanes insolubles content of 21.3wt%. The crude contains about 2vol% pentane and lighter components and has a Reid vapor pressure of 3.3psi (Table 3).

Bouri Vacuum Residue

Table 4 shows the general properties of Bouri vacuum residue. In addition to its extremely high n-heptanes insolubles content (approx. 80wt%), Bouri vacuum residue also has a high pour point of 69°C. Since it cannot be used as visbreaker feedstock, it is only possible to produce reduced pour point heavy fuel oils if a considerable amount of middle-distillate is used as cutter stock.

It may not be possible to produce a vacuum residue cut point as high as 565°C without encountering some coking problems in the vacuum heater or in the vacuum column due to asphaltene precipitation.

Table.3. Bouri Crude Oil General Tests.

Property	Result	Method
Density @ 15°C g/ml	0.8987	IP 365/D4052
Specific Gravity @ 60°F	0.8992	Calculation
API Gravity @ 60°F	25.86	Calculation
Characterisation Factor	11.7	Calculation
Total Sulphur % wt.	1.86	IP 336/D4294
Mercaptan Sulphur ppm wt.	46	IP 342 Mod/ D3227 Mod
Total Nitrogen % wt.	0.169	IP 379 Mod/ D4629 Mod
Pour Point °C (°F)	+ 9 (+ 48)	IP 15/D97
Viscosity @ 70°F, cSt	57.41	IP 71/D445
Viscosity @ 100°F, cSt	18.62	IP 71/D445
Vanadium ppm wt.	14.0	IP 377 Mod
Nickel ppm wt.	12.6	IP 377 Mod
Sodium ppm wt.	5.7	IP 377 Mod
Calcium ppm wt.	3.7	IP 377 Mod
Potassium ppm wt.	0.3	IP 377 Mod
Conradson Carbon % wt.	2.3	IP 13/D189
Asphaltenes % wt.	3.3	IP 143
n-Heptane insolubles % wt.	21.3	D893
Reid Vapour – Pressure KPa (psi)	23 (3.3)	IP 69/D323
Flash Point °C (°F)	< –20 (< – 4)	IP 170
Hydrogen Sulphide ppm wt.	< 1	IP PM – BJ
Neutralisation Number, mg KOH/g	0.07	IP 177/D664
Bottom, Sediment and Water % vol.	< 0.05	IP 359/D4007
Ash content % wt.	< 0.01	IP 4/D482
Salt (as NaCl) mg/litre (lbs/1000 bbls)	1.8 (0.63)	D3230

In practice it is possible that the vacuum residue cut point may have to be restricted to 500°C (or less). Only a commercial operation could determine this practical cut point, as laboratory testing is not representative.

Providing a market can be found for high sulphur coke, Bouri vacuum residue could be used as coker feedstock for the production of fuel grade coke. Due to its low penetration value it is unlikely that Bouri vacuum residue could be used as feedstock for bitumen manufacture. However, it is possible that a blend of Bouri and other Libyan vacuum residues (i.e. Es Sider) could be used as bitumen plant feedstock.

Table 4. Bouri Yields and Inspections of vacuum Residue.

Property	Result	Method
Boiling Range °C	565+	Method
Vol. % on Crude	21.7	
Wt. % on Crude	25.1	
Density @ 15 °C g/ml	1.0413	IP 365/D4052
Gravity°API	4.30	Calculation
Specific Gravity @ 60° F	1.0419	Calculation
Total Sulphur % wt.	3.36	IP 336
Pour Point °C (°F)	+69	IP 15/D97
Viscosity @ 100°C, cSt Nickel ppm wt. Vanadium ppm wt.	13,230 60.3 69.3	IP 71/D445 IP 377 Mod IP 377 Mod
Micro Carbon Residue % wt.	28.4	ASTM D4530
Asphaltenes % wt.	14.4	IP 143
n-Heptane insolubles % wt.	81.8	ASTM D893
Molecular Weight	> 500	Calculation
Calofric Value MJ/Kg gross	41.52	Calculation
Calofric Value MJ/Kg gross	9917	Calculation
Sodium ppm wt.	24.3	IP 377 Mod
Calcium ppm wt.	14.0	IP 377 Mod
Potassium ppm wt.	1.1	IP 377 Mod
Ash content % wt.	0.036	IP 4/D482

