Assessment of different methods to determine the total wax content of crude oils

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Published on: Energy & Fuels 26:10 (2012) 6352–6357

https://doi.org/10.1021/ef301190s

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Abstract

Wax formation by temperature decrease is a serious issue in the petroleum industry, since it makes the production difficult and can lead to important economic losses. As a result, a large effort has been made in order to predict the occurrence of this phenomenon as accurately as possible. Thermodynamic models are commonly used to predict the main parameters involved in the wax precipitation process. Models with wide basis require as most common input information the n-paraffin distribution and the total wax content (C_{20+} fraction).

The aim of this work is to check the capabilities of different experimental techniques to determine the C_{20+} content of different crude oils. For that purpose, High Temperature Gas Chromatography (HTGC) and Differential Scanning Calorimetry (DSC) analyses (direct analysis of the raw crude oil) were used, showing reasonable agreement. Likewise, the wax precipitation of the raw crude oils was performed to obtain the direct C_{20+} content. Such experiments lead to clearly higher values than those obtained by HTGC and DSC analyses because of the presence of trapped crude oil in the precipitated solid. After that porosity correction carried out by ^{1}H-NMR, DSC and sequential elution chromatography techniques, the obtained results indicate that both ^{1}H-NMR, DSC analyses yield more consistent results.

An empirical correlation was developed to determine the C_{20+} content from the API gravity and the pour point of the selected crude oils. The correlation was applied to a number of crude oils, obtaining a reasonable agreement between experimental and calculated C_{20+} values, which shows that the validity of that correlation is wider than previous unreliable equations.

Keywords: total wax content, wax porosity, differential scanning calorimetry, ^{1}H-NMR, HTGC, liquid chromatography.

1. Introduction

Paraffinic waxes present in petroleum crude oils may crystallize at low temperature and precipitate as a solid material, causing problems in pipelines, oil production and processing equipments [1-3]. For that reason, the quantification of wax precipitation is necessary to anticipate solutions for future problems in wells and implies the determination of the wax appearance temperature (WAT) and the amount of wax formed as a function of the temperature (wax precipitation curve, WPC). The prediction of these magnitudes is frequently carried out by thermodynamic models [4-10], which require as input parameter the knowledge of the n-paraffin distribution as close as possible to the actual fluid. Nevertheless, obtaining the n-paraffin distribution experimentally is not an easy task and the research in this area is ongoing. The n-paraffin distribution can be described by two parameters: the total n-alkane content (C_{20+}) and their decay [11]. Both of them can be determined directly by analyzing the raw crude oil by different experimental techniques (Differential Scanning Calorimetry and Gas Chromatography) [12-16] or by analyzing the wax fraction precipitated from the crude oil [17]. When the experimental C_{20}^{+} values are not available it can be estimated by using empirical correlations, most of which are only valid for specific crude oils [11].

DSC is a technique widely used to study the solid liquid equilibrium in crude oils[18-23]. This technique allows the transformation of the measured heat into wax mass and therefore the quantification of wax content. However, it presents some difficulties related to the integration process, for example the transformation of heat flow into the corresponding mass. Coto et al. [18] have developed a new method which overcomes such limitations and allows for the determination of the WAT, the WPC and the n-paraffin distribution of petroleum mixtures by DSC.

High Temperature Gas Chromatography (HTGC) allows the direct detection and quantification of n-alkanes up to very high molecular weights, and provides both the total n-alkane content and its decay. One of the major unsolved problems in the use of this technique is the uncertainty in the determination of the baseline to integrate the chromatogram, because of the low signal/noise ratios and the presence of very diverse compounds [24, 25].

The quantification of the wax present in crude oils is usually carried out by using the UOP 46-85 standard test method, although some modifications are frequently used [15, 17]. These methods are used to isolate the wax present in the raw crude oil, which allows the determination of the total wax content. However, it is not possible to determine the true total wax content directly, because crude oil remains trapped along with the precipitated solid, which can have a noticeable effect on the total mass quantified. Although the experimental determination of trapped crude oil is not well established, ^{1}H-NMR and DSC analyses have been used for that purpose, showing promising results[26].

Very often, in the absence of analytical information, the wax content is estimated from some standard properties of the crude oil by using empirical correlations[11]. Usually, such correlations are obtained for specific crude oils and its validity is limited.

