

Investigation of the Processing of Libyan Crude Oil Residues into Carbon Fibers

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Abstract

The high cost of the present carbon fiber precursors led researchers to investigate new and cheaper sources. Hence, the scientists all over the world have been making their efforts to develop the material suitable to their native country and attempting to find a new way to make carbon fiber. This study aims to investigate the processing of Libyan oil residues into high quality carbon materials. Samples from Bouri, Es Sider and Amna crude oils were processed by vacuum distillation and air blowing methods to produce pitch precursors. Structural characterization has been carried out by various techniques such as softening point (SP), Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Vacuum distillation markedly decreased atomic H/C ratio and increased aromaticity as well as the softening point. FT-IR analysis of the produced pitches showed that the relative intensities of the bands associated with aliphatic structure decreased with increased softening point, while the bands of aromatic structure were found to be slightly increased. The formation of the oxygenated compounds was the major feature of air blowing technique. The softening point of the blown pitches could be raised to about 175 °C, giving relatively less weight loss (64%). Carbon fibers have been produced successfully from the Bouri oil residues. The Bouri vacuum distilled pitch was successfully melt-spun into fibers. The resulting fibers were stabilized by oxidation with air. The morphology of the Bouri carbon fiber was studied by scanning electron microscopy (SEM).

Keywords: Carbon fiber; petroleum pitch; chemical structure.

1. Introduction

The high cost of the present carbon fiber has led researchers to search for alternative and cheaper sources [1]. As a result of this, coal tar pitch, petroleum pitch and oil shale based pitches are studied for carbon fiber production. Petroleum pitch is the most cost-effective raw material for producing carbon fibers. In petroleum industry, various processes can be used to produce petroleum pitch such as, thermal treatment, vacuum or steam stripping and oxidation. The exact composition and properties of the petroleum pitch depend on the source of the original material. Pitch can be considered to be composed of four general classes of chemical

compounds: naphthenic aromatics, saturates, polar aromatics, and asphaltenes. Compared to the other fraction, asphaltene is the highest molecular weight, and it also has the highest aromaticity in a pitch. Because it tends to consist of large, alkylated, plate-like molecules of condensed aromatic rings, the asphaltene fraction is the most thermally stable portion of the pitch [2]. As the asphaltene fraction of a pitch increases, the softening point, thermal stability and carbon yield tend to increase [3]. The softening point, thermal stability and potential carbon yield of a given pitch depend on the chemical composition of that pitch.

Generally, carbon fibers are classified into three

main groups [4]. The first group of carbon fibers is derived from, polyacrylonitrile (PAN), which is characterized by high tensile strength. The second types are anisotropic carbon fiber based on mesophase pitch; they have high Young's modulus. The last groups are isotropic pitch-based carbon fibers; they are characterized by moderate mechanical properties and low price. Because of their low production cost, this group of carbon fibers found wide applications in the industry. In recent times, isotropic pitch based carbon fibers have been used as thermal insulation at high temperature gaskets, filters in various plastics and so on [5].

Extensive studies have been focused on the preparation of mesophase pitch precursors from different hydrocarbons [6–14]. However, the preparation of isotropic pitch has received little attention [15–17]. In this context, Libyan hydrocarbon sources may be considered as possible carbon fiber sources. Such research is expected to improve the economics of Libyan crudes utilization and to produce value added materials that are more expensive to produce from other sources.

2. Experimental

2.1. Materials

Bouri, Es Sider, and Amna 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 Table 2.1.

Bouri crude oil (BCO) is more typical of a Middle-East rather than a N. African crude. It is classified as an intermediate crude oil having a gravity of 25.9 °API and a total sulfur content of 1.86 wt.%. However, compared to other heavy crudes, Bouri has an unusually high n-heptanes insoluble content of 21.3 wt.%. In addition to its extremely high n- heptanes insoluble content (85 wt.%), Bouri vacuum residue also (BVR) has a high pour point of +69 °C.

