

## Evaluation of Methods for the Extraction and Characterization of Waxes from Crude Oils

Juan J. Espada,<sup>\*,†</sup> Joao A. P. Coutinho,<sup>‡</sup> and José L. Peña<sup>§</sup>

<sup>†</sup>Department of Chemical and Energy Technology, Escuela Superior de Ciencias Experimentales y Tecnología (ESCET), Universidad Rey Juan Carlos, c/ Tulipán s/n, 28933, Móstoles, Madrid, Spain, <sup>‡</sup>Centre for Research in Ceramics and Composite Materials (CICECO), Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal, and <sup>§</sup>Repsol Technology Centre, 28931, Móstoles, Madrid, Spain

Received November 16, 2009. Revised Manuscript Received December 23, 2009

Wax precipitation is one of the most important flow assurance problems. The adequate characterization of the content and composition of the waxes present in the oil is one of the major obstacles in dealing with this issue. In this work, two different methods for the extraction of waxes from different crude oils are compared. The methods used differ significantly with regard to the separation of waxes from asphaltenes. Further purification of paraffins for characterization was carried out using sequential elution chromatography. The *n*-paraffin distribution determined by gas chromatography along with wax melting temperature and total *n*-paraffin content determined by differential scanning calorimetry show remarkable differences in the waxes depending upon the precipitation method used. The separation carried out by method 1 allows for heavier *n*-alkanes to be retained but with a higher content of impurities, as revealed by their lower melting points and *n*-paraffin content. Method 2 provides a better purification of the waxes but at a cost of losing some of the heavier *n*-paraffins. The waxes recovered are shown to be macrocrystalline waxes, with H/C ratios above 2 and average molecular weights between 450 and 530. <sup>1</sup>H nuclear magnetic resonance (NMR) analyses show a very low content of aromatic hydrogen, indicating the good separation achieved by the sequential chromatographic method used to isolate waxes, while the <sup>13</sup>C NMR results indicate the structure of the waxes to be mainly formed by straight chains with methyl branches.

### 1. Introduction

Waxes present in petroleum mixtures can precipitate when the temperature decreases during oil production, transport in pipelines, or storage. The deposition of this solid material causes a pressure drop in pipelines by increasing the fluid viscosity and constraining the pipeline, thus reducing or even stopping the oil production or transport. Therefore, the correct prediction of wax deposition is crucial to optimize the operation and minimize the operational costs.<sup>1–3</sup>

The modeling of wax precipitation requires a good knowledge of the solid–liquid equilibrium involved. Different authors have proposed thermodynamic models to describe the process;<sup>4–7</sup> however, the research on this field is ongoing, and new developments have recently been reached.<sup>8–10</sup> The main difficulty is the scarcity of reliable oil characterization in

what concerns the wax fraction, which limits the application of these models.

Accordingly to their physical properties, structure and composition, waxes can be classified into paraffinic waxes (macrocrystalline), microcrystalline waxes, and petrolatums.<sup>11</sup> Macrocrystalline waxes are composed of mainly *n*-alkanes with chain length within C<sub>20</sub>–C<sub>60+</sub>. These waxes represent the major risks to produce wax deposition problems despite the low content of long-chain waxes in crude oils (often not superior to 2%). Microcrystalline or amorphous waxes show a high proportion of isoparaffins and naphthenes within the range C<sub>30</sub>–C<sub>60</sub>.<sup>12</sup>

The two main variables usually considered in wax precipitation studies are the wax appearance/disappearance temperatures (WAT/WDT) and the amount of wax precipitated as a function of the temperature [wax precipitation curve (WPC)].

The measurement of the WAT/WDT can be carried out by a number of methods proposed in the literature,<sup>13</sup> but most of them are highly unreliable.<sup>14,15</sup>

The total amount of waxes present in oil can be determined by different methods reported in the literature. Most require the use of an anti-solvent and allow for the total amount

\*To whom correspondence should be addressed. Telephone: 34-91-4888087. Fax: 34-91-4887068. E-mail: juanjose.espada@urjc.es.

(1) Lu, X.; Redelius, P. *Energy Fuels* **2006**, *20*, 635–660.  
(2) Dos Santos, J. S. T.; Fernandes, A. C.; Giuliatti, M. *Pet. Sci. Eng.* **2004**, *45*, 47–60.  
(3) Robin, L. I.; Westacott, R. E.; Ni, X. *Chem. Eng. J.* **2008**, *137*, 205–213.  
(4) Coutinho, J. A. P. *Ind. Eng. Chem. Res.* **1998**, *37*, 4870–4875.  
(5) Coutinho, J. A. P.; Daridon, J. L. *Energy Fuels* **2001**, *15*, 1454–1460.  
(6) Daridon, J. L.; Pauly, J.; Coutinho, J. A. P.; Montel, F. *Energy Fuels* **2001**, *15*, 730–735.  
(7) Ramirez-Jaramillo, E.; Lira-Galeana, C.; Manero, O. *Pet. Sci. Technol.* **2004**, *22*, 821–861.  
(8) Escobar-Remolina, J. C. *Fluid Phase Equilib.* **2006**, *240*, 197–203.  
(9) Coutinho, J. A. P.; Edmonds, B.; Moorwood, T.; Szczepanski, R.; Zhang, X. *Energy Fuels* **2006**, *20*, 1081–1088.  
(10) Mehrotra, A. K.; Bhat, N. V. *Energy Fuels* **2007**, *21*, 1277–1286.

(11) Nermen, H. M.; Magdy, T. Z. *Pet. Sci. Technol.* **2004**, *11*, 15553–15569.

(12) Monger-McClure, T. G.; Tackett, J. E.; Merrill, L. S. *SPE Prod. Facil.* **1999**, *14*, 4–10.

(13) Hammami, A.; Ratulowski, J.; Coutinho, J. A. P. *Pet. Sci. Technol.* **2003**, *21*, 345–358.

(14) Coutinho, J. A. P.; Daridon, J. L. *Pet. Sci. Technol.* **2005**, *23*, 1113–1128.