The aim of this work is to check the capabilities of different experimental techniques to determine the C_{20}^{+} content of different crude oils. Specifically, the C_{20+} content was quantified by using HTGC and DSC (direct analysis of the raw crude oil) and from the precipitated wax obtained by using a modification of Burger´s method. The comparison of the obtained results showed that Burger´s method yielded larger C_{20+} values than HTGC and DSC. This difference is due to the trapped crude oil (wax porosity) remaining in the precipitated solid. In this work, ^{1}H-NMR, DSC [26] and sequential elution chromatography [27] techniques were used to determine the wax porosity of the

precipitated wax for the studied crude oils. The obtained results were used to rectify the C_{20+} values obtained by Burger´s method, showing that the correction made with ^{1}H-NMR or DSC yield more consistent C_{20+} values.

Additionally, an empirical correlation was developed in this work to determine the C_{20+} content of the studied crude oils. That relation allows the calculation of this parameter from two physical properties of the crude oils, API gravity and pour point. The reliability of the correlation was checked by calculating the C_{20+} content of different crude oils, obtaining a reasonable agreement between experimental and calculated values.

2. Experimental Section

2.1. Crude oils. A total number of 32 gas-free crude oils provided by Repsol were used in this work. The origin and nature as well as API gravity and pour point as characteristic properties of the studied crude oils are listed in Table 1.

2.2. Determination of C_{20}^{+} content

High Temperature Gas Chromatography (HTGC). The analyses were carried out in a Varian Chrompack CP-3800 chromatograph, equipped with a Varian CP 7542 column 10 meters long, 0.53 mm internal diameter and 0.17 μm stationary phase thick and a flame ionization detector (FID). The analysis method, based on the ASTM D-2887, requires the dilution of the samples in carbon disulfide at a concentration of 5% (wt.) and their injection on column. Helium was used as carrier gas with a flow of 18 ml/min. The initial temperature of the column oven was 40 ºC, and it was heated up to 425 ºC using a rate of 16 ºC/min. Then, the temperature remained constant for 20 minutes. Retention times were calibrated from two different standard n-paraffin mixtures: a mixture of C_5 - C_{18} n-paraffins from Agilent Technologies and a C_{20} - C_{70} mixture from Supelco called Poliwax 500.

The composition of each n-paraffin regarding to the carbon number was determined by integrating the corresponding individual signals in the chromatogram, following the two integrations methods previously proposed in the literature [24, 25, 28]: valley to valley integration (method A) and integration to the baseline of the chromatogram (method B). In this work, an average value of the results obtained by both methods was used, since the use of the method A leads to an overestimation of the C_{20+} content; whereas the method B underestimates it [24,25].

Differential Scanning Calorimetry (DSC).

The C_{20}^{+} content was determined by DSC from the WPC, taking into account that it corresponds to the value of precipitated mass obtained at -20ºC. The experimental apparatus used was a DSC Mettler-Toledo DSC822e. The following temperature profile reported elsewhere[18] was used to obtain the cooling thermograms of the samples:

- Sample is heated at 3°C/min from 25 to 80°C to completely dissolve possible solid phase and to remove any thermal history. This temperature is held for 2 min.
- Sample is cooled down from 80 to -120 °C at 3°C/min.
- Sample is heated up from -120 to 80 °C at 3°C/min.

The WPCs of the samples were determined by means of an iterative scheme to integrate the DSC thermogram of the mixtures developed by Coto et al.[18]. At the start step, the DSC thermogram is integrated following the methodology, reported by these authors. Solid-liquid equilibrium (SLE) equations are used to compute values for the precipitation heat and temperature and new correlations between precipitation temperature, precipitation heat and number of carbon atoms are determined. DSC thermogram is integrated again using such new correlations and a new WPC curve is obtained. Usually 3 or 4 iterations are enough to obtain convergence.

Wax precipitation: modification of Burger´s method. The amount of paraffin waxes precipitated at -20 °C was determined following a modification [23] of the method reported by Burger et al.[17] The crude oil is dissolved in n-pentane and stirred during 30 min. Acetone is added to the mixture (acetone/n-pentane ratio of 3:1) and cooled to -20°C for 24 h. The solid phase is separated by filtration in a Buchner funnel using a Whatman 934-AH glass microfiber filter. The solid phase is re-dissolved in n-hexane to remove asphaltenes. After solvent removal, the final product is weighted. The determination of the wax content cannot be carried out directly, since a certain amount of crude oil remains trapped along with the precipitated wax. Consequently, the quantification of the trapped crude oil is required in this case.

