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Characterization of Libyan Waxy Crude Oils

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The prediction of wax formation and the understanding of the physicochemical characteristics of the wax phase are of major importance in flow assurance. The characterization of the oil and wax can provide useful estimates of the parameters and behavior required for operational engineering process developments and/or physical modifications to the processing of crude oils, aiming at the reduction of costs of production and transportation. Five Libyan crude oils and their waxes were characterized using various experimental techniques. Waxes were extracted using the Universal Oil Products (UOP) 46-64 method and purified by column chromatography. Differential scanning calorimetry (DSC) and cross polar microscopy (CPM) techniques were used to study the wax appearance temperature (WAT) for these crude oils. Waxes were characterized using gas chromatography (GC), nuclear magnetic resonance (NMR), and X-ray diffraction (XRD). The carbon number distribution was determined by gas chromatography−flame ionization detector (GC−FID). Extensive information about the structural composition of these waxes was performed using ^{13}C NMR, and information for the crystalline structure of these waxes was obtained using XRD. This study shows that the five Libyan crude oils studied have wax contents between 8 and 24 wt % with WAT in the range of 22.5−68.17 °C. The isolated waxes are shown to be paraffinic (macro-crystalline wax) with an orthorhombic structure.

Introduction

The heavy saturated fraction of crude oil, known as wax, tends to precipitate during the extraction and transport of crude oils as a result of the temperature (T) and pressure (P) drop of the fluid. As soon as the $P-T$ conditions fall within the solid region of the phase envelope, i.e., the temperature of the oil falling below the wax appearance temperature (WAT), there will be formation of deposits on the reservoir or pipelines. The wax deposition causes the plugging of pipelines and clogging of transport equipment, being a well-known and expensive problem in the petroleum industries.[1,2] A better understanding of the oil composition and the paraffinic hydrocarbons present in the crude oils can help face this problem both preventively and providing remediation whenever necessary. Several useful analytical techniques have been proposed in the petroleum industry to study the petroleum fluid characteristics in general, and they can provide adequate information concerning the wax formation to facilitate production developments and thus avoid shutdowns and operational problems, which cost billions of dollars per year during

oil production and transportation.[3] Although predictive models are available today for wax formation[4,5] and deposition[6,7] in crudes, they always required detailed compositional knowledge of the oils for an adequate performance.

The purpose of this study is to evaluate the characteristics of five different Libyan crude oils, as well as their waxes. These oils, named Remal, Sarir, Sedra, Bouri, and Farigh, were supplied by three companies, Waha, Eni-Oil, and Arabian Gulf Oil, operating in Libya through the National Oil Corporation. The oils were chosen because of the wax problems that they present during transport. The location of these wells is presented in Figure 1, showing the sedimentary basins of Libya. The Bouri oilfield off Libya's western coast is the largest producing offshore oilfield, estimated to contain 2 billion barrels in proven recoverable crude oil. The Sirte basin contains around 80% of Libya's established oil reserves and production. Sedra provides the largest contribution to crude oils export, whereas Sarir is regarded as the second most important contribution for exportation.[8] These Libyan waxy crude oils present problems in transportation through pipelines because of thermal environmental changes. These crudes, mainly during wintry weather or at night, present a decreasing flow of crude oil because of the deposition of a solid phase that obstructs the pipeline, and as result of that, the flow handling becomes difficult. Because of the long distance that the oils travel through the pipelines from the field to the coast terminals (e.g., the distance from the Sarir field to

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Figure 1. Map showing the location of the investigated oil wells.

the coast terminal is about 513.6 km), thermal or mechanical treatment and flow improvers are always applied to these crude oils to avoid the transportation problem, which severely increases their production costs.

In practice, the characterization of the oils and their waxes can be achieved through various physicochemical and compositional analyses, such as American Petroleum Institute (API) gravity and viscosity, WAT, wax content, and pour point, and further characterization of the waxes by gas chromatography (GC), differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), and X-ray diffraction (XRD), among others.[9,10] The information obtained by these techniques can be of great importance to explain the causes of wax deposition and to be able to understand, predict, and prevent it during transportation, production, and storage of petroleum.