(15) Elsharkawy, A. M.; Al-Sahhaf, T. A.; Fanhim, M. A. *Fuel* **1999**, *79*, 1047–1055.

of precipitated waxes to be obtained.<sup>11,16,17</sup> The method proposed by Burger et al.<sup>16</sup> is commonly used to precipitate waxes from crude oils,<sup>18,19</sup> and several modifications of it can be found in the literature.<sup>12,20</sup> One of the limitations of these methods is the separation of heavy paraffins from other high-molecular-weight compounds that precipitate together. Thanh et al. proposed a method to overcome this problem, avoiding the use of *n*-paraffin solvents in the separation of asphaltenes.<sup>21</sup> Recently, a new method based on a multi-stage fractional precipitation process to precipitate waxes from non-diluted crude oils has been proposed.<sup>22</sup> This method allows for the effect of the solvent to be avoided. Moreover, it allows for the WAT/WDT and the WPC to be determined.

Most of the methods developed to carry out wax precipitation are laborious and time-consuming. For that reason, great effort is being addressed for the development of reliable methods based on experimental techniques, such as nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), Fourier transformed infrared (FTIR) spectroscopy, etc.<sup>12,23–28</sup>

Dealing with flow assurance issues related to the wax precipitation process requires not only the assessment of the amount of precipitated wax but also a characterization of the precipitated solids. Different experimental techniques to characterize waxes precipitated from crude oils have been reported in the literature.<sup>11,20,29–31</sup> Musser and Kilpatrick<sup>20</sup> reported extensive work on the separation and characterization of waxes precipitated from different crude oils. Waxes were isolated from organics precipitated by means of a sequential elution chromatography procedure. The further characterization of the waxes indicated the presence of two types of waxes in the studied crude oils. The first type was composed of *n*-alkanes and isoalkanes with molecular weight between 350 and 600 and high values of the methylene/methyl ratio. The second type showed much lower values of the methylene/methyl ratio, indicating the presence of highly branched hydrocarbons.

Jayalakshmi et al.<sup>29</sup> characterized paraffin waxes by DSC and gas chromatography (GC), obtaining good agreement between both techniques for the prediction of the total amount of precipitated wax.

Nermen and Magdy<sup>30</sup> reported results on the characterization of wax isolated from different Egyptian crude oils. Waxes were isolated using urea-adducting analysis and characterized by <sup>1</sup>H NMR and FTIR experimental techniques. Waxes were mainly composed of a mixture of *n*-paraffins, branched-chain paraffins, and cycloparaffins.

Recently, Martos et al.<sup>31</sup> reported results on the characterization of the raw precipitated waxes obtained at different temperatures by fractional precipitation. DSC analyses were performed to obtain the WAT. Mass spectrometry analyses yielded the carbon number distribution. <sup>1</sup>H NMR was used to determine the aromatic content and the branching degree of the waxes.

The aim of this work is to study the effect of the extraction procedures on the characteristics and composition of the waxes extracted from crude oils. The waxes were extracted here from naphthenic and paraffinic crude oils using two different methods: one based on the method by Burger et al.<sup>16</sup> and other method based on that proposed by Thanh et al.<sup>21</sup> The waxes were separated from the raw precipitate using a modification of the sequential elution method reported by Musser and Kilpatrick.<sup>20</sup> *n*-Paraffin distribution of all waxes was determined by GC analysis. The amount of paraffin and the WDT were obtained by DSC analysis. These results indicate differences in the waxes regarding the precipitation method used. The amount of paraffin waxes experimentally obtained was compared to that predicted by DSC for the different crude oils, showing a lower value of paraffins when using the method by Burger et al. The elemental composition and molecular weight of waxes were determined by elemental analysis and gel permeation chromatography (GPC), respectively. Structural analysis of waxes carried out using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy indicated that these structures are mainly dominated by straight chains, with a low fraction of branching and also a low aromatic content.

## 2. Experimental Section

**Materials.** Four different crude oils were selected to carry out the different experiments. Crude oils A, B, and C were naphthenic from North Africa, West Africa, and South America, respectively. Crude oil D was paraffinic from North Africa. All crude oils were provided by Repsol. Methylene chloride, acetone, *n*-hexane, and toluene were all HPLC-grade. Petroleum ether was reagent-grade. Both the alumina (0.063–0.200 mm) and the silica gel (0.2–0.5 mm) were provided by Merck. Filters used in this work were Whatman 934-AH glass microfiber filters.

**Wax Precipitation.** Wax precipitation was carried out using two methods: a modification of the method proposed by Burger et al.<sup>16</sup> (method 1) and a modification of the method proposed by Thanh et al.<sup>21</sup> (method 2). In method 1, the crude oil is dissolved in petroleum ether and stirred for 30 min. The anti-solvent (3:1 acetone/*n*-pentane ratio) is added to the mixture and cooled to 253 K for 24 h. Thereafter, the solid phase present in the oil is separated by filtration in a Buchner funnel using a Whatman 934-AH glass microfiber filter. The precipitate is redissolved in *n*-hexane to separate the asphaltenes, and finally, the wax is weighted after solvent evaporation.

Method 2 requires a previous separation between waxes and asphaltenes by toluene extraction in a Soxhlet apparatus. A total of 1 g of crude oil is dissolved in toluene, and the mixture is adsorbed onto alumina previously activated at 473 K. After adsorption, the alumina is charged in a Soxhlet extractor and washed with toluene for 48 h. The toluene extract is concentrated, and the waxy fraction is precipitated following method 1, avoiding the washing step with *n*-hexane. The recovery of the

(16) Burger, E. D.; Perkins, T. K.; Striegler, J. H. *J. Pet. Technol.* **1981**, *3*, 1075–1086.

(17) Handoo, J.; Gupta, A. K.; Agrawal, K. M. *Pet. Sci. Technol.* **1997**, *15*, 347–356.

