

Research Article

An Enhanced-Solvent Deasphalting Process: Effect of Inclusion of SiO₂ Nanoparticles in the Quality of Deasphalted Oil

Juan D. Guzmán, Camilo A. Franco, and Farid B. Cortés

Grupo de Investigación en Fenómenos de Superficie, Michael Polanyi, Departamento de Procesos y Energía, Facultad de Minas, Universidad Nacional de Colombia, Sede Medellín, Medellín, Colombia

Correspondence should be addressed to Camilo A. Franco; cafrancoar@unal.edu.co and Farid B. Cortés; fbcortes@unal.edu.co

Received 17 January 2017; Revised 9 February 2017; Accepted 12 February 2017; Published 8 March 2017

Academic Editor: Victor M. Castaño

Copyright © 2017 Juan D. Guzmán et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this work, the effect of nanoparticles in deasphalting heavy oil and extra-heavy oil process at laboratory-scale based on the conventional solvent deasphalting process was studied and named enhanced-solvent deasphalting (*e*-SDA) process. This work evaluated the effect of the nanoparticles of SiO₂ in the separation efficiency based on deasphalted oil (DAO) fraction quality compared to the conventional process of deasphalting (SDA). Different effects have been assessed such as solvent to oil ratio, operating temperatures, type of solvent, and SiO₂ nanoparticles dosage. The DAO quality was based on the asphaltene and sulfur contents, API gravity, distillable fraction, and rheological properties. The improvement of the process from the use of nanoparticles was confirmed with important reductions in the asphaltene and sulfur contents in the DAO of up to 24% and 23%, respectively, in comparison with the SDA process. Also, the API gravity can be increased by approximately 14% with the *e*-SDA process. The rheological properties of the DAO were improved by the inclusion of nanoparticles showing reductions in the viscosities of the DAO greater than 50% in comparison with the conventional process. These results lead to the conclusion that the *e*-SDA process improves the DAO quality when compared with the typical deasphalting process.

1. Introduction

Growth in global energy demand of approximately 50% is expected by the year 2040, reaching approximately 400 millions of barrels of oil equivalent per day (mboe/d) [1]. Because of this growth, nonconventional sources of hydrocarbons, such as heavy oil (HO) and extra-heavy oil (EHO), with nearly 70% of world oil reserves [2], of which EHO reserves correspond to 32% of the global oil reserves [3], have much potential.

HO and EHO are characterized by high specific gravities and high viscosities [4]. According to the American Petroleum Institute (API) gravity, HO is defined by having an API gravity between 10° and 22.3° [4]. EHO has an API gravity less than 10° and a viscosity at reservoir conditions higher than 10000 cP [4–6]. HO and EHO reservoirs are widely distributed throughout the world in countries such as Venezuela, Canada, and Colombia [5, 7–9], imposing several technological challenges in their production, transportation, and refining in these countries [4, 10, 11]. One of the main

characteristics of HO and EHO is the high concentration of high molecular weight asphaltenes that are complex and highly polar compounds with large amounts of heteroatoms containing O, N, and S, as well as metals such as Ni, Fe, and V [12–15]. These heteroatoms and their location in the asphaltene structure cause these molecules to be the most polar constituents in crude oil, leading to their self-association and formation of large asphaltic flocs [16, 17]. For example, for HO and EHO, in which asphaltenes are in high concentrations [18, 19], the viscosity increases due to the significant influence of these molecules on the rheology resulting from the formation of a viscoelastic network [20–23]. Also, high concentrations of asphaltenes in HO and EHO that contain elevated concentrations of sulfur with strong C-S and C=S bonds drastically increase the viscosity [24, 25].

Technologies for viscosity reduction and/or upgrading of HO and EHO have been classified as *in situ* [26–37] and *on-site* [38–52] which are mainly focused on subsurface and surface processes, respectively. *In situ* upgrading techniques

such as in situ combustion (ISC) [26–28], thermal cracking, and its catalytic variations [33–37], as well as all technologies assisted by nanocatalysts [29–32], are technologies that operate at high temperatures and require considerable amounts of fuel and/or steam/gases, thereby limiting their utilization [53–55]. Other thermal methods commonly used for viscosity reduction (but without an upgrading process) are based on the fluids injected into the reservoir such as the steam-assisted gravity drainage (SAGD) process [56, 57], hot water flooding, and continuous or cyclic (*huff-n-puff*) steam injection [53, 55, 58, 59]. However, in these processes, the crude oil returns to its original viscosity when the temperature of the crude oil decreases [60, 61]. Other nonthermal techniques for viscosity reduction have been used in reservoirs including injection of diluents (naphtha and light crude oils) [62–64] and CO₂ injection in enhanced oil recovery (EOR) processes [65–67], among others. Nevertheless, these techniques could initiate the destabilization of the asphaltenes, which in some cases leads to formation damage due to their precipitation/deposition in the pore throats, reducing porosity and permeability and affecting reservoir wettability [17, 67–69]. Also, these techniques for the reduction of HO and EHO viscosities require continuous injections into the reservoir making this an expensive process due to the use of large volumes of diluents.