In this work, a number of these techniques were used to characterize the five Libyan crudes under study. The WAT was measured by DSC; the wax content was measured by the Universal Oil Products (UOP) 46-64 method; and the waxes recovered were further purified by column chromatography. The purified waxes were then analyzed by GC, DSC, NMR spectroscopy, and XRD spectrometry for a full characterization of their nature, as discussed below.

Experimental Section

After a preliminary characterization of the crude oils under study, their waxes were extracted and also characterized. The techniques used for the oils and waxes are described below.

Oil Characterization. *Viscosity and Density.* The viscosity and density measurements were carried on an Anton Paar Viscometer, model SVM3000, according to ASTM D445-06 and ASTM D5002-99, respectively,[11] at the temperatures of 40 and 80 °C. The standard S3 from Paragon Scientific was used to calibrate the viscometer. The samples were heated above the WAT before the viscosity measurements to ensure that all wax particles are dissolved.

API Gravity. The API gravity is used to estimate the quality of a crude oil. The values of API gravity for each crude oil were estimated on the basis of the following equation using density values at 40 °C, except for Remal that used values at 80 °C:

$$\text{API} = \frac{141.5}{\text{SG}} - 131.5 \tag{1}$$

WAT. The WAT was measured for the studied crudes using a Mettler DSC822e calibrated with indium and flushed with dry nitrogen. To measure the WAT, crude oil samples of about 10 mg were heated to 40 K above pour-point temperatures and then cooled with a cooling rate of 1 or 3 K/min to evaluate the effect of the cooling rate on the WAT. Three runs were carried for each oil, and average results are reported. The WAT was taken here as the onset temperature of the exothermal peak observed.

Pour Point. The pour point of a crude oil is the temperature at which the oil gels because of the crystallization of waxes. Pour-point temperatures of the crude oils were measured using the standard test method for the pour point, ASTM D97-06.[11]

Water Content. The water content of the crude oils studied was evaluated in the oil samples as received using a Metrohm 831 Karl Fischer (KF) coulometer.[12]

Wax Content. Because the composition, type, and properties of the waxes present in a crude oil differ with the crude oil source, it is important to extract them from the hydrocarbon matrix to evaluate their chemical composition and structural characteristics. The UOP 46-64 method[13] was used to extract the wax from the crude oil. A total of ca. 2 g of crude oil was dissolved in 500 mL of petroleum naphtha, and 15 g of Fuller's earth were added to the solution. The mixture was then filtered and evaporated. Finally, 200 mL of a mixture of 1:3 petroleum naphtha/acetone was added to the solution, and the liquid was chilled to about −17 °C and filtered by a cold filter funnel, after which the sample was washed with hot naphtha and the petroleum naphtha was evaporated to recover the wax. This was weighed, and the wax content was evaluated.

Molecular Weight. The average molecular weight of the crudes was determined by cryoscopic depression by the relation

$$M_{\text{w}} = \frac{1000k_{\text{f}}m_{\text{oil}}}{\Delta T_{\text{fus}}m_{\text{xyl}}} \tag{2}$$

using xylene as the solvent.

Wax Characterization. *Wax Purification.* Before characterization, the waxes extracted from the crudes according to the procedure described above were further purified by cleaning the waxes using a silica gel column to remove the polar material that remains after precipitation. The wax samples were dissolved in *n*-hexane and passed through a 50 cm silica chromatographic column. The procedure was based on the method described by Musser and Kilpatrick.[14]

GC. A Varian gas chromatograph (CP3800) with a flame ionization detector (FID) was used for the characterization of the wax composition. A capillary column CP-5, 30 m long and with 0.32 mm internal diameter and 0.25 μm film thickness, was used. The wax was dissolved in CS_2, and the samples were injected into the column using an auto-sampler, with the injector at a temperature of 250 °C, with a split/splitless ratio of 1:50. The detector temperature was 300 °C. Analysis was performed under a helium flow rate of 1.2 mL/min and a temperature program of 40−280 °C at 12 °C/min and held for 5 min at the highest temperature.

