Mesophase formation behavior in petroleum residues

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Abstract

Mesophase pitch is an important starting material for making a wide spectrum of industrial and advanced carbon products. It is produced by pyrolysis of petroleum residues. In this work, mesophase formation behavior in petroleum residues was studied to prepare environmentally-benign mesophase pitches, and the composition of petroleum residues and its influence on the mesophase formation was investigated. Two petroleum residues, i.e., clarified oil (CLO-1, CLO-2) obtained from fluid catalytic cracking units of different Indian petroleum refineries, were taken as feed stocks. A third petroleum residue, aromatic extract (AE), was produced by extraction of one of the CLO-1 by using N-methyl pyrrolidone solvent. These petroleum residues were thermally treated at 380°C to examine their mesophase formation behavior. Mesophase pitches produced as a result of thermal treatment were characterized physico-chemically, as well as by instrumental techniques such as Fourier-transform infrared spectroscopy, nuclear magnetic resonance, X-ray diffraction and thermogravimetry/derivative thermogravimetry. Thermal treatment of these petroleum residues led to formation of a liquid-crystalline phase (mesophase). The mesophase formation behavior in the petroleum residues was analyzed by optical microscopy. Mesophase pitch prepared from CLO-2 exhibited the highest mesophase content (53 vol%) as compared to other mesophase pitches prepared from CLO-1 and AE.

Key words: clarified oil, aromatic extract, mesophase pitch, optical microscopic analysis

1. Introduction

The main focus of petroleum refineries is the production of transportation and heating fuels, either by atmospheric distillation or by the cracking of distillates produced from vacuum distillation. Such petroleum refining processes generate some aromatic-rich petroleum residues. For example, the generation of substantial quantities of residue, i.e. clarified oil (CLO), from fluid catalytic cracking (FCC) is unavoidable during the production of large volumes of transportation fuels. In addition to being rich in aromatics these petroleum residues generally have a high C/H ratio and can be good feed stocks for making mesophase pitches, that is, petroleum pitches which contain mesophase spheres. Mesophase pitches are considered to be good starting material for many industrial and advanced carbon products, such as carbon fibres [1], needle coke [2], graphite electrodes [3-5], C-C composites [6], fine-grained sintered carbons [7,8], Li-ion battery anodes [9], mesocarbon microbeads [10,11], carbon foam [12] and plasma-facing components for fusion devices [13] etc.

The formation of mesophase pitch from petroleum residues depends mainly on residue composition and process conditions. Mesophase pitches produced by the thermal polymerization of aromatic rich fractions of crude oil generally consist of polycyclic aromatic hydrocarbons (PAHs) and have molecular weights ranging from 200 to 2000 [14,15]. The physico-chemical properties and chemical composition of petroleum residues have a great impact on mesophase formation behavior as well as the resulting mesophase pitch properties. It has been found that the molecular composition of petroleum residue greatly affects the mesophase development [2]. Different types of hydrocarbons, such as saturates, aro-

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matics, resins, asphaltenes, and heteroatoms like sulfur, oxygen, nitrogen, and impurities present in the petroleum residues affect the mesophase formation and the quality of mesophase pitches [16-19]. In general, saturate hydrocarbons favor gas evolution as a result of cracking during thermal treatment. Aromatic hydrocarbons promote polymerization and condensation reactions which help mesophase formation. But while aromatic molecules are desirable, but that does mean that all types of aromatic hydrocarbons favor the development of mesophase pitch. For example, long alkyl side chains attached to the aromatic ring are unfavorable because they can hamper mesophase growth [16]. Asphaltenes and resin are undesirable because they contain heteroatoms and inhibit the process of mesophase development. Asphaltenes present in petroleum residues are also responsible for the formation of less ordered mosaic structure [20].

Mesophase pitches are mainly produced from coal tar and petroleum feed stocks. Coal tar generally contains high ash content and high levels of PAH. In recent years, restrictive environmental regulations concerning the emission of toxic and carcinogenic pollutants into the atmosphere from coke ovens, and the closure of numerous coke plants in some countries, have stimulated the search for new pitches capable of replacing the coal tar pitches. In contrast, petroleum pitches prepared from polycyclic aromatics from petroleum feed stocks have lower ash content, fewer impurities, and are less toxic and carcinogenic, and so may be a good alternative generation of pitches [21-23]. Another problem associated with coal-tar pitch is the presence of inherent primary quinoline insolubles (QI) which impede its direct use for some applications, such as for making carbon fibres. For these reasons, petroleum pitches prepared from petroleum feed stocks are considered superior to coal tar pitches. Certain other advantages are associated with petroleum pitches: they require lower processing temperatures and the resulting carbon products are easily stabilized. Furthermore, the processing conditions of petroleum residues give rise to products with

different compositions and degrees of polymerization, which are key issues in the development of mesophase pitch.

Not all petroleum residues have the potential to produce mesophase pitch suitable for making carbon materials. Therefore, in the present paper, CLO-1, CLO-2 and aromatic extract (AE) were studied to examine the mesophase formation behavior of these petroleum residues. The structures and chemical compositions of the pitches were investigated using elemental analysis, Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and thermogravimetry/derivative thermogravimetry (TG/DTG). Finally, optical microscopy was used to examine the pattern of mesophase formation in different petroleum residues.

2. Experimental

2.1. Raw materials

In this study, we have taken three petroleum residues, namely two FCC, CLO-1, CLO-2 and one AE from different Indian petroleum refineries, for the preparation of petroleum mesophase pitches. The physico-chemical properties of CLO-1, CLO-2 and AE are given in Table 1. AR grade toluene and quinoline were used as solvents for determining the toluene insolubles (TI) and QI in the produced mesophase pitches.