Because of these adverse factors, technologies that could be applied at the wellhead would be an efficient alternative to the current technologies. Several techniques have been used for HO and EHO viscosity reduction at the surface, such as dilution with solvents and light hydrocarbons [39, 40] or solvent de-asphalting (SDA) [5]. SDA is one of these technologies which is often used by the oil and gas industry for *on-site* upgrading. It is considered to be a viable option because operating costs can be reduced by the recovering and recycling of the solvents [70]. SDA is an economical process to remove concentrated asphaltene or pitch, the dirtiest part of HO and EHO [70], and has been widely studied since the first attempts to separate or distilling oils in the 1920s [71, 72]. Since then, many efforts have been made to understand this process, the effect of the variables present involved, and how to improve it [73–77]. SDA is a physical process in which there is a separation of two phases, the deasphalted oil (DAO) and the residue or pitch [70]. The DAO is removed from the HO or EHO by solvent extraction using paraffinic hydrocarbons in which there is no chemical reaction between the crude oil feed and the paraffinic solvent [70, 78–82]. Researchers have evaluated the effects of the chemical nature of the solvent [70, 78–89], temperature [82, 90, 91], operating pressure [83–85, 90, 92, 93], and solvent to oil ratio [77, 79, 81, 94–96] on the yield of DAO and/or pitch, as well as the DAO quality in some studies. Improvements of the SDA through the addition of macro- and microadsorbent materials have been reported in the literature, showing improvements in the DAO yield and quality [97, 98]. In some patents, the use of microscale solids such as clay, silica, alumina, and zeolite materials have been reported, reaching a higher quality of the DAO [99, 100]. Regarding Si-based materials, Ikematsu et al. [101] proposed an improved SDA process by using SiO₂ microparticles. The authors proposed the use of amorphous

SiO₂ with a preferable particle size between 0.5 and 1.0 μm and surface area of 100–800 m²/g [101].

Nevertheless, there have not yet been studies reported in the scientific literature about the role of nanoparticles (NPs) and their impact on the separation efficiency of the SDA process. These nanomaterials may offer special advantages for the SDA process due to their high surface area to volume ratio and hence a large number of available active sites, making them capable of selectively adsorbing asphaltenes onto their surfaces and enhancing the removal of the asphaltenes [31, 102–108]. In previous studies [107, 109] our research group has found that silica nanoparticles have a high affinity for asphaltene molecules, which could impact the efficiency directly of the SDA process. Franco et al. [107] showed that silica-based nanoparticles adsorbed up to 5.5 mg/m² of asphaltenes in comparison with microparticulate silica. Therefore, this study focused on evaluating the effects of adding nanoparticles to a typical SDA process with the purpose of enhancing the quality of the DAO and optimizing this procedure using nanotechnology in process of designated enhanced-solvent deasphalting (*e*-SDA). Lee et al. [70] provided a typical SDA process scheme that includes a solvent extractor, DAO/solvent separator, and pitch stripper. The SDA process involves injecting an alkane into the crude oil to disrupt and to disperse its components causing the polar components to precipitate [5]. The present paper is the first step for proposing the *e*-SDA technology shown in Figure 1. The experimental tests carried out at the laboratory-scale lead to the proposed *e*-SDA process to include the cyclic addition and recuperation of nanoparticles and the catalytic conversion of the pitch for energy production. The *e*-SDA process produces a DAO having enhanced quality and CO₂ that could be used in the EOR process [65, 66].

In this study, laboratory-scale experimentation was made where the DAO and pitch yields are presented while focusing on the DAO quality by evaluating its asphaltene and sulfur contents, API gravity, distillable fraction, and rheological properties. The rheological properties were described using a power law model commonly employed for this type of fluid.

2. Material and Methods

2.1. Materials and Chemicals. A Colombian extra-heavy crude oil obtained from a reservoir located in the Department of Meta in Colombia's central region was used in these experiments. This EHO of 6.4°API had a content of asphaltenes and sulfur of 20.3 and 4.5 wt%, respectively. Its distillable fraction was approximately of 56% until 750°C. Two different paraffinic solvents were used in the deasphalting process: *n*-heptane (99%, Sigma-Aldrich, St. Louis, MO) and *n*-pentane (99%, Panreac, Barcelona, Spain). In this sense, the commercial fumed silica (SiO₂) nanoparticles (mean particle size of 7 nm and a surface area “S_{BET}” of 389 m²/g) that were used to enhance the SDA process were obtained from Sigma-Aldrich (St. Louis, USA).

2.2. DAO Separation and Characterization. The experimental procedure begins with the addition of the paraffinic solvents to the oil at a defined solvent to oil mass ratio (SOR) for

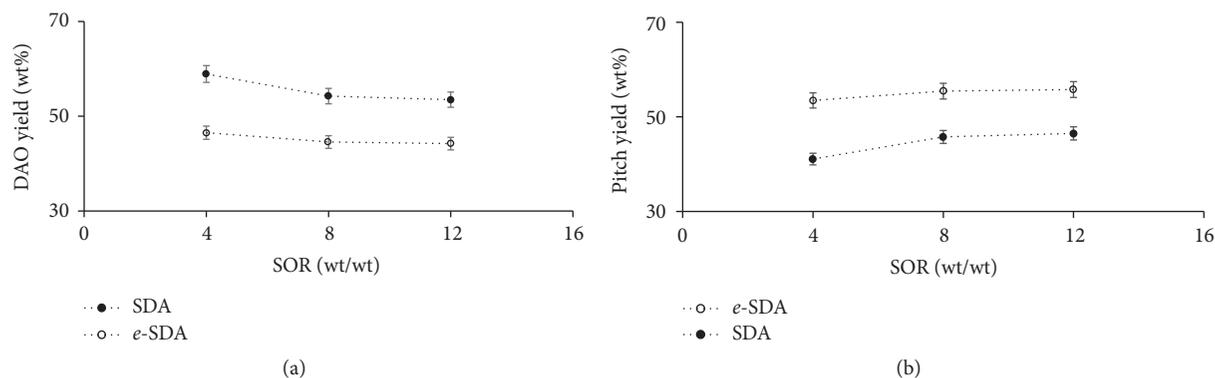


FIGURE 2: Effect of the solvent to oil ratio in (a) DAO and (b) pitch yields for the SDA and *e*-SDA processes using SiO₂ nanoparticles at a dosage of 5 wt% at 25°C and using *n*-heptane as the solvent.

be noticed that when n is equal to 1 (a Newtonian fluid), this parameter has units of cP and can be interpreted as the fluid viscosity independent of shear rate. For determining the goodness of fit of the employed model, the nonlinear chi-square (χ^2) analysis and root-mean-square error (RMSE%) were used [115].