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Table 1. Physical Properties for the Libyan Crude Oils Studied in This Work

crude oil samples	UOP wax content (wt %)	pour-point temperature (°C)	M_w	kinematic viscosity (mm^2 s^{-1})		density (g cm^{-3})		API gravity (deg)	water content (ppm)
				at 40 °C	at 80 °C	at 40 °C	at 80 °C		
Remal	18.8	51	331.5		18.680		0.886	25.13	
Bouri	15.0	12	249.7	20.475	7.225	0.883	0.860	25.70	820
Sarir	13.6	24	244.7	13.563	5.270	0.829	0.810	35.64	1327
Sedra	8.0	0	200.7	5.253		0.827		36.03	206
Faregh	24.1	21	217.2	4.446	2.557	0.790	0.772	43.47	576

Table 2. WAT at the Two Cooling Rates for the Studied Oils[a]

crude oil samples	WAT (°C) at 3 K/min	WAT (°C) at 1 K/min
Remal	67.3 ± 1.92	68.2 ± 0.38
Bouri	29.2 ± 0.54	29.7 ± 0.28
Sarir	48.7 ± 0.36	49.6 ± 0.10
Sedra	22.5 ± 0.04	23.2 ± 0.88
Faregh	42.1 ± 0.22	43.1 ± 0.14

[a] Uncertainty assigned is 2 times the standard deviation of the measurements.

Elemental Analysis. Elemental analysis (C, H, N, and S) for the purified waxes were carried out at the Centro de Apoio Científico e Tecnolóxico á Investigación (CACTI) of the University of Vigo (Spain) using a CHNS analyzer.

DSC. Thermal characterization of the waxes (melting temperatures and enthalpies) was carried out on a Mettler DSC822e calibrated with indium and flushed with dry nitrogen. The melting point of the waxes is taken as their peak temperature.

^{13}C NMR Spectra. Carbon NMR was used to provide a value for the relative proportions of aliphatic and aromatic carbons in the wax. Quantitative ^{13}C NMR spectra were collected on a Bruker Avance 300 spectrometer operating at 75.47 MHz. Wax samples were diluted at 50% in CDCl$_3$, and the spectra were recorded at 295 K with tetramethylsilane (TMS) as the internal reference. The inverse gate decoupling sequence, which allows for quantitative analysis and a comparison of signal intensities, was used with the following parameters: pulse angle, 30°; acquisition time, 3.48 s; relaxation delay, 60 s; data points, 32 000; and scans, 5000. Information concerning the different types of carbon present is based on the works by Carman et al.,[15] and Sperber et al.,[16] and the aromatic content is quantified according to ASTM D5292-99.[11]

XRD Spectra. Diffractograms of the waxes at room temperature were acquired on Philips X'Pert equipment, which operates in the reflection mode with Cu Kα radiation (λ = 1.5406 Å). Diffraction data were collected in a 2θ range from 2° to 60°, with a step of 0.02° and a time per step of 2 s, with incident and diffracted beam anti-scatter slits of 1°, divergence slit of 1°, and receiving slit of 0.1 mm, on a curved graphite diffracted beam monochromator.

Results and Discussion

Crude Oil Properties. Analyses were carried to characterize the five crude oils studied on this work. Specific gravity (SG), API gravity, viscosity, pour-point temperature, wax content, average molecular weight, and water content of each crude oil were measured as described above, and the results are reported in Table 1. The high pour point of Remal precluded the measurement of the viscosities and densities at 40 °C and also the water content.

The oil characterization shows that the crudes studied here are medium or light crude oils with high wax content. As

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**Table 3. Composition (wt %) of the Waxes Studied**

	Remal	Bouri	Sarir	Sedra	Faregh
C11		0.213			
C12		0.176			
C13		0.316			
C14		0.735			0.189
C15	0.405	1.763	0.460	0.394	0.480
C16	0.650	2.183	0.920	0.574	0.860
C17	1.030	2.865	2.065	1.148	1.233
C18	1.915	4.063	4.182	2.226	3.498
C19	3.598	5.083	7.054	4.831	4.543
C20	5.453	5.983	9.140	8.159	7.921
C21	7.679	6.207	10.443	10.489	11.267
C22	8.371	6.195	9.979	10.961	11.474
C23	8.804	5.392	9.577	10.300	9.834
C24	8.395	5.16	7.754	9.034	9.356
C25	8.331	4.203	7.040	7.670	6.949
C26	7.710	3.839	5.674	6.043	6.338
C27	7.378	3.297	4.662	5.503	5.058
C28	6.120	3.8	3.797	4.753	4.561
C29	5.477	2.816	3.236	4.070	3.427
C30	4.163	2.504	2.440	3.364	2.873
C31	3.126	2.259	1.713	2.646	1.928
C32	2.158	1.848	1.242	1.927	1.648
C33	1.595	1.554	0.989	1.535	1.127
C34	0.319	1.374		1.156	1.113
C35		1.228		1.006	0.896
C36		0.736			0.485
C37		0.653			
C38		0.546			
C39		0.354			
C40		0.351			
total *n*-alkanes	92.68	77.70	92.37	97.79	97.06
iso- and cycloalkanes	7.32	22.30	7.63	2.21	2.94

