

EVALUATION OF AN HPHT UNIT COUPLED WITH NIR PROBE TO DETERMINE ASPHALTENES PRECIPITATION ONSET UNDER DIFFERENT PRESSURES

EVALUACIÓN DE UNA UNIDAD HPHT ACOPLADA CON SONDA NIR PARA DETERMINAR EL INICIO DE LA PRECIPITACIÓN DE ASFALTENOS BAJO DIFERENTES PRESIONES

Daniel Rezende da Silva¹, João Pedro Dias Capuchinho¹, Edilson Domingos da Silva¹, Daniela Hartmann^{1,2}, Marcia Cristina Khalil de Oliveira³, Elizabete Fernandes Lucas^{*1,2}

¹Universidade Federal do Rio de Janeiro, Instituto de Macromoléculas/LMCP, Rua Moniz Aragão, 360, bloco 8G/CT2, 21941-594, Rio de Janeiro, RJ, Brazil

²Universidade Federal do Rio de Janeiro, Programa de Engenharia Metalúrgica e de Materiais/COPPE/LADPOL, Av. Horácio Macedo, 2030, bloco F, 21941-598, Rio de Janeiro, RJ, Brazil

³Centro de Pesquisas da Petrobras, Av. Horácio Macedo, 950, 21941-915, Rio de Janeiro, RJ, Brazil

*Corresponding author: elucas@ima.ufrj.br

Recibido: 11 de julio, 2023. **Aprobado:** 11 de septiembre, 2023. **Versión final:** 18 de septiembre, 2023.


Abstract

Asphaltenes are characterized as the crude oil fraction with the highest molar mass and polarity, presetting mainly (poly) aromatic groups. The flocculation and deposition of asphaltenes causes large losses to the oil industry. Understanding the phase behavior of asphaltenes under conditions closer to those found in reservoirs is important. Therefore, LMCP/UFRJ started operating a high-pressure high-temperature (HPHT) unit coupled to a near-infrared spectrometer probe that can use different flocculants. This work describes the development of a procedure as well as the validation of the results obtained from this unit. Due to the complex composition of crude oil, model systems (MS) were prepared with asphaltenes extracted with n-pentane (C5I) and n-heptane (C7I). The experiments were carried out at atmospheric pressure, titrated with n-heptane, and at 100 and 300 bar titrated with propane. As expected, C7I asphaltenes were more unstable, presenting lower precipitation onset than C5I asphaltenes under ambient conditions and higher pressures. However, for both MS, the stability increased with rising pressure when using propane as a solvent. The proposed method to evaluate asphaltenes precipitation onset was effective for MS in toluene and dead crude oil, and is a promising alternative for investigation of different types of crude oil.

Keywords: Asphaltenes, Near-infrared, Phase Behavior, High Pressure, Propane Titration.

Cómo citar: Da Silva, D. R., Dias, J. P., Da Silva, E. D., Hartmann, D., Khalil, M. C., & Lucas, E. F. (2023).

EVALUATION OF A HPHT UNIT COUPLED WITH NIR PROBE TO DETERMINE ASPHALTENES PRECIPITATION ONSET UNDER DIFFERENT PRESSURES. *Fuentes, el reventón energético*, 21 (2). 45-60.

<https://doi.org/10.18273/revfue.v21n2-2023004> 

Resumen

Los asfaltenos se caracterizan por ser la fracción de petróleo crudo con mayor masa molar y polaridad, preestableciendo principalmente grupos (poli)aromáticos. La floculación y deposición de asfaltenos provoca grandes pérdidas a la industria petrolera. Es importante comprender el comportamiento de fase de los asfaltenos en condiciones más cercanas a las que se encuentran en los yacimientos. Por lo tanto, la LMCP/UFRJ comenzó a operar una unidad de alta presión y alta temperatura (HPHT) acoplada a una sonda de espectrómetro de infrarrojo cercano que puede utilizar diferentes floculantes. Este trabajo describe el desarrollo de un procedimiento, así como la validación de los resultados obtenidos de esta unidad. Debido a la compleja composición del crudo, se prepararon sistemas modelo (MS) con asfaltenos extraídos con n-pentano (C5I) y n-heptano (C7I). Los experimentos se realizaron a presión atmosférica, titulados con n-heptano, ya 100 y 300 bar titulados con propano. Como era de esperar, los asfaltenos C7I fueron más inestables, presentando un inicio de precipitación más bajo que los asfaltenos C5I en condiciones ambientales y a presiones más altas. Sin embargo, para ambos MS, la estabilidad aumentó con el aumento de la presión al usar propano como solvente. El método propuesto para evaluar el inicio de la precipitación de asfaltenos fue efectivo para MS en tolueno y crudo muerto, y es una alternativa prometedora para la investigación de diferentes tipos de crudo.

Palabras clave: Asfaltenos, Infrarrojo Cercano, Comportamiento de Fase, Alta Presión, Titulación de Propano.

1. Introduction

Crude oil can be fractionated into various compounds that are divided based on the composition of different groups of molecules. Different types of solids can also exist in crude oil. Of these, asphaltene solids are the most prominent (Fakher et al., 2020b). Asphaltenes are considered one of the most complex components of crude oil due to the diversity of chemical structures that constitute them, which makes it very difficult to generalize a specific structure.

Asphaltenes are usually classified by their solubility class rather than their structure, whereby they are insoluble in low molecular weight n-alkanes and soluble in aromatic compounds such as benzene and toluene (Groenzin and Mullins, 2000; Fakher et al., 2020b; Peralta Sanchez et al., 2017; Marín Velazquez 2021). Asphaltenes deposition can reduce oil well productivity as well as clogging production pipes and oil treatment facilities. Due to their amphiphilic nature, asphaltenes also have surface activity and are able to adsorb at the oil-water interface and on clay mineral surfaces. The adsorption of asphaltenes on the surface of clay minerals plays an important role in the oil industry by altering wettability, which makes difficult to treat oil sands, for example (Maravilha et al., 2021). The worldwide cost associated with deposition of asphaltenes during production and processing operations is on the order of billions of dollars per year. Asphaltenes precipitation can occur through changes, albeit subtle, in pressure, temperature, oil composition and shear rate, among other factors (Rogel et al., 2015).

Variations in oil composition can affect this balance and result in precipitation of asphaltenes. Gas injection, one of the enhanced oil recovery (EOR) techniques, is closely involved with the precipitation of asphaltenes

in reservoirs. Nitrogen, natural gas, light hydrocarbons and carbon dioxide are typical gases used for EOR (Mohammadi et al., 2013). The oil properties change depending on the production conditions, the fluids injected into the reservoir, and the pressure changes as the hydrocarbons are produced. Various solvents can also be injected into the reservoir, including steam, surfactants, CO₂, nitrogen, methane, ethane, propane, butane, and others. In a study of thermal recovery methods, co-injecting steam and propane was found to promote an increase in crude oil production (James, Rezaei and Chatzis, 2008). The injection of light hydrocarbon gases, such as ethane and propane, can induce a significant oil swelling degree in the case of unconventional reservoirs. The swelling creates a localized pressure gradient, which causes the oil to be swept from the pores into the fractures (Habibi et al., 2017). In a simulation study considering a CO₂-propane mixture, the researchers observed a very high solvent force of propane in mobilizing the oil in shale cores. The solvent force of the gas refers to the mass transfer capacity of the lighter hydrocarbon fraction to the oil, making the oil less viscous and consequently increasing its mobility in producing wells (Li, Sheng and Xu, 2017). However, as the solvent begins to interact with the oil, asphaltenes may no longer be stable in the medium due to a change in equilibrium conditions (Demirbas, 2002; Fakher et al., 2020a). The problems resulting from the presence of asphaltenes in oil come from its destabilization, affecting several aspects of flow assurance. The mitigation of these problems is therefore important for crude oil production. One of the first steps in preventing asphaltenes deposition is to obtain accurate information about the structure of asphaltenes and their properties, especially stability. One of the methods to evaluate the stability of asphaltenes is to determine the

onset of their precipitation, which can be defined as the minimum amount of precipitating agent necessary to induce the beginning of the asphaltenes precipitation, measured in grams of sample (Golshahi et al., 2019; Guerrero-Martin et al. 2023; Guerrero-Martin et al. 20018).

