

Effect of Temperature on Asphaltenes Precipitation: Direct and Indirect Analyses and Phase Equilibrium Study

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ABSTRACT: Asphaltenes precipitation is still a challenge for the petroleum industry during crude oil production and processing. Pressure, composition, and temperature variation can induce asphaltenes destabilization and aggregation, leading to fouling and flow blocking in pipelines and wellbore pores. The present work aims to investigate the effect of temperature on asphaltene precipitation using *n*-heptane as the precipitant alkane. Three different Brazilian crude oils, here named BR1, BR2, and BR3, were studied at temperatures of 5, 25, and 50 °C, using two different asphaltene yield and precipitation onset analyses, defined as direct and indirect methods. It has been found that when temperature rises, there is a decrease in the asphaltenes precipitation yield, together with an increase in the precipitation onset, which could be related to the increase in the asphaltenes solubility. Temperature effects on the onset seem to be influenced by crude oil properties, being less significant for more stable asphaltenes. Asphaltenes precipitation phenomenon was properly modeled by the intermediate of the Regular Solution Model, showing a low molecular weight asphaltene distribution when temperature rises. When indirect method is used, it has been seen that new fractions of heavy compounds aggregate and precipitate at a second precipitation stage under an *n*-heptane excess.

1. INTRODUCTION

Crude oil is a complex mixture of hydrocarbons and non-hydrocarbon compounds ranging from methane to highly condensed molecular weight, e.g., resins and asphaltenes. Asphaltenes are the heaviest and the most polar group in crude oil, comprising a condensation of polynuclear aromatic layers with peripheral aliphatic chains containing heteroatoms, e.g., nitrogen, sulfur, and oxygen, and trace metals, such as vanadium, nickel, and iron.¹ In practical applications, they can be defined as the fraction of crude oil soluble in aromatic hydrocarbons, such as benzene and toluene, but insoluble in light alkanes, as *n*-pentane (nC5), *n*-hexane (nC6), and *n*-heptane (nC7).^{2,3}

Pressure, temperature, or composition gradient during oil production could act as a destabilizer agent for asphaltenes, leading to precipitate. As a consequence, asphaltenes could form aggregates and nanosized particles that grow into clusters and may cause important industrial problems by fouling and blocking wellbore pores, production, and transportation pipelines or even in the refinery plant.^{4–8}

Generally, asphaltene precipitation procedure is done by the addition of a paraffinic precipitant (nC5, nC6, and nC7) to crude oil samples to induce the asphaltenes flocculation. However, it has been reported in the literature that precipitant physicochemical properties could affect the asphaltenes precipitation yield as follows: at high concentrations of paraffins, short-chain *n*-alkanes behave as stronger precipitants than long ones,⁹ while at low precipitant concentrations, longer chain length alkanes (ranging from 7 to 10 carbon molecules) increase the asphaltene precipitation onset to a maximum.¹⁰ The precipitation onset, or flocculation point,^{11,12} could be defined as the minimum amount of precipitant that is responsible for asphaltenes aggregation and destabilization start point.

Besides the precipitant influence, temperature also plays an important role in asphaltene stability, with two competitive effects on asphaltenes precipitation. When temperature rises there is an increase in asphaltene solubility, causing a decrease in the mass of asphaltene precipitated. On the other hand, the viscosity of the oil–precipitant mixture decreases when temperature rises, which leads to an increase in the effective diffusivity of the particles and, consequently, a faster aggregation of the asphaltenes.¹³

Therefore, the effect of temperature on asphaltene precipitation is still controversial. Maqbool et al. have demonstrated that at higher temperatures the mass of asphaltene precipitated is smaller, but the precipitation onset time is shorter, due to the effect of viscosity on the aggregation of asphaltenes.¹³ On the contrary, Bjoroy et al. stated that the increase in temperature leads to higher asphaltene onset values, although there is a consensus about the decrease in the precipitation yields.¹²

Recently, Yang et al. proposed that one subfraction of asphaltene (the heavy part of asphaltenes) became more insoluble with the increase in temperature, increasing the precipitation. On the contrary, a second subfraction (the light part, which contains lower average molecular weights, less aromatic, and a lesser content of heteroatoms than the heavy one) became more soluble and precipitated less at higher temperatures.⁹ This suggests that the determination of the asphaltene properties is crucial to the understanding of the influence of temperature on their precipitation.

Different approaches for evaluation of temperature effects in asphaltene precipitation were available in the literature,

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Table 1. Recent Studies in Temperature Effects, Experimental, and Modelling Approaches for Asphaltene Precipitation^a

ref	precipitation techniques	solvent	aging time	temp	model
Yarranton et al. (2018) ¹⁴	direct (gravimetric using model oil)	n-C7	24 h	21 °C	Regular Solution Theory
Johnston et al. (2017) ¹⁵	direct and indirect (gravimetric)	n-C5	24 h	21–250 °C (pressures up to 13.8 MPa)	Modified PR-EOS
Tavakkoli et al. (2015) ⁴	direct and indirect (spectroscopic)	n-C7	1 h, 24 h, 1 week, 1 month	ambient conditions	—
Bjorøy et al. (2012) ¹²	direct (gravimetric)	n-C5, n-C6, n-C7	16 h	22, 30, 45, 60, and 90 °C	Empirical Model
Tharanivasan et al. (2011) ¹⁶	direct (gravimetric)	n-C7	24 h	ambient conditions	Regular Solution Theory
Maqbool et al. (2009) ¹⁷	direct (gravimetric)	n-C7	>100 h	ambient conditions	—
Calles et al. (2008) ¹⁸	direct (gravimetric)	n-C5, n-C6, n-C7	24 h	25, 36.5, and 50 °C	—
Sabbagh et al. (2006) ¹⁹	direct (gravimetric)	n-C7	24 h	0, 23, and 50 °C	PR-EOS
Akbarzadeh K. et al. (2005) ²⁰	direct (gravimetric)	n-C7	24 h	0, 23, and 50 °C	Regular Solution Theory

^aAbbreviations: n-C7, *n*-heptane; n-C6, *n*-hexane; n-C5, *n*-pentane; PR-EOS, Peng–Robinson equation of state.

involving different experimental procedures. Table 1 summarizes the recent studies made in this area, highlighting experimental approaches and phase behavior modeling for asphaltene precipitation. One can note that most of these studies consider asphaltenes solubility curves by intermediate of a direct precipitation method, i.e., evaluating the gradual asphaltene precipitation by direct analysis of precipitated material yield. However, a few studies are focused on the residual asphaltenes content that remains in solution after a precipitation procedure. The analysis of the remaining asphaltenes is known as an indirect method for asphaltene solubility analysis and presents advantages in sensibility and versatility for high pressure analysis.⁴ Also, it is interesting to mention that although asphaltene precipitation is recognized as a slow kinetic process, most of the phase equilibria studies were made by considering a typical time of 24 h for equilibration. Reproducible results in asphaltene precipitation yields have been found at times above 16 h,¹² with minor kinetic effects at higher precipitant concentrations.¹³

From this, it could be noted that there is a lack of studies that involve the effects of temperature on asphaltene precipitation by using both direct and indirect methods. The aim of this paper is to investigate the effect of temperature at asphaltene precipitation for three Brazilian crude oils (BR1, BR2, BR3), by using *n*-heptane as the precipitant alkane at three different temperatures (5, 25, and 50 °C) by intermediate of two different methods, direct (BR1, BR2, and BR3) and indirect (BR1, BR2). Also, effects of temperature on asphaltene precipitation were evaluated by intermediate of typical phase equilibria models.