2.2. SARA analysis of petroleum residues

For deeper insight into the composition of the petroleum residues, these residues were separated into SARA-fractions (i.e. saturates, aromatics, resins and asphaltenes) by using standard procedures [24] based on adsorption chromatography. Fig. 1 shows the distribution of saturates, aromatics, resins and asphaltenes type hydrocarbons in these petroleum residues.

Table 1. Physico-chemical properties of CLO-1, CLO-2 and AE

Characteristics	Test method	CLO-1	CLO-2	AE
Density d_4^{15} gm/mL	IP 190	0.9251	1.0924	1.1157
BMCI	By calculation	51.00	131	139
Viscosity at 70°C (cSt)	ASTM D 445	11.82	69.91	186.95
MCR %wt	ASTM D 4530	1.01	9.26	5.10
Sulfur %wt	ASTM D 4294	1.28	1.01	2.23
Pour point (°C)	ASTM D 97	45	6	24
UV characterization				
Mono aromatic (wt%)		19.8	27.1	19.7
Di-aromatic (wt%)		14.3	20.7	16.6
Poly aromatic (wt%)		28.4	51.1	63.6
Total aromatic (wt%)		62.5	98.9	99.9
Total saturate (wt%)		37.5	1.1	0.1

CLO: clarified oil, AE: aromatic extract, BMCI: Bureau of Mines Correlation Index, MCR: micro carbon residue.

Fig. 1. SARA analysis of clarified oils (CLO-1, CLO-2) and aromatic extract (AE).

2.3. UV, visible, near infrared spectroscopic analysis of petroleum residues

UV spectroscopy was used to determine total aromatics and their distribution in the petroleum residues (CLO-1, CLO-2 and AE), and are given in Table 1. Estimation of total aromatics and their distribution (mono-, di- and poly- aromatics) in the petroleum residues was done by UV-VIS-NIR spectrophotometer of Lambda-19, Perkin-Elmer make. For UV analysis, solutions of the three petroleum residues were made in spectroscopic grade iso-octane (2-2-4-tri-methyl-pentane). UV spectra were recorded in the wavelength region of 335-190 nm. All measurements were made using 1 cm cubic quartz cells under the same experimental conditions. Estimation of mono-, di-, and poly-nuclear aromatics in the three petroleum residues was done using varying molar absorptivities of mono-, di-, and poly-nuclear compounds at 197, 230, and 260 nm respectively.

2.4. Preparation of mesophase pitches

The process steps followed for production of the petroleum mesophase pitches are depicted in Fig. 2. The petroleum residues were thermally treated to examine their mesophase formation behavior. For thermal treatment, 325 g of the feed stock was charged in a laboratory scale glass reactor consisting of gas purging and measurement of the reaction temperature. Thermal soaking was performed at 380°C by maintaining a heating rate of 5°C/min under continuous purging with nitrogen gas. The rate of purged nitrogen gas was maintained at 150 mL/min using a wet gas flow meter to create an inert reaction atmosphere and to provide enough turbulence for the viscous pitch material. All thermal soaking experiments were carried out at atmospheric pressure. The petroleum pitches prepared from CLO-1, CLO-2 and AE were respectively named CLO-1-380(1), CLO-1-380(2), CLO-1-380(3), CLO-1-380(4), CLO-2-380(1), CLO-2-380(2),

CLO-2-380(3), AE-380(1), AE-380(2), and AE-380(3), where first two values represent the petroleum residue type, the third represents thermal soaking temperature and the fourth represents the petroleum pitch sample number. Sample nos. CLO-1-380(1), CLO-1-380(2) and CLO-2-380(1) could not be characterized because they were not converted into petroleum pitches.

2.5. Characterization of mesophase pitches

The physico-chemical properties of the mesophase pitches prepared from the three different petroleum residues were determined by ASTM methods, and included softening point (SP, Mettler Toledo FP90, ASTM D-3104), coking value (CV, ASTM D-4530), TIs (ASTM D-4312) and QIs (ASTM D-2318). The physico-chemical properties of the pitches are given in Table 2.

Elemental analysis, i.e. carbon, hydrogen, nitrogen and sulphur contents of mesophase pitches were determined using Elementar Vario Micro Cube.

The microstructures of the mesophase pitches were studied using a polarized light optical microscopy technique. The ASTM D 4616-95 test procedure was used to determine the mesophase content (MC) in the pitch samples. The mesophase formation in the pitches was examined using a state-of-the-art NIKON Optical Microscope. Pitch samples were first embedded in an epoxy resin and then the embedded pitch samples were ground using silicon carbide abrasive papers of various grit numbers. The ground pitch samples were then polished with alumina powder of different micron sizes. The grinding and polishing were done by hand, using water as a lubricant. The polished pitch samples were examined using a polarized light microscope under 500× magnification. The percentage of mesophase in the pitch samples was determined by manual counting in vol% by taking five observations of each sample in different directions and taking the average of the same. The MC was calculated quantitatively by using the following equation:

$$\% \text{ Mesophase content} = \frac{\text{Mesophase Counts}}{1000(\text{Total Counts})} \times 100$$

FT-IR spectra of the mesophase pitches were recorded on a Perkin Elmer spectrometer using dried KBr pellets. All spectra were recorded in the range of 4000-600 cm^{-1} . Absorbance of all mesophase pitches was calculated from these spectra by normalization and baseline correction of these spectra.