Near infrared spectroscopy (NIR) is an appropriate technique to measure asphaltenes precipitation onset during titration with a flocculating solvent. The test is relatively simple and fast, highly accurate, informative, and uses a small sample volume. However, it is important to note that the methods to determine the precipitation onset in general are carried out in the laboratory under ambient conditions, with controlled parameters, to make the analysis reproducible. In an oil reservoir, asphaltenes precipitation occurs under conditions of higher temperatures and pressures, and these characteristics are particular to each field (Liu et al., 2015). There are devices that can identify the asphaltenes precipitation onset, but the results are affected by the gas used to pressurize the system (Hartmann et al., 2016). On the other hand, pressure-volume-temperature (PVT) cells are not able to identify the exact precipitation onset point, and the equipment that does this is very expensive (Hirschberg et al., 1984; Creek, Wang and Buckley, 2008; Romero et al., 2019; Romero et al., 2021).

Therefore, here we describe an operational procedure for the high-pressure and high-temperature (HPHT) unit built for the LMCP/IMA/UFRJ, which monitors the system with a NIR probe. We also describe the phase behavior of polar fractions under conditions close to those found in reservoirs as a way to determine the asphaltene precipitation onset using propane as a flocculating agent in model systems of C5I and C7I asphaltenes in toluene.

2. Experimental Development

Materials

Chemicals

n-Pentane 98% was acquired from Isofar Indústria e Comércio de Produtos Químicos Ltda., Duque de Caxias, Rio de Janeiro, Brazil; n-heptane P.A. 99% was acquired from LabSynth Produtos para Laboratórios Ltda., Diadema, São Paulo, Brazil; cyclohexane ≥

99%, toluene ≥ 99% and commercial toluene were supplied by Vetec Química Fina Ltda., Duque de Caxias, Rio de Janeiro, Brazil; propane ≥ 99.5% was acquired from White Martins Gases Industriais Ltda, Rio de Janeiro, Rio de Janeiro, Brazil. The heavy crude oil sample, called P01, was provided by CENPES/Petrobras, Rio de Janeiro, Brazil, with the following characteristics: °API 21.1, saturates, aromatics, resins and asphaltenes contents of 45.5%, 32.8%, 19.2% and 2.4%, respectively, and pour point of -45 °C (ISO 12185, 1996; ASTM D6560, 2000; ASTM D-97, 2012). Except for the commercial toluene, which was distilled and dried over alumina, all materials were used as received.

Obtaining the Asphaltenes Fractions

Asphaltenes were separated from P01 crude oil based on a modification of a standard method IP 143 (IP 143/01, 2001). About 30 grams of the oil was added to 1 liter of precipitant solvent (n-pentane or n-heptane) and kept under moderate stirring for 48 hours. The precipitate was vacuum filtered through filter paper at room temperature repeatedly. The filter paper containing the unpurified asphaltenes precipitate was folded, air-dried and placed in an extraction cartridge, which was inserted into a Soxhlet extractor containing 500 mL of the precipitated solvent. The system was then refluxed until the circulating solvent became colorless. The solid residue was solubilized in 500 mL of toluene in a Soxhlet extractor and the solution of asphaltenes in toluene was kept separate until complete evaporation of the toluene. Finally, the dried sample was placed in a glass vial wrapped in aluminum foil to prevent oxidation. These procedures were repeated until obtaining enough asphaltenes to carry out the investigation, after having obtained 14.55 g and 4.22 g of C5I and C7I asphaltenes, respectively.

Characterization of the C5I and C7I Asphaltenes Fraction

The asphaltene samples were characterized by Fourier-transform infrared spectroscopy (FTIR) and CNHS elemental analysis. The FTIR spectra were obtained at room temperature, in attenuated total reflection mode (ATR) with wavelength ranging from 4000 to 400 cm⁻¹ and resolution of 4 cm⁻¹, using a Nicolet™ IS 50 spectrometer from Thermo Fisher Scientific. The mass percentages of carbon, hydrogen, nitrogen and sulfur were quantified by combustion followed

by chromatography in a PerkinElmer CHNS/O 2400 Analyzer based on the ASTM D5291 method (ASTM D5291, 2012). Oxygen was determined indirectly by difference. This analysis allows the determination of the degree of unsaturation of the sample by calculating the C/H or H/C ratio (Speight, 2007). The analyses were performed in duplicate, and the results are expressed as averages.

Preparation of Model Solutions of Asphaltenes in Toluene

The model systems were prepared at 1.00 wt/v% of C5I or C7I asphaltenes in toluene, using volumetric flasks. The system remained in an ultrasonic bath for 60 minutes until complete solubilization of the asphaltenes.

Determination of the Asphaltenes Precipitation Onset

Under ambient conditions of pressure and temperature, the studies of asphaltenes precipitation

onset using the model systems were carried out by titrating n-heptane and monitoring the result with a near infrared spectroscopy (NIR) probe (Fig. 1), using the Bruker Matrix-F spectrometer (Garreto et al., 2010; Garreto, Mansur and Lucas, 2013; Lucas, Spinelli and Khalil, 2015). About 7 grams of model solution was weighed in a glass container specific for the test and kept under magnetic stirring for 5 minutes before starting the tests, which were performed for 40 min. at an n-heptane flow rate of 1 mL/min to read the absorbance at wavelength of 1600 nm (Santos et al., 2017). In the beginning of the analysis, the absorbance tends to decrease because of sample dilution. However, when precipitation occurs by the formation of molecular aggregates, the absorbance increases, thus making the method very useful to detect the asphaltenes precipitation onset in the flocculant volume in which the absorption intensity is minimal (Oh, Ring and Deo, 2004; Garreto et al., 2010). The asphaltenes precipitation onset was expressed as volume of n-heptane (mL) per sample mass (g).

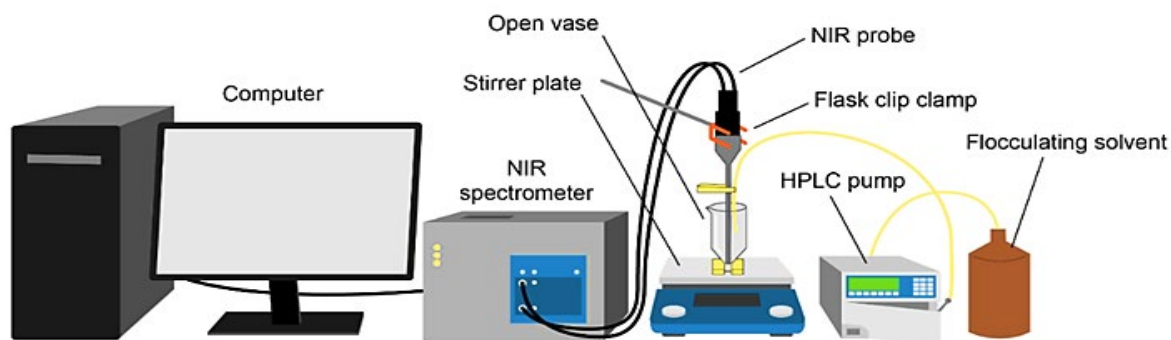


Fig. 1. Scheme to determine the asphaltenes precipitation onset by near-infrared spectroscopy in ambient conditions (adapted from Garreto et al., 2010).

Likewise, the asphaltenes precipitation onset was also evaluated under different pressure conditions. An HPHT unit (with automatic titrator, variable volume cell and NIR probe), built by Top Industrie Company, was used (Fig. 2). The NIR probe is resistant up to 400 bar and was supplied by Custom Sensor Technology

(CST), here called CST NIR probe to distinguish it from the NIR probe used in the conventional experiments to determine asphaltenes precipitation onset under ambient conditions (Fig. 1).

