

## Influence of Refinery Asphalt Residue Addition on Flow: A Study Using Waxy Model-System

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One of the main phenomena causing problems in the oil industry is the precipitation of waxes, which can crystallize and form deposits, clogging lines and reducing flows. Many studies have been conducted seeking to overcome this problem, mainly through application of chemical to increase flow. Some studies have shown that the asphaltenes present in crude oil can also be involved in the process of wax deposition. In this study, model systems were investigated to determine the influence of a natural additive, a chemical additive and their combined use on the fluidity of the samples. The natural additive, consisting of a refinery asphalt residue (ASPR), was studied in relation to the influence of its aggregation states on the fluidity of the wax model systems. All samples were evaluated through the pour point test, according to the ASTM D-97 standard. The results indicated that both the ASPR and the commercial poly(ethylene-co-vinyl acetate) can improve the fluidity. Synergistic effect, using both together, was verified by the significant reduction of pour point for model systems with wax content as high as 13% m v<sup>-1</sup>. That action was closely related to the concentration of ASPR and its aggregation state, as indicated by tests with different wax concentrations.

**Keywords:** wax precipitation, pour point depressant, polymer additives, refinery asphalt residue

### Introduction

Although the world is shifting to the use of energy sources other than fossil fuels, mainly due to the problems related to environmental risks, society is still highly dependent on petroleum. Therefore, strong attention is devoted to the technological development of the oil and gas industry, including for exploitation of more complex oil fields and to overcome existing problems related to extraction of hydrocarbons.

The transport of multiphase fluids (water, oil and gas) is a complicated operation that poses various risks to lines and equipment, such as organic and/or inorganic deposits, formation of hydrates, and corrosion, among others.<sup>1</sup> The identification, quantification and mitigation of these risks to guarantee production without interruptions is called flow assurance, which is particularly complicated in offshore

systems.<sup>2,3</sup> The “flow assurance” expression was first used by Petrobras, the Brazilian deep-water pioneer, in the early 1990s.<sup>4,5</sup>

Petroleum is a complex fluid, with wide variation of several aspects, including its composition. One of the components of crude oil that is especially vexing to the oil and gas industry is wax (paraffin), which is a mixture of saturated hydrocarbons with high molar mass that under certain conditions crystallizes, increasing the oil’s viscosity and forming deposits that can require shutdown of production lines for remediation, generating significant losses.<sup>6-10</sup>

Waxes are in the group of saturated hydrocarbons present in crude oil, with the general designation C<sub>n</sub>H<sub>2n+2</sub>, with linear, branched or cyclic chains.<sup>10-12</sup> Temperature variation is the main parameter involved in the formation of wax deposits. The oil from offshore reservoirs usually has initial temperature of 70-120 °C, but during production, the oil flows through undersea pipes in regions where the water temperature is about 4 °C. The large temperature drop can

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cause precipitation of the waxes.<sup>10,13-15</sup> Among the principal factors that affect the deposition of waxes are the quantity and molar mass of the waxes present in the oil, the temperature, and the shear conditions imposed by the flow.<sup>16-18</sup>

The wax appearance temperature (WAT), the gelling temperature (Tgel) and pour point are the main intrinsic properties of petroleum in relation to the solubility of waxes.<sup>17-24</sup>

One of the methods to assure oil flow is to use additives that reduce the pour point and/or inhibit the formation of wax deposits.<sup>25-27</sup> These inhibitors are mostly composed of polymers that have a hydrocarbon part in their chain, enabling interaction with the wax, and a polar part that is responsible for modifying the morphology of the wax crystals that are formed, inhibiting their aggregation.<sup>23,28</sup> Among the polymers typically used for the purpose of reducing the pour point is the poly(ethylene-*co*-vinyl acetate) (EVA), in which ethylene forms the nonpolar chain that interacts with the wax and vinyl acetate (VA) forms the polar part that impedes aggregation.<sup>17,29-34</sup>

However, asphaltenes, also present in crude oil, have the ability to interfere in the wax precipitation process, acting as an inhibitor, although the mechanism of this process is not yet fully understood.<sup>35</sup> Both the inhibitors and asphaltenes have the ability to improve the oil fluidity. Several studies<sup>36-41</sup> have shown that the performance of inhibitors is altered by the presence of asphaltenes. In this respect, researchers have proposed that asphaltenes can modify the morphology of wax crystals.<sup>36-41</sup>