Table 4. Elemental Analysis and H/C Ratio of the Waxes Extracted from the Oils and Total Aromatic Carbon Content of the Waxes under Study Measured by ^{13}C NMR

	C (wt %)	H (wt %)	H/C	C(ar) NMR (wt %)
Remal	85.28	14.72	2.07	0.7
Bouri	85.52	14.48	2.03	1.1
Sarir	85.66	14.34	2.01	0.9
Sedra	86.02	13.98	1.95	1.8
Faregh	85.09	14.91	2.10	0.6

expected, the wax content correlates well with the API gravity and the viscosity of the crudes at 40 °C. The crudes with a larger wax content present lower API gravities and higher viscosities.

The WAT is the temperature at which some heavy paraffinic molecules start to precipitate from solution. WAT is considered as one of main guidelines for system design, production operations, and the planning of the exploration of a reservoir.[9] The WATs for the five oils have been measured using DSC as the onset temperature of the exothermal peak observed upon cooling. Results for the WAT measured at the two cooling rates used are reported in Table 2. Although the WATs measured at the lowest cooling rate are consistently higher, the difference between these are in general within the uncertainty of the measurements estimated as
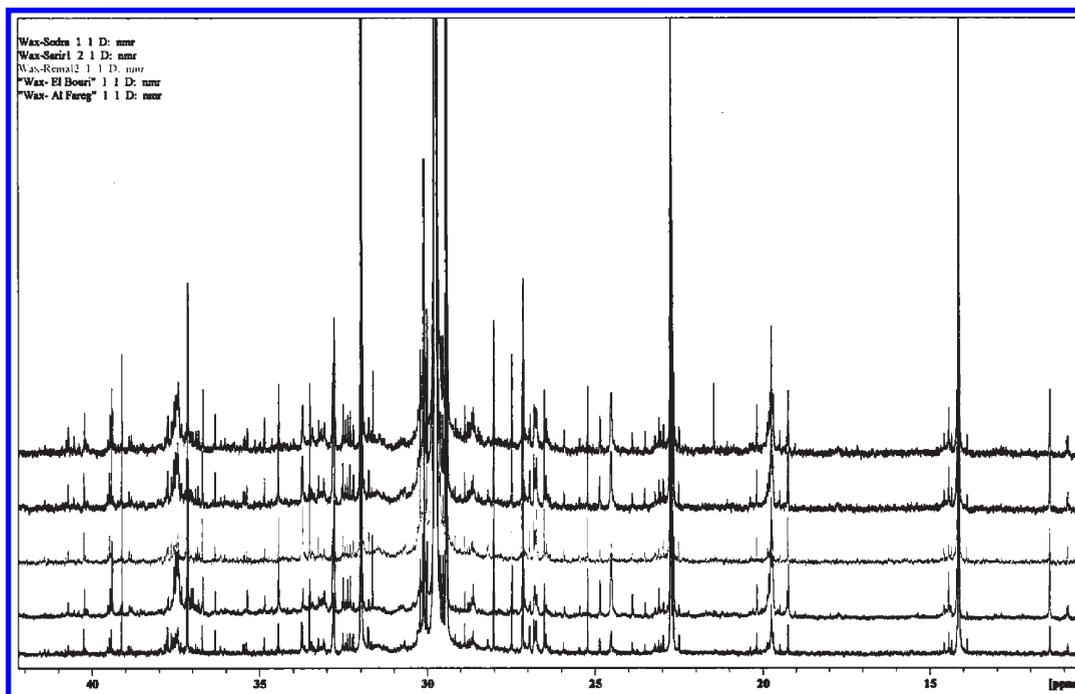
Figure 2. ^{13}C NMR spectra for the waxes studied in the aliphatic region. The spectra correspond, from top to bottom, to Sedra, Sarir, Remal, Bouri, and Faregh.