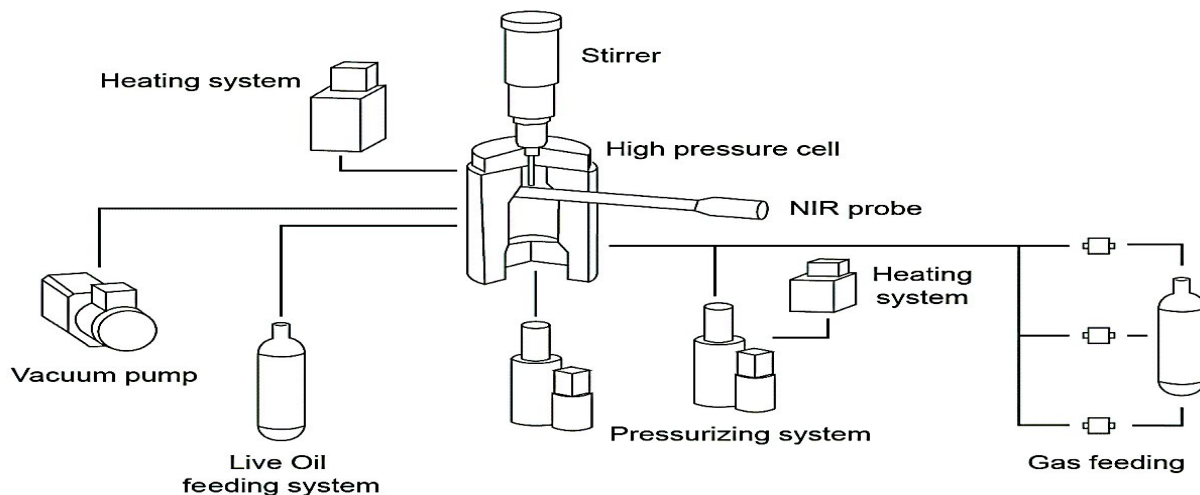


Fig. 2. Scheme of the high-pressure high-temperature unit to determine asphaltenes precipitation onset.

The cell for titration operates with maximum and minimum volumes of about 200 mL and 70 mL, respectively. For the analysis, the minimum volume of sample is required to pressurize the system. The stirrer is placed at the top of the cell. The heating is achieved in the cell through a circulating thermostatic bath. The adjustment is made by the bath display and the temperature is monitored by the sensor placed in the test cell. The cell pressure adjustment is performed by the hydraulic pump connected to the cell. The pressure in the pump is regulated and transferred to the cell through the pressure valve. Before starting the experiment, the system is kept for about 15 minutes under stirring at 1300 rpm at the selected pressure to stabilize the sample in the cell of the HPHT unit.

The line with the titrant is pressurized under the test conditions and the NIR spectroscope is configured using the required parameters. Simultaneously, the titrant pump and valve, and the LabVIEW computer program are initiated. The LabVIEW software is responsible for monitoring the variables and recording data during the test. The titrant flow rate is selected and input in the software. All experiments were performed at least in duplicate, the values were reported as the average of the measurements, and experimental errors were expressed as the standard deviation.

The experiments were carried out with the aim of evaluating the asphaltenes precipitation at higher pressure than ambient, as a function of the type of flocculating agent, the pressure and the characteristics of the asphaltenes fractions in the model systems. The results were compared with those obtained under ambient condition. The determination of the asphaltenes precipitation onset under different pressures allows studying the systems by simulating specific environmental and field conditions (Hartmann et al., 2016). The experiments were performed using about 90 g of sample. Table 1 shows the experimental conditions used to determine the asphaltenes precipitation onset in P01 crude oil and in the model system of C5I or C7I asphaltenes at 1.0 wt/v% in toluene.

Table 1. Experiments carried out to evaluate the asphaltenes phase behavior at room temperature, under different pressures (atmospheric, 100 and 300 bar) in a crude oil sample and model systems, using n-heptane or propane as titrant

Sample	Test conditions			
	Concentration (wt/v%)	Solvent	Pressure (bar)	Titrant
Crude oil P01	50.0	n-Heptane	Atmospheric	n-Heptane
	100.0	-	100 300	Propane
C5I asphaltenes	1.0	Toluene	Atmospheric	n-Heptane
			100 300	Propane
C7I asphaltenes	1.0	Toluene	Atmospheric	n-Heptane
			100 300	Propane

3. Results and Discussion

This section presents the characterization of C5I and C7I asphaltenes fractions according to FTIR and CHNS analysis; the development of the procedure to measure asphaltenes precipitation onset using the HPHT unit, when titrating the sample with propane and monitoring the precipitation with a CST NIR probe (including the probe validation); determination of the asphaltenes precipitation onset under ambient conditions when titrating the sample with n-heptane; and the determination of the asphaltenes precipitation onset at different pressures when titrating the sample with propane.

Characterization of C5I and C7I Asphaltenes Fractions

The FTIR spectrum of C5I asphaltenes showed strong absorption at 2920, 2850, 1455, 1375 and 730 cm^{-1} due to the presence of CH_2 and CH_3 groups. The presence of bands close to 1600, 860, 795 and 750 cm^{-1} identified aromaticity. The portion of lateral aliphatic hydrocarbons to the polycondensed aromatic rings was indicated by the presence of bands at 2920, 2850, 1450, 1375 and 730 cm^{-1} . The C=O and C–O absorption bands were also evident in the spectrum at 1695–1710 and 1032 cm^{-1} (bands that typically appear in asphaltenes spectra) (Akmaz et al., 2011). These results corroborate the works of other authors who have investigated functional groups of asphaltenes fractions from different origins (Ali, Kukhari and Hasan, 1989; Aske, Hallevik and Sjöblom, 2001; Peralta-Martínez et al., 2008). Table 2 summarizes the main groups and assignments provided by FTIR for the analysis of asphaltenes.

Table 2. Characteristic FTIR spectrum groups and assignments for asphaltenes samples

Wavelength (cm^{-1})	Group	Assignment
2923 e 2853	CH_2 e CH_3	Stretching vibration
1605	C=C e C=O	Aromatic nucleus vibrations
1457	CH_3	Symmetrical stretching vibration
1376	CH_3	Asymmetrical stretching vibration
1032	$\text{C}_2\text{S}=\text{O}$	---
870 e 800	CH	Out-of-plane vibration of ring
750	---	Vibration of four hydrogens adjacent to the aromatic ring

The FTIR spectrum of C7I asphaltenes showed essentially the same peaks observed in the C5I fraction, as expected. Differences were found only in the relative intensities. The spectrum of C7I asphaltenes showed more intense bands corresponding to 1600, 860 and 750 cm^{-1} , associated with aromaticity. Furthermore, the relative intensities of the bands at 1600/2920 and 2850 cm^{-1} were higher in the spectrum of C7I asphaltenes, also indicating a greater number of aromatic groups. The results showed that the extractions of different asphaltenes fractions were carried out successfully, since as expected, the C7I asphaltenes sample had a more polar characteristic than the C5I sample. The more polar compounds are more concentrated in the C7I asphaltenes fraction, while in the C5I fraction the polar compounds are mixed with less polar ones (Honse et al., 2012).

The results of elemental analysis are shown in Table 3. As expected, the highest values were observed for carbon and hydrogen contents due to the essentially hydrocarbon characteristic of crude oil and its asphaltenes fractions. In the oil sample, the contents of heteroatoms, mainly S and O, were insignificant. Comparison of the results of the oil with those of the asphaltenes samples revealed an increase in the concentration of N, S and O in the asphaltenes fractions, which was expected considering the theory of compositional continuity of crude oil, according to which the concentration of heteroatoms varies proportionally with polarity (Boduszynski, 1987; Lordeiro et al., 2021). Furthermore, the H/C ratio was higher for oil sample, in agreement with the fact that the asphaltenes molecules contain polyaromatic rings, where carbon-carbon double bonds predominate.

Table 3. Contents of carbon, hydrogen, nitrogen, sulfur, and oxygen in P01 crude oil and C5I and C7I asphaltenes fractions. The oxygen content was determined by the difference of the other elements and their contribution added to the sulfur percentage. Percentages are reported as the average of two analyses.

Sample	Elements (%)					H/C	N/C
	C	H	N	Total	S - O		
Crude oil P01	85.40 ± 0.07	13.60 ± 0.11	0.90 ± 0.07	99.90	0.10 ± 0.03	0.159	0.011
C5I asphaltenes	88.07 ± 0.03	9.69 ± 0.11	1.97 ± 0.08	99.73	0.27 ± 0.06	0.110	0.022
C7I asphaltenes	87.77 ± 0.09	9.14 ± 0.10	2.09 ± 0.05	99.00	1.00 ± 0.06	0.104	0.024

Comparison of the results obtained for the fractions of C5I and C7I asphaltenes showed that the carbon and hydrogen contents decreased slightly with increasing polarity while the nitrogen and sulfur contents tended to increase, as well as the concentrations of non-quantifiable components. This group, which cannot be quantified by this technique, may include the elements iron, nickel, vanadium, but mainly oxygen. Furthermore, the H/C ratio also varied, reinforcing the subtle differences in aromaticity between the C5I and C7I asphaltenes fractions observed in the FTIR analyses. Differences in H/C ratios may have been due to higher levels of cyclic compounds in the C7I fraction.