(18) Sjoblom, J.; Mingyuan, L.; Hoiland, H.; Johansen, E. J. *Colloids Surf.* **1990**, *46*, 127–139.

(19) Ronningnsgen, H. P.; Bjorndal, B.; Hansen, A. B.; Pedersen, W. B. *Energy Fuels* **1991**, *5*, 895–908.

(20) Musser, B. J.; Kilpatrick, P. K. *Energy Fuels* **1997**, *12*, 715–725.

(21) Thanh, N. X.; Hsieh, M.; Philip, R. P. *Org. Geochem.* **1999**, *30*, 119–132.

(22) Coto, B.; Martos, C.; Peña, J. L.; Espada, J. J.; Robustillo, M. D. *Fuel* **2008**, *87*, 2090–2094.

(23) Pedersen, W. B.; Hansen, A. B.; Larsen, E.; Nielsen, A. B. *Energy Fuels* **1991**, *5*, 908–913.

(24) Létoffé, J. M.; Claudy, P.; Kok, M. V.; Garcin, M.; Volle, J. L. *Fuel* **1995**, *74*, 810–817.

(25) Roehner, R. M.; Hanson, F. V. *Energy Fuels* **2001**, *15*, 756–763.

(26) Lu, X.; Kalman, B.; Redelius, P. *Fuel* **2008**, *87*, 1543–1551.

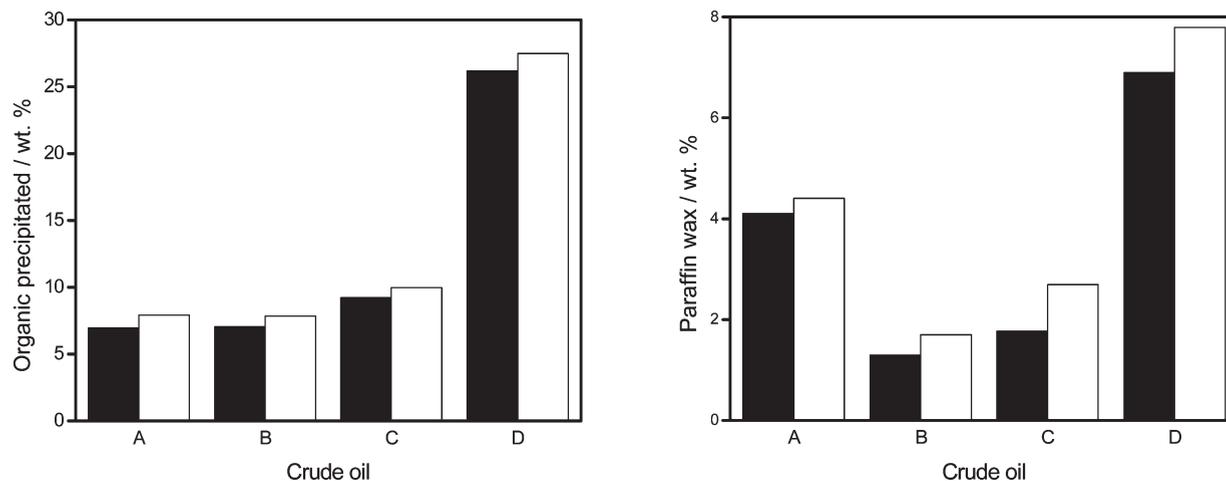
(27) Coto, B.; Martos, C.; Espada, J. J.; Robustillo, M. D.; Peña, J. L. *Fuel* (2009), doi:10.1016/j.fuel.2009.12.010.

(28) Paso, K.; Kallevik, H.; Sjöblom, J. *Energy Fuels* **2009**, *23*, 4988–4994.

(29) Jayalakshmi, V.; Selvavathi, V.; Sekar, M. S.; Sairam, B. *Pet. Sci. Technol.* **1999**, *17*, 843–856.

(30) Nermen, H. M.; Magdy, T. Z. *Pet. Sci. Technol.* **2005**, *23*, 483–493.

(31) Martos, C.; Coto, B.; Espada, J. J.; Robustillo, M. D.; Gomez, S.; Peña, J. L. *Energy Fuels* **2008**, *22*, 708–714.



**Figure 1.** Precipitated solid and purified waxes from the studied crude oils: (■) method 1 and (□) method 2.

polar fraction (asphaltenes and resins) is carried out in two steps. The material adsorbed onto the alumina is first extracted with *n*-pentane for at least 2 h and, afterward, with a mixture of chloroform/methanol (95:5). The eluate is concentrated and precipitated with pentane.

**Wax Purification.** The waxes were separated from the polar fraction following a modification of the sequential elution procedure proposed by Musser and Kilpatrick.<sup>20</sup> The organic precipitated obtained by methods 1 and 2 were dissolved in methylene dichloride, and the mixture was adsorbed onto silica gel previously activated at 393 K overnight. Methylene dichloride is removed in an oven at 313 K. Two glass chromatographic columns of 50 cm long in series were used to separate paraffin waxes from the precipitated solid. The bottom column was charged with fresh activated silica, and the top column was partially charged with fresh activated alumina and the adsorbed organic precipitated. *n*-Hexane was charged in a 250 mL reservoir attached to the top column. The paraffinic compounds were collected after eluting 200 mL of *n*-hexane. Finally, *n*-hexane was removed by rotatory evaporation, and the final material was weighed. The wax obtained from this procedure is white or pale yellow, unlike the black material recovered after precipitation.

**GC.** Paraffin waxes were dissolved in a dichloromethane/carbon disulfide mixture (1:1, vol) and analyzed using gas-phase chromatography on a Varian 6890 chromatograph equipped with an on-column injector and a 50 × 0.53 mm Chromapack CP-wax 52CB capillary column, with a temperature program of 3 K/min from 323 to 593 K.<sup>32</sup>

**DSC.** The experimental apparatus used was a DSC Mettler-Toledo DSC822e. The samples used weighed 40–50 mg. The procedure followed consists of a previous step, in which the sample is heated at 3 K/min from 293 to 353 K and maintained there for 2 min, to completely dissolve the possible solid phase. After that, the sample is cooled at 3 K/min from 353 to 153 K and kept at that temperature for 2 min. Finally, the sample is heated from 153 to 353 K at 3 K/min.