2 times the standard deviation. It can thus be assumed that the WATs measured at the two cooling rates are statistically identical. It is also quite remarkable that, although the WAT would be expected to increase with the wax content of the oil, there seems to be no straight relation between the two, with Faregh presenting one of the highest wax contents, while its WAT is inferior to those of Remal and Sarir. This is a clear indication that the WAT is dependent upon not only the wax content but also the wax composition, as previously suggested.[9] The pour point, however, displays a very good linear dependency upon the WAT for all fluids of 23 ± 3 K below the measured WAT. The WAT is thus, for these crudes, a good indicator of their pour point.

Wax Composition. The wax composition was determined by means of a GC–FID analysis according to the procedure described above. The *n*-alkane distributions and the content of non-*n*-alkanes on the oil are reported in Table 3. The results indicate that all of the waxes extracted are highly paraffinic macrocrystalline waxes. They vary from being essentially made up of *n*-alkanes, as is the case for Sedra and Faregh, to oils, such as Bouri, that, although highly paraffinic, present a non-*n*-alkane content slightly above 20 wt %. The two other oils, Remal and Sarir, present waxes very rich in *n*-alkanes, with the *n*-alkane content above 90 wt %.

To obtain more detailed information on the composition of the waxes, in particular, to evaluate the amount of tertiary and aromatic carbons present in the wax, elemental analysis and ^{13}C NMR were used. The peaks on the NMR spectra were assigned to carbon types according to the suggestion of Carman et al.[15] and Sperber et al.[16]

The elemental analysis, reported in Table 4, presents H/C ratios higher than 2 for all waxes, except Sedra, with a H/C ratio of 1.95. These values are typical of macrocrystalline paraffinic waxes with a high degree of saturation.

Figure 2 shows the ^{13}C NMR spectra for the five waxes in the aliphatic region. As can be seen, the signals of the straight hydrocarbons dominate, with a few signals of branched

Table 5. Characterization of the Aliphatic Portion of the Waxes by ^{13}C NMR

structure		ppm	Remal	Bouri	Sarir	Sedra	Faregh
α-CH$_3$	CH$_3$	14.14	5.073	4.134	5.329	4.474	5.861
1B$_1$		20.06	0.048	0.23	0.116	0.144	0.152
1B$_2$		11.46	0.07	0.36	0.123	0.142	0.076
1B$_{3-6}$		14.54	0.053	0.111	0.077	0.068	0.06
β-CH$_2$	CH$_2$	22.85	5.381	4.46	5.497	4.72	5.96
γ-CH$_2$		32.16	5.691	4.301	5.695	4.839	6.301
δ-CH$_2$		29.9	53.966	39.409	52.189	49.896	56.693
αδ$^+$-B$_1$		37.48	0.193	0.557	0.402	0.319	0.249
αδ$^+$-B$_2$		34	0	0.071	0	0	0
αδ$^+$-B$_{3-6}$		34.48	0.083	0.519	0.17	0.199	0.119
βδ$^+$-B$_1$		27.26	0	0	0	0	0
βδ$^+$-B$_{2-6}$		27.21	0.112	0.32	0.496	0.465	0.12
γδ$^+$-B$_1$		30.28	0.445	0.557	0.517	0.505	0.384
γδ$^+$-B$_{2-6}$		30.39	0	0.024	0	0	0
2B$_2$		27.59	0.148	0.296	0.185	0.255	0.16
CHB$_1$	CH	33.16	0.094	0.298	0.148	0.133	0.075
CHB$_2$		34.61	0.036	0.154	0.092	0.114	0.045
CHB$_{3-6}$		37.01	0.41	0.964	0.435	0.496	0.32
CN1	CN	26.84	0.093	0.145	0.094	0.102	0.113
CN2		33.85	0.271	0.286	0.285	0.261	0.212
percentage identified			72.167	57.196	71.851	67.131	76.901
percentage not identified			27.833	42.804	28.149	32.869	23.099
percentage of tertiary carbon			0.54	1.416	0.675	0.743	0.44

hydrocarbons. The aromatic carbon content was estimated according to the ASTM D5292-99[17] using the following equation:

$$\% \, C(ar) = [A/(A+B)] \times 100 \qquad (3)$$

where *A* is the peak area of the aromatic portion of the spectra (100–170 ppm), while *B* is the peak area of the aliphatic portion of the spectrum (10–70 ppm). The results