Development of the Procedure to Measure the Asphaltenes Precipitation Onset under High Pressure and Temperature Conditions (HPHT)

The development of the procedure to determine the asphaltenes precipitation onset using the HPHT unit was performed in two steps: the validation of the CST NIR probe and the establishment of the analytic procedure.

The probe used in the HPHT unit (CST NIR probe) has a different manufacturer than the probe used in a conventional system that operates under ambient conditions. Therefore, it is important to be sure that the results obtained from the HPHT unit are equal or similar to those obtained from the conventional system, so that they can be compared when developing a study using both systems. The CST NIR probe was designed to be used at high sample concentrations. The probe window material is made of sapphire, with a 4.55 mm pathlength and 220 mm insertion length, while the conventional external probe has a 5 mm pathlength. Furthermore, the CST probe presents unique features, such as withstanding pressures and temperatures up to 400 bar and 100 °C. To compare the response of the CST probe with that obtained in the system under ambient condition, it was carefully removed from pressure cell and used in the conventional system, under the same conditions employed with the standard probe (room temperature and atmospheric pressure) (Fig. 1).

The validation experiments were performed with the P01 crude oil sample pre-diluted in n-heptane and with the model solutions of C5I asphaltenes at 1.0 and 0.5 wt/v% in toluene. Fig. 3 shows one of the curves obtained from each duplicate experiment. Fig. 3a shows that the curves of asphaltenes precipitation onset for the P01 crude oil, obtained under the same conditions but changing the probe, were closely similar, which was also observed for the curves obtained with the model systems at different concentrations (Fig. 3b and 3c). The absorbance values were different for the different probes during the analyses, so that we used two y axes to present the curves close to each other. This occurred for the three samples, and it can be attributed to the construction and detection characteristics intrinsic to each probe.

The asphaltenes precipitation onset values obtained in these analyses are summarized in Table 4. The onset values are reported as the average of the tests performed in duplicate. For P01 crude oil and the model system containing 0.5 wt/v% of asphaltenes in toluene, there was a slight reduction of the onset obtained by the CST probe compared to that obtained by the conventional one ($\Delta = 0.25$ and 0.21 respectively). On the other

hand, the results were practically equal for the model system containing 1.0 wt/v% of asphaltenes in toluene ($\Delta = 0.03$), which is probably related to the higher sensitivity of the CST probe for measurements at higher concentrations. From the appearance of the curves (Fig. 3b and 3c) it can be seen that the CST probe does not have the same sensitivity as the conventional probe for more diluted systems, since it was not possible to observe the phenomenon of the initial drop in the absorbance signal for the solution model containing 0.5 wt/v% asphaltenes C5I-P01 (Fig. 3c). In this case, it is not possible to specify which point represents the lowest absorbance, since there is an irregularity in the measured signal until the moment the absorbance value increases abruptly, which was taken as indicative of asphaltenes precipitation and formation of aggregates. Therefore, meaning that the CST probe is not suitable for highly diluted model systems. However, in general good reliability was observed in the results obtained with the CST probe, because although the results were not the same as those obtained with the conventional probe, there was a correlation in relation to the stability trend of the three samples evaluated, besides the good correlation in terms of onset values, given by an acceptable experimental variation (Δ).

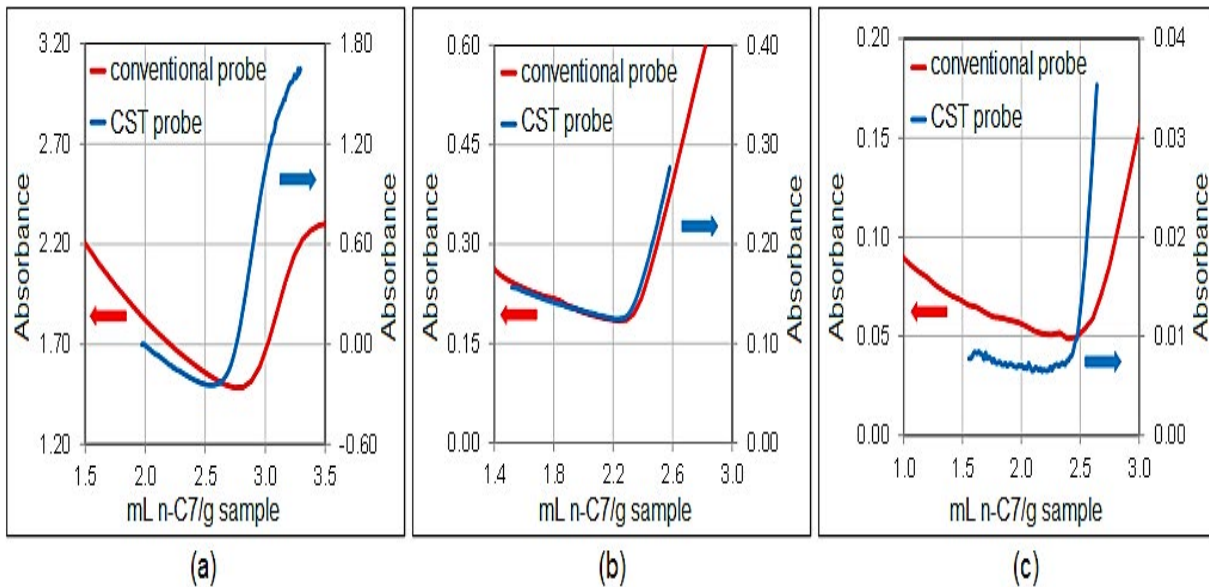


Fig. 3. Curves of absorbance as a function of n-heptane volume (mL) per gram of sample, obtained in the conventional system under ambient conditions, using the CST and conventional probes, for: (a) P01 crude oil; (b) model system of C5I asphaltenes at 1.0 wt/v% in toluene; and (c) model system of C5I asphaltenes at 0.5 wt/v% in toluene.

Table 4. Asphaltenes precipitation onset values obtained from the experiments shown in Fig. 3.

Sample	Asphaltenes precipitation onset (mL n-C7/g sample)		Δ onset
	Conventional probe	CST probe	
P01 crude oil	2.79 ± 0.04	2.54	0.25
Model system C5I (1.0 wt/v%)	2.25 ± 0.01	2.22	0.03
Model system C5I (0.5 wt/v%)	2.39 ± 0.01	2.18	0.21

After the validation of the CST probe, the operating method of the HPHT unit was established by performing several tests. First, an experiment was carried out by titrating n-heptane into the P01 crude oil at pressure of 1 bar (minimum operating pressure of the HPHT unit), under stirring at 1300 rpm. The result obtained with CST probe in the conventional system was used as reference. Therefore, we tried to reproduce the same conditions: 1 bar (close to atmospheric pressure); room temperature (20-25 °C); P01 crude oil sample pre-diluted with n-C7; n-heptane as flocculating agent; and flow rate of n-C7 equal to 1.0 mL/min. This result was then compared with that obtained by the CST probe in the conventional system (Fig. 3a, Table 4). The asphaltenes precipitation onset found in this first experiment was equal to 1.90 mL n-C7/g sample, which was very different from the value of 2.54 mL n-C7/g sample found for the CST probe in the conventional system. As the test pressure was extremely low for the usual operating parameters of a high-pressure unit, it was difficult to guarantee that the pressure in the test cell was set to 1 bar. Experimentally, this was noted through the irregular displacement of the motorized pump, which allows for a variation in the internal volume of the system. During the test at 1 bar the pump displaced one step when experimentally 2 to 2.5 steps are expected in a regular test. In theory, moving the pump by one step would only allow the addition of a volume of titrant equal to 50 mL, but this has not been verified. In this specific test, two volumes of titrant were added or two complete pumps (100 mL), which shows an imbalance in the initial pressure that seems to have affected the result found. Thus, as demonstrated that the test pressure was not adequate (1 bar) for the operational parameters of the HPHT unit, it was difficult to guarantee that the pressure in the cell was stable at 1 bar throughout the experiment. Therefore, other tests were performed with adjustment of some parameters.