Special calibration for low temperature was carried out using pure *n*-alkanes in the range from *n*-C<sub>7</sub> to *n*-C<sub>18</sub>, thus covering a temperature range between 183 and 303 K.

**Elemental Analysis.** An Elementar Vario EL III CHNS analyzer was used to determine the content of C and H of each sample. Analysis is carried out by combustion of the sample with an oxygen flow of 65 mL/min. Combustion gases flow through different columns, are selectively separated, and are detected by thermal conductivity. Sulphanilic acid was used as the standard for the calibration and

analyzed after each experiment to check the quality of measurements. The precision for each determination was ±0.3 wt %.

**<sup>1</sup>H NMR.** A Bruker DRX 500 NMR spectrometer (C/H dual 5 mm probe, frequency of 500 MHz) was used to identify and quantify different types of hydrogen atoms. Samples were prepared by dissolving 15–20 mg of the sample in 0.45 mL of CDCl<sub>3</sub> used as the solvent in 5 mm sample tubes. The number of scans was 64, with a 30° pulse and a 1 s delay time between scans.

**<sup>13</sup>C NMR.** The same equipment was used to identify and quantify the different types of carbon atoms. Concentrations of samples were within 50–80 mg/mL dissolved in CDCl<sub>3</sub> in 5 mm sample tubes. The number of scans was 64, with a 30° pulse and a 1 s delay time between scans.

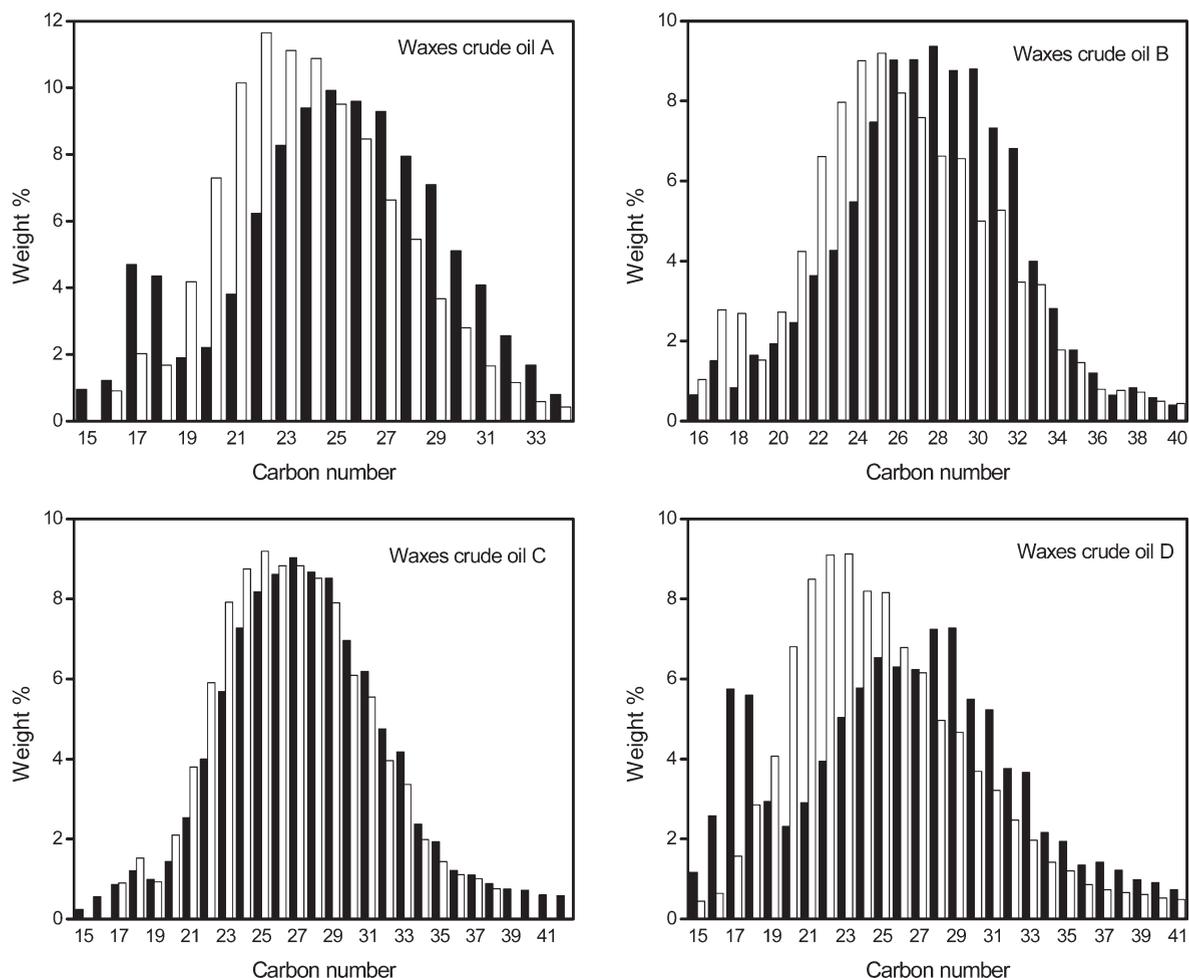
**GPC.** The average molecular weight of the waxes was determined by GPC. An Alliance GPCV 2000 equipped with refractive index and viscosimeter detectors and three different columns (two PLgel 10 μm MIXTED-B, 300 × 7, 5 mm, and a PLgel 10 μm 10E6 Å, 300 × 7, 5 mm) was used in this work. The mobile phase was 1,2,4-trichlorobenzene; the flow rate was 1 mL/min; and the temperature was 145 °C. Samples were dissolved in 1,2,4-trichlorobenzene in a concentration of about 1.5 mg/mL. The calibration was obtained from pure *n*-paraffins used as the standard.