Es Sider crude oil (SCO) is classified as an intermediate crude oil having a gravity of 37 °API and a total sulfur content of 0.39 wt.%. The crude's product quality yield structure is similar to that of Brent. Es Sider vacuum residue (SVR) has a nickel +vanadium of about 60 ppm, Sulphur content of about 1.0 wt.% and a pour point of 54 °C.

Amna crude oil (ACO) is more typical of a Middle-East rather than a North African crude. It is classified as an intermediate crude oil having a gravity of 36.7 °API, a total sulfur content of 0.17 wt.% and a pour point of +24 °C. Amna vacuum residue (AVR) has vanadium + nickel content of approximately 4 ppm, a sulphur content of 0.30 and a pour point of 63 °C.

2.2. Pitch preparation

2.2.1. Vacuum distillation of crude oils

25 liters of each crude oils were distilled in the Kontes Martin (ASTM D2892) apparatus under atmospheric pressure to 175 °C and then under vacuum at a pressure of 10 mm Hg to 400 °C. The vacuum distilled on the Sarina High Vacuum (ASTM P196) still at 0.3 mm Hg to 565 °C. The vacuum residues obtained from these three crude oils (Bouri, Es Sider and Amna) were coded as BVR, SVR, and AVR.

2.2.2. Air blowing

Air blowing is known to be one of the methods used to raise the softening point of pitches and produce precursors preferable to general purpose carbon fiber. In this study, 50 g of vacuum distilled samples of Bouri (BVR) was subjected to air blowing at 250 °C, 275 °C, and 300 °C in an electric furnace for several hours. A thermocouple was directly immersed into the liquid pitch for exact measurement of pitch temperature. The blown air was introduced into the bed of pitch at room temperature at a calibrated flow rate of 225 ml/min. During the blowing, softening point of the pitch was monitored at every hour by a ring and ball method. Yield of air blown pitches were determined from the weight the pitch remaining in the reactor.

2.3. Melt spinning

The selected pitches were spun into pitch fibers of 10 to 15 µm in diameter through a single spinneret with a capillary diameter of 300 µm (capacity about 8 gram) that is operated under nitrogen. The Bouri pitch precursors were spun under 30-40 Psi at different temperature according to their softening point temperature. Ambient air quenched the fiber as it is extruded from the capillary, and the cooled fiber was collected on a fiber wind-up device. The distance from the spinneret to the wind up device was about 30 cm for all spinning experiments.

Table 2.1: General characteristic of the parent crude oils and their vacuum residues.

Sample	$^{\circ}$ API at 15.6 $^{\circ}$ C	S wt. %	PP $^{\circ}$ C	HI wt. %	V & N ppm
BCO	25.9	1.86	+9	21.3	14 & 12
BVR	4.7	3.12	+69	85.0	58 & 50
SCO	37	0.39	9	0.73	2 & 7
SVR	10.2	0.97	54	6.79	14 & 45
ACO	36.7	0.17	+24	–	1.12 & 0.34
AVR	14.6	0.30	63	–	2.78 & 0.89

S: Total Sulphur, PP: Pour Point, HI: n-Heptane Insoluble, V: Vanadium, N: Nickel.

2.4. Characterization of crude oils and their vacuum residues

FT-IR spectra of all parent oils and vacuum distilled pitches were obtained with a Nicolet 20 SXC FT-IR spectrophotometer. Samples were first dissolved in carbon disulphide and then smeared uniformly on pre-weighed KBr windows. Using the band assignments established for complex organic molecules, the FT-IR spectra were used to a qualitative comparison of the molecular nature of the samples.

TGA measurements were conducted in a Stanton-redcroft STA-781 thermo analyzer. Samples were deposited on platinum crucibles, using sample mass of 20 mg. Experiments were carried out under nitrogen at a flow rate of 50 ml/min using heating rate of 5 $^{\circ}$ C/min over the 293-973 K temperature interval. TGA analysis was also applied to determine the coke yield. 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 (2 g.), 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 25 mm. The morphology of the produced fibers was observed by scanning electron microscopy (SEM).