4. Results

4.1. Solvent to Oil Ratio Effects. In this section, the results of solvent to oil ratio (SOR) effect on the DAO yield and the quality of SDA and *e*-SDA processes are presented. Figure 2 shows the DAO and pitch yields for both processes using *n*-heptane at a nanoparticles dosage of 5 wt% and a fixed temperature of 25°C. Increasing the SOR reduces the DAO yield (Figure 2(a)) and consequently increases the pitch yield (Figure 2(b)). These results are in agreement with those reported by several authors [77, 79, 81, 94–96] in which this behavior is explained by the solvating power of solvent [81]. To further understand this phenomenon, it is necessary to consider resins in addition to asphaltenes that are responsible for considerable changes in the solvent power [81]. As the SOR increases, more resins are solubilized by the solvent and these are unable to act as peptizing (or interfacial) agents of asphaltenes [116–119] leading to their aggregation and precipitation [81, 116–119]. Hence, as the SOR increased, the pitch yield increased while the DAO yield decreased proportionally [79, 82].

On the other hand, the *e*-SDA process using SiO₂ nanoparticles has considerable effects on the DAO and pitch yields compared with the SDA process. It is worth mentioning that the silica nanoparticles selectivity to asphaltenes due to the presence of acid centers such as hydroxyl silanol (Si-OH) on their surface [119–121] and their interaction with the polar groups of asphaltenes are expected. Also, the DAO yields in the *e*-SDA process are lower in comparison with traditional SDA, and consequently the pitch yields are larger in the *e*-SDA process (Figure 2(b)). This increase of pitch can be explained by the adsorption phenomena between the silica nanoparticles and asphaltenes that has been widely studied and is determined by the affinity between adsorbent (SiO₂ nanoparticles) and adsorbate (asphaltenes), the asphaltene

self-association over the surface of the nanoparticles, and their maximum adsorption capacity [122]. Franco et al. [107] studied asphaltene adsorption in different nanoparticles and found that the process strongly depends on of the surface structure and chemistry of the nanomaterial. In this way, SiO₂ nanoparticles added to the deasphalting process adsorb asphaltenes on their surface and enhance their precipitation and separation from the crude oil matrix. However, the trend obtained by DAO and pitch yields over the wide range of SOR evaluated can be considered constant, as seen in Figure 2(a), indicating that the amount of solvent needed for the de-asphalting process can be reduced significantly by the addition of nanoparticles. Additionally, it has been demonstrated that nanoparticles impact the viscosity of oil by altering the aggregation system of asphaltenes [123, 124]. This may modify the efficiency of the deasphalting process by lowering the system viscosity, reducing the mass-transfer resistance between fractions, and thereby increasing the asphaltene extraction efficiency [98].

Figure 3 presents the DAO quality in three panels related to (a) asphaltene content, (b) sulfur content, and (c) °API for both SDA and *e*-SDA processes. For the SDA process increasing the SOR decreased the asphaltene content in the DAO, as shown in Figure 3(a). This situation can be explained because increasing the SOR leads to reducing the asphaltene solubility causing them to precipitate [81, 116–119]. For this reason, as the SOR increased, more asphaltenes were precipitated [83, 84] and therefore the DAO quality increased. These results are widely confirmed by previous studies that measured the content of asphaltene in DAO [70, 82, 85]. Regarding the sulfur content of the DAO, this is directly related to asphaltene content [82], which can be seen in Figure 3(b). As the asphaltene content of the DAO decreased, the sulfur content decreased, showing the same trend as the asphaltene content as SOR increased. Thus, Figure 3(c) shows that increases of the SOR increased the API gravity of the DAO. This result is consistent with the reductions in the asphaltene and sulfur contents [125].

The DAO quality was also affected by the addition of nanomaterials in the *e*-SDA process. As seen in Figure 3(a), the asphaltene content of the DAO was lower for all SOR values in comparison with the system without nanoparticles.