2. MATERIALS AND METHODS

Three different Brazilian crude oils samples (one from an onshore field and two from offshore fields) supplied by Petrobras have been used in this work. Table 2 shows some physicochemical analyses for BR1, BR2, and BR3 (API gravity, viscosity, wax appearance temperature, and saturate, aromatics, resins, and asphaltenes (SARA) composition). API and viscosity were determined by using an Anton-Paar SVM 3000 viscodensimeter. Wax appearance temperature (WAT) was determined by viscosity–temperature analysis, as described elsewhere.²¹ SARA analysis was performed by following a single-stage *n*-heptane addition, as described by Alboudwarej et al.²² for asphaltene content and ASTM D2007 M for SAR determination. Standard uncertainties (*u*) are reported as $u(T) = 0.01$ K, $u(\eta) = 0.02\eta$ mPa s, and $u(\rho) = 0.0015$ g cm^{−3}, where *T* is the temperature, η is the viscosity, and ρ is the density. Experimental uncertainties for saturate, aromatic, resin, and asphaltene

Table 2. API Density, Viscosity, and SARA Measurements for Crude Oils

crude oil	BR1	BR2	BR3
° API	16.5	17.7	11.7
viscosity (20 °C), mPa·s	2203	1774	—
viscosity (60 °C), mPa·s	106.5	101.7	1780
S ± 2, wt %	32	37	38
A ± 2, wt %	27	25	24
R ± 3, wt %	35	32	24
A ± 0.05, wt %	6.34	6.29	6.58
WAT ± 1, °C	24	25	45

(SARA) were determined by four independent repeated measurements, giving saturate and aromatic contents, ± 2 wt %; resin content, ± 3 wt %; asphaltene content, ± 0.05 wt %.

Temperature effects on asphaltene precipitation were evaluated by a direct and an indirect method, as could be seen in Figure 1. For the direct method, mixtures of crude oils and *n*-heptane (as precipitant) were prepared, and the resulting precipitated phase was collected, with their mass determined by a gravimetric method. Nevertheless, residual nonprecipitated asphaltene present in the supernatant phase was considered in the indirect method. Asphaltenes yields obtained from direct and indirect methods were compared to the original asphaltenes content of the crude oil, by intermediate of a mass balance. Direct and indirect methodology are described in the following sections.

2.1. Direct Determination of Asphaltene Precipitation Curve.

For ambient temperature, crude oil–heptane mixtures were prepared for each oil at 25 °C. A known mass of crude oil was diluted with a specified mass ratio of *n*-heptane with concentrations varying from 40 to 90 wt %, inside a transparent plastic centrifuge tube. The samples were mixed and sonicated for 15 min and then left to settle for 24 h at room temperature. Afterward, the tubes were centrifuged at 4500 rpm for 10 min. The supernatant liquid phase, containing crude oil and *n*-heptane, was saved for the indirect method analysis, and the precipitated asphaltene cake at the bottom was washed once with *n*-heptane. Washed samples were stirred and sonicated once more at the same previous conditions and kept aging for another 24 h. At last, the tubes were centrifuged again, the supernatant phase, containing *n*-heptane and any residual crude oil, was discarded, and the precipitated asphaltene samples were dried in an oven at 65 °C until their weights presented a mass variation below 0.0005 g. The asphaltenes yields were calculated as the percentage by mass of asphaltene precipitated per mass of crude oil, and the precipitation onsets were estimated by linear extrapolation of the asphaltene yield curves to zero yield.

For the measurements at high temperature, crude oil–heptane mixtures samples were prepared as discussed earlier, with the sonication done using water at 50 °C and the aging steps done with the tubes kept

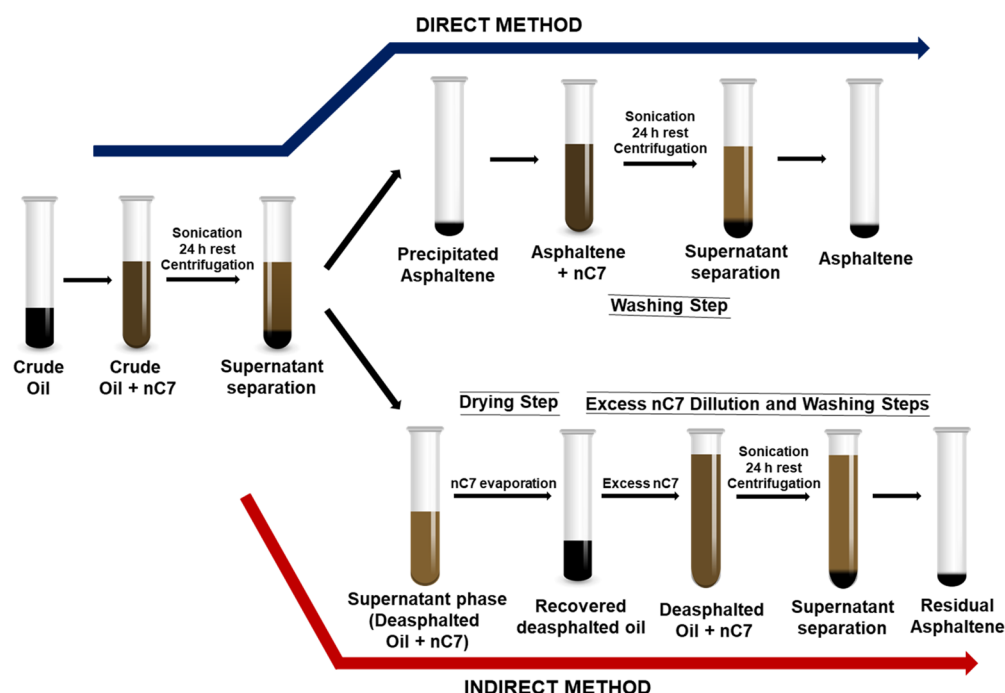


Figure 1. Procedure of the direct and indirect method of asphaltene precipitation determination.

in an oven with the temperature maintained at 50 °C. It is important to mention that centrifugation procedure has been done at room temperature. Evaporation losses were determined, and final deviation of *n*-heptane concentration varied from less than 3 wt % for low precipitant ratio mixtures (less than 60 wt % of *n*-heptane) to 1.2 wt % for the higher *n*-heptane concentration ones.