The presence of asphaltenes, even in low concentrations, can cause problems for the petroleum industry, such as by precipitating or affecting the stability of emulsions, making difficult the demulsification process. Moreover, asphaltenes can facilitate or hamper the precipitation of waxes.<sup>35,42-44</sup> Hence, analysis of this fraction has attracted wide attention of researchers, and it has been demonstrated that the solubility of asphaltenes is related not only to the pressure and temperature of the crude oil, but also to the composition of the oil and the number of carbons of the solvent used to deasphalt the oil.<sup>45-47</sup> Some studies have shown the importance of resins in the stabilization of asphaltenes<sup>48-50</sup> while others have indicated the importance of the percentage of aromatics in composition of the crude oil.<sup>34,51</sup> However, it is necessary to better understand the mechanism of this process, along with the influences exerted by components of the medium, ratio of concentrations, and ideal aggregation state of the asphaltenes, among other variables that can affect the process of inhibiting deposition of waxes. Recent studies<sup>35,39,41,52,53</sup> have been focused on the synergistic effect of asphaltenes and wax deposition inhibitors based on polymers, showing that asphaltenes can improve the performance of the additive.

Due to the importance of finding ways to control the formation of wax deposits so as to improve the operational fluidity and thus reduce losses, it is necessary to perform studies to learn how the compounds present in crude oil affect its fluidity. Several studies<sup>37-42,46,49,50</sup> have been published in this respect, and others are in progress, applying different methods of analysis, various forms of inducing aggregation, and different types of samples, among other aspects. Nevertheless, further research is necessary. In particular, as already known, the asphaltic residue from petroleum obtained during the refining process contains a high concentration of asphaltenes. Therefore, it is reasonable to propose that such residue presents strong potential to affect the pour point of crude oil by acting on the waxes. However, to the best of our knowledge, no specific study has been published examining this hypothesis.

Therefore, this work evaluates the influence of individually adding a refinery asphalt residue (ASPR) or polymer based on poly(ethylene-*co*-vinyl acetate) (EVA10) on the flow assurance of a synthetic paraffin system by inducing aggregation of asphaltenes, and the possible synergistic effect of using both additives in combination.

## Experimental

### Materials

Commercial toluene (distilled at 110 °C and dried with alumina),<sup>54</sup> and 99.5% *n*-heptane were supplied by Isofar Ind. Com. Produtos Químicos Ltda, Duque de Caxias, Brazil. Paraffin with melting point in the 53-57 °C range (76.1% *n*-alkanes and 23.9% iso and cycloalkanes)<sup>23</sup> was supplied by Sigma-Aldrich Ltda., Duque de Caxias, Brazil. Poly(ethylene-*co*-vinyl acetate) (EVA HM728) was supplied by Braskem Ltda, Duque de Caxias, Brazil, with vinyl acetate content of 10 mol% and molar masses of  $\bar{M}_n = 48,100 \text{ g mol}^{-1}$  and  $\bar{M}_w = 176,420 \text{ g mol}^{-1}$ ,<sup>23</sup> called EVA10. Finally, the asphalt residue (ASPR) from crude oil refining was supplied by Duque de Caxias Refinery, Duque de Caxias, Brazil.

### Characterization of the asphaltic residue (ASPR)

The ASPR was characterized by: Fourier transform infrared spectroscopy (FTIR), using Nicolet ISO50 FT-IR (Thermo Scientific, Waltham, USA), attenuated total reflection (ATR) in the range of 4000 to 400  $\text{cm}^{-1}$  and 4  $\text{cm}^{-1}$  of resolution, analyzing sample on ATR at room temperature; thermogravimetric analysis, using a Q500, TA Instruments, New Castle, USA, from 30 to

600 °C at 20 °C min<sup>-1</sup>, under N<sub>2</sub>; elemental analysis, using PerkinElmer 2400 CHNS/O Serie II, Waltham, USA, burned at 950 °C and reduction temperature of 500 °C; and microcalorimetry, using a Setaram DSC VII-D3830 Caluire, France, from 80 to -10 °C at 0.48 °C min<sup>-1</sup>.

#### Preparing the model systems

The model systems were prepared with the solvents toluene (solvent for asphaltenes) and *n*-heptane (non-solvent for asphaltenes) in different proportions; wax at concentrations of 5 or 10% m v<sup>-1</sup>; refinery asphalt residue (ASPR) at concentrations of 0.00, 0.10, 0.25, 0.50 or 1.00% m v<sup>-1</sup>; and EVA10 at concentrations of 0 or 0.05% m v<sup>-1</sup>. For the purpose of analyzing the effects of all the contributions, the model systems were composed of: (i) solvent + wax; (ii) solvent + wax + ASPR; (iii) solvent + wax + EVA10; and (iv) solvent + wax + ASPR + EVA10.