2.3. Determination of wax porosity

As reported in the literature, the determination of trapped crude oil (wax porosity) in precipitated waxes is required to determine the total wax content of a crude oil[22, 23]. There is a wide variety of techniques used to calculate the wax porosity[29-31]. In this work, ^{1}H NMR, HTGC and sequential elution chromatographic were used.

^{1}H NMR Spectroscopy. A Varian Mercury Plus NMR spectrometer (C/H dual 5 mm probe, frequency of 400 MHz) was used to quantify the different types of hydrogen atoms. Samples were dissolved in $CDCl_3$ in 5 mm sample tubes. The number of scans was 64, with a 30° pulse and a 1s delay time between scans. Then, the wax porosity of the precipitated samples was determined by ^{1}H NMR spectroscopy following a procedure reported elsewhere [29]. This methodology assumes that wax porosity (ε) can be estimated by determining the content of aromatic protons in the sample, because their presence is exclusively due to the crude oil remaining in the precipitated solid. Consequently, the wax porosity can be calculated as follows:

$$\varepsilon(wt.\%) = 100 - \left(\frac{H_{arC} - H_{arS}}{H_{arC}} \cdot 100 \right) \quad (1)$$

where H_{ar} denotes the content of aromatic hydrogen atoms (in wt.%); C and S subscripts refer to Crude oil and Precipitated sample, respectively.

Differential scanning calorimetry (DSC). The DSC analyses were carried out using the experimental conditions reported above. The wax porosity was calculated following a methodology developed by Coto et al.[26]. These authors state that the wax porosity can be obtained from the total paraffin fraction of the sample, usually accepted to be the one obtained at -20°C. Consequently, the wax porosity of the precipitated sample at -20°C can be calculated as follows:

$$\varepsilon = 1 - y \quad (2)$$

where y is the total paraffin content (by wt.) obtained from the DSC analysis of the mixture precipitated at -20°C.

Chromatographic Separation of Trapped Crude Oil (CS). This method is based on a modification [32] of the sequential elution procedure proposed by Musser and Kilpatrick [27] and it is used to determine the total wax content of a crude oil. This method allows for the separation of the saturate and the aromatic fraction of the precipitated solid obtained by Burger´s method.

The wax porosity of the sample can be calculated from the saturate fraction as follows:

$$\varepsilon_{\text{i SCCE SAT}} = 1 - s_i \quad (3)$$

where s_i indicates the amount of saturate compounds in the precipitated samples at -20ºC.

On the other hand, the wax porosity can be also determined from the aromatic fraction of the sample, as follows:

$$\varepsilon_{i\ cs_{Ar}} = \frac{m_{tc\,f}}{m_f} \cdot 100 = \frac{m_{Ar_f}}{m_f \cdot x'_{Ar_c}} \cdot 100 \qquad (4)$$

where,

$m_{tc\,f}$: Mass of trapped crude oil in the precipitated sample.

m_f : Mass of the precipitated fraction.

m_{Ar_f} : Mass of aromatic compounds in the precipitated fraction determined by sequential elution chromatography.

x'_{Ar_c} : Corrected mass fraction of aromatic compounds obtained in the raw crude oil, determined from the following equation:

$$x'_{Ar_c} = \frac{x_{Ar_c} \cdot m_c}{m_c - (m_c \cdot x_{light_c})} \qquad (5)$$

where,

m_c : Mass of raw crude oil.

x_{light_c} : Mass fraction of light compounds obtained in the raw crude oil determined by SARA anaysis[25].

3. Results and discussion

3.1. Determination of C_{20}^+ content

The total precipitated solid at -20ºC of the crude oils was experimentally determined from the wax precipitation curve obtained by DSC (percentage of precipitated solid at -20 ºC, as it is shown in Figure 1), by HTGC and by the modified Burger´s method used in this work [23]. The obtained results, summarized in Table 2, reveal how the amount of precipitated solid obtained by the modified Burger´s method is clearly higher than those obtained by the other techniques used. The observed differences are due to the presence of trapped crude oil in the precipitated fractions [25, 29, 30]. Consequently, it is necessary to

determine the wax porosity of these samples in order to compare the results obtained by these methods.