Then, for the lowest temperature experiment, the same procedure described above has been employed. However, the sonication was carried out at 5 °C, with the aging steps in a temperature-controlled water-bath maintained at 5 °C, and the centrifugation procedure was done in a refrigerated centrifuge at 5 °C.

2.2. Indirect Determination of Asphaltene Precipitation Curve. For the indirect determination of the precipitation curve, the separated supernatant liquid phase originating from the direct method was dried in an oven (at $T = 65$ °C) until complete *n*-heptane evaporation, with the asphaltene-deficient crude oil fraction remaining. Asphaltene content was determined by adding an excess ratio of *n*-heptane (7:1 vol/mass for *n*-heptane and crude oil respectively), following the same procedure used for the direct method. The indirect method was applied also for 5, 25, and 50 °C. Triplicate repetitions of each experiment were made to determine its experimental uncertainties.

2.3. Asphaltenes Characterization. In order to determine possible wax precipitation, chemical and thermal analyses were made for the asphaltenes obtained at 90% of *n*-heptane for each oil at the different temperatures. The asphaltenes alkyl contents were analyzed by attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR) using an Angilent Cary 630 ATR-FTIR spectrometer. The alkyl content of the precipitate solids was determined by the percentual area of 2920/2850, 1453, and 1374 cm^{-1} bands in the ATR-FTIR spectrum, as described elsewhere.^{23–25} Moreover, elemental analysis (carbon, hydrogen, and nitrogen) was obtained on a Perking Elmer 2400 Series II CHN-S/O, according manufacturer standard procedures.

Also, the same samples were analyzed by differential scanning calorimetry (DSC) using a Shimadzu DSC-50, calibrated with indium (In) powder standard (99.999% pure). Each sample (5–10 mg) was placed in an aluminum cell seal and heated from 25 to 120 °C at the rate of 5 °C/min under nitrogen atmosphere with a flow rate of 50 mL/min. In this temperature range thermal effects were determined and associated with wax reorganization and melting.^{26,27} From the obtained

heat flow curves, the enthalpy of crystallization was calculated as the area of the endothermic peaks and the baseline between the peaks' onset and endset.²⁸ Finally, an approximation of the content of crystalline phase of waxes was calculated considering that crude oil waxes are a mixture of paraffins with an enthalpy of crystallization near to 200 J/g.^{28,29}

2.4. Thermodynamic Modeling. Asphaltenes precipitation curves were modeled using a modified Regular Solution Method, described by Akbarzadeh et al.¹⁴, used widely in the literature.^{15–18} The model was fitted for asphaltenes yield curves at 25 °C and later employed predictively to estimate the effects of the temperature variations. Briefly, the model is based on a liquid–liquid equilibrium between the heavy dense phase (consisting of asphaltene and resins) and the light phase, composed of the solvent and all the oil fractions (saturates, aromatics, resins, and asphaltenes in equilibria). The crude was divided into SARA molar fractions, and the equilibrium constant for each fraction was determined as follows:

$$K_i^{\text{hl}} = \frac{x_i^{\text{h}}}{x_i^{\text{l}}} = \exp \left[\frac{v_i^{\text{h}}}{v_m^{\text{h}}} - \frac{v_i^{\text{l}}}{v_m^{\text{l}}} + \ln \left(\frac{v_i^{\text{l}}}{v_m^{\text{l}}} \right) - \ln \left(\frac{v_i^{\text{h}}}{v_m^{\text{h}}} \right) + \left(\frac{v_i^{\text{l}}}{RT} (\delta_i^{\text{l}} - \delta_m^{\text{l}})^2 - \frac{v_i^{\text{h}}}{RT} (\delta_i^{\text{h}} - \delta_m^{\text{h}})^2 \right) \right] \quad (1)$$

where x represents the molar fraction, v is the molar volume, δ is the solubility parameter, T is the absolute temperature, R is the universal gas constant, subscripts i indicate the i th component (saturates, aromatics, resins, asphaltene, or *n*-heptane as solvent) and m mixture properties, and superscripts l and h denote the light and heavy phase, respectively.

The mole fraction, the molar volume, and the solubility parameter for each component are required to apply this model. For saturates, aromatics, and resins, recent papers report that there is no considerable variation in those fractions properties when compared with previous SAR data of different crude oils from around the globe.^{14,20} Mean molar weight for SAR fractions are given in Table 3. Correlations for density, ρ , and solubility parameters, δ , as a function of temperature are available from a small data set collected by Akbarzadeh et al.²⁰ and improved by Tharanivasan,³⁰ as follows:

$$\rho_{\text{saturates}} = 1069.54 - 0.6379T \quad (2)$$

Table 3. Molar Weight for SAR Fractions^{14,30} at 25 °C and 1 atm

compound/group	molar weight, g/mol
saturates	460.0
aromatics	522.0
resins	1040.0

$$\rho_{\text{aromatics}} = 1164.73 - 0.5942T \quad (3)$$

$$\rho_{\text{resins}} = 1044 \quad (4)$$

$$\delta_{\text{saturates}} = 23.021 - 0.0222T \quad (5)$$

$$\delta_{\text{aromatics}} = 26.333 - 0.0204T \quad (6)$$

For *n*-heptane, densities values of 694.97 kg/m³ at 5 °C, 678.0 kg/m³ at 25 °C, and 658.85 kg/m³ at 50 °C were used. These data were obtained from NIST REFPROP database version 7. The calculation of solubility parameter for *n*-heptane as a function of temperature was made by using the Akbarzadeh et al.¹⁴ correlation, developed for *n*-alkanes, given by

$$\delta_{n-C7} = \delta_{n-C7(25^\circ\text{C})} - (0.0232 \cdot (T - 298.15)) \quad (7)$$

where the solubility parameter of *n*-heptane at 25 °C, $\delta_{n-C7(25^\circ\text{C})}$, is 15.2 MPa^{0.5}.³¹

Asphaltenes molar weight was determined by fitting the model to the asphaltenes yield curve for the BR1, BR2, and BR3 crude oils at 25 °C. Molar weight of asphaltenes were described by a two-parameter gamma distribution^{20,32,33} as follows:³⁴

$$f(MW_a) = \frac{(MW_a - MW_m)^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} \exp\left(-\frac{MW_a - MW_m}{\beta}\right) \quad (8)$$

where MW_m is the molecular weight of the monomeric asphaltene unit, α determines the shape of the distribution, MW_a is the molecular weight of asphaltene, $f(MW_a)$ is the frequency at given molecular weight MW_a , and β is stated by

$$\beta = \frac{MW_{\text{avg}} - MW_m}{\alpha} \quad (9)$$

where MW_{avg} is the average molecular weight of the asphaltenes aggregates. The asphaltene molecular weight domain was considered between 750 and 7200 Da. Those values are in accordance with Mullins et al.³⁵ and have been used successfully in our previous work.²¹ Values for α and MW_{avg} are used to fit the model to experimental data.