3. Results and Discussion

3.1. General properties of the parent crude oils and their vacuum distilled residues

Some properties of Bouri Es Sider and Amna crude oils and their vacuum distilled residues are com-

pared in Table 3.1. Vacuum distillation decreased atomic H/C ratio and increased aromaticity as well as the softening point. The softening point temperatures of the vacuum distilled pitches increased with decreasing H/C ratios in the order of AVR < SVR < BVR. The Bouri vacuum distilled residue showed a softening point of 60 $^{\circ}$ C compared with 40 and 42 $^{\circ}$ C for Es Sider and Amna vacuum distilled residues, respectively. Since the atomic H/C ratios of vacuum distilled pitches, measured from elemental analysis results, showed that BVR has a lower value than SVR and AVR fractions. This indicates that the BVR is more aromatic than SVR and AVR fractions. The aromaticity (H/C atomic ratio) and the softening points of the vacuum distilled pitches were found to be dependent on the nature of the original crude oil. It is generally known that the lower the hydrogen-to-carbon ratio, the greater the degree of ring condensation, regardless of whether the rings aromatics or naphthenic in nature [18]. Moreover, the vacuum distilled residues were subject to characterization studies by determining the asphaltene, yield and sulphur content. The results of which are compiled in Table 3.1. The distillation under vacuum increased the sulphur content while decreased hydrogen to carbon ratio (H/C). This indicates heteroatoms especially S tends to concentrate in the heavy fractions. It should be also noted that the BVR has the highest asphaltene content (16.0%) and yield (25.1%) compared with SVR and AVR. These finding indicate that the chemical constitution of the heavy fractions (asphaltene) depends upon the nature of the starting materials (i.e., the original hydrocarbons or its fractions).

3.2. Characterization of samples by FT-IR

Figure 3.1 shows the infrared spectra of the parent crude oils. The spectra show characteristic absorption bands corresponding to aromatic structures

Table 3.1: Properties of the parent crude oils and their vacuum residues.

Sample	As wt.%	SP °C	EA wt.%				Yield wt.%
			S (%)	C (%)	H (%)	H/C	
BCO	3.30	<15	1.86	85.99	11.90	0.83	–
BVR	16.0	60	3.12	84.33	9.99	0.70	25.1
SCO	0.53	<15	0.39	83.00	12.30	0.89	–
SVR	3.80	42	0.97	83.02	11.08	0.80	15.2
ACO	0.22	<15	0.17	81.09	13.18	0.97	–
AVR	0.49	40	0.30	87.17	11.94	0.82	21

As: Asphaltene, SP: Softening Point (°C), EA: Elemental Analysis (wt.%), S: total Sulfur, C: Carbon, H: Hydrogen, H/C: Atomic ratio, Yield: cut yield on crude (wt.%).

at (3050, 1600, 870, 810, 750 cm^{-1}) and aliphatic structures at (2966, 2922, 2850, 1450, 1379 cm^{-1}) [19, 20]. The bands at 3050 cm^{-1} in the spectra are mainly attributed to the stretching mode of C-H aromatic hydrocarbons, while the bands in the 1600 cm^{-1} region are assigned to the stretching of aromatic C=C groups. Bands in the region 900 to 700 cm^{-1} are usually assigned to the out of plane bending of aromatic C-H groups. The bands in the 2970-2700 cm^{-1} and the bands in the 1450-1377 cm^{-1} are due to the stretching and bending modes of saturated aliphatic hydrocarbons, respectively [21]. The FT-IR spectra of the parent crude oils showed that the relative intensities of aliphatic C-H bands (CH_2 and CH_3 ; 3000-2850 cm^{-1}) were stronger than those of aromatic C-H band (around 1600 2), and CH_2 bands (around 2927 cm^{-1}) stronger than those of CH_3 bands (around 2954 cm^{-1}). This indicates that these materials contained significant amounts of aliphatic components, especially naphthenic rings. The sharp strong bands at 2927 cm^{-1} clearly arise from the saturated C-H stretching vibrations of alkyl substituents (methylene groups CH_2) and the very weak bands near 3050 cm^{-1} , suggest that the aromatic rings are highly substituted. In general, the absorbance at 3050 and 2927 cm^{-1} allows evaluation of the concentrations of aromatic and aliphatic bonds in the samples [22].