Breaga Crude Oil

Table 5 shows the general properties of Breaga crude oil. It is classified as a paraffinic intermediate crude oil having a gravity of 42.4°API and a total sulphur content of 0.22wt%. The crude is lighter than some other Libyan crudes and therefore, its product quality and structure is closer to that of an Algerian rather than a North Sea crude. The crude flows readily at room temperature with a viscosity of 5.3cSt at 21.1°C and a pour point of -9°C. A nickel and vanadium content are 0.5 and 0.8ppm respectively are extremely low even for a light, low sulphur crude. The conradson carbon residue content of 1.5wt% is about average for this type of crude, approximately 7.6vol% of the crude consists of pentane and lighter components. The Reid vapour pressure is 7.8psi.

Breaga Vacuum Residue (BrVR)

Table 6 shows the general properties of Breaga vacuum residue. Due to its low sulphur and metals content, Breaga vacuum residue is excellent coker feedstock for anode grade production. Due to its high penetration value, Breaga vacuum residue is not suitable as feedstock for bitumen manufacture.

Table 5. Brega Crude Oil General Tests.

Property	Result	Method
Density @ 15°C g/ml	0.8131	IP 365/D4052
Specific Gravity @ 60°F	0.8135	Calculation
API Gravity @ 60°F	42.44	Calculation
Characterisation Factor	12.2	Calculation
Total Sulphur % wt.	0.22	IP 336/D4294
Mercaptan Sulphur ppm wt.	44	IP 342 M/ D3227 M
Total Nitrogen % wt.	0.09	IP 379 Mod/ D4629m
Pour Point °C (°F)	- 9 (+ 16)	IP 15/D97
Viscosity @ 70°F, cSt	5.293	IP 71/D445
Viscosity @ 100°F, cSt	2.696	IP 71/D445
Vanadium ppm wt.	0.8	IP 377 Mod
Nickel ppm wt.	0.5	IP 377 Mod
Sodium ppm wt.	2.5	IP 377 Mod
Calcium ppm wt.	1.5	IP 377 Mod
Potassium ppm wt.	0.3	IP 377 Mod
Conradson Carbon % wt.	1.50	IP 13/D189
Asphaltenes % wt.	0.16	IP 143
n-Heptane insolubles % wt.	0.41	D893
Reid Vapour – Pressure KPa (psi)	54 (7.8)	IP 69/D323
Flash Point °C (°F)	< –20 (< –4)	IP 170
Hydrogen Sulphide ppm wt.	< 1	IP PM – BJ
Neutralization Number, mg KOH/g	0.09	IP 177/D664
Bottom, Sediment and Water % vol.	< 0.05	IP 359/D4007
Ash content % wt.	< 0.01	IP 4/D482

Sirtica Crude Oil (SCO)

Sirtica is classified as an intermediate crude oil having a gravity of 41.1°API and a total sulphur content of 0.42wt% (Table 7). Its product quality and structure are close to that of Zuetina, except it is a little more naphthenic. Sirtica Crude Oil has a pour point of -9°C and a viscosity of 4.5cSt at 21.1°C and flows readily at room temperature. Its conradson carbon residue content of 2.1wt% is about normal for this type of crude. Approximately 7.1vol% of the crude consists of pentane and lighter component sand it has a Reid vapor pressure of 7.8psi.

Sirtica Vacuum Residue

Sirtica vacuum residue has a nickel +vanadium content of approximately 40ppm, a Sulphur content of 1.38wt% and a pour point of 51°C (Table 8).

Table 6. Brega Yields and Inspections of vacuum Residue.