For use of ASPR or EVA10, we prepared the respective stock solutions described as follows. The material was dissolved in toluene under magnetic stirring for 90 min at 45 °C. In the cases where ASPR was used, after stirring, the system was submitted to ultrasound treatment (Ecosonics Q 9.5/40) for 30 min.

To prepare the model system, half of the required solvent volume (respecting the toluene/*n*-heptane ratio) was added to the paraffin, previously weighed. The system was submitted to magnetic stirring for 30 min at 45 °C. Then, the additive (ASPR and/or EVA10) was added (or not) along with the rest of the solvent, and the mixture was left under stirring for 60 min at 45 °C.

#### Determination of the asphaltenes precipitation onset

The precipitation onset of the model system of ASPR in toluene was determined by titration with *n*-heptane and monitoring the absorption intensity with a Matrix-F near-infrared (NIR) spectrometer equipped with an external probe system (Bruker, Billerica, USA, with optical path of 5 mm). The probe was first immersed in pure *n*-heptane to obtain the zero calibration. Then, the probe was immersed in the model system, to which *n*-heptane was added at a flow of 1 mL min<sup>-1</sup> with a positive displacement pump (Jasco PU-2087 Plus, Hachioji, Japan). The system was kept under magnetic stirring for the 60 min. The result was a graph of the absorption intensity (at 1600 nm) in function of the volume of *n*-heptane (mL). The start of precipitation was identified by noting the volume *n*-heptane in which the absorption intensity was minimal, and the precipitation onset was expressed in terms of mL of *n*-heptane *per* mL of the model system.

#### Determination of the pour point

The pour point test determines the temperature at which movement of the oil under the effect of gravity no longer occurs, according to the procedure described in ASTM D97.<sup>55</sup>

A glass cuvette was filled with 40 mL of sample and left at rest for at least 24 h, and then was heated up to 45 °C. Four thermostatic baths were used at different temperatures: 24 °C (Thermo Haake C40P bath, Waltham, USA), 0 °C (Thermo Scientific A40 (AC200), Waltham, USA), -18 °C (Julabo 900F, Seelbach, Germany), and -33 °C (Julabo F81HL, Seelbach, Germany). The cuvette was placed into the bath at 24 °C and the temperature was read using a thermometer inside the sample. For every 3 °C decrease in temperature, the sample was tilted to observe its flow. The cuvette was sequentially changed to the other bath when the sample temperature achieved the bath temperature. The pour point was defined as the temperature at which the sample stopped flowing plus 3 °C. For the samples that remained fluid at -24 °C, the pour point is reported as < -24 °C. The maximum standard deviation of the measurements was ± 1.5 °C.

## Results and Discussion

#### Characterization of the asphaltic residue (ASPR)

The ASPR was characterized by: Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TGA), elemental analysis (CHNSO), X-ray fluorescence, and microcalorimetry. The FTIR spectrum exhibited bands related to CH<sub>2</sub> and CH<sub>3</sub> groups (2917-2849, 1459 and 1375 cm<sup>-1</sup>), C-H bond at 1028 cm<sup>-1</sup>, aromatic C=C at 1595 cm<sup>-1</sup>, aromatic C-H below 1000 cm<sup>-1</sup>, and C<sub>2</sub>S=O at 1028 cm<sup>-1</sup>. The spectrum is very similar to that observed for the asphaltenes C7I,<sup>56</sup> excepting by the band intensities. The thermogravimetric analysis recorded only one degradation step with the maximum mass loss at ca. 470 °C and 18% of ash content. The elemental composition (C = 85% m m<sup>-1</sup>, H = 10% m m<sup>-1</sup>, N = 0.6% m m<sup>-1</sup>, and S = 5.4% m m<sup>-1</sup>) of the ASPR could evidence the presence of the sulfur in the molecular structures. No exothermic peak was detected by microcalorimetry, evidencing the absence of high molar masses waxes in the ASPR, or their amount is not significant.

#### Aggregation of the asphaltic material in function of adding *n*-heptane

The pour point analysis was conducted to assess the impacts on the fluidity of the wax model systems. For

this purpose, we analyzed the effects of aggregation of the asphaltic material when using different proportions of toluene/*n*-heptane, along with the action of the additive EVA10 and the possible existence of a synergistic effect between the asphaltic material and EVA10 on the fluidity of the samples.