Figure 2 shows the results obtained by DSC and HTGC analysis. As can be seen, reasonable agreement was achieved for the C_{20+} values obtained by both analyses, despite their different approaches. In addition, both techniques show consistent results since in general, the total wax content values are higher for paraffinic crude oils than that obtained for the naphthenic ones. This can be explained because the former are enriched on n-paraffin compounds; meanwhile the latter contain other constituents as iso-paraffin and naphthenic compounds. The C_{20+} content of the aromatic crude oils must be taken with caution since their very low n-paraffin content makes its quantification not fully reliable.

3.2. Wax porosity

The trapped crude oil (wax porosity) of each precipitated fraction was calculated using the methods based on ^{1}H-NMR, DSC and sequential elution techniques, described in the Experimental Section. The results, depicted in Figure 3, show that precipitated mixtures contain an important amount of crude oil, in agreement with the results reported elsewhere [25, 29, 30].

The method based on sequential elution of saturates (CS_{sat}) leads to a clear underestimation of the wax porosity and the subsequent overestimation of C_{20+}, as it was expected, because not all saturate compounds can be considered n-paraffin. In order to overcome this drawback, a further separation of the aromatic compounds was included (CS_{ar}), obtaining values of wax porosity similar to ^{1}H-NMR and DSC techniques, although somewhat higher for light crude oils. This fact may be due to losses of light compounds during the evaporation of the solvents used to carry out the chromatographic separation.

^{1}H-NMR and DSC analyses yield similar values of wax porosity, showing their consistency for most of the samples.

Table 3 shows the C_{20+} values obtained by precipitation corrected with the wax porosity values determined by the DSC, ^{1}H-NMR and CS_{AR} techniques. As can be observed, the values of C_{20+} corrected by DSC and ^{1}H-NMR are very similar and show differences respect to the values yielded by CS_{AR}, as expected.

Figure 4 shows the C_{20+} values obtained by precipitation corrected by DSC, ^{1}H-NMR, CS_{AR} and those obtained from the WPC of the raw crude oil, considered as benchmark in this work. As can be observed, the total wax content values corrected by DSC and ^{1}H-NMR are very similar to that obtained from the WPC, although slightly lower in general.

3.3. Empirical correlations

Although the C_{20+} content is usually determined by experimental techniques, it can be calculated using empirical correlations, as that reported by Coutinho and Daridon [11]. These authors found a simple relationship between the C_{20+} content and the molecular weight, but it can be properly used only for North Sea paraffinic crude oils.

These correlations are usually valid only for a specific type of crude oils and their extrapolation to other ones with different characteristics is not fully reliable. Thus, the correlation proposed by Coutinho and Daridon[11] was applied to the crude oils studied in this work, obtaining poor results for most of them.

In order to overcome this drawback, an empirical correlation to determine C_{20+} was developed using the crude oils listed in Table 4, which present different origin and nature. From the available properties, the following relation between the C_{20+} content with both API gravity and pour point (PP, ºC) was obtained:

$$\ln C^{+}_{20\,WPC} = 2.0137 - \frac{229.65279}{\left(API^{\circ}\right)^{2}} + 0.03344\ PP \qquad (6)$$

The calculated C_{20+} values and the absolute deviations (δ_i) with respect to those obtained from the WPC are summarized in Table 4. The absolute average deviation was calculated as follows:

$$\delta = \frac{\Sigma_{i=1}^{n} \delta_i}{n} \qquad (7)$$

The obtained average value, δ = 0.8, reported in Table 4 is similar to the absolute difference between C_{20+} values obtained by HTGC and DSC shown in Table 3. This indicates that the uncertainty of the obtained fit equation is similar to that of the experimental techniques.

Figure 5 represents the crude oils shown in Table 4 and the surface of the mathematical function obtained for the selected crude oils, whose API gravities range between 10.7 and 42.6 and their pour points are within the range of -38 to 39°C.

In order to check the reliability of the obtained correlation it was applied to the crude oils shown in Table 5 that were not included in the correlation procedure. The calculation of wax content for crude oils with pour point <-38 ºC (see Table 1) was carried out taking into account a PP value of -38 ºC in the absence of accurate data. However, the results show low deviations respect to the C_{20+} value obtained experimentally from the WPC_{DSC}, despite of these crude oils are near the lower limit of applicability of the correlation. For the rest of crude oils, low deviations between experimental and predicted C_{20+} values were obtained as can be seen in Table 5. The absolute average deviation value determined by equation (7) was 0.6, similar to that determined for the crude oils used in the fitting of the proposed correlation.