Figure 3.2 shows the FT-IR spectra obtained for the Bouri crude oil (BCO), for the material obtained after heat treatment in air at 275 °C for 1 hour (BAb1) and 5 hours (BAb5). In general, the major air blowing products are carbonyl C=O (1700 cm^{-1}), phenoxyl (1280 cm^{-1}) and hydroxyl functional groups formed at aliphatic side chain [15]. After air blowing at 275 °C for 5 hours the

band 1700 cm^{-1} appears. The appearances of this band reflect higher oxygen content of the air-blown pitches. Also, for BAb5, new beak appears at about 1530 cm^{-1} , which could be attributed to nitro groups. A weak and broad but distinct band was observed at about 1030 cm^{-1} and attributed to aryl-aryl ether [23]. As expected, both BAb1 (275 °C - 1 hour) and BAb5 (275 °C - 5 hours) are considerably more aromatic in nature as deduced from the strong bands at 1600 and 700-900 cm^{-1} , BAb5 being comparatively more aromatic. Unexpectedly, no clear absorbance was observed at 1100 to 1300 cm^{-1} in the air-blown pitches attributable to carbon-oxygen-carbon single bond asymmetric stretching.

3.3. Characterization of air blown pitches by thermogravimetric analysis (TGA)

Figure 3.3 shows thermogravimetric analysis (TGA) of air blown pitches at temperature of 300 °C for 1, 3, and 5 hours. These pitches obtained at these corresponding times were coded as 300-1, 300-3 and 300-5. Thermogravimetric analysis records the weight loss of a sample as the temperature is raised at uniform rate. In the case of these pitches, it may be seen, that weight loss occurs as a multiple steps beginning at temperatures in the range 380-420 °C and ending at 600-700 °C.

The relationship between the softening point and the weight loss of the air blown pitches from the Bouri vacuum residue are shown in Table 3.2. It shows that the magnitude of weight loss at 600 °C varied from 73% (BVR) to 64% at 300 °C for 5 hours. Furthermore, a small, continuous weight loss occurred above 700 °C, especially for 300-5 sample. The magnitude of weight loss in this high temperature was generally smaller and lower than 10% of

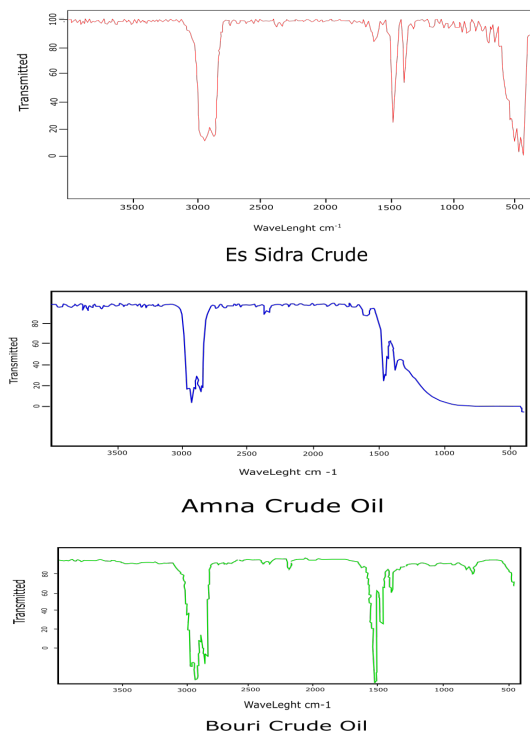


Figure 3.1: FT-IR spectra of the parent crude oils.

the sample weight at the beginning of the experiment. As expected the softening point of pitches increased with decrease in the weight loss (see Table 3.2). The softening point of the blown pitches could be raised to about 175 °C, giving relatively less weight loss (64%). It should be noted that 300-5 sample exhibits a relatively lower weight loss than the rest of pitches over the whole temperature interval studied. This agrees with the fact that this sample has the highest softening point which indicates the presence of less volatile constituents than the other samples.