We first determined the asphaltene precipitation onset of the model systems (ASPR in toluene), to ascertain the influence of the solvent on the asphaltene aggregation state. Then, we conducted pour point tests to evaluate the influence on the samples' fluidity.

The aggregation behavior of the asphaltic material was evaluated by determining the asphaltene precipitation onset by titration of the system with *n*-heptane and monitoring the intensity of absorption by near-infrared spectrometry (NIR).<sup>57</sup> The greater the stability of the asphaltenes in the medium, the higher will be the volume of *n*-heptane necessary to cause precipitation.<sup>35</sup> We analyzed the ASPR in toluene model systems at concentrations of 2 and 5%  $m\ v^{-1}$ . The results are presented in Figures 1a and 1b, respectively.

The curves had the expected behavior, i.e., lower absorption intensity as the sample was diluted with higher concentrations of *n*-heptane. When this addition of *n*-heptane reaches a certain level, the asphaltenes in the toluene/heptane mixture start to precipitate, forming molecular aggregates, which tend to increase the absorption. By this method of analysis, the asphaltenes precipitation onset is expressed as the volume of *n*-heptane corresponding to the minimum absorption intensity, and is expressed as mL of *n*-heptane *per* 1 mL of the system in question. Since we used 10 mL of sample, we divided the volume of *n*-heptane by 10 to calculate the asphaltene precipitation onset. These onset values in the model systems with 2%  $m\ v^{-1}$  ASPR (Figure 1a) and 5%  $m\ v^{-1}$  ASPR (Figure 1b) were 2.6 and 2.8 mL of *n*-heptane *per* mL of sample, respectively. These asphaltene precipitation onset

values are considered relatively high, indicating the good stability of the asphaltenes in the asphalt residue dispersed in toluene. Furthermore, these values were very near each other, indicating that the concentration of asphaltic material, within the range studied, did not exert a significant influence on the precipitation onset, which is dictated by the solubility parameter of the medium that induces the precipitation of the more unstable molecules in the system gradually with the reduction of the solubility parameter.

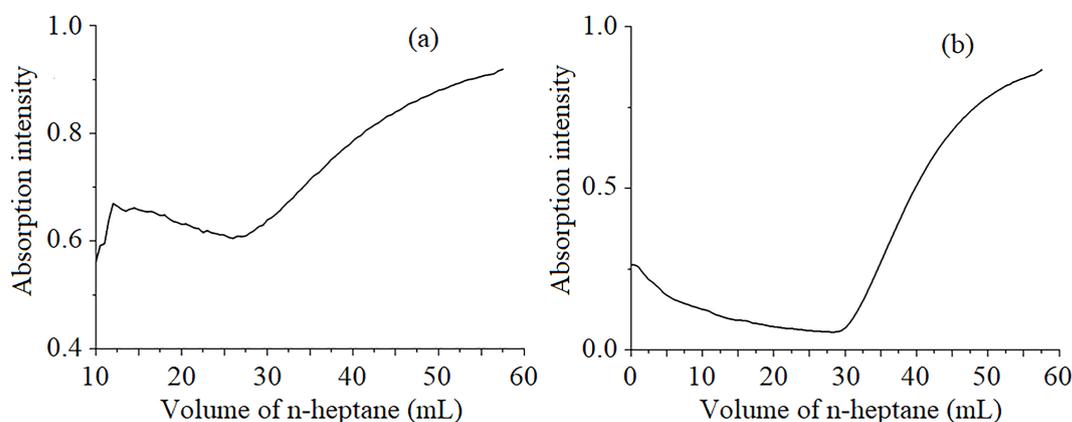
These asphaltene precipitation onset values of the ASPR in toluene model systems at 2 and 5%  $m\ v^{-1}$  correspond, respectively, to toluene/heptane ratios of 28/72 v/v and 26/74 v/v. Beyond these point, higher proportions of *n*-heptane provoke greater aggregation state of the asphaltenes.

#### Evaluation of the behavior of the model systems by pour point measurements

In this section we evaluate the influence of each component of the model systems on the pour point of the samples. For this purpose, all the samples were prepared following the same protocol and the results are subdivided into: (i) model systems in pure toluene; and (ii) model systems in mixtures of toluene/*n*-heptane.