Property	Result	Method
Boiling Range °C	565+	Method
Vol. % on Crude	8.3	
Wt. % on Crude	10.1	
Density @ 15 °C g/ml	0.9870	IP 365/D4052
Gravity°API	11.78	Calculation
Specific Gravity @ 60° F	0.9876	Calculation
Total Sulphur % wt.	0.74	IP 336
Pour Point °C (°F)	+51	IP 15/D97
Viscosity @ 50°C, cSt	30,000 *	D341
Viscosity @ 80°C, cSt	-	IP 71/D445
Viscosity @ 100°C, cSt	565.4	IP 71/ D445
Nickel ppm wt.	4.7	IP 377 Mod
Vanadium ppm wt.	7.8	IP 377 Mod
Micro Carbon Residue % wt.	16.7	ASTM D4530
Asphaltenes % wt.	2.7	IP 143
n-Heptane insolubles % wt.	0.64	ASTM D893
Molecular Weight	590	Calculation
Calofric Value MJ/Kg gross	43.35	Calculation
Calofric Value MJ/Kg gross	10354	Calculation
Sodium ppm wt.	25.0	IP 377 Mod
Calcium ppm wt.	15.0	IP 377 Mod
Potassium ppm wt.	0.9	IP 377 Mod
Ash content % wt.	0.021	IP 4/D482

* No Flow at temperature / Extrapolated using D341

Table 7. Sirtica Crude Oil General Tests.

Property	Result	Method
Density @ 15°C g/ml	0.8194	IP 365/D4052
Specific Gravity @ 60°F	0.8198	Calculation
API Gravity @ 60°F	41.11	Calculation
Characterisation Factor	12.1	Calculation
Total Sulphur % wt.	0.42	IP 336/D4294
Mercaptan Sulphur ppm wt.	110	IP 342 Mod/ D3227 M
Total Nitrogen % wt.	0.12	IP 379 Mod/ D4629 M
Pour Point °C (°F)	- 9 (+ 16)	IP 15/D97
Viscosity @ 70°F, cSt	4.534	IP 71/D445
Viscosity @ 100°F, cSt	2.935	IP 71/D445
Vanadium ppm wt.	1.5	IP 377 Mod
Nickel ppm wt.	3.5	IP 377 Mod
Sodium ppm wt.	18.6	IP 377 Mod
Calcium ppm wt.	4.7	IP 377 Mod
Potassium ppm wt.	0.4	IP 377 Mod
Conradson Carbon % wt.	2.1	IP 13/D189
Asphaltenes % wt.	0.46	IP 143
n-Heptane insolubles % wt.	0.84	D893
Reid Vapour – Pressure KPa (psi)	54 (7.8)	IP 69/D323
Flash Point °C (°F)	< –20 (<–4)	IP 170
Hydrogen Sulphide ppm wt.	< 1	IP PM – BJ
Neutralization Number, mg KOH/g	0.10	IP 177/D664
Bottom, Sediment and Water % vol.	< 0.05	IP 359/D4007
Ash content % wt.	< 0.01	IP 4/D482

However, heavy fuel oils of reduced point can be made by using vacuum residue as visbreaker feedstock and back blending, the visbreaker residue with FCC light cycle oil and decant oil. Despite its metal content, Sirtica vacuum residue has a relatively high carbon residue content and is therefore, suitable as coker feedstock for the production of anode grade cock. Sirtica vacuum residue has both moderate penetration value and asphaltenes content. If required, it be used as feedstock for bitumen manufacture. However, due to its superior quality it is unlikely that its use as bitumen feedstock could be economically justified.

Characterization of Samples by Thermogravimetric (TGA)

Thermogravimetric analysis records the weight loss of a sample as the temperature is raised at uniform rate. Figure 3 shows TGA of the parent crude oils. For all the three crude oils weight loss occurs as first stage beginning at temperature 26C° and ending at 600°C. The values of weight loss at 600°C, 94.54% BCO, 97.33% BrCO and 100% for SCO. The weight loss of BCO was lower than the weight loss of BrCO and (SCO). As expected these results indicated that Bouri Crude Oil consists of a higher percentage of heavy fraction (i.e. asphaltene).

Figure 4 shows TGA of Bouri crude oil (BCO) and its asphaltene, maltene and vacuum residue. In this case, weight loss occurs as a multiple step beginning at temperatures in the range 50-400°C and ending at 570-600°C. The magnitudes of weight loss at 600°C was 94.54% (BCO), 48.96% asphaltene (BA), 94.04% maltene (BM), and 83.35% Bouri vacuum residue. These results indicated that the magnitudes of weight loss at

Table 8. Sirtica Yields and Inspections of vacuum Residue.