The mesophase pitch samples were characterized using liquid-state ^1H NMR and ^{13}C NMR spectroscopy. The spectra of these samples were recorded on a Bruker AV-III 500 NMR spec-

Fig. 2. Schematic diagram of the processing of petroleum decant oil to produce pitches.

Table 2. Mesophase pitch properties

Sample	N ₂ gas flow rate mL/min	Soaking time (h)	SP (°C)	CV (wt%)	TI (wt%)	QI (wt%)	MC (vol%)	I _{Ar} ^{a)}
CLO-1-380(1)	150	5.00	ND	14.30	0.98	0.20	ND	-
CLO-1-380(2)	150	7.30	ND	28.63	6.00	0.29	ND	-
CLO-1-380(3)	150	10.00	120	58.0	37.3	4.6	8	0.46
CLO-1-380(4)	150	10.15	150	65.6	48.1	8.3	19	0.48
CLO-2-380(1)	150	5.00	ND	31.54	7.98	0.31	ND	-
CLO-2-380(2)	150	7.30	90	49.1	25.9	2.2	BCL	0.43
CLO-2-380(3)	150	9.00	145	69.3	57.8	20.7	53	0.54
AE-380(1)	150	5.00	90	47.2	24.9	2.7	BCL	0.37
AE-380(2)	150	7.30	130	58.0	41.7	6.6	8	0.41
AE-380(3)	150	8.30	152	65.2	51.7	12.3	34	0.42

SP: softening point, CV: coking value, TI: toluene insoluble, QI: quinoline insoluble, MC: mesophase content, ND: not determined, BCL: below countable limit, CLO: clarified oil, AE: aromatic extract.

^{a)} Aromaticity index determined by FT-IR spectroscopy [33].

trometer with ¹H larmer frequency of 500.1 MHz. For ¹H NMR and ¹³C NMR spectroscopic analysis, solutions of the petroleum residues, and the pitches that were prepared from them, were made in CDCl₃ and tetra-methyl-silane (TMS) was used as an internal reference. For ¹H NMR analysis a solution of 10 wt% of the sample was prepared in CDCl₃, while for ¹³C NMR analysis the concentration of the sample was increased to about 40 wt%.

XRD analysis of the pitch samples was carried out using a Cu K α source radiation in D 8 advance diffractometer of Bruker, Germany make. The diffractometer was operated in step scan mode with 0.2° steps in the range of 2°-80° (2 θ) at a scan rate 1°/min. The diffractograms were used to calculate crystallite size (L_c) and interlayer spacing (d_{002}) of the pitch samples.

The pyrolysis behavior of the mesophase pitches was studied by thermogravimetric analysis (TG/DTG). TG/DTG experiments were carried out using a TA SDT 2960 analyzer. About 10 mg of mesophase pitch sample was taken in crucible, which was then introduced in the thermo balance. The temperature was increased from 40°C to 900°C at a heating rate of 10°C min⁻¹ under a nitrogen flow of 100 mL/min.

3. Results and Discussion

3.1. Analysis of petroleum residues

The physico-chemical properties of the petroleum residues are given in Table 1. Analysis of the properties of these petroleum residues showed that the density of CLO-1 was 0.9251 g/mL and CLO-2 was 1.0924 g/mL. This indicates that CLO-1 contains fewer aromatics than CLO-2. This fact was also supported by the Bureau of Mines Correlation (BMCI) value--a measure of aromaticity of these petroleum residues. The higher BMCI value of CLO-2 (131) than CLO-1 (51) confirmed that CLO-2 was more aromatic in nature than CLO-1. The higher

pour point of CLO-1 (45°C) as compared to CLO-2 (6°C) was also an indication of the presence of fewer aromatics and more paraffins in CLO-1. Due to the presence of more aromatics, CLO-2 produced higher carbon residue. This analysis of the petroleum residues showed that CLO-2 was a better feed stock for producing mesophase, because more aromatics in the petroleum residue increase the chances for mesophase formation.

To improve the aromaticity of CLO-1, it was solvent extracted to remove paraffinic hydrocarbons. After solvent extraction it was observed that there was a significant improvement in the aromaticity of CLO-1. After extraction, the aromaticity (BMCI 139) of CLO-1 extract (AE) exceeded CLO-2 aromaticity (BMCI 131) and it appeared that AE was the most suitable petroleum residue for making mesophase pitch.

The physico-chemical properties of petroleum residues give a general indication about the potential for mesophase formation in the petroleum residues. For deeper understanding of the individual hydrocarbon types present in the petroleum residues, SARA analysis of these residues was carried out.

Results of the SARA analysis of the three petroleum residues are presented in Fig. 1. The SARA analysis shows that CLO-1 contains the highest amount of saturates, i.e. 71.07 wt%, and the lowest aromatics, i.e. 23.08 wt%, among all the residues, and it is predominantly paraffinic in nature. CLO-2 contains more aromatics (30.65 wt%) than CLO-1 (23.08 wt%) but less than AE (54.60 wt%). AE, which was obtained by solvent extraction of CLO-1, is enriched and contains the highest amount of aromatics (54.60 wt%) with the least amount of saturates (30.92 wt%), and is predominantly aromatic in nature. This analysis showed that CLO-1 was paraffinic in nature, AE was aromatic in nature, while CLO-2 was of intermediate nature between these two feed stocks. Generally, Aromatic compounds play a significant role in the formation of mesophase in petroleum residues, while saturated compounds do not directly contribute much mesophase formation, because Aromatics are the basic chemical structures

Fig. 3. Physico-chemical properties (SP, CV, TI, QI, and MC) of synthesized petroleum pitches prepared from three different petroleum feeds with varying thermal soaking time. CLO: clarified oil, AE: aromatic extract.