Asphaltenes density, ρ_a , was estimated using the exponential relation as a function of the molar weight of the asphaltene aggregates proposed by Barrera et al.:³²

$$\rho_a = \left(1100 + 100 \left(1 - \exp\left(-\frac{MW_a}{3850}\right) \right) \right) \quad (10)$$

The estimation of the solubility parameter of asphaltenes and resins has been accomplished by using the correlation presented by Tharanivasan et al.¹⁶ as follows:

$$\delta = (A(T)\rho)^{1/2} \quad (11)$$

and,

$$A(T) = 0.579 - 0.00075T \quad (12)$$

where $A(T)$ function is considered approximately equal to the monomer specific heat of vaporization in J/kg, and δ and ρ are the solubility parameter (MPa^{0.5}) and density (kg/m³) of the resin or asphaltene, respectively.

From those data, the phase distribution was performed using Rachford–Rice flash calculations.³⁶ The asphaltenes molar weight distribution was fitted to the asphaltene yield at 25 °C for all crude oils. The model was fitted by the minimization of the average absolute relative deviation percent %AARD as objective function, defined below:

$$\%AARD = 100 \cdot \sum \frac{1}{N} \left| \frac{(y_{\text{exp}} - y_{\text{modeled}})}{y_{\text{exp}}} \right| \quad (13)$$

where y_{exp} represents the experimental asphaltene yield, y_{modeled} the modeled asphaltene yield, and N the number of experimental data.

After the model was fitted at 25 °C, the asphaltenes molar weight distribution was obtained. This result was used to predict the effect of temperature in asphaltene yield curves at 5 and 50 °C. The average absolute deviation AAD was calculated for both the fitted and the predicted asphaltene yields at different temperatures as follows:

$$AAD = \sum \frac{1}{N} |y_{\text{exp}} - y_{\text{modeled}}| \quad (14)$$

3. RESULTS AND DISCUSSION

3.1. Effect of Temperature on Asphaltene Precipitation.

Figures 2, 3, and 4 show asphaltenes yield against *n*-

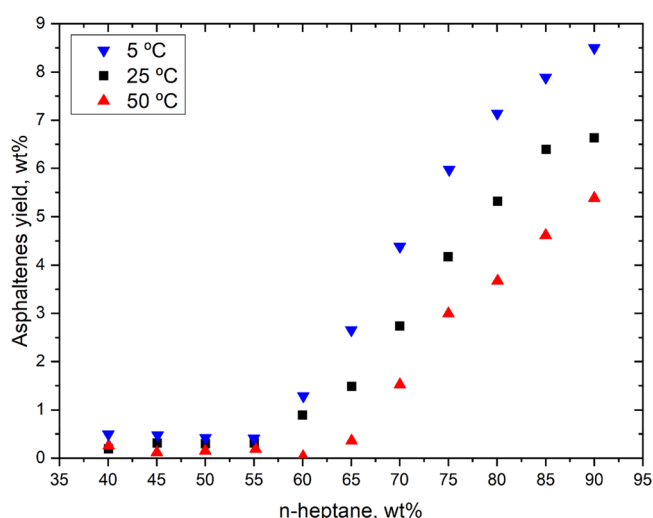


Figure 2. Asphaltene yield from BR1 crude oil diluted with *n*-heptane at 5, 25, and 50 °C, obtained by direct method (experimental errors within ± 0.2 wt %).

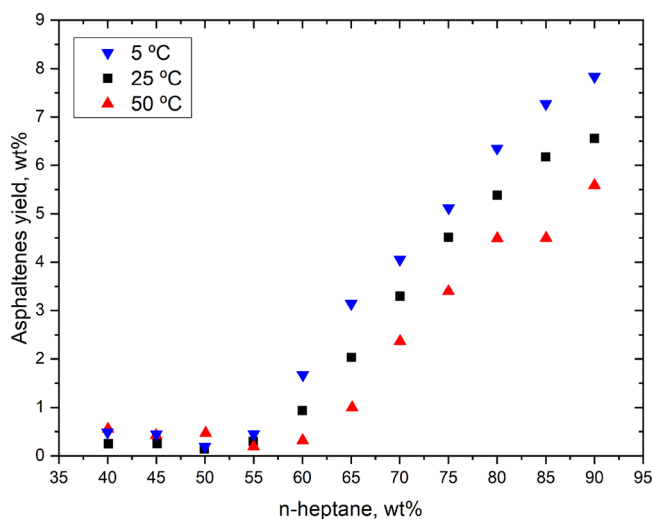


Figure 3. Asphaltene yield from BR2 crude oil diluted with *n*-heptane at 5, 25, and 50 °C, obtained by direct method (experimental errors within ± 0.2 wt %).

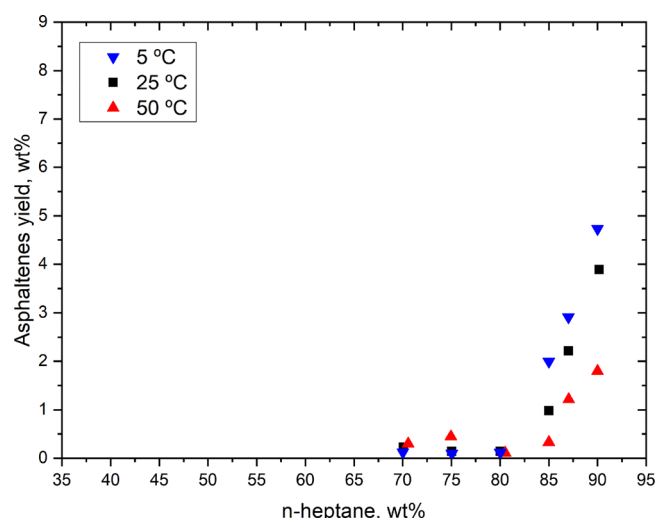


Figure 4. Asphaltene yield from BR3 crude oil diluted with *n*-heptane at 5, 25, and 50 °C, obtained by direct method (experimental errors within ± 0.2 wt %).

heptane wt % using direct method for the BR1, BR2, and BR3 crude oils at the different temperatures tested. For all crude oils studied, the effect of temperature on asphaltenes yield presented a similar behavior.

It can be noted that as temperature increases, there was a decrease in the asphaltenes yield, as well as an increase in the precipitation onset. The biggest asphaltene yield was observed for BR1 crude oil at 5 °C, with 8.5 wt % asphaltene yield at 90% of *n*-heptane, dropping to 7.7 wt % at 25 °C, and then to 5.4 wt % at 50 °C. For BR2 crude oil the maximum asphaltene yield was found for 5 °C, with 7.8 wt %, going down to 6.5 wt % at 25 °C, and 5.6 wt % at 50 °C. Finally, BR3 crude oil showed an asphaltene yield of 4.7 wt % for 5 °C, dropping to 3.9% at 25 °C, and 1.8% at 50 °C. As expected, asphaltenes yield decreases by increasing the temperature.