### 3. Results and Discussion

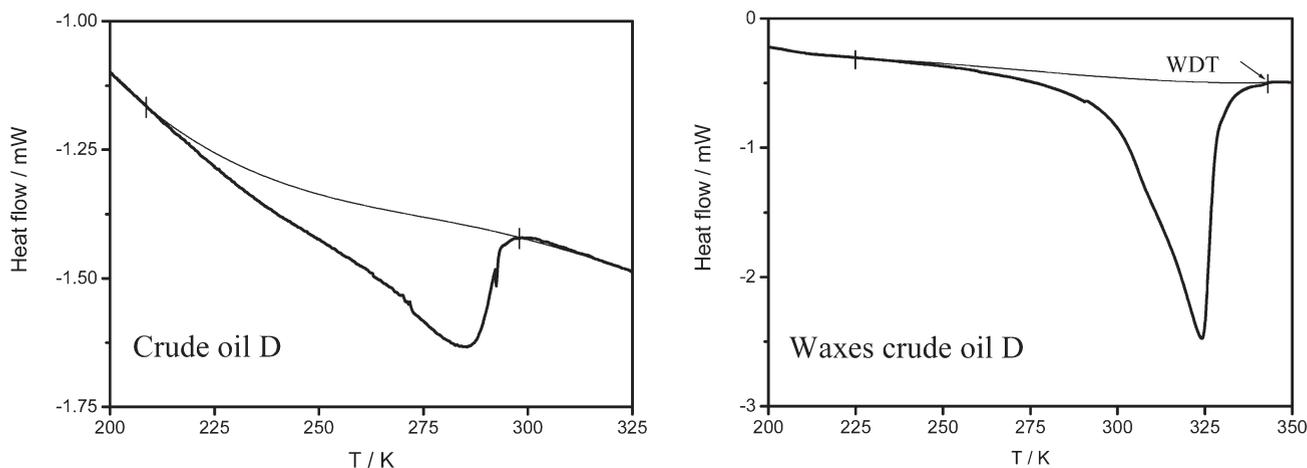
**Wax Precipitation and Purification.** In this work, the waxes were precipitated from the selected crude oils using the two methods described above (methods 1 and 2). The amount of solid precipitated by each method is shown in Figure 1. As can be seen, no remarkable differences between the two methods are observed, although method 2 produces consistently a somewhat higher amount of precipitated wax than method 1. Crude oil D (highly paraffinic) presents the highest content of precipitated solid.

Sequential elution chromatography was used to separate paraffin waxes from the other precipitated materials. The experimental procedure followed was a modification of that reported by Musser et al.,<sup>20</sup> as described above. Figure 1 also shows the results obtained for the studied crude oils. The decrease in the wax content after purification very much depends upon the nature of the oil and the amounts of the other fractions coprecipitated during the first extraction step. Although the wax content in oil A is not much affected by the purification step, the other oils present a purified wax content that is 2–3 times lower than the amount of wax extracted in the first step. Again, the amount of wax retrieved by method 2 is consistently higher than that obtained by method 1, and now this difference is even more

(32) Coutinho, J. A. P.; Gonçalves, C.; Marrucho, I. M.; Pauly, J.; Daridon, J. L. *Fluid Phase Equilib.* **2005**, *233*, 28–33.



**Figure 2.** GC spectra for waxes purified from the selected crude oils: (■) method 1 and (□) method 2.



**Figure 3.** DSC thermogram during heating of crude oil D and its purified wax.

significant than after step 1, evidence of a superiority of method 2 on the extraction of waxes from crude oils. This result must be related to the difference in the separation of asphaltenes between the two methods. While *n*-hexane is used in method 1 to separate the asphaltenes, no solvent is used in method 2.

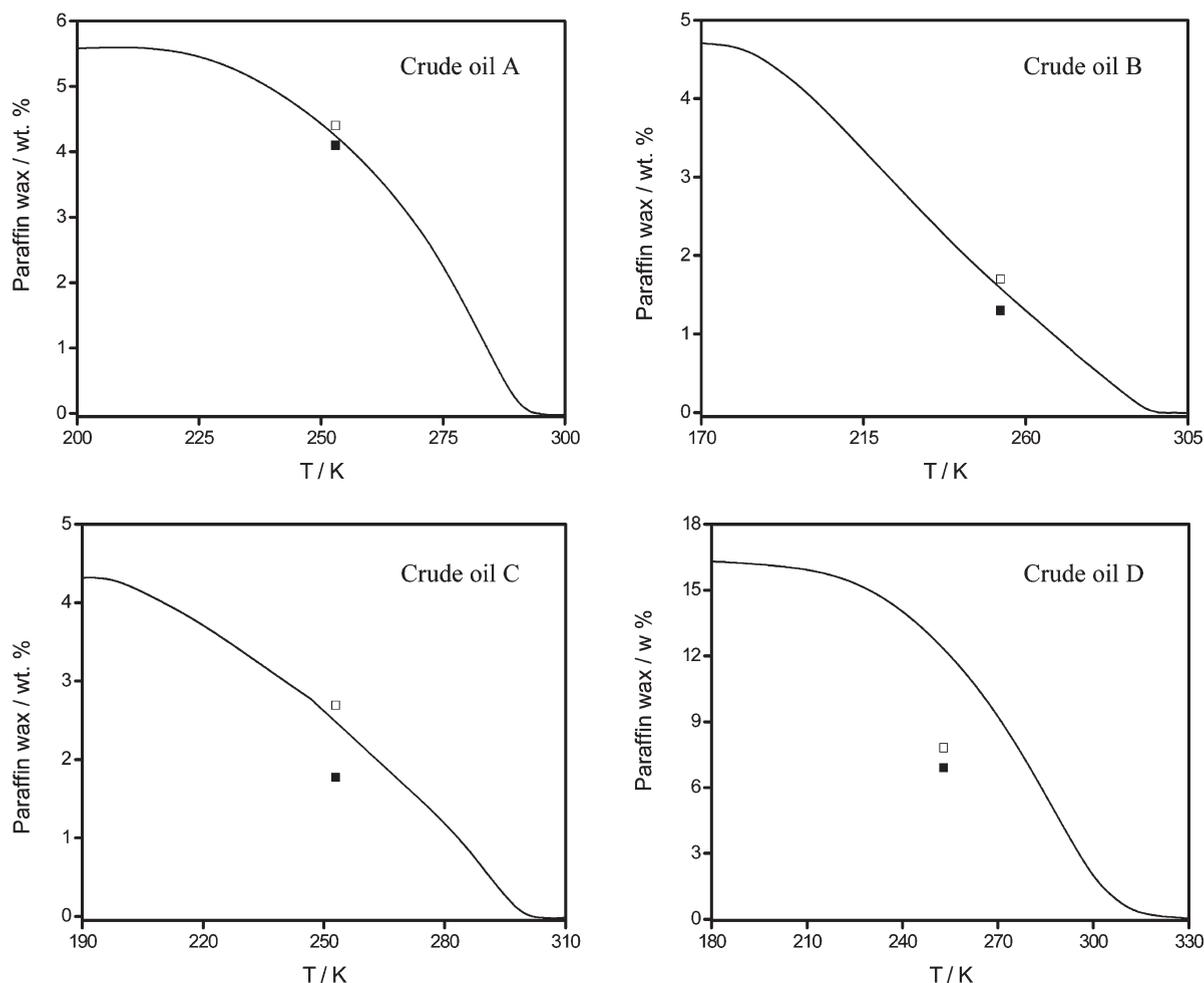
**GC.** To obtain *n*-paraffin distribution of waxes precipitated using methods 1 and 2, GC analysis of the purified waxes was carried out according to the procedure described above. The results obtained are presented in Figure 2. As can