In the following tests, the pressure was increased from 1 to 2 bar, making it possible to stabilize the pressure

in the cell. Despite being higher, the pressure of 2 bar is still a very low in comparison with the high pressures to which oil is subjected in the reservoir. The stirring was reduced from 1300 rpm to 1000 rpm, because a large noise amplitude variation of the signal was observed when using 1300 rpm. Fig. 4 shows the curve obtained for the P01 crude oil under the same conditions described in the previous paragraph, at 2 bar and 1000 rpm. For comparison, the curve already exhibited in Fig. 3a for the CST probe used in the conventional system is also shown. Despite an increase in the onset value when the measurement was made in the unit cell (from 2.54 to 2.95 mL n-C7/g P01 crude oil), the curves (absorbance x onset) are well adjusted. This difference can be attributed to the small difference in the pressures and to the probe's exposure in an open/light or closed/dark system. From then on, it can be inferred that the asphaltenes precipitation onset values obtained with the HPHT unit are valid and reproducible when the conditions are kept constant, and the HPHT unit is properly operated. A detailed description of the HPHT unit and its operation can be found in the Silva (2022) (Silva et al., 2022).

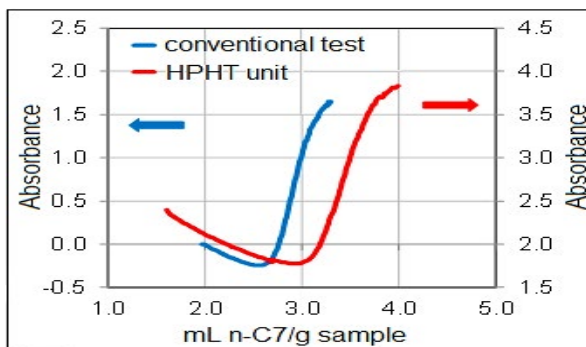


Fig. 4. Determination of the asphaltenes precipitation onset of P01 crude oil, using CST probe, in the HPHT unit at 2 bars. The curve obtained for the P01 crude oil using CST probe in the conventional system (Fig. 3a), at ambient conditions, is already showed for comparison.

Determination of the Asphaltenes Precipitation Onset under Ambient Conditions

Various techniques can be used to monitor asphaltenes precipitation. Among these techniques, spectrometry techniques using ultraviolet-visible (UV-Vis) and near infrared (NIR) wavelengths stand out. These techniques are based on the asphaltenes particles scattering light. Light scattering is detected by the equipment as the absorbance of the solution increases. A spectrometer allows comparing the amount of light passing through the sample to how much light passes through the reference (blank). In turn, the asphaltenes particles scatter some of the incident light, so less light reaches the detector than through the reference (blank). The spectrometer reads the phenomenon as if the scattered light was being absorbed by the solution/sample (Cruz et al., 2019; Fakher et al., 2020b).

In the analysis to determine the asphaltenes precipitation onset, graphs of absorbance as a function of the volume of flocculant added to the sample were obtained, as already shown in Fig. 3 and 4. At the beginning of the test, the asphaltenes molecules are dispersed in the crude oil or solution, which has a characteristic absorbance for each sample. In general, the addition of the flocculating agent causes only a dilution in the solution, reducing the absorbance. When a sufficient volume of flocculant agent is added to cause the precipitation of asphaltenes, the presence of precipitates causes an increase in the intensity of absorption and the effects of dilution of the solution and light scattering compete, causing the reduction in absorbance to deviate from a linear relationship. With the addition of more flocculant, the amount of precipitated material increases, and the effects of light scattering outweigh those of dilution, with an increase in absorbance signal being observed. In this evaluation, the precipitation onset is taken at the point where the absorption intensity is minimum, despite the presence of asphaltenes particles dispersed in solution (IP 143/01, 2001; Mansur, Melo and Lucas, 2012; Lucas, Spinelli and Khalil, 2015).

The onset values thus determined allow evaluating the stability of crude oils in terms of asphaltenes precipitation. There is an empirical scale of asphaltenes stability in crude oils as a function of the precipitation onset determined under ambient conditions, which classifies a crude oil as very stable, stable, unstable and very unstable, as described by Altoé et al. (2014).

Table 5 summarizes the results of asphaltenes precipitation onset of P01 crude oil and the model systems of C5I and C7I asphaltenes, under ambient conditions, obtained from the absorption intensity curves as a function of n-heptane volume added to the sample, with profiles similar to those reported in the literature (Barreira et al., 2018; Nunes et al., 2019). The results are expressed as the average value between measurements. The excellent reproducibility of the analysis is highlighted based on variations smaller than 0.1 mL of n-heptane/g of sample.

Table 5. Asphaltenes precipitation onset values obtained under ambient conditions for P01 crude oil and model systems prepared with C5I or C7I asphaltenes at 1.0 wt/v% in toluene, titrated with n-heptane.

Sample	Asphaltenes precipitation onset (mL n-heptane/g sample)
P01 crude oil	2.79 ± 0.04
Model system of C5I asphaltenes	2.25 ± 0.01
Model system of C7I asphaltenes	1.93 ± 0.01

The results obtained for P01 crude oil (2.79 mL n-heptane/g of sample) classify it as an oil with high stability in terms of asphaltenes precipitation under ambient conditions. Comparisons between the phase behavior of oil and the model systems, as well as between the two model systems prepared with C5I and C7I asphaltenes, can also be performed.

The difference between the values found, especially between P01 crude oil and the model system C7I stands out, in addition to the specificity of the n-alkane used in the asphaltenes extraction and in the methodology used in the separation of the asphaltenes fraction. It is known that resins play an important role in stabilizing asphaltenes in solution, interacting with asphaltenes and with saturated compounds, behaving as a surfactant given its amphiphilic structural characteristic. Thus, the removal of resins during the purification step in the extraction of asphaltenes eliminates this additional stabilization provided by this class of molecules. This is one of the accepted theories based on experimental observation that the model systems required a smaller volume of precipitating agent to start the asphaltenes phase separation.

As seen in the topic about the characterization of asphaltene fractions, the fraction insoluble in n-heptane (C7I) is more polar than that insoluble in n-pentane (C5I). This is a characteristic caused by extraction with n-alkanes. Commonly, n-alkanes with lower carbon numbers provide higher yields in the extraction of asphaltenes, encompassing a greater variety of molecules referring to molecular mass, but this greater dispersion of molecular mass reduces the polarity of the fraction. For example, in the precipitated fractions with n-C7, n-C8, n-C9, and mainly n-C10 molecules, it is expected to find asphaltenes with a greater number of functional groups and heteroatoms, which confer greater polarity and therefore less stability. Thus, when the flocculant agent is added to the solution, the more polar and thus less stable fraction separates first from the phase, which characterizes a smaller volume of flocculant necessary for this phenomenon to occur. Therefore, the lower onset value found for the model system C7I compared to the system C5I agrees with the literature (Wang and Buckley, 2003; Akbarzadeh et al., 2007; Ting et al., 2007).

Determination of the Asphaltenes Precipitation Onset with Propane Titration under Different Pressures

In this step, experiments were carried out with the objective of evaluating the response of the HPHT unit under different pressures on the phase behavior of asphaltenes in the oil sample and in model systems through the gas injection process. Propane was used in these experiments.

Given the novelty of the process and the challenges encountered, in the first analyses we made an adjustment in the operation of the HPHT unit. The P01 crude oil was analyzed until the curve profile obtained with the propane titration was similar to the previously known profiles. In one of the reproduction tests at 100 bar, the profile of the precipitation onset curve did not fit well to the curves of the graphs obtained previously. This result can be explained by the fact that during the pressurization of the pressure cell in one of the steps, the pressure did not remain constant due to a leak in one of the valves. At this stage of the test, the test cell was already registering 100 bars of pressure, and probably the depressurization to adjust the leaky valve mischaracterized the test condition, making the precipitation onset measurement different from the previous results. In this type of experiment, special attention must be given to the occurrence of depressurization in the cell after starting a specific test.

Once the sample has reached the intended temperature, it is not recommended to stop the test, depressurize the cell, and restart the analysis at that point. This step may change the properties of the crude oil, leading to misinterpretations about the asphaltene phase behavior of the sample under study. In these cases, it is advisable for the analysis to be interrupted, the system cleaned, and a new sample loaded in the cell to begin a new test.