Figure 6 shows the comparison between C_{20+} values experimentally obtained from WPC to those calculated by the correlation developed in this work. As can be observed, a good agreement was obtained.

4. Conclusions

HTGC and DSC analyses can be used to quantify C_{20+} content of raw crude oils showing reasonable agreement. Nevertheless, wax precipitation technique allows the determination of C_{20+}, but these values must be corrected due to the presence of trapped crude oil in the precipitated solid.

Among the different methods used to calculate the trapped crude oil, ^{1}H-NMR and DSC analyses yield consistent results for paraffinic and most of the naphthenic crude oils studied in this work.

It is possible to develop a relationship between the C_{20+} content, the API gravity and the pour point of the studied crude oils. The C_{20}^{+} values calculated using this correlation were in good agreement with those obtained experimentally by DSC analysis for most of the crude oils tested.

Acknowledgements

The authors thank Repsol for providing the crude oils and for the financial support through the research project “Aseguramiento de flujo de crudos de petróleo: Estudio de la precipitación de parafinas”.

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Figure captions

Figure 1. Wax precipitation curve of a crude oil and wax content at -20 ºC.

Figure 2. C_{20}^{+} content of some crude oils obtained by HTGC and DSC analyses.

Figure 3. Wax porosity values of precipitated samples at -20ºC obtained by different techniques

Figure 4. Comparative results of C_{20+} content corrected with the porosity values calculated by different techniques.

Figure 5. Mathematical function of the correlation proposed in this work

Figure 6. Comparison between experimental and calculated C_{20}^{+} values obtained by using the correlation developed in this work

Table 1. Crude oils used in this work.

Crude oil	*Origin*	*Type*	*Nature*	*API*	*Pour Point (°C)*
A-1	North Sea	Light	Paraffinic	37.50	-6
A-2	North Sea	Light	Paraffinic	36.00	-15
B-2	North Africa	Light	Paraffinic	45.00	<-38
B-3	North Africa	Light	Paraffinic	36.77	24
B-5	North Africa	Light	Paraffinic	42.18	<-38
C-1	West Africa	Medium	Paraffinic	29.44	0
C-2	West Africa	Light	Paraffinic	42.68	-9
E-1	Middle East	Light	Paraffinic	33.40	-33
F-1	Asia	Light	Paraffinic	35.88	-9
G-2	Mediterranean	Very light	Paraffinic	41.69	3
G-3	Mediterranean	Light	Paraffinic	30.94	6
G-4	Mediterranean	Light	Paraffinic	32.88	6
D-13	South America	Medium	Paraffinic	29.41	39
D-14	South America	Medium	Paraffinic	29.41	30
D-17	South America	Light	Paraffinic	35.78	-12
D-19	South America	Medium	Paraffinic	27	3
A-3	North Sea	Medium	Naphthenic	25.57	0
B-1	North Africa	Light	Naphthenic	34.17	0
C-3	West Africa	Medium	Naphthenic	29.75	<-38
D-3	South America	Medium	Naphthenic	30.88	-24
D-7	South America	Medium	Naphthenic	24.41	-3
D-9	South America	Heavy	Naphthenic	20.85	-38
D-10	South America	Medium	Naphthenic	26.71	-21
D-11	South America	Heavy	Naphthenic	20.68	<-38
D-12	South America	Heavy	Naphthenic	19.40	<-38
D-15	South America	Medium	Naphthenic	24.35	-15
E-5	Middle East	Light	Naphthenic	33.94	-30
D-2	South America	Heavy	Aromatic	10.80	21
D-5	South America	Heavy	Aromatic	10.94	18
D-8	South America	Heavy	Aromatic	11.79	9
D-16	South America	Heavy	Aromatic	18.6	-30
D-18	South America	Heavy	Aromatic	18.98	3

Table 2. C_{20+}values obtained by DSC, HTGC and wax precipitation techniques.