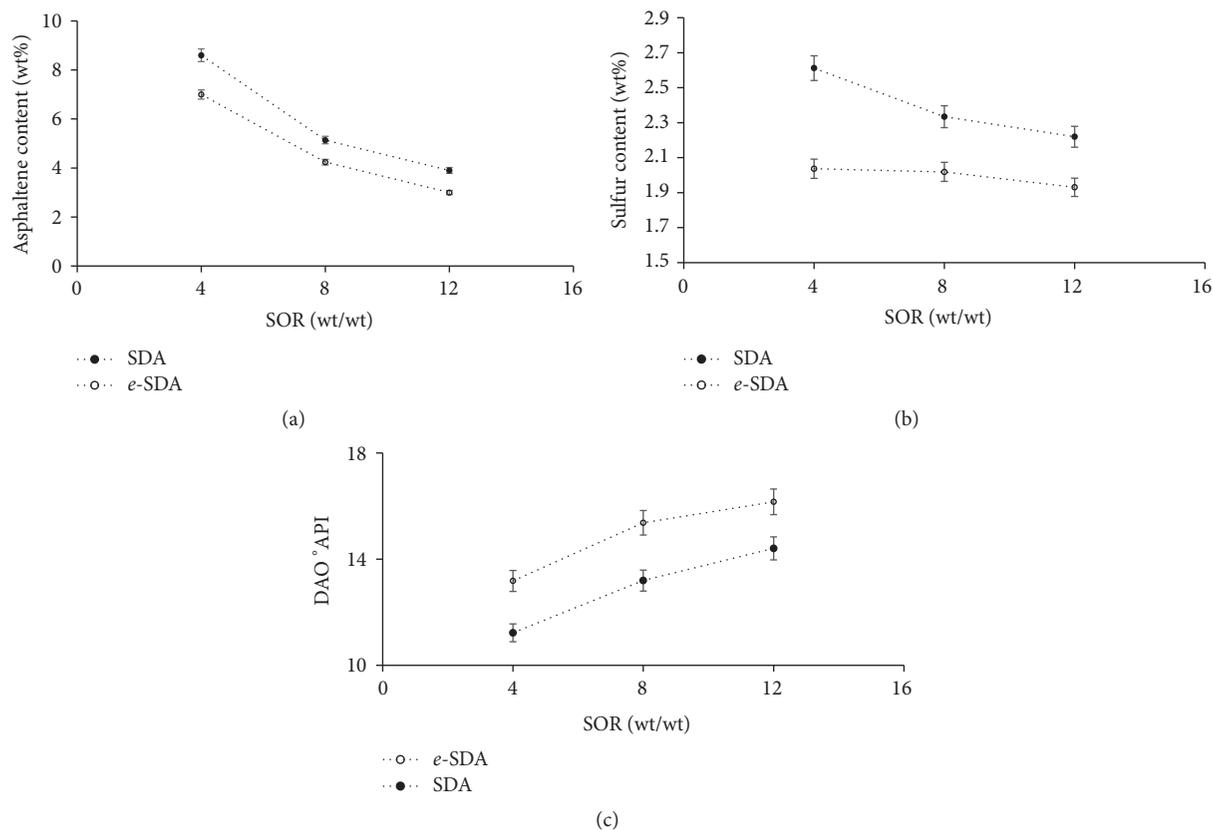


FIGURE 3: Effect of solvent to oil ratio on DAO quality related to (a) asphaltene and (b) sulfur content and (c) API gravity for the SDA and *e*-SDA processes using SiO₂ nanoparticles at a dosage of 5 wt% at 25°C and using *n*-heptane as the solvent.

This improvement in quality can be mainly explained by the interaction between the asphaltenes and the nanoparticles that remain in the pitch fraction, which also explains the sulfur content values of the *e*-SDA process that were clearly lower than those of the SDA process because of the direct relationship between the asphaltene and sulfur contents [82]. The sulfur content is nearly constant as the SOR increased and could be due to the fact that O- and N-containing asphaltenes are more prone to get adsorbed on the silica nanoparticles than those containing sulfur [119, 121]. Additionally, Figure 3(c) shows that the *e*-SDA process improved the °API values of the DAO for all of the SOR values. This remarkable result is also related to the reduction of the DAO asphaltene content values in *e*-SDA versus the traditional SDA process [125]. This result can be contrasted with the simulated distillation results that show that the distillable fractions for all DAO samples (either SDA or *e*-SDA) were approximately 100% up to 750°C.

Rheological measurements were conducted by triplicated to evaluate the DAO quality. Figure 4 shows the viscosity, shear stress, and the fitting with the Oswald-de Waele model as a function of shear rate for (a) crude oil and for DAO obtained from tests made with SOR values of (b) 4, (c) 8, and (d) 12. The estimated parameters of the Oswald-de Waele model are summarized in Table 1. As shown in Figure 4(a), the crude oil had the expected shear-thinning behavior frequently known as pseudo-plastic behavior [114].

This is confirmed by the n parameter value in Table 1, which is clearly less than 1.

The DAO obtained from the SDA process with an SOR of 4 (Figure 4(b)) also exhibited a shear-thinning behavior. However, in this case, the n value is 0.906 and, being almost 1, had a nearly Newtonian behavior with a K value of 73321 cP·s ^{$n-1$} that is related to the fluid viscosity at a shear rate value of 1 s⁻¹. For the same SOR = 4, the *e*-SDA process considerably improved the DAO rheological properties as can be seen clearly from the results shown in Figure 4 and Table 1. The parameters of the Oswald-de Waele model (n of 0.979 and K of 35522 cP·s ^{$n-1$}) indicate an approximately Newtonian behavior with a viscosity of 35522 cP. The last parameter indicates that adding SiO₂ nanoparticles reduces expected viscosity of the DAO by more than 50%. For an SOR value of 8 in the SDA process (Figure 4(c)), the DAO rheological characteristics presented a similar trend with an approximately Newtonian behavior and viscosity of 19552 cP. For the same SOR, when the *e*-SDA process was conducted with SiO₂ nanoparticles, the rheological properties of the DAO were improved, having a viscosity of 11883 cP that indicates a viscosity reduction of 42% on the typical SDA process conducted without nanoparticles. The same performance was observed for the DAO with an SOR of 12 in which the viscosity was reduced from 10670 to 8504 cP in the SDA and *e*-SDA processes, respectively. These rheological results are interesting because these fluid