Property	Result	Method
Boiling Range °C	550+	Method
Vol. % on Crude	10.3	
Wt. % on Crude	12.6	
Density @ 15 °C g/ml	1.0038	IP 365/D4052
Gravity°API	9.39	Calculation
Specific Gravity @ 60° F	1.0042	Calculation
Total Sulphur % wt.	1.38	IP 336
Pour Point °C (°F)	+51	IP 15/D97
Viscosity @ 50°C, cSt	100,000 *	D341
Viscosity @ 100°C, cSt	1108	IP 71/D445
Nickel ppm wt. Vanadium ppm wt.	28.4 11.3	IP 377 Mod IP 377 Mod
Micro Carbon Residue % wt.	16.5	ASTM D4530
Asphaltenes % wt.	3.2	IP 143
n-Heptane insolubles % wt.	1.7	ASTM D893
Molecular Weight	530	Calculation
Calofric Value MJ/Kg gross	42.85	Calculation
Calofric Value MJ/Kg gross	10,235	Calculation
Sodium ppm wt.	25.4	IP 377 Mod
Calcium ppm wt.	10.9	IP 377 Mod
Potassium ppm wt.	0.6	IP 377 Mod
Ash content % wt.	0.012	IP 4/D482

600°C increase in the order of parent crude oil< maltene< asphaltenes, respectively. It should be noted the same trend for the Breaga and Sirtica crude oils and their fractions have been observed as shown in (Figs. 5 and 6).

As expected, the weight loss of samples decreased with increase in the heavy fractions. The asphaltene sample exhibits a relatively lower weight loss than the rest of samples over the whole temperature interval studied. This agrees with the fact that this sample has the highest heavy fraction, which indicates the presence of less volatile constituents than the other samples. This finding is consistent with the IR and NMR analysis.

Characterization by Infrared Spectroscopy

Infrared spectroscopy (IR) has found increasing use as instrumental analysis methods for coal, pitch, carbon fiber, and other carbon materials (El Akrami *et al*, 1997; Putzig *et al*, 1992; Guillien *et al*, 1992). This spectroscopy has been used to identify various types of hydrocarbons (aliphatic,

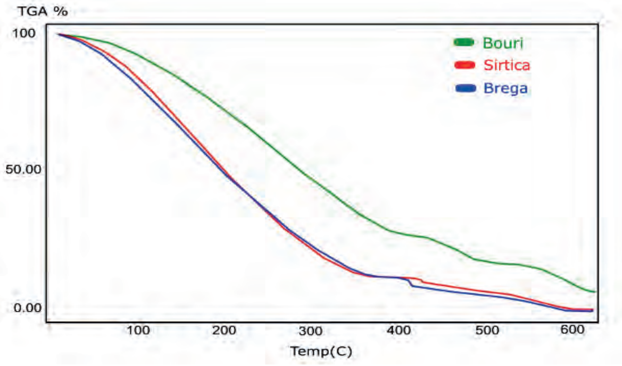

Fig. 3. TGA of the parent crude oils (Breaga, Sertica and Bouri).

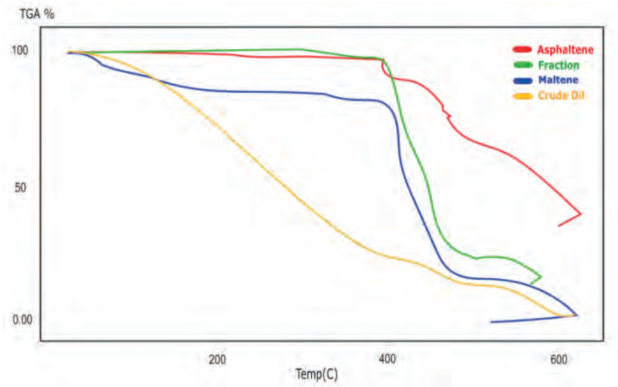

Fig. 4. TGA of Bouri crude oil (BCO) and it's asphaltene (A), maltene (M) and vacuum residue (Fraction F).