Table 3.2: Relationship between the softening point and the weight loss of the air blown pitches from Bouri vacuum residue.

Sample	Softening point °C	Weight loss wt. %
BVR	60	73
300-1	100	71
300-3	157	68
300-5	175	64

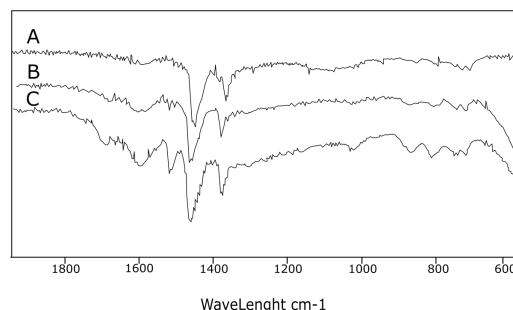


Figure 3.2: FT-IR spectra of the BCO (A) and its air blowing pitches; BAb1(B) and BAb5 (C).

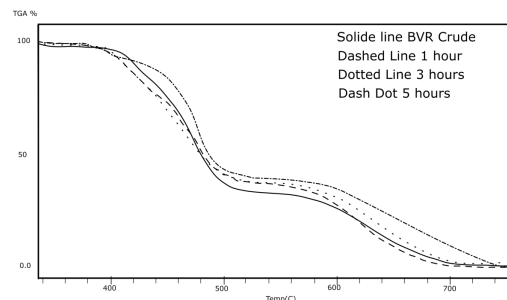


Figure 3.3: TGA curves for the air blown pitches.

3.4. Spinning and Stabilisation

Selected pitches obtained with different air blown conditions were processed by melt spinning. Reasonable amounts of continuous pitch fibers were successfully produced from Bouri petroleum pitches, using a mono-hole spinneret at temperatures between 185 and 280 °C, under nitrogen pressure. Only the samples with relatively high softening points were spun, the samples with low softening points were not used because of the difficulties that would involve their subsequent stabilization. In order to get a comparable evaluation of the spinnability of the various pitch combinations, the spinning parameters were not varied. The only variable parameter was the spinning temperature. It has been found that the average spinning temperature is about 40 °C higher than the softening temperature. Since, it is common practice in the art to characterize in part a precursor pitch by its softening point. Thus, the softening point may be used as a close approximate to determine the desired spinning temperature. Figures 4.1, 4.2, 4.3 show SEM micrographs of the successfully produced fibers from Bouri oil pitches. According to the original pitch precursor and soft-

ening point the melt spun fibers were oxidatively stabilized at 110, 160, 220 °C for different periods of time. The heating rate up to the stabilization temperature was 3 °C/min. Other heating rates were also examined. As shown in these figures there are no evident cracks or pores and very smooth surfaces with uniform diameters of the stabilized fibers have been produced. This means that the lack of fluctuation of diameter along the fiber axes was recognized. The average diameter of the as-spun fiber was about 15 μm, and it could be reduced by increasing the take-up speed. The thinner- diameter fiber would be expected to have higher tensile strength, since the molecular structure within the fiber tends to be oriented along the fiber axis, and the thin fiber has more orientation and more uniform radial temperature distribution during stabilization. It should be noted that these fibers are clearly separate and have retained the original fiber shape.

4. Conclusions

The following conclusions can be drawn from the results obtained in this study.

1. This study represents the first successful production of carbon fibres from Libyan precursors. It suggested that the Bouri vacuum residue is a promising material as carbon fiber precursors.
2. Both vacuum distillation and air blowing were effective methods for increasing the softening point of the pitch materials.
3. FT-IR spectra of blown pitches showed that the high yield and formation of oxygenated compounds such as carbonyl and phenoxy groups are the major feature of the air blowing technique.
4. Structural characterization by TGA and FT- IR showed that distillation of lighter fractions, increase in the softening point and dehydrogenation raised their aromaticity.
5. In summary, the distillate from Bour crude oil has the potential for conversion into carbon fibres once the appropriate route has been defined. It might also be appropriate for conversion into petroleum coke or even into mesophase-based powders for so-called 'sinterable' carbons. However, a detailed study is required to process the distillate into the appropriate form and to optimise the fibre production conditions.