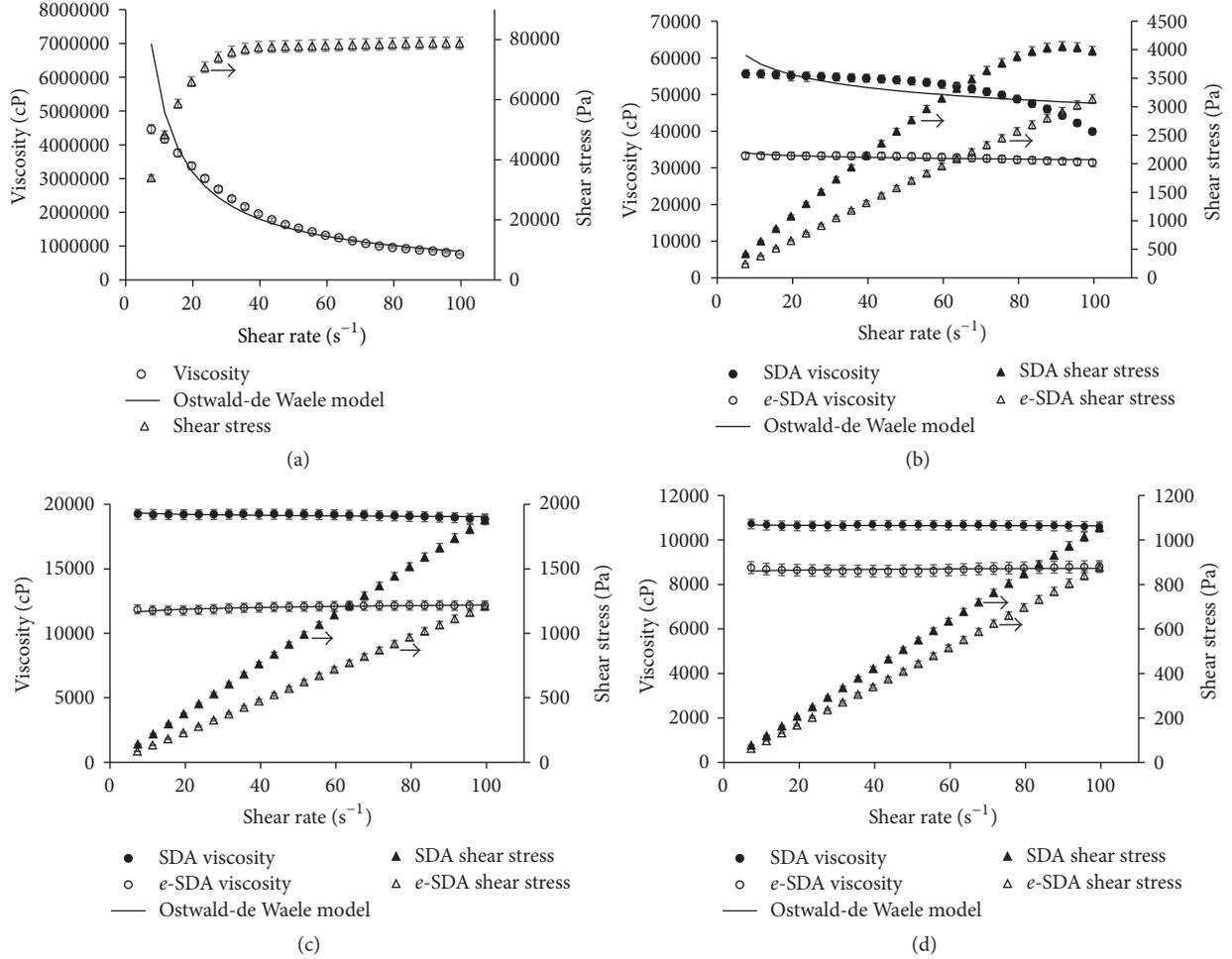


FIGURE 4: Viscosity and shear stress as a function of shear rate for (a) crude oil and DAO after SDA and *e*-SDA with SOR values of (b) 4, (c) 8, and (d) 12 at 25°C with a fixed dosage of SiO₂ nanoparticles of 5 wt% and with *n*-heptane as the solvent.

TABLE 1: Ostwald-de Waele estimated parameters for rheological experiments on crude oil and DAO after SDA and *e*-SDA with SOR values of 4, 8, and 12 at 25°C with a fixed dosage of SiO₂ nanoparticles 5 wt% and *n*-heptane as the solvent.

Sample	SOR	K (cP·s ^{<i>n</i>-1})	n (dimensionless)	RSME%	χ^2
Crude oil	0	37051877	0.180	9.29	3.45
	4	73321	0.906	6.20	2.37
SDA	8	19552	0.994	0.44	0.18
	12	10670	0.999	0.18	0.08
<i>e</i> -SDA	4	35522	0.979	1.15	0.48
	8	11883	1.017	0.40	0.14
	12	8504	1.006	0.70	0.29

properties determine the crude oil and DAO transporting conditions. In Figure 4 it is observed that the inclusion of SiO₂ nanoparticles significantly reduced the shear stress and the yield point in comparison with the SDA process in the absence of nanoparticles.

Finally, for the deasphalting process conducted with and without nanoparticles, at all of the assessed SOR values, the estimated solvent losses were lower than 1.0 wt%.