Table 3. Normalized integration data based on the ^1H NMR and ^{13}C NMR spectra

Sample	^1H NMR								^{13}C NMR			
	$\text{H}_{\text{ar(mono)}}$ (%)	$\text{H}_{\text{ar(di)}}$ (%)	$\text{H}_{\text{ar(poly)}}$ (%)	$\text{H}_{\text{ar}}\%$	$\text{H}_{\alpha}\%$	$\text{H}_{\beta}\%$	$\text{H}_{\gamma}\%$	$\text{H}_{\text{al}}\%$	$\text{H}_{\text{ar}}/\text{H}_{\text{al}}$	$\text{C}_{\text{sat}}\%$	$\text{C}_{\text{ar}}\%$	$\text{C}_{\text{ar}}/\text{C}_{\text{sat}}$
CLO-1	0.99	6.73	1.41	9.13	11.87	62.38	16.62	90.87	0.10	73.23	26.77	0.37
CLO-1-380(3)	3.15	49.01	19.99	72.15	26.32	1.48	0.05	27.85	2.59	6.92	93.08	13.45
CLO-1-380(4)	8.34	50.73	14.13	73.20	25.46	1.34	0	26.80	2.73	6.61	93.39	14.13
CLO-2	2.57	25.04	4.57	32.18	31.48	25.92	10.42	67.82	0.47	31.52	68.48	2.17
CLO-2-380(2)	3.06	48.82	12.73	64.61	32.19	3.21	0	35.40	1.83	8.95	91.05	10.17
CLO-2-380(3)	3.20	53.21	19.14	75.55	23.15	1.30	0	24.45	3.09	5.16	94.84	18.38
AE	1.40	29.71	5.83	36.94	37.21	17.85	8.00	63.06	0.59	29.51	70.49	2.39
AE-380(1)	5.41	46.53	11.85	63.79	33.54	2.52	0.15	36.21	1.76	7.89	92.11	11.67
AE-380(2)	4.53	51.69	13.50	69.72	29.37	0.89	0.02	30.28	2.30	5.92	94.08	15.89
AE-380(3)	4.79	55.19	14.67	74.65	24.55	0.76	0.05	25.36	2.94	4.06	95.94	23.63

NMR: nuclear magnetic resonance, CLO: clarified oil, AE: aromatic extract.

which act as nucleation points for the formation of mesophase, and the conversion of saturates into aromatics is not easy.

UV spectroscopy was also used to compare the aromaticity of the petroleum residues. UV spectroscopic analysis data of the three petroleum residues are presented in Table 1. The UV analysis showed that the order of total aromatics and poly aromatics in these petroleum residues is $\text{AE} > \text{CLO-2} > \text{CLO-1}$. This observation is consistent with the SARA analysis. It was

further observed that there is a different pattern in the percentage of di-aromatics in these residues, which is in the order of $\text{CLO-2} > \text{AE} > \text{CLO-1}$.

The ^1H NMR and ^{13}C NMR average structural parameters of the three petroleum residues are presented in Table 3. These data indicate that total aromatic hydrogen (H_{ar}) and total aromatic carbon (C_{ar}) are in the decreasing order of $\text{AE} > \text{CLO-2} > \text{CLO-1}$ which is in line with the SARA analysis and UV spectro-

scopic analysis (Table 1). These data show that AE and CLO-2 are predominantly aromatic in nature, while CLO-1 is paraffinic in nature.

To get a deeper understanding of the composition of these petroleum residues, some ^1H NMR and ^{13}C NMR average structural parameters were also analyzed. The lower percentage of H_a in CLO-1 (11.87%) showed that it contains aromatic molecules having a smaller number of alkyl side chains attached on them as compared to CLO-2 and AE. Further, the length of alkyl side chains attached to aromatic molecules in CLO-1 is longer, as evident from its higher value of H_β as compared to CLO-2 and AE. The high value of H_γ in CLO-1 also indicates that the alkyl side chains attached to aromatic molecules are more branched in structure than in CLO-2 and AE.

Earlier work carried out by other researchers has shown that the molecular composition of petroleum feed stocks plays an important role in the mesophase development [25].

3.2. Analysis of mesophase pitch characteristics

The elemental analyses of the petroleum pitches prepared from the three petroleum residues are presented in Table 4. The results of the elemental analysis show that the petroleum pitches mainly consist of carbon (>90.40%) with a little amount of nitrogen and sulfur. It was further observed that for each petroleum residue, the percentage of carbon and the C/H ratio in the pitches increases with increasing thermal soaking time. However, the percentage of hydrogen and sulfur decreases. This increase in the percentage of carbon and decrease in the percentage of hydrogen is due to the polymerization and condensation reactions which take place during thermal soaking [26]. During thermal soaking of petroleum residues, cracking of alkyl side chains also occurs because the length of alkyl side chains attached to the aromatics is reduced. This is evident from the lowering of the H_β value. However, the petroleum pitches still contain some side chains with shorter chain length with increasing thermal soaking time. Further, in the second stage these side chains tend to crack at the alpha position to the aromatic ring [27]. This leads to the formation of free radicals, which on dimerization leads to formation of aryl-aryl bridges in the pitch dimers. Therefore, the C/H ratio increases with increasing thermal soaking time.