	Crude Oil	*$C_{20+\ DSC}$ (wt. %)*	*$C_{20+\ HTGC}$ (wt. %)*	*$C_{20}{}^{+}{}_{WAX\ PRECIPITATION}$ (wt. %)*
Paraffinic	A-1	4.4	5.3	15.3
	A-2	3.2	4.4	16.5
	B-2	2.7	3.4	10.8
	B-3	14.8	10.4	35.2
	B-5	1.6	3.1	3.8
	C-1	4.8	4.9	23.6
	C-2	3.5	4.4	7.8
	E-1	3.2	3.4	10.7
	F-1	4.4	3.9	11.8
	G-2	6.5	5.9	NA
	G-3	5.6	5.8	12.9
	G-4	5.7	4.4	10.3
Naphthenic	A-3	5.1	6.3	13
	B-1	5.2	2.8	9.3
	C-3	1.5	4.1	7.6
	D-3	3.8	4.4	10.4
	D-7	4.3	2.5	13.2
	D-9	2.2	3.3	10.7
	D-10	2.9	1.4	12.6
	D-11	1.3	0.5	16.9
	D-12	1.3	-	18.7
Aromatic	D-2	1.4	-	16.1
	D-5	2.2	-	22.7
	D-8	1.0	-	12.8

Table 3. C_{20}^{+} content obtained after subtracting the trapped crude oil determined by the different techniques.

	Crude Oil	*C_{20}^{+} ε_{DSC} (wt. %)*	*$C_{20}^{+}\varepsilon_{H\text{-}NMR}$ (wt. %)*	*C_{20}^{+} $\varepsilon_{CS\ AR}$ (wt. %)*
Paraffinic	A-1	4.3	3.8	5.5
	A-2	3.1	3.3	2.1
	B-2	2.5	2.1	1.2
	B-3	13.7	13.4	0.0
	B-5	1.1	1.2	0.0
	C-1	5.7	5.2	1.2
	C-2	3.4	3.4	3.6
	E-1	2.4	2.1	6.4
	F-1	3.1	3.0	3.2
	G-3	4.9	4.8	1.2
	G-4	4.6	4.5	4.6
Naphthenic	A-3	2.3	2.6	3.0
	B-1	3.7	4.2	3.7
	C-3	1.3	1.4	0.0
	D-3	2.6	2.9	3.5
	D-7	3.2	3.4	1.2
	D-9	1.9	1.7	2.2
	D-10	2.0	1.9	1.1
	D-11	2.7	1.0	0.0
	D-12	0.6	0.7	3.6
Aromatic	D-2	0.8	0.3	0.0
	D-5	1.6	1.1	5.2
	D-8	0.4	0.4	0.0

Table 4. C_{20}^{+} content values determined by WPC (DSC) and calculated by the correlation, equation (6), developed in this work (crude oils involved in the fitting).

Crude Oil	$C_{20}^{+}{}_{WPC}$ *(wt. %)*	$C_{20}^{+}{}_{calculated}$ *(wt. %)*	δ_i
A-1	4.4	5.2	0.8
A-2	3.2	3.8	0.6
B-3	14.8	14.1	0.7
C-1	4.8	5.7	0.9
C-2	3.5	4.9	1.4
E-1	3.2	2.0	1.2
F-1	4.4	4.6	0.2
G-3	6.6	7.2	0.6
G-4	5.7	7.4	1.7
A-3	5.1	5.3	0.2
B-1	5.2	6.2	1.0
D-3	3.8	2.6	1.2
D-7	4.3	4.6	0.3
D-9	2.2	1.2	1.0
D-10	2.9	2.7	0.2
D-2	1.4	2.0	0.6
D-5	2.2	1.9	0.3
D-8	1.0	1.9	0.9
D-13	20.3	21.2	0.9
D-14	17.2	15.7	1.5
			δ= 0.8

Table 5. C_{20}^{+} content values determined by WPC (DSC) and those calculated by the correlation, equation (6), developed in this work (predicted values).

Crude Oil	$C_{20}^{+}{}_{WPC}$ *(wt. %)*	$C_{20}^{+}{}_{calculated}$ *(wt. %)*	δ_i
B-2	2.7	1.8	0.9
B-5	1.6	1.9	0.3
G-2	6.5	7.3	0.8
E-5	3.2	2.3	0.9
C-3	1.5	1.6	0.1
D-11	1.3	1.2	0.1
D-12	1.3	1.1	0.2
D-15	3.0	3.1	0.1
D-16	1.3	1.4	0.1
D-17	3.6	4.2	0.6
D-18	2.5	4.4	1.9
D-19	4.6	6.0	1.4
			δ= 0.6

Figure 1.