For analyses by NIR spectrometry, either under ambient pressure or at higher pressures, the sample signal gain is an important parameter to consider. Variations in this parameter between one analysis and another can greatly affect the profiles found. The factors that affect the determination of the sample signal gain in the NIR spectrometry software are closely linked to the ability of the radiation emitted by the probe to “see” the sample. Conditions such as inefficient cleaning of the probe window between one experiment and another and temperature variations can influence the definition of the sample signal gain that will be adjusted for the experiment.

As an observation for the samples titrated by gases at high pressure, as developed in this work, it is necessary to know the density of the flocculant in the different experimental conditions of pressure and temperature. Density data for propane at experimental pressures and temperature were obtained from the National Institute of Standards and Technology. The value found for the density of propane in the tests at 25°C at 100 bar was 492.4 kg/m³ for example. For the correct control of the volume of pressurized flocculant added (mL) to the test cell, it is necessary that the mass meter coupled to the system is operating correctly.

When using the appropriate procedure, the absorption intensity curve as a function of the titration with propane of the P01 crude oil presented the profile shown in Fig. 5a: a significant drop in the absorbance from the initial measurement, characterized by the dilution of the system; a minimum absorbance, identifying the point of precipitation onset; and a rapid increase in absorbance due to aggregation and precipitation of asphaltene particles, causing light scattering. At the end of the preliminary evaluations with propane as a flocculating agent and the determination of the asphaltene precipitation onset of the P01 crude oil titrated by propane, it was possible to confirm the applicability of the operational procedure established for the HPHT unit. After the measurements of the asphaltene precipitation onset in the P01 crude oil, the

evaluation of the precipitation onset of the C5I and C7I model systems at 1.0 wt/v% in toluene was carried out, also titrated with propane at 100 and 300 bar (Fig. 5b).

The curve forms were confirmed. Table 6 summarizes the asphaltenes precipitation onset values obtained from the graphs in Fig. 5.

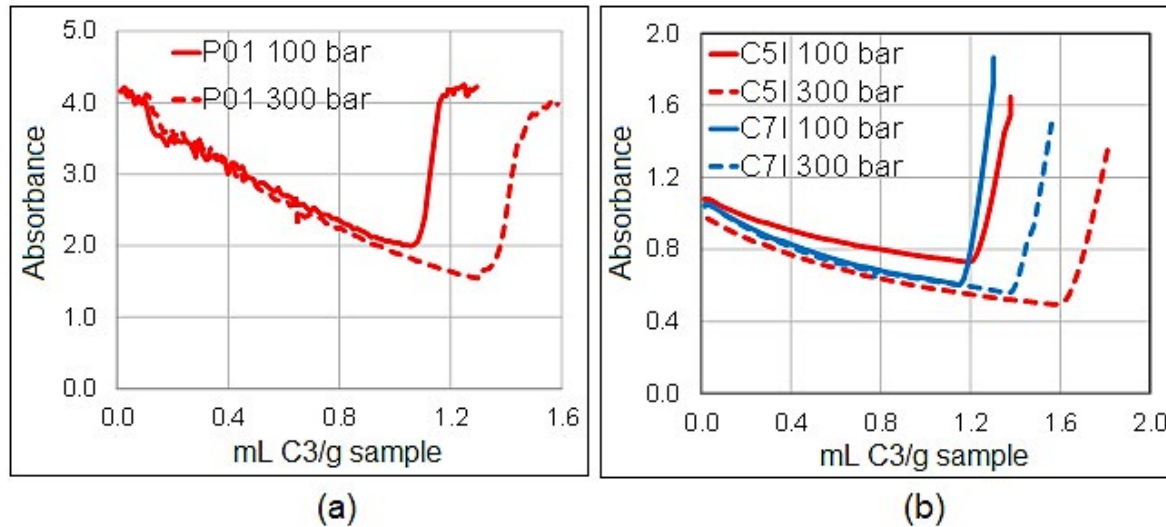


Fig. 5. Asphaltenes precipitation onset of P01 crude oil (a) and model systems C5I and C7I at 1.0 wt/v% in toluene (b), titrated with propane at 100 and 300 bar.

Table 6. Asphaltenes precipitation onset of P01 crude oil and model systems prepared with C5I and C7I asphaltenes at 1.0 wt/v% in toluene, titrated with propane at 100 and 300 bar

Sample	Pressure (bar)	Asphaltenes precipitation onset (mL propane/g sample)
P01 crude oil	100	1.06 ± 0.00
	300	1.27 ± 0.04
Model system of C5I asphaltenes	100	1.22 ± 0.03
	300	1.54 ± 0.04
Model system of C7I asphaltenes	100	1.13 ± 0.04
	300	1.41 ± 0.05

The results for P01 crude oil showed that increasing the pressure from 100 to 300 bar, using propane as titrant, increased the stability of asphaltenes. Comparison with the test carried out with n-heptane close to atmospheric pressure (2.79 mL n-C7/g sample – Table 5) indicated that greater stability was achieved for the system titrated with n-heptane, even at lower pressures. As observed for crude oil, in both model systems, the precipitation onset increased when raising the pressure from 100 to 300 bar, confirming the increase in stability with rising pressure within the analyzed pressure range.

For the model system containing C5I asphaltenes, precipitation onset was reduced from 2.25 mL n-C7/g sample (atmospheric pressure – Table 5) to 1.22 mL C3/g

sample (100 bar). This behavior of reduced stability with the use of propane at 100 bar in comparison with the use of n-heptane at close to atmospheric pressure was similar to that observed for crude oil. Comparison of the results obtained for the crude oil and the model system of C5I asphaltenes at the pressure of 100 bar of propane revealed that the crude oil was more unstable. This behavior was opposite to that observed at ambient conditions with titration by n-heptane, where normally the model solution has lower precipitation onset in relation to that of the crude oil, since the resins, which are considered to stabilize asphaltenes in crude oil, were eliminated during the asphaltenes extraction process, which makes the asphaltenes in the model system more susceptible to precipitation by the flocculating agent.

The test using the C5I asphaltenes model system at 100 bar titrated with propane was repeated using a smaller sample mass (from ~90 g to ~60 g). The curve profile was maintained, and the precipitation onset values did not change (1.22 ± 0.02 mL propane/g sample), validating the obtainment of good results with smaller sample mass even using a cell with relatively large capacity. This reduction in sample mass for the test has the advantages of lower volume of flocculating agent spent during the test, as well as a reduction in analysis time.

Comparison of the results obtained under the same pressure conditions for the two different model systems showed, as expected, that the system containing C5I asphaltenes was more stable than that containing C7I, for both evaluated pressures. As discussed for the characterization of fractions C5I and C7I, the asphaltenes insoluble in n-heptane were more unstable, since they are more polar and show lower heterogeneity in terms of chemical structures when compared to the portion insoluble in n-pentane. This outcome agrees with the results displayed in Table 6.

This correlation between pressure and asphaltenes stability was different from that reported by Hartmann et al. (2016), who also used propane as titrant, because they observed that the stabilization decreased as increasing pressure (Hartmann et al., 2016). Such a discrepancy may be related to the differences in the operating principles of the devices: They used argon to pressurize the flocculation equipment, which had an influence on the results at higher pressures, besides the limitations related to the detection of precipitation onset for darker oil samples and model solutions with high concentration of asphaltenes; we used a system that is directly pressurized by a hydraulic pump, that is, it does not exist any interference of a gas dissolution in a sample evaluation. Therefore, we consider our new results more reliable.

4. Conclusions

The increase of pressure (from atmospheric to 300 bar) promoted an increase in the stability of asphaltenes using propane as a flocculating agent, both for the crude oil sample and the model systems of C5I or C7I asphaltenes at 1.0% wt/v in toluene. Therefore, we can highlight that the model system satisfactorily represents the trend of phase behavior of asphaltenes as a function of pressure. The model systems studied in this work, although very simple, allowed minimizing the variables in relation to more complex systems, used to determine the phase behavior of asphaltenes in

crude oil. The use of model systems enabled studying the influence of other fractions (aromatics and resins) on the stabilization of asphaltenes. For the samples investigated in this work, the fraction of resins had a greater influence on the stabilization of asphaltenes than the other fractions in the samples of the model system compared to the crude oil sample under pressure above atmospheric, because of the opposite behavior to that observed by NIR monitoring under ambient conditions.