be seen, in all cases, the waxes precipitated using method 1 show a displacement of the distribution toward heavier alkanes than those obtained using method 2.

**DSC.** The use of DSC has been widely described in the literature<sup>12,27,32–34</sup> as a procedure for the characterization

(33) Coutinho, J. A.; Ruffier-Méray, V. *Fluid Phase Equilib.* **1998**, *148*, 147–160.

(34) Queimada, A. J. N.; Dauphin, C.; Marrucho, I. M.; Coutinho, J. A. P. *Thermochim. Acta* **2001**, *372*, 93–101.



**Figure 4.** Comparison between DSC analysis and experimental results. (Line) Crude oil WPC obtained by DSC analysis and (symbols) precipitated wax: (■) method 1 and (□) method 2.

and quantification of wax precipitated from crude oils and refined products. This technique has the advantage of simplicity and fast response, which makes it appropriate for routine assays. In a typical DSC analysis, a sample is heated/cooled at a constant rate, the heat transfer is registered, and the phase transition can be determined by quantifying the differences in heat flows. Figure 3 shows the thermogram obtained for a heating run of crude oil D and that for the wax precipitated from the same crude. As can be seen, the DSC analysis of the crude oil shows a broader signal than that of the precipitated wax as a result of the larger distribution of paraffins in the crude, because the studied extraction methods will precipitate essentially the  $C_{20+}$  fraction, as shown in Figure 2, and also the presence of the solvent.

In this work, the thermograms were integrated using a procedure previously proposed.<sup>31</sup> The integration process yields the WDT and the WPC.

Figure 4 shows the comparison between the amount of paraffin wax obtained by methods 1 and 2 after purification and that predicted by the WPC calculated by DSC analysis for the studied crude oils. The amount of precipitated wax predicted using the DSC analyses is in good agreement with that experimentally obtained by both methods for naphthenic crude oils (A, B, and C), with method 2 displaying slightly superior results. A larger discrepancy between predicted and experimental results is observed for crude oil D. This deviation may result from a limitation of the method used to

**Table 1. Melting Points and Melting Enthalpies of the Waxes Precipitated by Methods 1 and 2**

wax crude oil	WDT (K)		$\Delta H$ (J g <sup>-1</sup> )	
	method 1	method 2	method 1	method 2
A	322.5	325.0	125.4	130.1
B	332.2	336.3	76.2	95.6
C	338.2	343.6	124.7	152.6
D	321.8	339.6	91.6	105.9

purify paraffin waxes from highly paraffinic crude oils. Further studies are required to elucidate this point.

The melting point of a wax is related to the type of compounds present in the wax. It is well-known that the melting points of *n*-paraffins should be higher than those of branched alkanes. Table 1 shows the melting points and the enthalpies of melting for the precipitated waxes. For waxes precipitated using method 1, both magnitudes are consistently lower than those precipitated using method 2, despite the heavier alkanes present, as revealed by the GC analyses. These results suggest differences between the waxes extracted by the two methods concerning not only their composition but also their structure.

The WPCs of the purified waxes were also estimated from the DSC analyses. The total *n*-paraffin content was assumed as the maximum value of solids predicted by the WPC. Figure 5 shows the WPC of the wax precipitated from crude oils A (naphthenic) and D (paraffinic) using methods 1 and 2.