(17) Petitjean, D.; Schmitt, J. F.; Laine, V.; Bouroukba, M.; Cunat, C.; Dirand, M. *Energy Fuels* **2008**, *22*, 697–701.
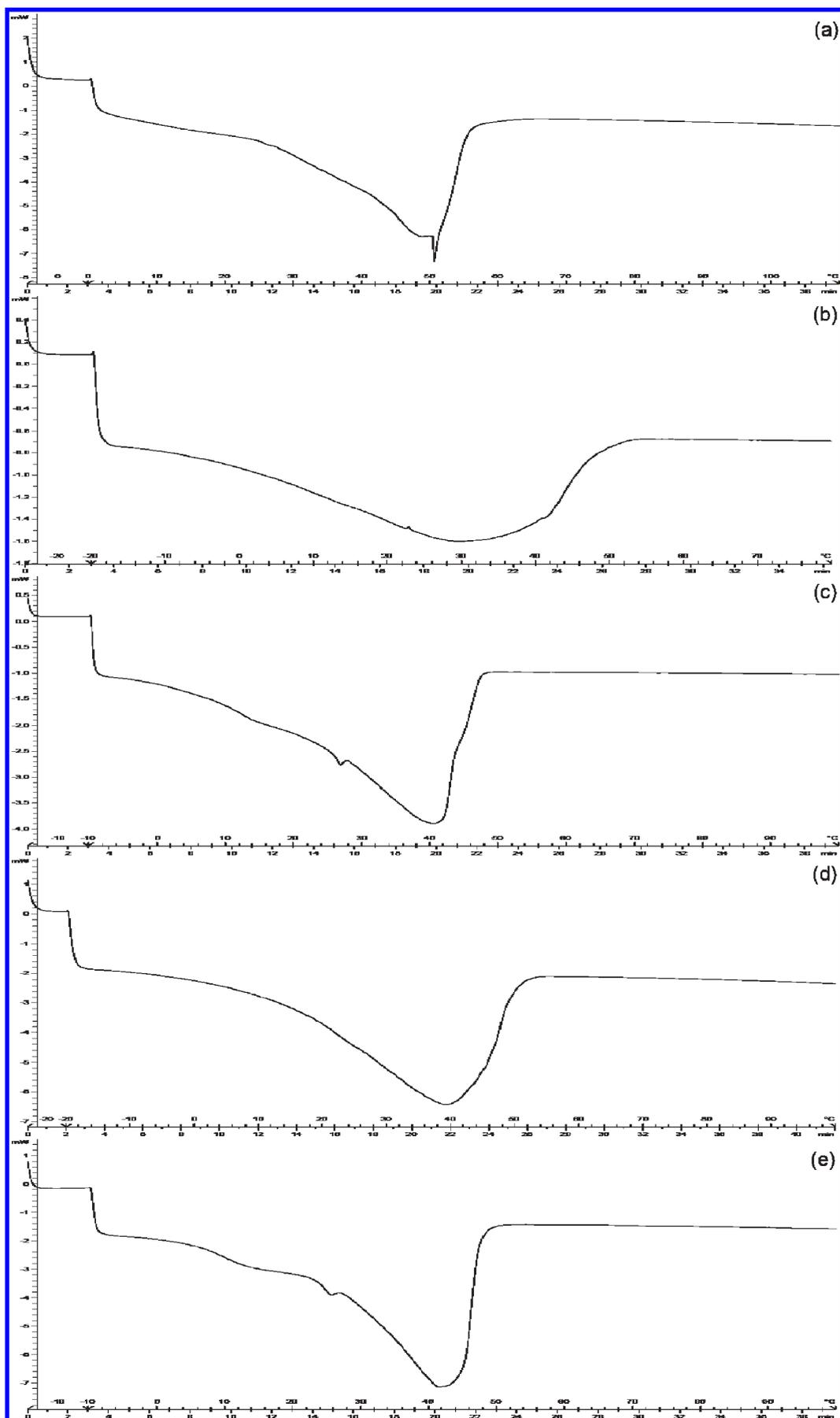
Figure 3. Thermograms for (a) Remal, (b) Bouri, (c) Sarir, (d) Sedra, and (e) Faregh.