The physico-chemical properties of the petroleum pitches and their variation with thermal soaking time are presented in

Table 2 and Fig. 3 respectively. In the case of CLO-1, the first two samples, i.e. CLO-1-380(1) and CLO-1-380(2), were not converted into pitch after thermal soaking times of 5.00 h and 7.30 h respectively. This may be due to the paraffinic nature of CLO-1. The saturates present in CLO-1 (71.07 wt%) are not easily converted into aromatics and therefore not into pitch. When the thermal soaking time was further increased to 10.00 h and 10.15 h, the CLO-1 was converted into two pitches, i.e. CLO-1-380(3) and CLO-1-380(4), respectively. As thermal soaking time increased the values of the physico-chemical properties of the pitches also increased, i.e. SP, CV, TI, QI and MC, as shown in Fig. 3 and Table 2. This was due to the additional polymerization and condensation of aromatics, removal of hydrogen, and the formation of larger aromatic molecules.

In the case of petroleum pitches prepared from CLO-2, after thermal soaking of 5.00, 7.30 and 9.00 h three samples were produced, i.e. CLO-2-380(1), CLO-2-380(2) and CLO-2-380(3), respectively. The first sample, CLO-2-380(1), was not converted into pitch, but remained in liquid form. Since CLO-2 feed contains relatively more aromatic (30.65 wt%) than CLO-1 (23.08 wt%), CLO-2 required less thermal soaking time to convert into pitch as compared to CLO-1. Increases were observed in the values of the physico-chemical properties of the other two pitch samples with increasing thermal soaking time.

Similarly, in the case of AE, three petroleum pitch samples, i.e. AE-380(1), AE-380(2) and AE-380(3) were produced after thermal soaking of 5.00, 7.30 and 8.30 h, respectively. Due to the additional aromatics present in AE (54.60 wt%), it was quickly converted into pitches. With this petroleum residue, an increase in physico-chemical properties was also observed with increasing thermal soaking time, similar to CLO-2.

When petroleum residues are thermally soaked, first, smaller aromatic molecules are formed by thermal polymerization, condensation and de-alkylation reactions [28]. These smaller aromatic molecules are then polymerized and condensed and form planar aromatic molecules. These aromatics are stacked together and form liquid crystal or mesophase spheres. Further, these mesophase spheres coalesce with each other [29] and form bulk mesophase. Due to the higher aromaticity of CLO-2 and AE, greater polymerization and condensation reactions took place in these petroleum residues, and consequently, pitches prepared from these exhibited higher values of SP, CV, TI, QI, MC and I_{ar} as compared to pitches prepared from CLO-1, as shown in Table 2 and Fig. 3.

During thermal soaking of the petroleum residues, smaller aromatic molecules are converted into bigger, high molecular weight, aromatic molecules by polymerization and condensation of aromatic free radicals, which are formed by the cracking of C-C and C-H bonds. As a result, there is an increase in the values of physico-chemical properties of the petroleum pitches. Further polymerization of petroleum pitches enhances SP and CV and semi-coke is formed, which ultimately leads to formation of an infusible anisotropic coke [29]. It is also evident that the increase in the physico-chemical properties of mesophase pitches is well correlated with the increase of C/H ratio, including degree of aromatization. The data discussed above indicates that the enhancement in the physico-chemical properties takes place through structural changes of the pitch molecules caused by the conversion of the lighter fractions of the pitch into heavier ones, and the formation of more and bigger aromatic units.

Table 4. Elemental analysis of mesophase pitches (wt%)

Sample	C	H	N	S	C/H
CLO-1-380(3)	91.33	6.08	0.05	2.54	1.26
CLO-1-380(4)	92.28	5.30	0.04	2.38	1.46
CLO-2-380(2)	91.33	6.56	0.21	1.90	1.17
CLO-2-380(3)	93.40	5.15	0.23	1.22	1.52
AE-380(1)	90.40	6.49	0.04	3.07	1.17
AE-380(2)	91.04	6.03	0.05	2.88	1.27
AE-380(3)	91.79	5.80	0.06	2.35	1.33

CLO: clarified oil, AE: aromatic extract.

3.3. Optical microscopy analysis

Figs. 4 and 5 show polarized light micrographs of the pitches prepared from the three petroleum residues. These pitches have different MC as shown in Table 2. To make the pitches, although the thermal soaking temperature was the same (380°C), the thermal treatment time was different. MC, as determined by plane polarized light optical microscopy, varied from 8 to 53 vol% in the different pitches. The difference in the MC in the petroleum residues can be related to differences in the molecular composition of these residues.

In pitches CLO-1-380(3) and CLO-1-380(4) prepared from petroleum residue CLO-1, it was observed that although the petroleum residue was paraffin rich, mesophase formation took place, and MC increased with increasing thermal soaking time, as shown in Fig. 4. Due to the low level of aromatics (23.08 wt%) in CLO-1 the MC could be increased only up to 19 vol% with thermal soaking of 10.15 h.

The growth of mesophase spheres in pitch is also affected by the viscosity of the feed stocks. A lower feed viscosity generally helps the formation of mesophase spheres [30,31]. In the case of petroleum residue CLO-1, it was observed that the growth in size of mesophase spheres was good, and this may be due to the lower viscosity of CLO-1, which provided a better environment for the mesophase spheres to grow. The low asphaltene content (0.55 wt%) of CLO-1 also helped the proper growth of mesophase spheres.