4.2. Temperature Effects. Procedures were conducted with *n*-heptane as the solvent at an SOR of 8 with a SiO₂ nanoparticles dosage of 5 wt% and a fixed temperature of 70°C to assess the temperature effects. The results are summarized in Table 2 and are in agreement with the literature reports, which found that, within the range evaluated, increasing the temperature increases the pitch yield and reduces the DAO yield [82, 90, 91]. This can be seen for both the SDA

TABLE 2: Yield and quality of the DAO after the SDA and *e*-SDA processes at 70°C using a SiO₂ nanoparticles dosage of 5 wt% and an SOR of 8 with *n*-heptane as the solvent.

Variable	Process	
	SDA	<i>e</i> -SDA
Yield		
Pitch (%)	51.7 ± 0.1	60.5 ± 0.1
DAO (%)	48.3 ± 0.1	39.5 ± 0.1
DAO quality		
Asphaltene content (%)	3.43 ± 0.01	2.96 ± 0.01
Sulfur content (%)	2.04 ± 0.01	1.55 ± 0.01
°API	14.39 ± 0.02	16.15 ± 0.02

and *e*-SDA processes and can be explained by increases in the differences in the solubility parameters and molar volumes between the solvent and crude oil as temperature rises, leading to a larger region of immiscibility in a solvent—pitch—DAO system [82]. In this sense, increasing system temperature has a similar effect compared to that when the molecular weight of used solvent is decreased. For the SDA, the DAO yield decreased from 54.3% at 25°C to 48.3% at 70°C. Increasing the temperature in the *e*-SDA process improved the asphaltene separation as indicated by a decrease of the DAO yield from 44.6% to 39.5%. This situation suggests that there is a synergistic effect between the nanoparticles and temperature that improved the DAO and pitch separation that is controlled by adsorption on the nanoparticles and the increased diffusion of asphaltenes through the feedstock to the pitch by increased thermal motion [98].

The temperature effects on DAO quality are shown in Table 2. For the SDA process, the temperature improved the DAO quality, showing that asphaltene content was reduced from 5.14% at 25°C to 3.43% at 70°C. This type of behavior was also noticed in sulfur content that was reduced from 2.33% at 25°C to 2.04% at 70°C. The DAO quality was especially related to the asphaltene content. It increased as the temperature is increased, as expected for the typical SDA process [82, 90, 91]. As noted above, the sulfur content and °API are also related to the asphaltene content, and this explains their behavior in this investigation [78, 82, 125]. For the *e*-SDA process, temperature plays the same role in improving DAO quality. The DAO asphaltene content was reduced from 4.24% at 25°C to 2.96% at 70°C. Consequently, the DAO sulfur content was also improved, decreasing from 2.02% to 1.56%. Table 2 shows that the physicochemical properties of the DAO were enhanced by the *e*-SDA process in comparison with the SDA process by increasing API gravity and by reducing both the asphaltene and sulfur contents at 70°C. Meanwhile, the solvent losses were also lower than 1.0 wt% in the processes conducted at 70°C.

Figure 5 shows the rheological properties of the DAO obtained from SDA and *e*-SDA processes at 70°C, and the estimated parameters for the Oswald-de Waele model are presented in Table 3. These results show that, at 70°C, the DAO samples obtained from both processes exhibited

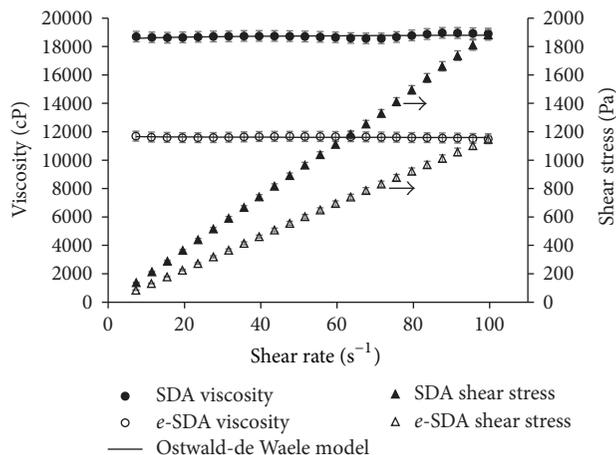


FIGURE 5: Viscosity and shear stress of the DAO as a function of shear rate for the SDA and *e*-SDA processes at 70°C using a SiO₂ nanoparticles dosage of 5 wt% and an SOR of 8 with *n*-heptane as the solvent.

TABLE 3: Ostwald-de Waele estimated parameters from rheological experiments for DAO after the SDA and *e*-SDA processes with an SOR of 8 at 70°C using SiO₂ nanoparticles and *n*-heptane as the solvent.

Parameter	SDA	<i>e</i> -SDA
K (cP·s ^{<i>n</i>-1})	18410	11699
n (dimensionless)	1.005	0.998
RSME%	0.53	0.40
χ^2	0.19	0.17

approximately Newtonian behavior. For SDA, the Ostwald-de Waele estimated parameters were $n = 1.005$ and hence K can be considered as sample viscosity equal to 18410 cP. These results from the SDA process at 70°C denote a marked improvement over those at 25°C (Table 1). The same type of response was observed for the *e*-SDA process and can be noted in estimated parameters: $n = 0.998$ and $K = 11699$ cP. These results demonstrate that nanoparticles can improve the deasphalting process at 70°C by reducing the resulting DAO viscosity by approximately 37%.