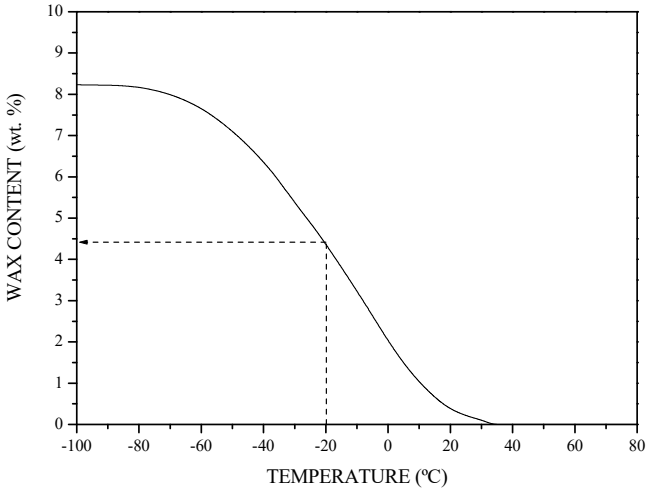

WAX CONTENT (wt. %)
TEMPERATURE (ºC)
10
9
8
7
6
5
4
3
2
1
0
-100
-80
-60
-40
-20
0
20
40
60
80

Figure 2.

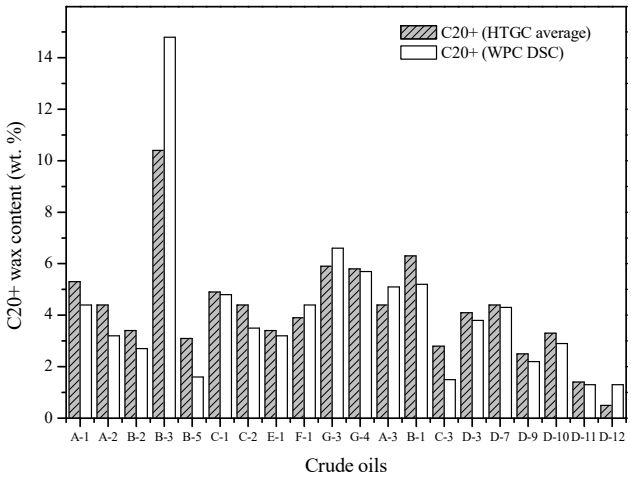

C20+ (HTGC average)
C20+ (WPC DSC)
C20+ wax content (wt. %)
0
2
4
6
8
10
12
14
A-1
A-2
B-2
B-3
B-5
C-1
C-2
E-1
F-1
G-3
G-4
A-3
B-1
C-3
D-3
D-7
D-9
D-10
D-11
D-12
Crude oils

Figure 3.

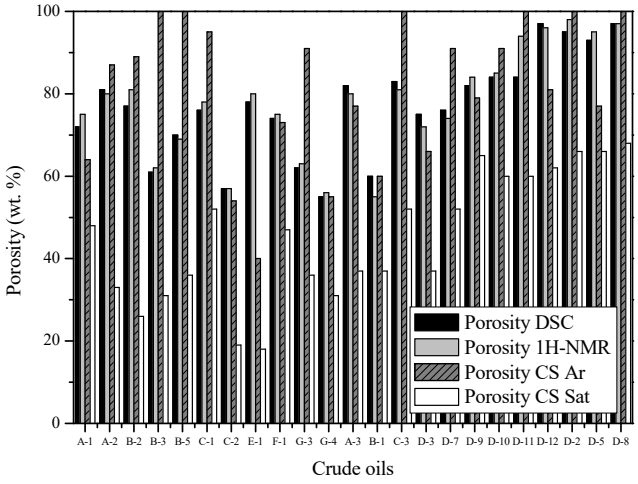

Porosity (wt. %)
100
80
60
40
20
0
A-1
A-2
B-2
B-3
B-5
C-1
C-2
E-1
F-1
G-3
G-4
A-3
B-1
C-3
D-3
D-7
D-9
D-10
D-11
D-12
D-2
D-5
D-8
Crude oils
Porosity DSC
Porosity 1H-NMR
Porosity CS Ar
Porosity CS Sat

Figure 4.