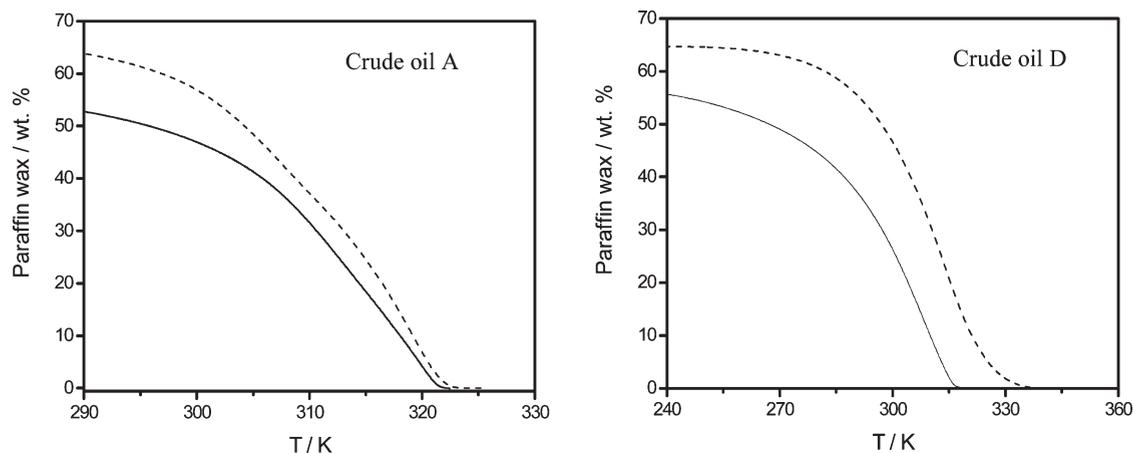


Figure 5. WPC of waxes precipitated from crude oils A and D: (—) method 1 and (---) method 2.

Table 2. Elemental Analysis and Molecular Weights for the Waxes Precipitated by Methods 1 and 2

wax crude oil	method 1					method 2				
	C (wt %)	H (wt %)	S (wt %)	H/C	molecular weight	C (wt %)	H (wt %)	S (wt %)	H/C	molecular weight
A	84.83	14.62	0.56	2.07	461	84.56	15.14	0.30	2.15	456
B	85.13	14.72	0.16	2.07	433	84.72	15.10	0.78	2.14	427
C	85.51	14.41	0.08	2.02	531	84.51	15.32	0.17	2.17	498
D	85.10	14.73	0.17	2.08	514	84.64	15.15	0.21	2.15	529

As can be seen, the waxes extracted by method 1 show lower *n*-paraffin contents than those obtained by method 2.

The lower melting point and total *n*-paraffin content obtained for the waxes precipitated using method 1 may seem at first to be in discrepancy with GC results, because these waxes show heavier *n*-alkanes and wider *n*-paraffin distributions. This discrepancy can be explained because of the presence of impurities in the precipitated material, which lowers the wax melting point and *n*-paraffin content estimated by DSC. Therefore, method 1 allows for heavier *n*-alkanes to be recovered but with less purity. On the other hand, method 2 is better at purifying the waxes (more paraffinic) but at a cost of losing some of the heavier *n*-alkanes.

**Elemental Analysis and GPC.** Table 2 shows the elemental composition analysis and the molecular weight of the waxes extracted by methods 1 and 2. As can be seen, in all cases, the H/C ratio was higher for waxes precipitated using method 2, showing that the waxes extracted and purified using this method are better purified and composed essentially of branched or linear paraffins, with little content of other types of compounds.

All waxes were also analyzed by GPC to assess their average molecular weight. GPC is an experimental technique widely used to characterize saturate compounds of petroleum fractions,<sup>35,36</sup> including precipitated waxes.<sup>20</sup> In this work, an average molecular weight between 400 and 550 was obtained for all of the waxes. In agreement with the chromatographic analyses, the molecular weights of the waxes obtained with method 1 are in general higher than those from method 2.

**<sup>1</sup>H NMR Spectroscopy.** All waxes were analyzed by <sup>1</sup>H NMR. This technique allows for the type and content of

Table 3. <sup>1</sup>H NMR Results for the Waxes Precipitated by Methods 1 and 2

wax crude oil	H <sub>ar</sub> (mol %)	H <sub>α</sub> (mol %)	H <sub>β</sub> (mol %)	H <sub>γ</sub> (mol %)	H <sub>β</sub> /H <sub>γ</sub>
Method 1					
A	1.02	0.61	81.32	17.05	4.77
B	0.92	11.77	66.26	21.04	3.15
C	0.79	9.32	68.53	21.37	3.21
D	1.86	8.40	69.80	19.93	3.50
Method 2					
A	1.04	11.35	73.11	14.49	5.04
B	0.19	6.95	77.07	15.79	4.88
C	0.24	9.93	74.38	15.45	4.81
D	1.24	5.87	74.51	18.38	4.05

the different hydrogens to be determined. Table 3 shows the experimental results, in which the percentages of H<sub>ar</sub> (hydrogen atoms in aromatic rings), H<sub>α</sub> (hydrogen atoms next to functional groups), H<sub>β</sub> (methylene hydrogen atoms), and H<sub>γ</sub> (methyl hydrogen atoms) were obtained by integration of the corresponding peak areas, as reported by Martos et al.:<sup>31</sup> H<sub>ar</sub> (9.2–6.5 ppm), H<sub>α</sub> (3.8–1.8 ppm), H<sub>β</sub> (1.80–1.03 ppm), and H<sub>γ</sub> (1.03–0.40 ppm). This information allows for the branching degree and the aromatic content of the waxes to be determined. As can be seen in Table 3, the aromatic content of all waxes was inferior to 2%, in good agreement with elemental analysis and again showing that the procedures adopted for wax purification allow for a very good removal of non-saturated fractions. Waxes precipitated using method 2 showed higher values of the H<sub>β</sub>/H<sub>γ</sub> ratio, which indicates a higher content of *n*-paraffins than in those obtained using method 1, in agreement with the results discussed above.

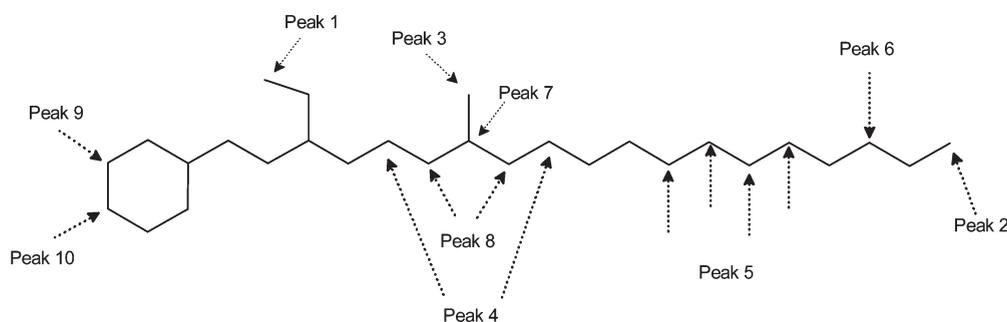
**<sup>13</sup>C NMR Spectroscopy.** Waxes precipitated by methods 1 and 2 were also analyzed by <sup>13</sup>C NMR. This technique has been widely used for the characterization of heavy

(35) Al-Zaid, K.; Khan, Z. H.; Hauser, A.; Al-Rabiah, H. *Fuel* **1998**, *77*, 453–458.