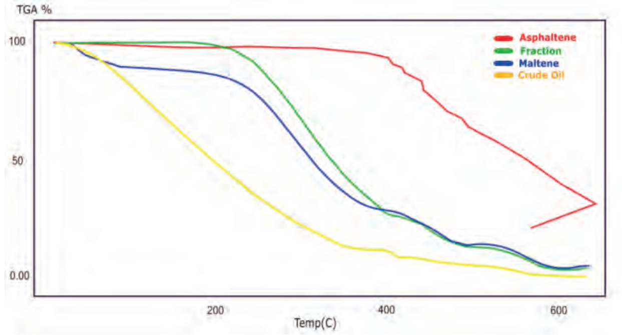

Fig. 5. TGA of Breaga crude oil (BrCo) and it's asphaltene (A), maltene (M) and vacuum residue (Fraction F).

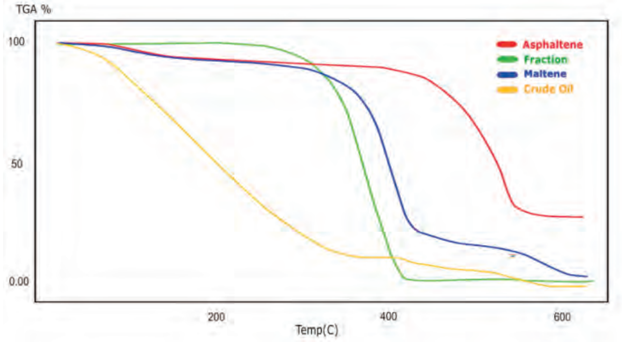

Fig. 6. TGA of Sirtica crude oil (SCO) and it's asphaltene (A), maltene (M) and vacuum residue Fraction (F).

aromatic, etc.) and functional groups that are present overlapped bands.

Figure 7 shows the IR spectra of the parent (BVR) and solvent extracted fractions (asphaltene and maltene). The spectra show characteristic absorption bands corresponding to aromatic structures at (3050, 1600, 870, 810,750cm-1) and aliphatic structures at (2960, 2922, 2855, 1450, 1379cm-1) Reference (El Akrami *et al*, 1997) The bands at 3050cm-1 in the spectra are mainly attributed to the stretching mode of C-H aromatic hydrocarbons, while the bands in the 1600cm-1 region are assigned to the stretching of aromatic C=C groups. Bands in the region 900 to 700cm-1 are usually assigned to the out-of-plane bending of aromatic C-H groups. The bands in the 2970-2700 and the bands in the 1450-1377cm-1 are due to the stretching and bending modes of saturated aliphatic hydrocarbons, respectively (El Akrami *et al*, 1997). The broad strong band observed at 1400-1600, and the sharp strong bands at 2150 and 2300 cm-1 are due CS_2 which was used as solvent for some of the samples. It should be noted that the bands at 1600 and 1450cm-1 are overlapped.

Compared to asphaltene fraction, the maltene, which constitute the bulk of the BVR, appear to have a lower degree of conjugation (or ring condensation) and less substitution on the aromatic rings in view of the higher hydrogen aromaticity as inferred from the higher intensity of the composite bands at 700-900cm-1. The maltene fraction was found to be more paraffinic than the asphaltene fraction. The whole BVR gave a spectrum that is very similar to that of the maltene. The asphaltene, on the other hand, is the most aromatic fraction of the BVR sample, as can be seen from the comparison of the intensities of the respective aliphatic and aromatic with those of other samples. In Figure 8 the IR spectra of parent crude oils showed that the relative intensities of aliphatic C-H bands (CH_2 and CH_3; 3000-2850cm-1) were stronger than those of aromatic C-H band (around 1600cm-1), and CH_2 bands (around 2927cm-1) stronger than those of CH_3 bands (around 2954cm-1). This indicates that these materials contained significant amounts of aliphatic components, especially naphthenic rings (Seshadri *et al*, 1985). The sharp strong bands at 2927cm-1 clearly arise from the saturated C-H stretching vibrations of alkyl substituents (methylene groups -CH_2) and the very weak bands near 3050cm-1, suggests that the aromatic rings are highly substituted. In general, the absorbances at 3050 and 2927cm-1 allow evaluation of the concentrations of aromatic and aliphatic bonds in the samples (Seshadri *et al*, 1985).