The asphaltenes phase behavior under pressure conditions above ambient was satisfactorily evaluated using a high-pressure high-temperature (HPHT) unit coupled to a NIR spectrometer probe. This device was built for this purpose and has a significantly lower cost than others commercially available for the same purpose. Besides this, it does not use gases for pressurization, which can interfere with the stability of asphaltenes and/or influence the action of the flocculant solvent of interest in a specific study. The HPHT unit's operating procedure was successfully established, and the probe response used under higher pressure was validated. In the evaluation of the probe coupled to the pressure cell, a significant reduction in the concentration of the asphaltenes solution resulted in an inconclusive profile for the determination of the precipitation onset under ambient conditions. This result was expected, because the probe construction characteristics are tailored to investigate solutions with higher concentration. The similar shapes of the curves of absorbance versus volume of flocculant and the agreement of the results obtained indicate the reliability of the analyses carried out with the HPHT unit. The proposed method to evaluate asphaltenes precipitation onset was effective for model systems of asphaltenes in toluene and dead crude oil and is a promising alternative for investigation of different crude oil types, including live crude oil.

5. Acknowledgements

The authors thank the financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq 303583/2019-3 and CNPq/PIBITI) and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ E-26/200.974/2021). The authors of this study are grateful for the support of Agência Nacional do Petróleo, Gás Natural e Biocombustíveis/FINEP (PRH-16.1) and Centro de Pesquisas, Desenvolvimento e Inovação Leopoldo Américo Miguez de Mello/Petróleo Brasileiro S.A (Cenpes/Petrobras).

References

- [1] Akbarzadeh, K., Hammami, A., Kharrat, A., Zhang, D., Allenson, S., Creek, J., Kabir, S., Jamaluddin, A., Marshall, A., Rodgers, R., Mullins, O.C., & Solbakken, T. (2007) Asphaltenes—Problematic but Rich in Potential. *Oilfield Review*, 19, 22–43. <https://www.slb.com/-/media/files/oilfield-review/p22-43-english>
- [2] Akmaz, S., Iscan, O., Gurkaynak, M. A., & Yasar, M. (2011). The Structural Characterization of Saturate, Aromatic, Resin, and Asphaltene Fractions of Batiraman Crude Oil. *Petroleum Science and Technology*, 29 (2), 160–171. <https://doi.org/10.1080/10916460903330361>
- [3] Ali, M. F., Bukhari, A., & Misbah-ul-Hasan. (1989). Structural Characterization of Arabian Heavy Crude Oil Residue. *Fuel Science and Technology International*, 7 (8), 1179–1208. <https://doi.org/10.1080/08843758908962284>
- [4] Altoé, R., De Oliveira, M. C. K., Lopes, H. E., Teixeira, C., Cirilo, L. C. M., Lucas, E. F., & Gonzalez, G. (2014). Solution behavior of asphaltic residues and deasphalted oil prepared by extraction of heavy oil. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 445, 59–66. <https://doi.org/10.1016/j.colsurfa.2013.12.082>
- [5] American National Standard Test Method for Determination of Asphaltenes (Heptane Insolubles) in Crude Petroleum and Petroleum Products. West Conshohocken, 2000. ASTM D 6560 – 12/IP-143
- [6] American National Standard Test Method for Instrumental Determination of Carbon, Hydrogen and Nitrogen in Petroleum Products and Lubricants, ASTM D5291, 2010
- [7] American National Standard Test Method for Pour Point of Petroleum Products, ASTM D-97, 2012
- [8] Aske, N., Kallevik, H., & Sjöblom, J. (2001). Determination of Saturate, Aromatic, Resin, and Asphaltenic (SARA) Components in Crude Oils by Means of Infrared and Near-Infrared Spectroscopy. *Energy Fuels*, 15(5), 1304–1312. <https://doi.org/10.1021/ef010088h>
- [9] Barreira, F. R., Reis, L. G., Nunes, R. de C. P., Filipakis, S. D., & Lucas, E. F. (2018). Asphaltenes Precipitation Onset: Influence of the Addition of a Second Crude Oil or Its Asphaltene Fractions (C3I and C5I). *Energy Fuels*, 32 (10), 10391–10397. <https://doi.org/10.1021/acs.energyfuels.8b01749>
- [10] Boduszynski, M. M. (1987). Composition of heavy petroleum. 1. Molecular weight, hydrogen deficiency, and heteroatom concentration as a function of atmospheric equivalent boiling point up to 1400.degree.F (760.degree.C). *Energy Fuels*, 1 (1), 2–11. <https://doi.org/10.1021/ef00001a001>
- [11] Creek, J. L., Wang, J., & Buckley, J. S. (2008). Asphaltene Instability Induced by Light Hydrocarbons. *All Days - Offshore Technology Conference*. <https://doi.org/10.4043/19690-MS>
- [12] Cruz, A. A., Amaral, M., Santos, D., Palma, A., Franceschi, E., Borges, G. R., Coutinho, J. A. P., Palácio, J., & Dariva, C. (2019). CO2 influence on asphaltene precipitation. *The Journal of Supercritical Fluids*, 143, 24–31. <https://doi.org/10.1016/j.supflu.2018.08.005>
- [13] Demirbaş, A. (2002). Asphaltene yields from five types of fuels via different methods. *Energy Conversion and Management*, 43(8), 1091–1097. [https://doi.org/10.1016/S0196-8904\(01\)00085-1](https://doi.org/10.1016/S0196-8904(01)00085-1)
- [14] Fakher, S., Ahdaya, M., Elturki, M., & Imqam, A. (2020). An experimental investigation of asphaltene stability in heavy crude oil during carbon dioxide injection. *Journal of Petroleum Exploration and Production Technology*, 10 (3), 919–931. <https://link.springer.com/article/10.1007/s13202-019-00782-7>
- [15] Fakher, S., Ahdaya, M., Elturki, M., & Imqam, A. (2020). Critical review of asphaltene properties and factors impacting its stability in crude oil. *Journal of Petroleum Exploration and Production Technology*, 10(3), 1183–1200. <https://doi.org/10.1007/s13202-019-00811-5>
- [16] Garreto, M. S. E., Gonzalez, G., Ramos, A. C., Lucas, E. F. (2010). Looking for a Model Solvent to Disperse Asphaltene. *Chemistry & Chemical Technology*, 4 (4), 317–323. <https://doi.org/10.23939/chcht04.04.317>