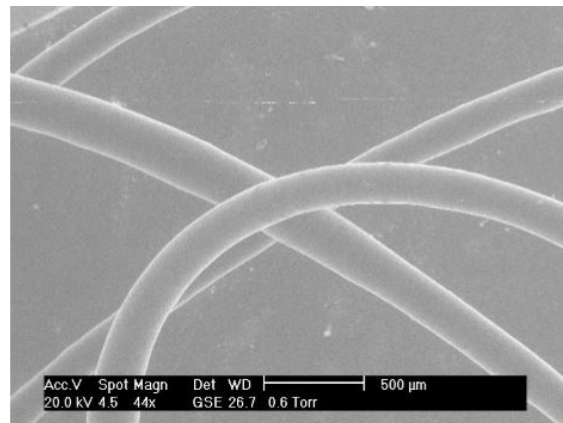


Figure 4.1: SEM micrographs of carbon fibers successfully prepared from Bouri oil pitches.

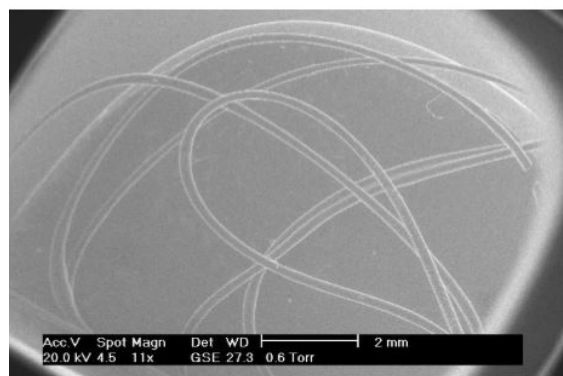
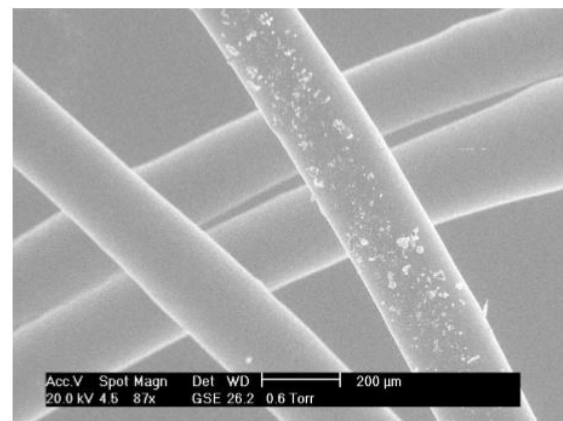


Figure 4.2: SEM micrographs of carbon fiber successfully prepared from Bouri oil pitches.

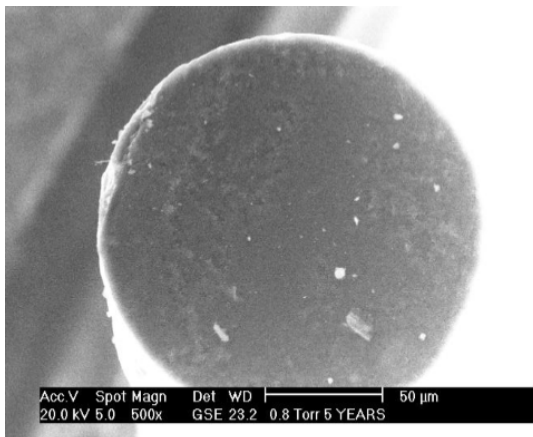


Figure 4.3: Fracture surfaces of fibers showing a uniform texture for Bouri oil sample.

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