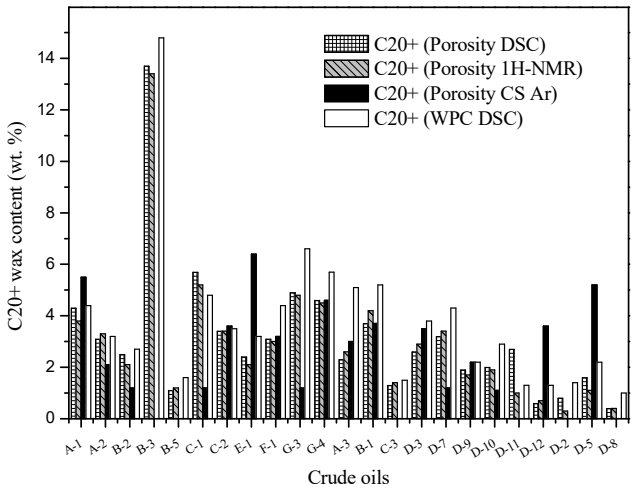

C20+ (Porosity DSC)
C20+ (Porosity 1H-NMR)
C20+ (Porosity CS Ar)
C20+ (WPC DSC)
C20+ wax content (wt. %)
0
2
4
6
8
10
12
14
A-1
A-2
B-2
B-3
B-5
C-1
C-2
E-1
F-1
G-3
G-4
A-3
B-1
C-3
D-3
D-7
D-9
D-10
D-11
D-12
D-2
D-5
D-8
Crude oils

Figure 5.

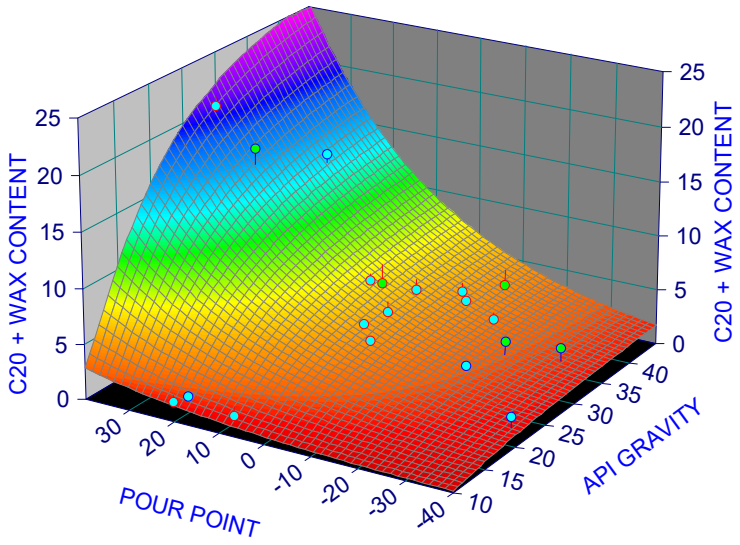
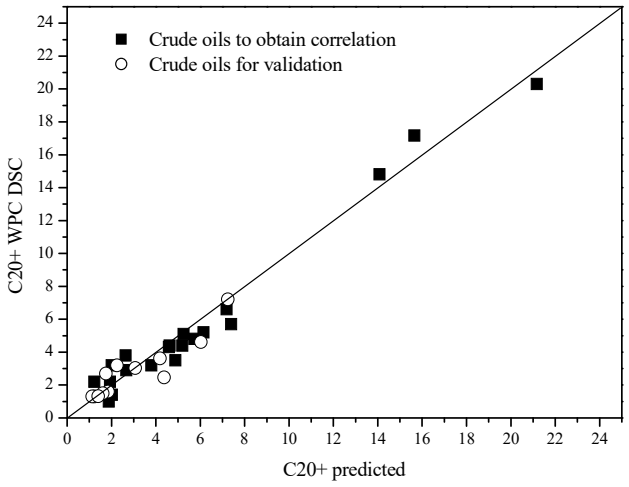

C20 + WAX CONTENT
25
20
15
10
5
0
30
20
10
0
-10
-20
-30
-40
POUR POINT
10
15
20
25
30
35
40
API GRAVITY
C20 + WAX CONTENT
25
20
15
10
5
0

Figure 6.


Crude oils to obtain correlation
Crude oils for validation
C20+ WPC DSC
C20+ predicted
0
2
4
6
8
10
12
14
16
18
20
22
24