In the case of sample CLO-2-380(1) prepared from petroleum residue CLO-2 no pitch formation was observed even after 5 h of thermal soaking. In pitch sample CLO-2-380(2) mesophase formation started after 7.30 h of thermal soaking but the MC in this pitch were below countable limit (BCL). In the third pitch sample CLO-2-380(3), which was produced by thermal soaking for 9.00 h, formation of mesophase in substantial quantity (53 vol%) took place. It was further observed that the formation of mesophase between 7 to 9 h was very fast, as shown in Fig. 4. In the CLO-2-380(3) sample it can be clearly seen that the mesophase spheres have started to coalesce and bulk mesophase formation has begun. It was further observed that due to the

presence of more aromatics in CLO-2, more mesophase formation (53 vol%) took place in a shorter thermal soaking time of 9.0 h in CLO-2-380(3) pitch, as compared to CLO-1, which is paraffinic in nature, in which only 19 vol% mesophase formation took place in 10.15 h in CLO-1-380(4) pitch.

Similarly, for AE, the pitch sample AE-380(1) exhibited a mesophase BCL after 5.0 h. This was increased to 8 vol% in AE-380(2) after 7.30 h, and further increased to 34% in AE-380(3) after 8.30 h, as shown in Fig. 5. It was further observed that although the AE was more aromatic in nature than CLO-2, the MC in AE pitches was less than in CLO-2 pitch. Analysis of the petroleum residues properties showed that perhaps di-aromatics play an important role in the formation of mesophase. The petroleum residue CLO-2 contains more di-aromatics (20.7 wt%) than AE, which contains 16.6 wt% di-aromatics. Due to this, more mesophase formation took place in CLO-2 than AE pitch. It appears that di-aromatics help to promote mesophase formation, while polyaromatics promote coke formation.

As thermal soaking time increases, the growth of aromatic molecules and the formation of more mesophase takes place, due to the greater extent of polymerization condensation reactions [32,33]. The development of long range of molecular order in the pitch is attributed to both increasing molecular weight and a loss of sp³-type chemical bonding. Such chemical reactions lead to the formation of large planar molecules. As the thermal soaking progresses, the size of the mesophase spheres grows and then they coalesce to form large mesophase spheres which separate from the lower density isotropic pitch phase and slowly settle [28]. Mesophase spheres observed in these cases, in size Figs. 4 and 5, are heterogeneous. If the chemical reactions continue, petroleum pitches pass through a fluid stage and are finally converted into infusible coke during carbonization. In the early stages of carbonization, free radicals are formed due to the thermal rupture of C-C and C-H bonds in reactive components. Polymerization proceeds mainly via a free radical mechanism, leading to molecular size enlargement (aromatic growth) and the formation of oligomeric systems (mesogens).

It was observed that although all the petroleum residues have different aromaticity, mesophase formation was observed in

Fig. 4. Polarized light optical microscopic images of synthesized petroleum pitches. CLO: clarified oil.

Fig. 5. Polarized light optical microscopic images of synthesized petroleum pitches. AE: aromatic extract.

all the feed stocks, and the order of mesophase formation was CLO-2 > AE > CLO-1. The study suggests that mesophase formation is dependent on the presence of a proper balance in the concentrations of paraffins and aromatics in the petroleum residues. Paraffins are required for the generation of free radicals, and aromatics are required for the growth of mesophase formation. A higher percentage of di-aromatics helps to form more mesophase. The petroleum residue should also have sufficient viscosity so that poly aromatics can move in the feed and accumulate in the form of mesophase spheres.

3.4. FT-IR analysis

The FT-IR spectra of the petroleum pitches are shown in Fig. 6. The results can provide information about the functional groups present in the pitch samples and how they change with thermal soaking. There are few significant differences in the FT-IR spectra of all the mesophase pitches. All the pitches exhibit bands with less resolution and intensity. A high degree of rigidity in the mesophase pitch samples is expected from the large size polynuclear aromatic hydrocarbons present in them.

The functional groups of all the mesophase pitches were observed to be aromatic (3048, 1609, 880, 805, 751, and 745 cm^{-1}) and aliphatic (2913 and 1447 cm^{-1}) groups. FT-IR spectra of all the petroleum pitches showed a less intense peak at $\sim 3048 \text{ cm}^{-1}$ which is due to aromatic C-H stretching. The peak at $\sim 1605 \text{ cm}^{-1}$ may be due to stretching of aromatic C=C (multiple bonds). These two bands indicate that aromatic rings are present in the mesophase pitches. The band at 1447 cm^{-1} in all the mesophase pitches may be assigned to methylene C-H in-plane bending. This band indicates that some aliphatic carbons are also present in the mesophase pitches. These aliphatic carbons are generally attached to aromatic molecules as side chains.

The bands at ~ 875 , ~ 805 and $\sim 750 \text{ cm}^{-1}$ in all the mesophase pitches indicate that there may be substitutions at the aromatic rings. Another band present at $\sim 750 \text{ cm}^{-1}$ indicates the presence of four adjacent aromatic hydrogen atoms in the polynuclear aromatic ring. This study confirmed that large size substituted polynuclear aromatics are present in the pitches.

From the FT-IR spectroscopy, aromaticity indices were also calculated using the formula $I_{Ar} = \text{Abs}_{3050} / (\text{Abs}_{3050} +$

$\text{Abs}_{2920})$ [34], and are reported in Table 2. The aromaticity index listed in Table 2 shows that CLO-2-380(3) exhibits the highest I_{Ar} value (0.54) along with the highest MC (53 vol%). The results indicate that the aromaticity of the pitches increases with the increase in thermal soaking time, because the degree of polymerization and condensation of aromatics increases with thermal soaking time. These features imply the progressive loss of hydrogen during the formation of the pitches, which is consistent with increases in the sizes of the polycyclic aromatic units. The increase of the C/H ratio (Table 4) and MC (Table 2) also support this finding.