#### Model systems in pure toluene

To evaluate the influence on a model system prepared only using toluene as the solvent, we analyzed the pour point of samples containing: (i) toluene + wax; (ii) toluene + wax + ASPR; (iii) toluene + wax + EVA10; and (iv) toluene + wax + ASPR + EVA10, with varying concentrations of wax and ASPR. The respective concentrations (%  $m\ v^{-1}$ ) along with the pour point values are presented in Table 1. The results are discussed



**Figure 1.** Curves of adsorption intensity in function of volume of *n*-heptane using 10 mL of the ASPR in toluene model systems prepared with: (a) 2%  $m\ v^{-1}$  ASPR and (b) 5%  $m\ v^{-1}$  ASPR.

separately in terms of variation of the pour point in function of the concentrations of wax and ASPR and the joint action of ASPR and EVA10. The concentrations of ASPR and EVA10 are expressed in relation to the volumes of the model system.

**Table 1.** Pour point of (i) toluene + wax, (ii) toluene + wax + ASPR, (iii) toluene + wax + EVA10 and (iv) toluene + wax + ASPR + EVA10 systems

EVA10 concentration / (% m v <sup>-1</sup> )	ASPR concentration / (% m v <sup>-1</sup> )	Pour point (± 1.5) / °C		
		Wax concentration / (% m v <sup>-1</sup> )		
		5	10	13
0.00	0.00	6	21	18
	0.10	–	< –24	6
	0.25	< –24	< –24	3
	0.50	< –24	9	15
	1.00	< –24	12	18
0.05	0.00	< –24	–3	3
				< –24 <sup>a</sup>
	0.10	–	–	–21 <sup>b</sup> –9 <sup>c</sup>

Since the limit of the measurement system is –24 °C, the pour point of all the samples that did not stop flowing at this temperature are indicated as < –24 °C. <sup>a</sup>System prepared by first adding the EVA10 to the wax followed by homogenization of the ASPR; <sup>b</sup>system prepared by first adding the ASPR to the wax followed by homogenization of the EVA10; <sup>c</sup>system prepared by first adding the EVA 10 to the ASPR followed by homogenization of the wax. EVA10: poly(ethylene-co-vinyl acetate) with 10 mol% vinyl acetate; ASPR: asphaltic residue from refinery.

#### Influence of wax concentration

Initial analysis of the systems without the addition of ASPR or EVA10 for the three wax concentrations showed that, as reported in the literature,<sup>23</sup> the increase of the wax content resulted in an increase of the pour point. The increase of the wax concentration from 5 to 10% m v<sup>-1</sup> caused an increase of 15 °C in the pour point. However, the increase beyond that concentration did not cause a significant difference in the system's pour point, as can be noted in the result of the concentration of 13% m v<sup>-1</sup> wax, which was within the experimental error range in comparison with the pour point at 10% m v<sup>-1</sup> wax.

#### Influence of the ASPR concentration

With regard to the influence of adding ASPR on the fluidity of the system, in general, this caused a reduction of the pour point. However, this influence was dependent both on the wax concentration and ASPR concentration: within the concentration ranges studied (5 to 13% m v<sup>-1</sup> wax and 0.10 to 1.00% m v<sup>-1</sup> ASPR), the fluidity of the system was greater for lower concentrations both of wax and ASPR.

The influence of the wax concentrations on the pour point was confirmed with the addition of ASPR, since

for any ASPR concentration analyzed, the pour point increased with rising wax concentrations. This influence existed even for the ASPR concentration of 0.25% m v<sup>-1</sup>, because although the systems containing 5 and 10% m v<sup>-1</sup> wax presented pour point values < –24 °C, the system with 5% m v<sup>-1</sup> wax reached –24 °C still highly fluid, i.e., far from a temperature at which it would stop flowing, while the system at 10% m v<sup>-1</sup> wax reached –24 °C almost completely solid.

At 5% m v<sup>-1</sup> wax, the pure model system already had a relatively low pour point (6 °C), and all the ASPR concentrations significantly reduced the pour point. In other words, at < –24 °C it was not possible to observe the influence of the ASPR concentration on reducing the pour point. At 10% m v<sup>-1</sup> wax, the effect of the ASPR concentration was more pronounced: the systems containing 0.10 and 0.25% m v<sup>-1</sup> ASPR underwent a very significant reduction of the pour point, from 21 °C to < –24 °C, while the systems containing 0.50 and 1.00% m v<sup>-1</sup> underwent less pronounced pour point reductions, from 21 °C to ca. 12 °C (the differences for 9 and 12 °C were within the error range of the analysis). It is curious to note that, although the pour point values of the pure waxy model systems could be considered similar at 10 and 13% m v<sup>-1</sup> wax, the addition of ASPR maintained its effect on lowering the pour point for the system containing 13% m v<sup>-1</sup> wax, although the reduction was smaller (from 18 °C to 6 and 3 °C, respectively, for the ASPR concentrations of 0.10 and 0.25% m v<sup>-1</sup>, within the experimental error interval). That reduction was only observed for the lower ASPR concentrations, since at 0.50 and 1.00% m v<sup>-1</sup> there was no variation of the pour point of the system containing 13% m v<sup>-1</sup> wax.