are reported in Table 4, where it can be seen that Sedra has the highest content of aromatic carbon, with the other waxes presenting an aromatic carbon content equal or inferior to 1%. A good correlation was observed between the H/C ratio and the aromatic carbon content obtained from ^{13}C NMR spectra, allowing for an explanation for the lower H/C ratio observed for Sedra in the elemental analysis.

Using the peak identification mentioned above, an identification of the different carbon types was carried out and is reported in Table 5 using the nomenclature suggested by Sperber et al.[16]

The ^{13}C NMR spectra show that the waxes are formed essentially by alkyl chains with very limited amount of carbons in cyclic structures (CN < 0.5%) or tertiary carbons (CH), with the exception of Bouri, with a content of tertiary carbons close to 1.5%. The tertiary carbon content also seems to be related to the higher content of non-identified structures in Bouri wax. This indicates that the content of isoparaffins in Bouri must be higher than in the other waxes, as also suggested by the GC−FID analysis, and it must have some impact on the crystalline structure of the wax.

Melting Characteristics of the Waxes. DSC was used in this study to further characterize the structure of the waxes

through the determination of their melting temperatures and heats of fusion. Panels a−e of Figure 3 show the thermograms for the various wax samples studied, while Table 6 presents the measured melting point temperatures, as well as the heats of fusion. These values show how the thermograms are affected by the wax composition. Remal, which presents the wax with a higher *n*-alkane content, displays a sharp peak with a narrow melting range and high heat of fusion. As the non-*n*-alkane content increases, the melting range becomes broader and the heats of fusion decrease. Bouri, with its relatively high content of branched paraffins, presents a very broad melting peak and the lowest heat of melting (83.0 J/g), indicating that this wax has a much lower crystallinity than the other waxes. A small secondary peak is observed for Faregh and Sarir at temperatures close to 25 °C, which may be due to a solid−solid phase transition of *n*-alkanes. The large heats of melting observed are typical of macrocrystalline waxes.

A good correlation between the measured melting points and heats of fusion is observed for these waxes, with higher melting points corresponding to the higher heats of fusion. A good correlation is also observed between the heats of fusion/melting temperatures and the content of tertiary carbon reported in Table 5. The lower the tertiary carbon content, the higher the crystallinity of the wax and, thus, its melting temperature and heat of fusion.

XRD of the Waxes. To obtain information on the crystalline structure of the waxes extracted from the oils under investigation, XRD was performed here on the purified wax samples. The diffractograms of the five waxes are presented in Figure 4. The crystallinity of the samples can be associated