Asphaltenes precipitation onsets at different temperatures are presented in Figure 5. From these data, it could be stated that for BR1 and BR2 crude oils there is a significant effect of the temperature on the precipitation onset, with an increase in asphaltene onset when temperature increases. This effect could

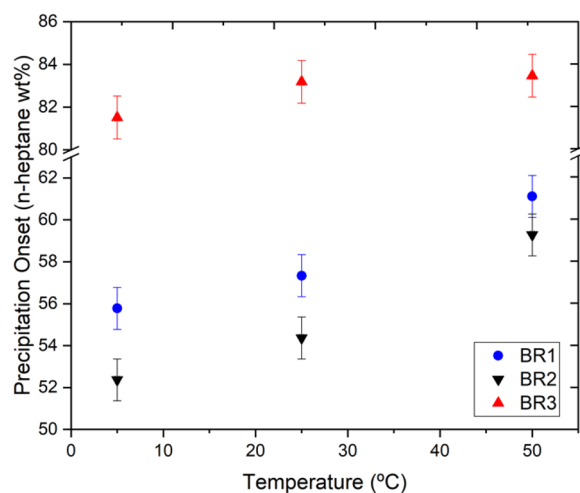


Figure 5. Variation on the asphaltene precipitation onsets of the crudes BR1, BR2, and BR3 as a function of the temperature.

be related to asphaltenes higher stability when temperature increases.²⁰ Nevertheless, for BR3 crude oil, the effect of the temperature could be negligible. Although higher precipitation onset was observed, that could be associated with the asphaltene stability.

As temperature increases, a variation in the solubility of asphaltenes diluted in *n*-heptane is expected. At higher temperatures, asphaltene solubility seems to increase with a total reduction of asphaltene yield, with a shift in the precipitation onset to the right (increasing *n*-heptane content). Otherwise, at the lower temperatures, the precipitation yield increases and asphaltenes becomes more instable, shifting the precipitation onset to the left (decreasing *n*-heptane content). Once again, with a reduction in temperature, solubility effect on asphaltenes becomes relevant. It could be possible that some crude oil heavy fraction precipitated at 5 °C, resulting in an increase in asphaltenes yields when compared with 25 °C.

It is remarkable that asphaltene yield at the lower temperature tested (5 °C) is higher than the total asphaltene content obtained from crude oil characterization (Table 2), especially for BR1 and BR2 crude oils. For this reason, chemical and thermal analyses for the solids precipitated at different temperatures were done. Alkyl content and elemental analysis of the asphaltenes obtained at different temperature are presented in Table 4. It could be noted that there is no relevant statistical

Table 4. Chemical Analysis of Precipitated Solids Obtained at 5, 25, and 50 °C for the Different Crude Oils

asphaltene/ temp	alkyl +1, wt %	C + 0.7, wt %	H + 0.1, wt %	N + 0.03, wt %	H/C + 0.02, atomic ratio
BR1/5 °C	27	85.3	9.1	1.60	1.27
BR1/25 °C	29	85.4	9.2	1.59	1.28
BR1/50 °C	27	86.2	9.0	1.64	1.24
BR2/5 °C	28	85.8	9.2	1.60	1.27
BR2/25 °C	30	85.7	9.1	1.65	1.27
BR2/50 °C	25	85.6	9.0	1.62	1.26
BR3/5 °C	30	84.5	9.5	1.49	1.34
BR3/25 °C	28	83.7	9.1	1.59	1.29
BR3/50 °C	27	83.8	9.2	1.56	1.30

variation in asphaltenes properties when temperature changes. These results could indicate that no paraffinic coprecipitation occurs when temperature decreased. In fact, the precipitation phenomenon is attributed to asphaltene deposition.

In addition, DSC analyses of the precipitated solids obtained at different temperatures are present in Figure 6 for BR2 crude oil sample. From these analyses it can be noted that two thermal effects are present: one at 74 °C, detected for all samples, and another around 100 °C, more evident for the samples obtained at 25 and 5 °C. These endothermic events could be associated with paraffin melting and reorganization, allowing the estimation of the wax content of the solids from the area of these thermal peaks.²⁸ For all samples, the estimated wax content was below 0.15 wt %, confirming no major precipitation of waxes with the asphaltenic solids. It is important to mention that similar results have been observed for BR1 and BR3.

3.2. Indirect Analysis of Asphaltene Precipitation. The precipitation onset measured by indirect method is presented in Figures 7 and 8, showing residual crude oil asphaltenes content as a function of the *n*-heptane proportion of the first precipitation step.

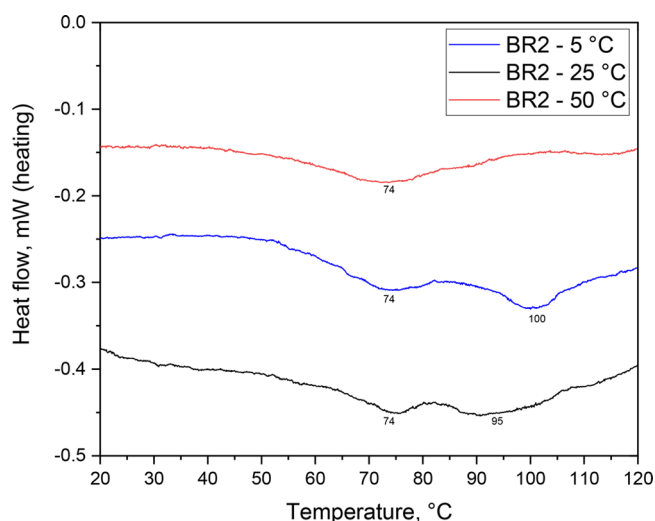


Figure 6. Heat flow curves of asphaltenes from crude BR2 at temperatures of 5, 25, and 50 °C.

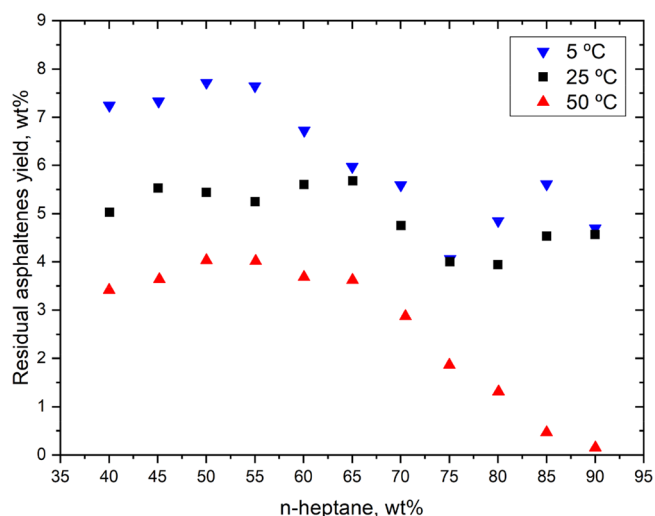


Figure 7. Residual asphaltene precipitation yield from indirect method as a function of the *n*-heptane proportion of the first precipitation step (direct method) for crude BR1 at temperatures of 5, 25, and 50 °C (experimental errors within ± 0.2 wt %).