High concentrations of asphaltenes in the system result in a tendency to worsen fluidity because of the presence of heavier elements. Therefore, the ASPR concentrations of 0.50 and 1.00% m v<sup>-1</sup> already were large enough to explain the higher pour points observed. According to Lei *et al.*<sup>58</sup> a relationship exists between the concentration of asphaltenes (which is related to their aggregation state) and the solubility of wax in crude oil in a temperature range from 40 °C (wax appearance temperature of petroleum) to 35 °C, in which they suggested the existence of a critical asphaltene concentration, below which the quantity of wax dissolved at each temperature increases with rising concentration of asphaltenes. However, above this critical point, the quantity of wax dissolved at each temperature diminishes with rising concentration of asphaltenes. In other words, above a critical asphaltene concentration, the wax becomes increasingly less soluble in the medium with increasing concentration of asphaltenes. Based on

this information, we believe that 0.50% m v<sup>-1</sup> ASPR was above the critical concentration, since the system's fluidity worsened in comparison with lower ASPR concentrations.

#### Influence of adding EVA10

In relation to the influence of the additive EVA10, the same trend was observed as for the addition of ASPR with respect to the influence of wax concentrations on the model system. The additive diminished the pour point of the samples in all the wax concentration ranges studied, but this reduction gradually waned with increasing wax content, as expected.<sup>23</sup>

#### Joint influence of ASPR and EVA10

To ascertain the possible synergistic effect of adding ASPR and EVA10 together, we selected the most critical wax concentration in relation to the fluidity of the system (13% m v<sup>-1</sup>), the lowest ASPR concentration studied at which we observed a significant reduction of the pour point (0.10% m v<sup>-1</sup>), and the concentration of EVA10 of 0.05% m v<sup>-1</sup>, which also caused a reduction of the pour point. Furthermore, to analyze the possible influence of the order of including the additives in the system, we used samples prepared in three different ways: (a) addition of EVA10 in wax and toluene followed by 30 min of homogenization at 45 °C and subsequent addition of ASPR with 1 more hour of homogenization at 45 °C; (b) addition of ASPR in wax and toluene followed by 30 min of homogenization at 45 °C and subsequent addition of EVA10 with 1 more hour of homogenization at 45 °C; and (c) addition of ASPR and EVA10 in toluene followed by 30 min of homogenization at 45 °C and subsequent addition of wax with 1 more hour of homogenization at 45 °C.

Independently of the method of preparation, there was synergy between the two additives, since all the pour point values obtained (< -24/-21/-9 °C) were lower than those observed when using each component separately at any of the ASPR concentrations studied.

With regard to the differences caused by the distinct order of adding each component, this had a significant influence on the fluidity of the system. In other words, the efficiency of each additive in reducing the pour point differed in function of the addition order. For the systems in which the EVA10 or ASPR was added separately to the wax in toluene (systems a and b), the pour point values were lowest (respectively < -24 and -21 °C), i.e., greater efficiency for these preparation methods. In turn, the preparation with joint addition of EVA10 and ASPR, although causing a good reduction of the pour point (from 18 to -9 °C), had the worst performance in comparison with the other two systems, where the additives were added individually.

The analyses carried out so far evidence that EVA and asphaltic materials act on the crystallization phases of the waxes by influencing the process of growth of aggregates. In the case of this study, we can suggest that the large performance difference observed for the sample in which ASPR and EVA10 were added together might have been a consequence of interactions between these two species, since both have polar groups able to interact with each other, making them less available to interact with the wax.