3.5. ^1H NMR and ^{13}C NMR analysis

NMR is a powerful and widely used tool for characterizing pitches. ^1H NMR gives detailed structural information about the periphery of the molecules. The NMR spectra give a direct measurement of the distribution of protons in differing chemical environments, such as hydrogen attached to aromatic carbons, hydrogen in an alkyl group or hydrogen attached to a carbon atom in a bridging position between two aromatic rings etc. [35,36]. The ^1H NMR spectra is divided into two regions, i.e., aromatic hydrogen (H_{ar}) between 6.0-9.0 ppm and aliphatic hydrogen (H_{al}) between 0.5-4.5 ppm. The ^1H NMR spectral regions were subdivided according to the nature of the hydrogen present in the samples, as shown in Table 5.

The ^1H NMR data of the three different petroleum residues and their pitches are given in Table 3. The data indicate that before thermal treatment, the petroleum residues contained higher amounts of H_{al} than H_{ar} . As the thermal soaking of residues progressed these H_{al} were thermally cracked down at α , β and γ positions to give a benzylic type free radical, which then polymerized to form aromatic bridge structures. The initiation step involves thermally induced free radical formation via homolysis of the C-H bond. Therefore, by increasing thermal soaking time, the percentage of H_{ar} was enhanced in all the pitches, with a simultaneous decrease in H_{al} . Also, the hydrogen aromaticity index ($\text{H}_{ar}/\text{H}_{al}$) [36] of the prepared pitches increased with increasing thermal soaking time. Thus, the higher $\text{H}_{ar}/\text{H}_{al}$ of the petroleum pitches suggests that the polymerization/condensation reactions involved in the thermal soaking occur at the expense

Fig. 6. Fourier-transform infrared spectroscopy patterns of synthesized petroleum pitches. CLO: clarified oil, AE: aromatic extract.

of the aliphatic hydrogen.

^{13}C NMR spectroscopy offers complementary information about the internal structure of the petroleum pitches. The ^{13}C NMR data of the petroleum pitches are presented in Table 3. Like ^1H NMR spectra, ^{13}C NMR spectra are also divided into different regions depending on the nature of the carbon [35,36]. The ^{13}C NMR spectra can be divided into two regions, i.e. aromatic carbons (C_{ar}) between 100-160 ppm and saturate carbons (C_{sat}) between 5-50 ppm, as presented in Table 5. Similar to ^1H NMR, all the prepared pitch samples from the three different petroleum residues also show an increase in C_{ar} but a decrease in

C_{sat} with increasing thermal soaking time. The carbon aromaticity index ($\text{C}_{\text{ar}}/\text{C}_{\text{sat}}$) [37] is also increased.

These results suggest that during thermal soaking of the petroleum residues, polymerization/condensation reactions take place with the removal of aliphatic hydrogen, leading to the formation of highly aromatic molecules.

To sum up, polymerization reactions enhance the size of aromatic molecules. During thermal soaking of pitch, dehydrogenative polymerization of aromatics is an important step to make basic pitch molecules [38]. In the present study, this is supported by the decrease in total hydrogen content observed in elemental analysis (Table 4). A relationship was found between the aromaticity of the pitches and the C/H atomic ratio as determined from elemental analysis. Elemental analysis is a rapid and convenient method to estimate the aromaticity of pitches. This result also agrees with the result of I_{Ar} (Table 2).

3.6. XRD analysis

XRD curves of the prepared petroleum pitch samples are shown in Fig. 7, and the XRD parameters of these are presented in Table 6. All the XRD spectra of petroleum pitches show a wide peak at $2\theta \approx 25.6$ and 45.5 corresponding to graphite. It was observed that when the thermal soaking time of the pitches was increased, the sharpness of the peak was also increased. Increasing sharpness of the peaks at around 25.6 in the pitches indicates that the pitches are going to be more crystalline in nature and are moving towards a graphitic structure.

The crystallite size (L_c) and interlayer spacing (d_{002}) of pitches are listed in Table 6. The data listed in Table 6 shows that L_c increases and d_{002} decreases with increasing thermal soaking time. Furthermore, L_c increased with the increase in carbon content (Table 4) whereas d_{002} decreased with increasing carbon content (Table 4). The increased value of L_c with increasing thermal soaking time indicates the formation of large sized planar aromatic molecules which are stacked together to form mesophase. Mesophase further forms a turbostratic structure, i.e. intermediate between graphite and amorphous carbon. The minimum interlayer spacing between aromatic sheets was found to vary between 3.342 to 3.488 for these pitches. As the crystallinity of the mesophase pitches increases with increasing thermal soaking time, the interlayer spacing decreases, which indicates that

Table 5. ^1H NMR and ^{13}C NMR spectral divisions		
	Symbol	Definition
^1H NMR chemical shift range (ppm)		
0.5-1.1	H_γ	Aliphatic H in methyl or methylene γ to an aromatic
1.1-2.1	H_β	Aliphatic H in methyl or methylene β to an aromatic
2.1-4.5	H_α	Aliphatic H in methyl or methylene α to an aromatic
0.5-4.5	H_{al}	Total aliphatic hydrogen
6.0-7.1	$\text{H}_{\text{ar(mono)}}$	Mono-aromatic protons
7.1-8.2	$\text{H}_{\text{ar(di)}}$	Di-aromatic protons
8.2-9.0	$\text{H}_{\text{ar(poly)}}$	Poly-aromatic protons
6.0-9.0	H_{ar}	Total aromatic protons
-	$\text{H}_{\text{ar}}/\text{H}_{\text{al}}$	Hydrogen aromaticity index
^{13}C NMR chemical shift range (ppm)		
5-50	C_{sat}	Total saturate carbon
100-160	C_{ar}	Total aromatic carbon
-	$\text{C}_{\text{ar}}/\text{C}_{\text{sat}}$	Carbon aromaticity index

NMR: nuclear magnetic resonance.