4.3. Effect of the Type of Solvent. The solvent used in SDA and *e*-SDA processes has a high influence. Table 4 shows the DAO yield and quality from both processes when conducted with *n*-pentane and at 25°C a dosage of 5 wt% of SiO₂ nanoparticles. Comparing these results with those obtained when using *n*-heptane as the solvent (Figure 2), it is observed that reducing the carbon number of solvent reduced the DAO yield and hence increased the pitch or precipitated fraction yield [78–82, 84]. This is because increasing the molecular weight of the solvent allows it to solubilize heavier hydrocarbons [78, 84], as reflected in the solubility parameter of asphaltenes in different solvents [80]. This situation is similar in both the SDA and *e*-SDA processes. The DAO quality also followed this same phenomenon, and reducing the solvent molecular weight increases the DAO quality

TABLE 4: Yield and quality of the DAO after the SDA and *e*-SDA processes at 25°C using SiO₂ nanoparticles at a dosage of 5 wt% and an SOR of 8 with *n*-pentane as the solvent.

Variable	Process	
	SDA	<i>e</i> -SDA
Yield		
Pitch (%)	56.1 ± 0.1	65.3 ± 0.1
DAO (%)	43.9 ± 0.1	34.7 ± 0.1
DAO quality		
Asphaltene content (%)	2.34 ± 0.01	2.01 ± 0.01
Sulfur content (%)	1.55 ± 0.01	1.38 ± 0.01
°API	19.38 ± 0.02	21.11 ± 0.02

TABLE 5: Ostwald-de Waele estimated parameters from rheological experiments for the DAO after the SDA and *e*-SDA processes with an SOR of 8 at 25°C using SiO₂ nanoparticles at a dosage of 5 wt% and an SOR of 8 with *n*-pentane as the solvent.

Parameter	SDA	<i>e</i> -SDA
K (cP·s ^{<i>n</i>-1})	2500	2166
n (dimensionless)	0.994	0.991
RSME%	0.69	0.68
χ^2	0.25	0.24

[79, 81, 82]. For the SDA process, the DAO asphaltene content was reduced from 5.14% with *n*-heptane to 2.34% with *n*-pentane. The same trend occurred with sulfur content, which fell from 2.33% to 1.55%. Finally, the °API of the DAO improved considerably by increasing from 13.19 to 19.38 for *n*-heptane and *n*-pentane, respectively. This considerable improvement of the API gravity can be attributed to the resins and their influence on the deasphalting process [81, 116–119] and how they precipitated in higher proportion when the solvent had a lower molecular weight [82].

The *e*-SDA process also exhibited improvements regarding the DAO quality as the molecular weight of solvent was reduced. The asphaltene content fell from 4.24% with *n*-heptane (Figure 2) to 2.01% with *n*-pentane (Table 4) and the same trend was observed for the sulfur content. On the DAO °API, it increased from 15.37 to 21.11 with the use of *n*-heptane and *n*-pentane, respectively. The solvent losses were also less than 1 wt%. In this sense, there seemed to be a synergetic effect on the DAO quality between the reduction of solvent molecular weight and the use of SiO₂ nanoparticles.

Figure 6 and Table 5 summarize the rheological properties of DAO that were affected in several ways by the solvent used in the SDA and *e*-SDA processes. The results indicate nearly Newtonian behavior for the DAO obtained from both processes. These results were confirmed by the n parameters of Ostwald-de Waele models that equal 0.994 and 0.991, respectively. In this sense, the K values, interpreted as the viscosity, were 2500 cP for SDA and 2166 cP for *e*-SDA; that is, a reduction in resultant DAO viscosity of approximately 14% occurred with the *e*-SDA process. This viscosity reduction that was exhibited when using nanoparticles could be attributed mainly to the resin fraction of the DAO that played

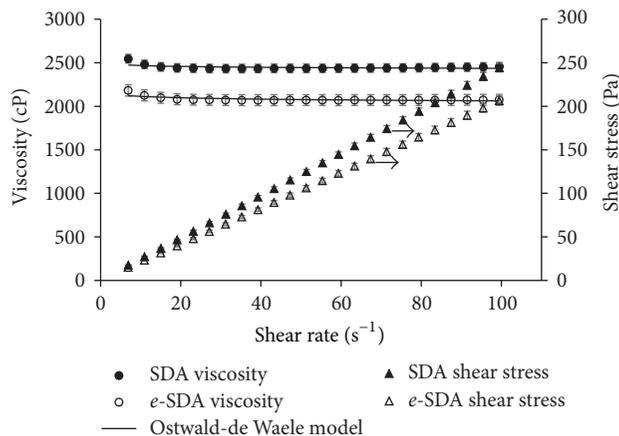


FIGURE 6: Viscosity and shear stress of the DAO as a function of shear rate for the SDA and *e*-SDA processes at 25°C using SiO₂ nanoparticles at a dosage of 5 wt% and an SOR of 8 with *n*-pentane as the solvent.

a key role in the formation of the viscoelastic network that drastically increased the EHO viscosity [20, 124]. It is known that resins are adsorbed simultaneously with asphaltenes on the nanoparticles [109] implying that a higher amount of the resins could remain in the pitch fraction. Hence, nanoparticles may have a synergistic effect with the solvent employed, *n*-pentane in this case, by enhancing the amount of resins adsorbed and thereby inhibiting the formation of the viscoelastic network, which translates into lower energy demand for fluid transportation and processing.