#### Model systems in mixtures of toluene/*n*-heptane

To evaluate the influence of the aggregation state of the asphaltenes on the pour point, we performed tests with the wax and ASPR dispersed in different toluene/*n*-heptane ratios, since heptane worsens the solubility of ASPR by inducing its aggregation. For this investigation, we used higher ASPR concentrations (0.50 and 1.00% m v<sup>-1</sup>), where they should have presented some degree of aggregation, and as discussed previously, had a lesser influence on the pour point, to ascertain a possible relationship between the worse fluidity and an increase of the aggregation state of the asphaltenes in the ASPR. The volume/volume ratios of toluene/*n*-heptane (T/H v/v) used and the pour points of the samples are reported in Table 2. For the purpose of comparison, the pour point values of the different wax concentrations in pure toluene and in the different concentrations of ASPR (presented in Table 1 and already discussed) are repeated in Table 2.

Influence of varying the composition of the toluene/*n*-heptane solvent system, without addition of ASPR, on the pour point

We performed a blank test, consisting of samples with wax in the mixtures of solvents without the presence of ASPR, where we observed that the toluene/*n*-heptane mixtures had little influence on the reduction of the pour point. The addition of *n*-heptane resulted in a lower pour point, which varied in function of the wax concentration in the system. However, in the system with 100% *n*-heptane, the pour point started increasing again, reaching values similar to those observed for the system with 100% toluene. This behavior, where the pour point was unchanged in the pure solvents toluene and *n*-heptane, is in line with the result reported by Alves *et al.*<sup>59</sup> but has not yet been systematically investigated. Another aspect to consider is that the influence caused by adding *n*-heptane also varied with the wax concentration, i.e., for a wax content of 5% m v<sup>-1</sup>, the decrease in fluidity was greater than for the system with wax concentration of 10% m v<sup>-1</sup>, which in turn was greater than for the system containing 13% m v<sup>-1</sup> wax,

**Table 2.** Pour point of toluene/*n*-heptane + wax and toluene/*n*-heptane + wax + ASPR systems with varied concentrations

ASPR / (% m v <sup>-1</sup> )	0.0			0.5			1.0		
	5	10	13	5	10	13	5	10	13
Wax / (% m v <sup>-1</sup> )	Pour point (± 1.5) / °C								
Toluene/ <i>n</i> -heptane (v/v)									
100/0	6	21	18	< -24	9	15	< -24	12	18
95/5	–	15	–	< -24	15	–	–	–	–
90/10	3	15	–	< -24	12	–	–	–	–
85/15	–	15	–	–	12	–	–	–	–
80/20	3	12	18	–	12	15	–	-9	6
75/25	–	12	18	–	9	–	–	< -24	3
70/30	-6	12	15	< -24	< -24	-9	–	< -24	-21
60/40	–	–	18	–	–	< -24	–	–	< -24
50/50	–	–	–	< -24	–	–	–	–	–
40/60	–	15	–	–	< -24	–	–	–	–
30/70	–	15	–	< -24	< -24	–	–	< -24	–
20/80	–	15	–	–	< -24	–	–	–	–
10/90	–	18	–	–	< -24	–	–	–	–
0/100	9	21	21	–	< -24	-6	–	< -24	–

Since the limit of measurement was -24 °C, all the samples that did not stop flowing at this temperature are classified as having pour point of < -24 °C. ASPR: asphaltic residue from refinery.

where the differences observed were almost all within the analytical error range.

**Influence of varying the composition of the toluene/*n*-heptane solvent system, with addition of ASPR, on the pour point**

By analyzing a system containing ASPR with varying toluene/*n*-heptane ratios, we expected the aggregation state of the asphaltenes to increase with rising content of *n*-heptane as of a determined composition of the mixture of solvents. As observed in Figure 1, for an ASPR concentration of 2% m v<sup>-1</sup>, the asphaltene precipitation onset happened with a toluene/*n*-heptane ratio of 28/72 v/v.

Analysis of the systems in the presence of ASPR (at 0.5 and 1.0% m v<sup>-1</sup>) showed that the addition of *n*-heptane led to a reduction of the pour point for all the wax concentrations, i.e., the increased aggregation of the ASPR resulted in better fluidity of the system. Therefore, the worse fluidity of the system with increasing ASPR concentration, observed previously, was not related to the aggregation state of the ASPR, but rather to the effect of increasing its concentration in the system, since ASPR is a heavy component and tends to worsen the fluidity. In the case of the system containing wax and ASPR, the action of the ASPR to minimize the wax agglomeration was offset by reduction of fluidity with increased ASPR concentration.