(36) Espada, J. J.; Coto, B.; Peña, J. L. *Energy Fuels* **2009**, *23*, 888–893.

Table 4.  $^{13}\text{C}$  NMR Chemical-Shift Assignments<sup>42</sup>

peak number	structure	chemical shift (ppm)
1	methyl group at the end of the ethyl branch	11.46
2	methyl group at the end of the alkyl chain (bound to primary carbon)	14.14
3	methyl branching more than four carbons away from terminal $\text{CH}_3$	20.06
4	methylene groups in $\beta$ carbon away from the methyl branch	27.36
5	methylene groups in straight chain	29.90
6	methylene groups in straight chain	32.16
7	tertiary carbon from a methyl branch	33.16
8	methylene groups in $\alpha$ carbon away from the methyl branch	37.48
9	naphthenic carbon	26.84
10	naphthenic carbon	33.85

Figure 6. Identification of  $^{13}\text{C}$  NMR signals.Table 5.  $^{13}\text{C}$  NMR Results for the Waxes Precipitated by Methods 1 and 2

peak number	waxes (mol %)							
	method 1				method 2			
	A	B	C	D	A	B	C	D
1	0.00	0.00	0.00	0.74	1.09	0.98	0.24	0.00
2	1.06	0.90	0.97	1.09	2.69	1.29	1.38	1.48
3	2.49	4.54	3.79	1.43	2.25	2.84	1.88	1.27
4	2.92	5.55	3.76	5.95	3.76	4.53	3.32	4.91
5	82.46	75.30	74.85	78.08	84.80	76.07	81.23	78.41
6	6.13	6.29	5.30	5.84	1.23	6.81	5.70	6.01
7	1.91	3.82	4.62	3.97	2.11	4.76	2.91	3.72
8	2.25	2.91	5.80	1.20	1.41	1.73	2.11	2.72
9	0.33	0.34	0.22	0.56	0.18	0.41	0.32	0.53
10	0.21	0.04	0.37	0.00	0.10	0.16	0.31	0.54
identified signal (%)	99.76	99.69	99.68	98.86	99.62	99.58	99.40	99.59

hydrocarbons.<sup>20,31,36–42</sup> The most interesting information obtained by  $^{13}\text{C}$  NMR for the wax structure concerns the length of alkyl chains and branching degree. In this work, the identification of the carbon signals was performed according to the work reported by Sperber et al.<sup>42</sup> Table 4 shows the chemical-shift assignment and the nomenclature used for the different carbon signals based on that proposed by these authors. Figure 6 depicts the identification of these signals on a model molecule.

(37) Netzel, D. A.; McKay, D. R.; Heppner, R. A.; Guffey, F. D.; Cooke, S. D.; Varie, D. L.; Linn, D. E. *Fuel* **1980**, *60*, 307–320.

(38) O'Donnell, D. J.; Sigle, S. O.; Berlin, K. D.; Sturm, G. P.; Vogh, J. W. *Fuel* **1980**, *59*, 166–174.

(39) Gillet, S.; Rubini, P.; Delpuech, J. J.; Escalier, J. C.; Valentin, P. *Fuel* **1981**, *60*, 221–225.

(40) Ali, F.; Khan, Z. H.; Ghaloum, N. *Energy Fuels* **2004**, *18*, 1798–1805.

(41) Verdier, S.; Coutinho, J. A. P.; Silva, A. M.; Alkilde, O. F.; Hansen, J. A. *Fuel* **2009**, *88*, 2199–2206.

(42) Sperber, O.; Kaminsky, W.; Geissler, A. *Pet. Sci. Technol.* **2005**, *23*, 47–54.

Table 5 shows the results obtained after NMR spectra integration. As can be observed, the structures of all waxes were mainly dominated by methylene carbon in straight chains with short branches. Thus, only methyl branches were detected for the considered waxes. Cyclic structures were detected in traces, thus revealing their low content in the analyzed waxes. The methyl content however is larger on the waxes obtained with method 1, again indicating the larger content of non-*n*-alkanes present on these waxes. According to the results obtained, all of the precipitated fractions are mainly formed by macrocrystalline waxes.

#### 4. Conclusions

Two methods for the precipitation and purification of waxes from crude oils were studied, and the waxes recovered from them were compared using various analytical techniques. The separation carried out by method 1 allows for heavier *n*-alkanes to be retained but with a higher content of impurities, as revealed by their lower melting points and *n*-paraffin content. Method 2 provides a better purification of the waxes but at a cost of losing some of the heavier *n*-paraffins.

All waxes recovered in this work were formed essentially by carbon and hydrogen, with H/C ratios above 2 and with average molecular weights ranging between 425 and 530 ( $\text{C}_{30}$ – $\text{C}_{40}$ ).

The aromatic content of the waxes was determined by  $^1\text{H}$  NMR, showing values of less than 1.3%.  $\text{H}_\beta/\text{H}_\gamma$  ratios over 3 indicated the presence of long chains in the structure of the paraffinic waxes.  $^{13}\text{C}$  NMR results indicated that the structure of the paraffins present in the waxes was mainly formed by *n*-alkanes.

**Acknowledgment.** The authors thank Repsol for providing the crude oil samples and the financial support through the research project “Aseguramiento de flujo de crudos de petróleo: Estudio de la precipitación de parafinas”. This work was carried out within the framework of Luso Spanish CRUP/CRUE Integrated Action E-85/09.