Table 6. Melting Point Temperatures and Heats of Melting for the Waxes Studied

	melting temperature (°C)	heat of melting (J g^{-1})
Remal	50.5	159.1
Bouri	30.2	83.0
Sarir	40.6	121.8
Sedra	39.2	119.7
Faregh	41.1	142.9
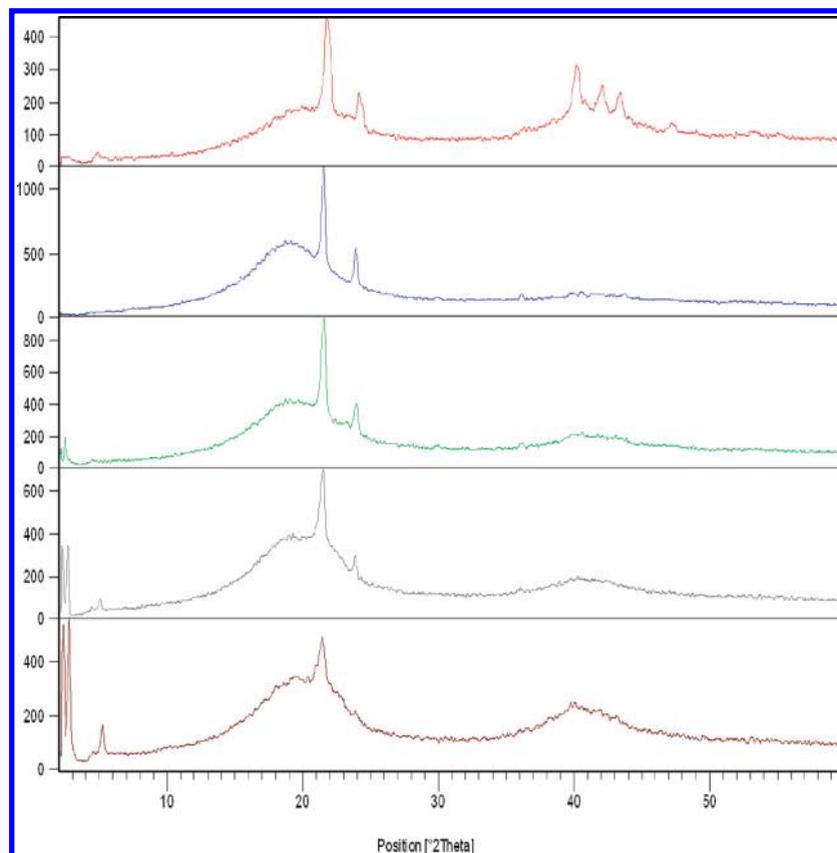
Figure 4. X-ray diffractograms of the studied waxes from top to bottom: (red) Remal, (blue) Bouri, (green) Sedra, (gray) Sarir, and (brown) Faregh, respectively.

with the $2\theta = 35-45$ region. Remal and Faregh are the most crystalline samples, while Bouri is the less crystalline sample. This is in good agreement with the observed heats of fusion. The low crystallinity of Bouri seems to be related with the large content in tertiary carbon of the Bouri waxes, as observed from the NMR spectra. Waxes with a higher iso-paraffin content present poor crystalline structures, and their mechanical properties are also modified.[17] These waxes are favorable from a flow assurance point of view because they are softer and easier to melt and, thus, remove from the pipelines by pigging.

To evaluate if a thermal treatment would have any effect on the crystalline habit of the waxes, diffractograms were collected for the purified wax samples and samples under-going different thermal treatments. No differences in the crystalline habit were observed with the thermal treatments.

Given the high *n*-alkane content of all of these waxes, it is not surprising that they all exhibit very similar XRD patterns. Their crystalline habit can be identified with an orthorhombic structure common in normal paraffins.[17,18]

Conclusions

Characterization of waxy crude oils and their waxes is necessary to be able to understand and predict their behavior to avoid various problems during production, transport, and processing, such as plugging and clogging of pipelines. It is thus very important to obtain reliable information concerning the nature of wax using a combination of various analytical techniques, because there is no single analytical method that can provide a complete picture on the chemical and physical nature of the wax. In this work, the characteristics of five Libyan waxy crudes, namely, Remal, Sarir, Sedra, Bouri, and Faregh, and their waxes were investigated.

Although the major characteristics of the oils seem to be in good agreement, displaying a good relationship between the average molecular weight, API gravity, viscosity, and wax content, it is shown here that the WAT is not just directly related with the wax content of the oil but also with its paraffin distribution. A correlation between the measured WAT and the pour points was also observed.

The results of ^{13}C NMR, elemental analysis, and GC−FID indicate, with a good agreement, that all of the studied Libyan crudes present macrocrystalline waxes, composed of essentially straight-chain saturated paraffinic hydrocarbons as *n*-alkanes. The aromatic content in the waxes was marginal, with the largest value of 2% being presented by Sedra. The waxes from Bouri have a higher quantity of isoparaffins than the other samples, with an important impact on their crystalline structure and, consequently, their melting characteristics.

The coherence between the results obtained from different analytical techniques helps to identify the most adequate, to provide the necessary information with lower effort and cost.

(18) Heyding, R.; Russell, K.; Varty, T.; St-Cyr, D. *Powder Diffr.* **1990**, *5*, 93–100.