We also observed the existence of a critical aggregation state, where the reduction of the pour point was very pronounced, leading to the minimum value detected for

the system (-24 °C), as of which the pour point values remained low. This behavior occurred for both ASPR concentrations used (0.5 and 1.0% m v<sup>-1</sup>) but was only perceptible for the highest wax concentrations (10 and 13% m v<sup>-1</sup>). For the samples with ASPR content of 0.50% m v<sup>-1</sup>, this critical point was between the ratios of 75/25 and 70/30 for 10% m v<sup>-1</sup> wax, and between 70/30 and 60/40 for 13% m v<sup>-1</sup> wax. For the highest wax concentration, the critical point occurred at an *n*-heptane concentration higher than that at 10% m v<sup>-1</sup> wax. It appeared that a higher wax content requires a greater aggregation of the asphaltenes. This same behavior happened for the system containing 1.0% m v<sup>-1</sup> ASPR, i.e., the highest wax concentration required a higher content of *n*-heptane in the mixture, inducing greater aggregation of the asphaltenes. Nevertheless, for the samples with 1.00% m v<sup>-1</sup> ASPR, this critical point occurred with lower *n*-heptane contents: between 80/20 and 75/25 for 10% m v<sup>-1</sup> wax and between 75/25 and 70/30 for 13% m v<sup>-1</sup> wax. Therefore, a higher wax concentration for the same ASPR concentration (0.50 or 1.00% m v<sup>-1</sup>) was associated with a higher ASPR aggregation state required to reach this critical point, i.e., a greater *n*-heptane content in the system. Furthermore, higher ASPR concentrations for the same wax concentration (10 or 13% m v<sup>-1</sup>) were associated with a lower *n*-heptane content required to reach the critical point, since the increase of the ASPR concentration in the medium already induced greater aggregation.

Considering the toluene/*n*-heptane ratio (28/72 v/v) at which the start of asphaltene precipitation was detected, or at which the aggregates formed were large enough to cause a variation in the absorption intensity in the titration test with *n*-heptane, we observed that the critical points possibly occurred with asphaltene particles much larger than detected in the asphaltene precipitation onset test.

Overall, this study showed that the behavior of the asphaltenes extracted from crude oil,<sup>35</sup> in the sense of reducing the pour point in function of the aggregation state, can also be achieved by using ASPR, which is a residue obtained from the oil refining process and does not require additional treatment. Moreover, it is more stable in the oil than the asphaltene fractions. This recent research is a new contribution to the collection of information that already exists in the literature.<sup>60</sup>

## Conclusions

The wax content was one of the main determinants of the fluidity of the systems studied here, i.e., greater wax concentrations were associated with higher pour points, besides significantly affecting the performance of the additives tested in this work.

The asphalt residue from oil refining (ASPR), in its dispersed state, even at low concentrations, caused a significant reduction of the pour point of the wax model system, and this reduction tended to increase with rising ASPR concentration, until reaching an optimal concentration, as observed for the synthetic chemical additives. At the lowest ASPR concentration (0.1% m v<sup>-1</sup>), the pour point diminished substantially, with a large improvement with a slight increase of the concentration to 0.25% m v<sup>-1</sup>, followed by a waning reduction of the pour point when further increasing the ASPR concentration to 0.5 and 1.0% m v<sup>-1</sup>. However, it is important to stress that the reduced efficiency of the ASPR at higher concentrations only occurred with respect to the lowest concentrations, since at all the concentrations studied, the pour point of the wax model system with the presence of ASPR was lower than that in the pure system.

The addition of aggregated ASPR in the wax model system increased its efficiency in reducing the pour point in relation to the ASPR in the dispersed state. The performance improved with increasing aggregation state up to a determined limit, and this limit after which no further gain was observed in reducing the pour point, was also strongly influenced by the wax content in the model system. By adjusting the aggregation state of the ASPR, it was possible to significantly lower the fluidity of the wax model system containing paraffin content as high

as 13% m v<sup>-1</sup>, which was not attained with the use of the commercial chemical additives.

Besides this, there was a synergistic effect from the joint use of poly(ethylene-co-vinyl acetate) (10 mol% in vinyl acetate) (EVA 10) and ASPR in the dispersed state, at low concentrations of both components, an effect that has promising industrial applications. The effect of this combined use was affected by the method of adding each component to the model system: the addition of one of the components to the solubilized wax with subsequent addition of the other component caused a greater reduction in the pour point (from 18 to about -20 °C) than adding the EVA/ASPR pair to the solubilized wax (from 18 to -9 °C), in a model system containing relatively high wax concentration (13% m v<sup>-1</sup>). In both cases, there is a gain in the system fluidity using a waste from refinery.

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