- [17] Garreto, M. S. E., Mansur, C. R. E., & Lucas, E. F. (2013). A model system to assess the phase behavior of asphaltenes in crude oil. *Fuel*, 113, 318–322. <https://doi.org/10.1016/j.fuel.2013.05.097>
- [18] Golshahi, N., Afra, S., Samouei, H., Nasr-El-Din, H., & Beraldo da Silveira Balestrin, L. (2019). Asphaltene Structural Changes Induced by Carbon Dioxide Injection. *Offshore Technology Conference Brasil*. <https://doi.org/10.4043/29730-MS>
- [19] Groenzin, H., & Mullins, O. C. (2000). Molecular Size and Structure of Asphaltenes from Various Sources. *Energy Fuels*, 14 (3), 677–684. <https://doi.org/10.1021/ef990225z>
- [20] Guerrero-Martin, C. A., Montes-Pinzon, D., Meneses Motta da Silva, M., Montes-Paez, E., Guerrero-Martin, L. E., Salinas-Silva, R., Camacho-Galindo, S., Lucas, E. F., & Szklo, A. (2023). Asphaltene Precipitation/Deposition Estimation and Inhibition through Nanotechnology: A Comprehensive Review. *Energies*, 16 (13), 4859. <https://doi.org/10.3390/en16134859>
- [21] Guerrero-Martin, C. A., Montes-Páez, E., Khalil de Oliveira, M. C., Campos, J., & Lucas, E. F. (2018). Calculating Asphaltene Precipitation Onset Pressure by Using Cardanol as Precipitation Inhibitor: A Strategy to Increment the Oil Well Production. *SPE Trinidad and Tobago Section Energy Resources Conference*. <https://doi.org/10.2118/191275-MS>
- [22] Habibi, A., Yassin, M. R., Dehghanpour, H., & Bryan, D. (2017). Experimental investigation of CO₂-oil interactions in tight rocks: A Montney case study. *Fuel*, 203, 853–867. <https://doi.org/10.1016/j.fuel.2017.04.077>
- [23] Hartmann, D., Lopes, H. E., Teixeira, C. L. S., de Oliveira, M. C. K., Gonzalez, G., Lucas, E. F., & Spinelli, L. S. (2016). Alkanes Induced Asphaltene Precipitation Studies at High Pressure and Temperature in the Presence of Argon. *Energy Fuels*, 30 (5), 3693–3706. <https://doi.org/10.1021/acs.energyfuels.5b02217>
- [24] Hirschberg, A., deJong, L. N. J., Schipper, B. A., & Meijer, J. G. (1984). Influence of Temperature and Pressure on Asphaltene Flocculation. *Society of Petroleum Engineers Journal*, 24 (03), 283–293. <https://doi.org/10.2118/11202-PA>
- [25] Honse, S. O., Ferreira, S. R., Mansur, C. R. E., Lucas, E. F., & González, G. (2012). Separation and characterization of asphaltenic subfractions. *Química Nova*, 35 (10), 1991–1994. <https://www.scielo.br/j/qn/a/jwQb4RPBnDGNbM59FvLMLQx/?lang=en>
- [26] Institute of Petroleum of London. IP 143/01 (2001) standard methods for analysis and testing of petroleum and related products, London.
- [27] ISO 12185 (1996) Crude petroleum and petroleum products -- Determination of density -- Oscillating U-tube method. Geneva: International Organization for Standardization.
- [28] James, L. A., Rezaei, N., & Chatzis, I. (2008). VAPEX, Warm VAPEX and Hybrid VAPEX - The State of Enhanced Oil Recovery for In Situ Heavy Oils in Canada. *Journal of Canadian Petroleum Technology*, 47 (04). <https://doi.org/10.2118/08-04-12-TB>
- [29] Li, L., Sheng, J. J., & Xu, J. (2017). Gas Selection for Huff-n-Puff EOR in Shale Oil Reservoirs Based upon Experimental and Numerical Study. *SPE Unconventional Resources Conference Calgary, Alberta, Canada*. <https://doi.org/10.2118/185066-MS>
- [30] Liu, T., Wei, H., Wang, X., Sun, D., & Ma, Z. (2015). Measurement of Asphaltene Precipitation Onset. *Recent Patents on Mechanical Engineering*, 8 (1), 3–15. <https://www.eurekaselect.com/article/63569>
- [31] Lordeiro, F., Altoé, R., Hartmann, D., Filipe, E., González, G., & Lucas, E. (2021). The Stabilization of Asphaltene in Different Crude Fractions: A Molecular Approach. *Journal of the Brazilian Chemical Society*, 32 (4), 741-756. <https://doi.org/10.21577/0103-5053.20200226>
- [32] Lucas, E. F., Spinelli, L. S., & Khalil, C. N. (2015). Polymers Applications in Petroleum Production. *Encyclopedia of Polymer Science and Technology*, 1-50. <https://doi.org/10.1002/0471440264.pst641>
- [33] Mansur, C. R. E., De Melo, A. R., & Lucas, E. F. (2012). Determination of Asphaltene Particle Size: Influence of Flocculant, Additive, and Temperature. *Energy Fuels*, 26(8), 4988–4994. <https://doi.org/10.1021/ef300365x>

- [34] Maravilha, T. S. L., Middea, A., Spinelli, L. S., & Lucas, E. F. (2021). Reduction of asphaltenes adsorbed on kaolinite by polymers based on cardanol. *Brazilian Journal of Chemical Engineering*, 38(1), 155–163. <https://doi.org/10.1007/s43153-020-00082-2>
- [35] Marín-Velásquez, T. D. (2021). Pronóstico de estabilidad de asfaltenos en petróleo crudo con base en análisis SARA mediante redes neuronales artificiales. *Fuentes, el reventón energético*, 19(2), 19-33. <https://doi.org/10.18273/revfue.v19n2-2021003>
- [36] Mohammadi, M., Akbari, M., Bahramian, A., Naeni, M. S., & Fakhroueian, Z. (2013). Inhibition effect of CO₂ on asphaltene precipitation for an Iranian crude oil and comparison with N₂ and CH₄. *Korean Journal of Chemical Engineering*, 30(2), 429–433. <https://doi.org/10.1007/s11814-012-0144-7>
- [37] Nunes, R., Valle, M., Reis, W., Aversa, T., Filipakis, S., & Lucas, E. (2019). Model Molecules for Evaluating Asphaltene Precipitation Onset of Crude Oils. *Journal of the Brazilian Chemical Society*, 30 (6), 1241-1251. <https://doi.org/10.21577/0103-5053.20190019>
- [38] Oh, K., Ring, T. A., & Deo, M. D. (2004). Asphaltene aggregation in organic solvents. *Journal of Colloid and Interface Science*, 271 (1), 212–219. <https://doi.org/10.1016/j.jcis.2003.09.054>
- [39] Peralta-Martínez, M. V., Vázquez-Ramírez, R., Blass-Amador, G., & Palacios-Lozano, E. M. (2008). Determination of Functional Groups in Mexican Vacuum Residua. *Petroleum Science and Technology*, 26(1), 91–100. <https://doi.org/10.1080/10916460600705816>
- [40] Peralta Sanchez, A. F., Blanco Sanchez, J. D., Reina Gonzalez, J. F., & Mantilla Ramirez, L. E. (2017). Transporte de crudo pesado por oleoducto usando el método de dilución: Un enfoque práctico para modelar la caída de presión y la precipitación de asfaltenos. *Fuentes, el reventón energético*, 15 (2), 7-17. <https://doi.org/10.18273/revfue.v15n2-2017001>
- [41] Rogel, E., Roye, M., Vien, J., & Miao, T. (2015). Characterization of Asphaltene Fractions: Distribution, Chemical Characteristics, and Solubility Behavior. *Energy Fuels*, 29 (4), 2143-2152. <https://doi.org/10.1021/ef5026455>
- [42] Romero, J. F., da Costa, M. F. L., Sampaio, J. P. G., Chacón Valero, A. M., Feitosa, F. X., & de Sant’Ana, H. B. (2021). Experimental phase behavior and solubility parameter for crude oil + methane [T = 311.15–373.15 K] and crude oil + methane + CO₂ mixtures [T = 343.15–383.15 K]. *Fuel*, 288, 119675. <https://doi.org/10.1016/j.fuel.2020.119675>
- [43] Romero, J. F., Feitosa, F. X., Fleming, F. P., & de Sant’Ana, H. B. (2019). Experimental study of the phase behavior of methane and crude oil mixtures. *Fuel*, 255, 115850. <https://doi.org/10.1016/j.fuel.2019.115850>
- [44] Santos, D., Filho, E. B. M., Dourado, R. S., Amaral, M., Filipakis, S., Oliveira, L. M. S. L., Guimarães, R. C. L., Santos, A. F., Borges, G. R., Franceschi, E., & Dariva, C. (2017). Study of Asphaltene Precipitation in Crude Oils at Desalter Conditions by Near-Infrared Spectroscopy. *Energy Fuels*, 31 (5), 5031-5036. <https://doi.org/10.1021/acs.energyfuels.7b00602>
- [45] Silva, D. R., Hartmann, D., Oliveira, M. C. K., & Lucas, E. F. (2022). Avaliação da precipitação de frações polares de petróleo induzida por propano, sob diferentes condições de pressão. *IBP - Rio Oil and Gas Expo and Conference*, 1-13. <https://doi.org/10.48072/2525-7579.rog.2022.448>
- [46] Speight, J. G. (2006). The Chemistry and Technology of Petroleum. (4th ed.). *CRC Press -Taylor & Francis Group*. <https://doi.org/10.1201/9781420008388>
- [47] Ting, P. D., Gonzalez, D. L., Hirasaki, G. J., & Chapman, W. G. (2007). Application of the PC-SAFT Equation of State to Asphaltene Phase Behavior. In: Mullins, O. C., Sheu, E. Y., Hammami, A., & Marshall, A. G. (eds), *Asphaltenes, Heavy Oils, and Petroleumomics*. *New York: Springer*, 301-327. https://doi.org/10.1007/0-387-68903-6_12
- [48] Wang, J., & Buckley, J. S. (2003). Asphaltene Stability in Crude Oil and Aromatic Solvents -The Influence of Oil Composition. *Energy Fuels*, 17 (6), 1445–1451. <https://doi.org/10.1021/ef030030y>