Fig. 7. X-ray diffraction patterns of synthesized petroleum pitches. CLO: clarified oil, AE: aromatic extract.

Table 6. X-ray diffraction parameter of mesophase pitches

Sample	Crystallite size (L_c)	Interlayer spacing (d_{002})
CLO-1-380(3)	14.40	3.463
CLO-1-380(4)	17.50	3.342
CLO-2-380(2)	15.80	3.480
CLO-2-380(3)	24.00	3.414
AE-380(1)	15.70	3.488
AE-380(2)	17.80	3.466
AE-380(3)	18.20	3.440

CLO: clarified oil, AE: aromatic extract.

the pitch is moving towards a crystalline graphitic structure. The effect of thermal soaking time on L_c agrees with the result of C/H ratio (Table 4) and I_{Ar} (Table 2).

3.7. TGA analysis

The thermal stability and pyrolysis behavior of the mesophase pitches were studied by TGA (Fig. 8, Table 7). The results indicate that in all the mesophase pitches the first weight loss occurred at temperature (T_i) around $<260^\circ\text{C}$ due to the removal of light molecular weight volatile compounds, and the second weight loss occurred at temperature (T_f) between 260°C and 555°C due to the removal of high molecular weight polymerized compounds. The tempera-

ture of initial weight loss (T_i), temperature of final weight loss (T_f), and temperature of maximum rate of weight loss (T_{max}), which were calculated from TG/DTG curves, increased as the thermal soaking time increased, as shown in Table 7 and Fig. 8. As the thermal soaking time increases, more polymerization and condensation reactions take place in the pitches, which results in the formation of large sized aromatic molecules. Therefore, Fig. 8 shows that all the mesophase pitch is thermally stable up to a temperature of 260°C and after this, degradation may take place.

It was observed that as the thermal soaking time increased, the weight loss occurred at both regions (T_i and T_f) of higher temperature, and this may be due to the higher degree of polymerization in the mesophase pitches. The DTG curves show that the temperature of maximum rate of weight loss (T_{max}) varied between 300°C and 357°C for the mesophase pitches. We also obtained the carbon yield of the mesophase pitches, by TGA curves, given in Table 7. The carbon yield obtained at 900°C also increased with the increase in thermal soaking time shown in Table 7, similar to CV listed in Table 2. This finding is also supported by the increasing values of physico-chemical properties (TI, QI, MC and SP) of mesophase pitches with increasing thermal soaking time.

4. Conclusions

This study on mesophase formation in petroleum residues leads to the following conclusions:

1) Analysis of the physico-chemical properties of the petroleum residues showed that they have different natures. The

Fig. 8. Thermogravimetry (left) and derivative thermogravimetry (right) curves of synthesized petroleum pitches. CLO: clarified oil, AE: aromatic extract.

Table 7. TG/DTG parameters of mesophase pitches

Sample	TG/DTG (°C)			
	T _i ^{a)}	T _f ^{b)}	T _{max} ^{c)}	Carbon yield ^{d)} (wt%)
CLO-1-380(3)	247	542	345	43.6
CLO-1-380(4)	255	548	352	50.1
CLO-2-380(2)	233	522	299	32.1
CLO-2-380(3)	240	552	315	55.6
AE-380(1)	240	530	304	34.1
AE-380(2)	243	544	308	43.6
AE-380(3)	260	550	357	54.3

TG/DTG: thermogravimetry/derivative thermogravimetry.

^{a)}Temperature of initial weight loss (°C).

^{b)}Temperature of final weight loss (°C).

^{c)}Temperature of maximum rate of weight loss (°C).

^{d)}Carbonaceous residue at 900°C (wt%).

SARA analysis showed that CLO-1 had more paraffinic hydrocarbons (71.07 wt%), while CLO-2 (30.65 wt%) and AE (54.60 wt%) contained more aromatic hydrocarbons.

2) The UV and NMR spectroscopic analyses showed that total aromatics, total aromatic hydrogen (H_{ar}) and total aromatic carbon (C_{ar}) of the petroleum residues were in the order AE > CLO-2 > CLO-1.

3) The optical microscopic analysis of mesophase pitches showed that the mesophase spheres in these pitches were heterogeneous in size. Among these three petroleum residues, CLO-2 exhibited more MC, (53%), as compared to AE (34%) and CLO-1 (19%). The percentage of MC was in the order CLO-2 > AE > CLO-1. This showed that although according to BMCI AE (139) was more aromatic than CLO-2 (131), greater mesophase formation was observed in CLO-2 due to the presence of a higher percentage of di-aromatics (as observed by UV) in CLO-2 (20.70 wt%). This indicates that di-aromatics play an important role in mesophase formation.

4) NMR data such as hydrogen aromaticity index (H_{ar}/H_{al}) and carbon aromaticity index (C_{ar}/C_{al}) of the mesophase pitches showed that with increasing thermal soaking time, polymerization/condensation reactions favored formation of aromatics, while the thermal cracking reduced aliphatic hydrogen.

5) XRD analysis showed that the crystallinity of the mesophase pitches increased with increasing thermal soaking time. The increasing crystallite size and decreasing interlayer spacing with increasing thermal soaking time indicates that the pitch is moving towards a crystalline graphitic structure.

6) TG/DTG analysis showed that as the thermal soaking time increased, weight loss occurred at both regions (T_i and T_f) at higher temperature, and the value of carbon yield obtained at 900°C also increased.

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