Figure 9 shows the infrared spectra of the asphaltenes fractions. Sirtica asphaltene exhibited a very weak band at 1600cm-1, the intensity of which is higher for the Bouri and Breaga asphaltenes Moreover the aliphatic C-H bands (2855-2960cm-1) and methylene/naphthenic C-H bending bands (1450cm-1) of Sirtica asphaltene were more intense than those of the Bouri and Breaga asphaltenes, indicating that most of the alkyl groups are in methylene or naphthalene form. Among the asphaltenes materials studied, Bouri asphaltene showed the highest aromatic nature as deduced from the absorption at 1600 and 700-900cm-1.

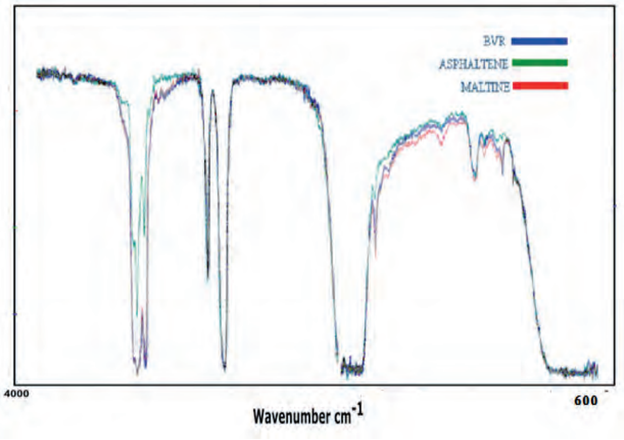

Fig. 7. IR spectra of the parent (BVR) and solvent extracted fractions.

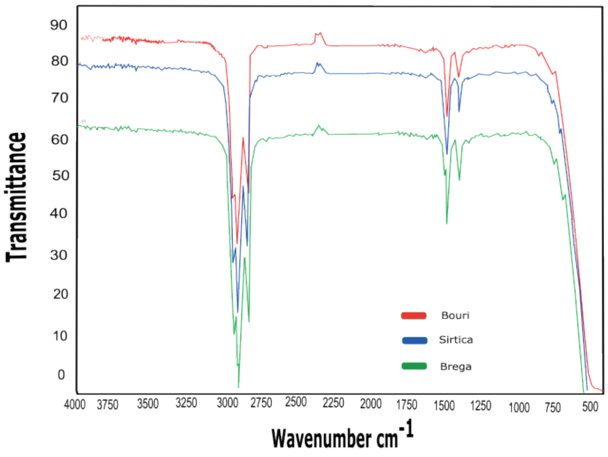

Fig. 8. IR spectra of the parent crude oils (Bouri, Sirtica and Brega).

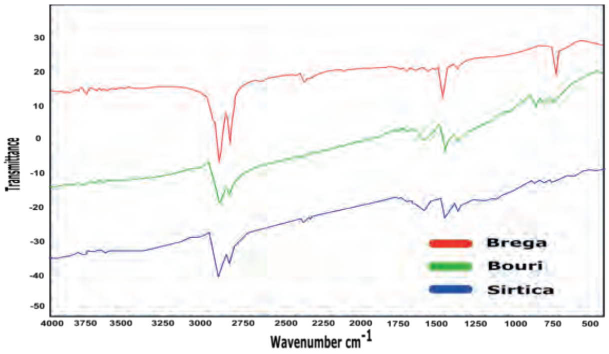

Fig. 9. IR spectra of the asphaltenes fractions.

CONCLUSIONS

Based on the results obtained in this study and the conditions under which they are obtained the following conclusions can be drawn.

- Due its high softening point and asphaltene content the Bouri vacuum residue is promising material as carbon fibre precursors.
- Due to its low sulphur and metals content, Breaga vacuum residue is excellent coker feedstock for anode grade production.
- Sirtica vacuum residue has both moderate penetration value and asphaltenes Content. It is possible that it could, if required, be used as feedstock for bitumen manufacture.
- Providing a market can be found for high sulphur coke, Bouri vacuum residue could be used as coker feedstock for the production of fuel grade coke.
- Vacuum distillation was an effective method in increasing the softening point of the crude oils.
- Vacuum distillation promoted the dehydrogenation and aromatization through reduction of aliphatic hydrogen.
- Structural characterization by softening point and IR showed that distillation of lighter fractions increased the softening point and dehydrogenation raised their aromaticity.

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