It was expected that the residual asphaltenes yield curves obtained from the indirect method should present a consistent mass balance, i.e., the summation of asphaltenes yield obtained from both methods (direct and indirect) would keep constant: for lower *n*-heptane content, asphaltene precipitation is negligible by using the direct method. For this reason, indirect method should present the maximum asphaltene yield. On the other hand, after precipitation onset, direct method determination shows a sharp raise in asphaltene yield by increasing *n*-alkane content. Therefore, for indirect method, asphaltene yield should decrease until zero once most of asphaltenes have been recovered by direct method.

However, only for the experiments made at high temperature (50 °C) was this behavior confirmed. For lower temperatures (25 and 5 °C), an unexpected behavior was detected, as shown in Figures 7 and 8. For instance, the expected decline of the curve after the onset point is interrupted. Instead, at around of 75 wt % of *n*-heptane dilution region, the precipitated residual asphaltene yield raises again. These results possibly indicate that

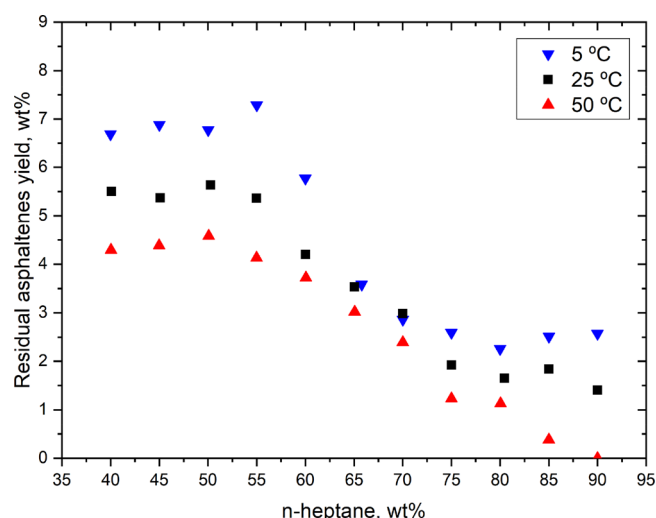


Figure 8. Residual asphaltene precipitation yield from indirect method as a function of the *n*-heptane proportion of the first precipitation step (direct method) for crude BR2 at temperatures of 5, 25, and 50 °C (experimental errors within ± 0.2 wt %).

a new fraction of heavy compound precipitates when the deasphalted oil is under a second precipitation stage. It is important to mention that these results were obtained after 24 h of equilibration, and at lower temperatures kinetics could be limited and residual asphaltene could remain in solution also by slow precipitation process.

3.3. Thermodynamic Modeling of Asphaltene Precipitation. Considering the asphaltenes yield obtained by the direct method as equilibrium data, phase equilibria were analyzed. Figures 9 and 10 depict experimental asphaltene

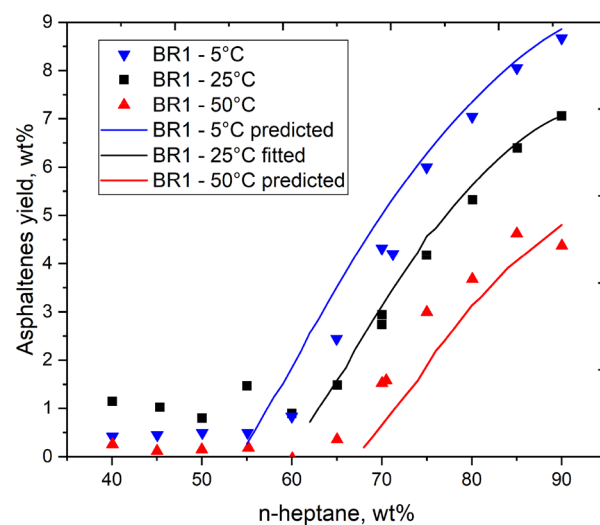


Figure 9. Fitted and predicted asphaltene precipitation yield in *n*-heptane from crude BR1 at temperatures of 5, 25, and 50 °C (experimental errors within ± 0.2 wt %).

yield curves compared with those obtained by using the Regular Solution Model. It can be noted that the model qualitatively predicts the experimental tendencies on asphaltenes yield for BR1 and BR2 crude oils, as a function of the temperature. Best results were obtained for 5 °C, with an AAD of 0.4 for BR1 crude oil and 0.8 for BR2, as shown in Table 5.

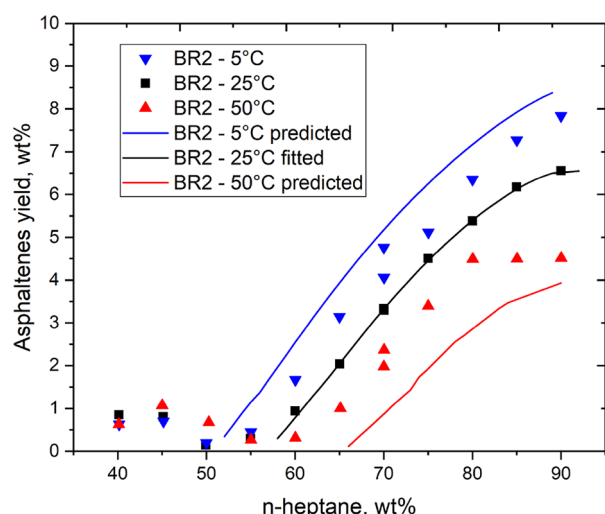


Figure 10. Fitted and predicted asphaltene precipitation yield in *n*-heptane from crude BR2 at temperatures of 5, 25, and 50 °C (experimental errors within ± 0.2 wt %).

Table 5. %AAD Deviations between Predicted and Experimental Asphaltenes Yield Curve at Different Temperatures

crude oil	AAD, %		
	5 °C	25 °C	50 °C
BR1	0.4	0.2	0.7
BR2	0.8	0.04	1.4
BR3	—	>5.0	—

As mentioned previously, asphaltenes molar weight distribution was used to adjust the precipitation model at 25 °C. From these results, the effect of the temperature was predicted for 5 and 50 °C. From Figure 11, the change in precipitate mass distribution at the different temperatures tested can be noted. For both crude oils (BR1 and BR2), a major proportion of higher molar weight precipitated asphaltenes was predicted when temperature decreases. On the other hand, the amount of higher molar weight precipitated asphaltenes predicted was lower as temperature increases. Modeling observation is in

accordance with experimental data, even using generic parameters obtained from the literature.

It is important to mention that for BR3 crude oil a poor adjustment was obtained from the model used in this work, possibly because of nontypical high asphaltenes stability (precipitation onset above 80 wt % of *n*-heptane).

4. CONCLUSIONS

In this paper the temperature effects in asphaltene precipitation were studied through direct and indirect methods. It was observed that at high temperature (50 °C), asphaltene yield obtained by both methods is in accordance with the asphaltene mass balance. Nevertheless, at lower temperatures (25 and 5 °C), the indirect analyses showed that heavy compounds fraction from deasphalted oil aggregate and precipitate at a second precipitation stage under a *n*-heptane excess. This result suggests that asphaltenes compounds could remain in the crude oil after a single stage deasphalting process with *n*-heptane at temperatures below 50 °C. Besides, no variations in alkyl content and H/C ratio of the precipitated material from direct method at the temperatures studied were observed. The use of the Regular Solution Model shows that there is a decrease in the amount of precipitate heavy molecular weight compounds by increasing temperature, related to solubility temperature dependence.

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Notes

The authors declare no competing financial interest.

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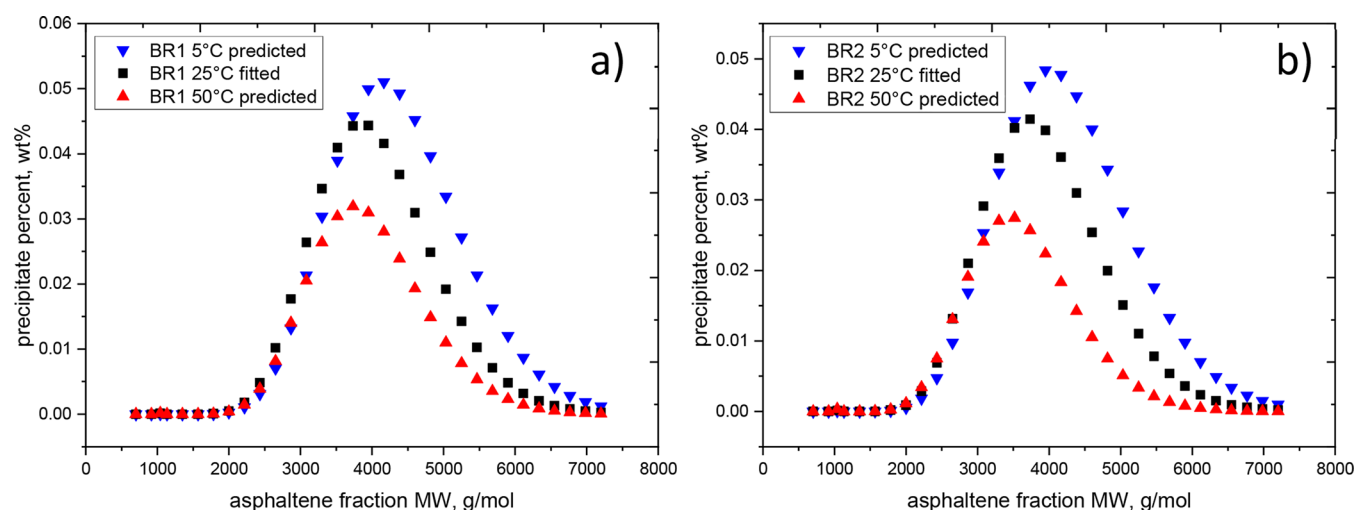


Figure 11. Modeled precipitation of the different asphaltenes molar weight classes for (a) BR1 and (b) BR2 at different temperatures.

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REFERENCES

- (1) Mullins, O. C. Rebuttal to Comment by Professors Herod, Kandiyoti, and Bartle on "Molecular Size and Weight of Asphaltene and Asphaltene Solubility Fractions from Coals, Crude Oils and Bitumen." *Fuel* **2007**, 86 (1), 309–312.
- (2) Speight, J. G. Petroleum Asphaltenes-Part 1: Asphaltenes, Resins and the Structure of Petroleum. *Oil Gas Sci. Technol.* **2004**, 59 (5), 467–477.
- (3) Chilingarian, G. V.; Yen, T. F. Chapter 1. Introduction to Asphaltenes and Asphalts, Vol. 2. In *Developments in Petroleum Science*; Yen, T. F., Chilingarian, G. V., Eds.; Asphaltenes and Asphalts, 2; Elsevier: Amsterdam, 2000; Vol. 40, pp 1–5.
- (4) Tavakkoli, M.; Panuganti, S. R.; Taghikhani, V.; Pishvaie, M. R.; Chapman, W. G. Precipitated Asphaltene Amount at High-Pressure and High-Temperature Conditions. *Energy Fuels* **2014**, 28 (3), 1596–1610.
- (5) Eskin, D.; Mohammadzadeh, O.; Akbarzadeh, K.; Taylor, S. D.; Ratulowski, J. Reservoir Impairment by Asphaltenes: A Critical Review. *Can. J. Chem. Eng.* **2016**, 94 (6), 1202–1217.
- (6) Civan, F. *Reservoir Formation Damage*; Gulf Professional Publishing: Houston, TX, 2015.
- (7) Ancheyta, J.; Trejo, F.; Rana, M.S. *Asphaltenes: Chemical Transformation during Hydroprocessing of Heavy Oils*; CRC Press: Boca Raton, FL, 2010.
- (8) Ancheyta, J. *Deactivation of Heavy Oil Hydroprocessing Catalysts: Fundamentals and Modeling*; John Wiley & Sons: New York, 2016.
- (9) Yang, Z.; Chen, S.; Peng, H.; Li, M.; Lin, M.; Dong, Z.; Zhang, J.; Ji, Y. Effect of Precipitating Environment on Asphaltene Precipitation: Precipitant, Concentration, and Temperature. *Colloids Surf., A* **2016**, 497, 327–335.
- (10) Wiehe, I. A.; Yarranton, H. W.; Akbarzadeh, K.; Rahimi, P. M.; Teclemariam, A. The Paradox of Asphaltene Precipitation with Normal Paraffins. *Energy Fuels* **2005**, 19 (4), 1261–1267.
- (11) Buckley, J. S.; Wang, J.; Creek, J. L. Solubility of the Least-Soluble Asphaltenes. In *Asphaltenes, Heavy Oils, and Petroeconomics*; Mullins, O. C., Sheu, E. Y., Hammami, A., Marshall, A. G., Eds.; Springer: New York, 2007; pp 401–437.
- (12) Bjørøy, Ø.; Fotland, P.; Gilje, E.; Høiland, H. Asphaltene Precipitation from Athabasca Bitumen Using an Aromatic Diluent: A Comparison to Standard n-Alkane Liquid Precipitants at Different Temperatures. *Energy Fuels* **2012**, 26 (5), 2648–2654.
- (13) Maqbool, T.; Srikiatwong, P.; Fogler, H. S. Effect of Temperature on the Precipitation Kinetics of Asphaltenes. *Energy Fuels* **2011**, 25 (2), 694–700.
- (14) Yarranton, H. W.; Powers, D. P.; Okafor, J. C.; van den Berg, F. G. A Regular Solution Based Approach to Modeling Asphaltene Precipitation from Native and Reacted Oils: Part 2, Molecular Weight, Density, and Solubility Parameter of Saturates, Aromatics, and Resins. *Fuel* **2018**, 215, 766–777.
- (15) Johnston, K. A.; Schoeggl, F. F.; Satyro, M. A.; Taylor, S. D.; Yarranton, H. W. Phase Behavior of Bitumen and N-Pentane. *Fluid Phase Equilib.* **2017**, 442, 1–19.
- (16) Tharanivasan, A. K.; Yarranton, H. W.; Taylor, S. D. Application of a Regular Solution-Based Model to Asphaltene Precipitation from Live Oils. *Energy Fuels* **2011**, 25 (2), 528–538.
- (17) Maqbool, T.; Balgoa, A. T.; Fogler, H. S. Revisiting Asphaltene Precipitation from Crude Oils: A Case of Neglected Kinetic Effects. *Energy Fuels* **2009**, 23 (7), 3681–3686.
- (18) Calles, J. A.; Dufour, J.; Marugán, J.; Peña, J. L.; Giménez-Aguirre, R.; Merino-García, D. Properties of Asphaltenes Precipitated with Different N-Alkanes. A Study To Assess the Most Representative Species for Modeling. *Energy Fuels* **2008**, 22 (2), 763–769.
- (19) Sabbagh, O.; Akbarzadeh, K.; Badamchi-Zadeh, A.; Svrcek, W. Y.; Yarranton, H. W. Applying the PR-EoS to Asphaltene Precipitation from n-Alkane Diluted Heavy Oils and Bitumens. *Energy Fuels* **2006**, 20 (2), 625–634.
- (20) Akbarzadeh, K.; Alboudwarej, H.; Svrcek, W. Y.; Yarranton, H. W. A Generalized Regular Solution Model for Asphaltene Precipitation from N-Alkane Diluted Heavy Oils and Bitumens. *Fluid Phase Equilib.* **2005**, 232 (1), 159–170.
- (21) Romero Yanes, J. F.; Feitosa, F. X.; do Carmo, F. R.; de Sant'Ana, H. B. Paraffin Effects on the Stability and Precipitation of Crude Oil Asphaltenes: Experimental Onset Determination and Phase Behavior Approach. *Fluid Phase Equilib.* **2018**, 474, 116–125.
- (22) Alboudwarej, H.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W.; Akbarzadeh, K. Sensitivity of Asphaltene Properties to Separation Techniques. *Energy Fuels* **2002**, 16 (2), 462–469.
- (23) García, M. d. C.; Carbognani, L. Asphaltene-Paraffin Structural Interactions. Effect on Crude Oil Stability. *Energy Fuels* **2001**, 15 (5), 1021–1027.
- (24) Paiva, F. L.; Marchesini, F. H.; Calado, V. M. A.; Galliez, A. P. Wax Precipitation Temperature Measurements Revisited: The Role of the Degree of Sample Confinement. *Energy Fuels* **2017**, 31 (7), 6862–6875.
- (25) Carbognani, L.; Espidel, J.; Izquierdo, A. Chapter 13. Characterization of Asphaltenic Deposits from Oil Production and Transportation Operations. In *Developments in Petroleum Science*; Yen, T. F., Chilingarian, G. V., Eds.; Asphaltenes and Asphalts, 2; Elsevier: Amsterdam, 2000; Vol. 40, pp 335–362.
- (26) Santos, D.; Amaral, M.; Filho, E. B. M.; Dourado, R. S.; Coutinho, J. A. P.; Borges, G. R.; Franceschi, E.; Dariva, C. Revisiting the Methodology for Asphaltenes Precipitation. *J. Pet. Sci. Eng.* **2019**, 178, 778–786.
- (27) Dirand, M.; Bouroukba, M.; Briard, A.-J.; Chevallier, V.; Petitjean, D.; Corriou, J.-P. Temperatures and Enthalpies of (Solid + Solid) and (Solid + Liquid) Transitions of n-Alkanes. *J. Chem. Thermodyn.* **2002**, 34 (8), 1255–1277.
- (28) Ganeeva, Yu. M.; Yusupova, T. N.; Romanov, G. V.; Gubaidullin, A. T.; Samigullina, A. I. The Composition and Thermal Properties of Waxes in Oil Asphaltenes. *J. Therm. Anal. Calorim.* **2015**, 122 (3), 1365–1373.
- (29) Létoffé, J. M.; Claudy, P.; Kok, M. V.; Garcin, M.; Volle, J. L. Crude Oils: Characterization of Waxes Precipitated on Cooling by d.s.c. and Thermomicroscopy. *Fuel* **1995**, 74 (6), 810–817.
- (30) Tharanivasan, A. K. *Asphaltene Precipitation from Crude Oil Blends, Conventional Oils, and Oils with Emulsified Water*. Ph.D. Thesis, University of Calgary, Calgary, Alberta, 2012.
- (31) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton, FL, 2002.
- (32) Barrera, D. M.; Ortiz, D. P.; Yarranton, H. W. Molecular Weight and Density Distributions of Asphaltenes from Crude Oils. *Energy Fuels* **2013**, 27 (5), 2474–2487.
- (33) Powers, D. P.; Sadeghi, H.; Yarranton, H. W.; van den Berg, F. G. A Regular Solution Based Approach to Modeling Asphaltene Precipitation from Native and Reacted Oils: Part 1, Molecular Weight, Density, and Solubility Parameter Distributions of Asphaltenes. *Fuel* **2016**, 178, 218–233.
- (34) Powers, D. P. *Characterization and Asphaltene Precipitation Modeling of Native and Reacted Crude Oils*. Ph.D. Thesis, University of Calgary, Calgary, Alberta, 2014.
- (35) Mullins, O. C.; Sabbah, H.; Eyssautier, J.; Pomerantz, A. E.; Barré, L.; Andrews, A. B.; Ruiz-Morales, Y.; Mostowfi, F.; McFarlane, R.; Goual, L.; et al. Advances in Asphaltene Science and the Yen-Mullins Model. *Energy Fuels* **2012**, 26 (7), 3986–4003.
- (36) Alboudwarej, H.; Akbarzadeh, K.; Beck, J.; Svrcek, W. Y.; Yarranton, H. W. Regular Solution Model for Asphaltene Precipitation from Bitumens and Solvents. *AIChE J.* **2003**, 49 (11), 2948–2956.