4.4. Effects of Nanoparticle Dosage. Using SiO₂ nanoparticles in the *e*-SDA process in dosages of 2.5 and 10 wt% of crude oil mass generated differences with the same process conducted with a fixed dosage of 5 wt%, in both DAO yield and quality. Figure 7 shows the yield of (a) DAO and (b) pitch as a function of the nanoparticles dosage. As can be noticed, increasing nanoparticles dosage decreases DAO yield and increases pitch yield. This behavior can be explained by the relation between adsorbate and adsorbent. Increasing the mass of the adsorbent and hence the total surface area available for adsorption by mass unit generates that larger amounts of asphaltenes that could be adsorbed on the nanoparticles surface. This situation leads to the fact that as SiO₂ nanoparticles dosage increases, more asphaltenes are adsorbed, and DAO yield decreases while pitch yield increases. These results are in agreement with those reported by several authors [120, 122, 124, 126–129], but considering the total mass of adsorbed asphaltenes instead of the relation between the mass of adsorbed asphaltenes and the mass of adsorbent.

Figure 8 shows the DAO quality in three panels related to (a) asphaltene content, (b) sulfur content, and (c) °API for *e*-SDA process at different SiO₂ nanoparticles dosage. The asphaltene content of the DAO reduces as nanoparticles dosage increases. This situation can be explained by the same situation abovementioned; increasing the total surface area for asphaltene adsorptions leads to their precipitation

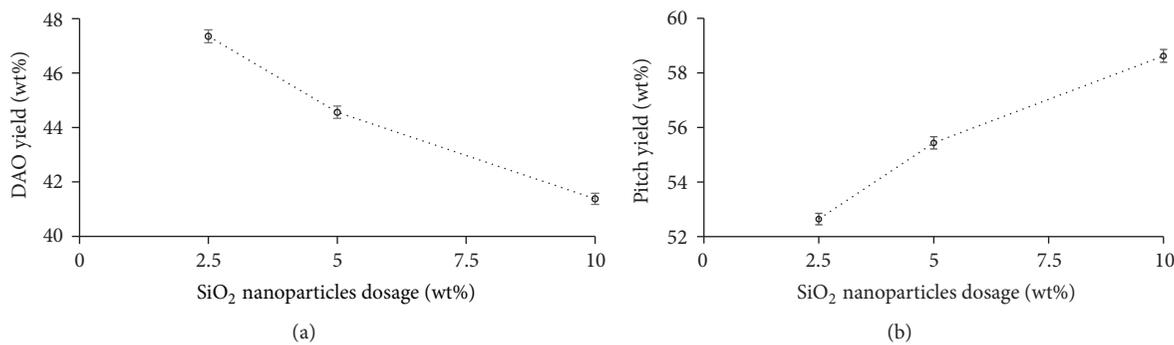


FIGURE 7: Effect of the SiO₂ nanoparticles dosage in (a) DAO and (b) pitch yields for the *e*-SDA process at SOR value of 8 at 25°C and using *n*-heptane as the solvent.

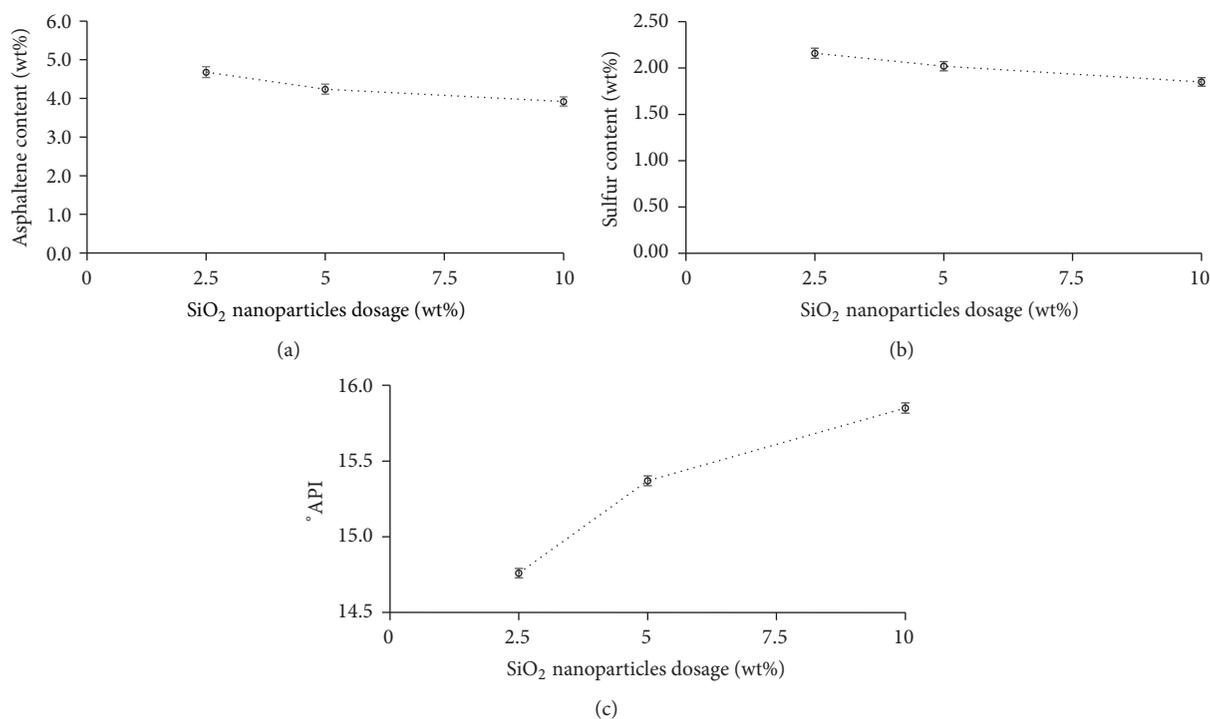


FIGURE 8: Effect of SiO₂ nanoparticles dosage in DAO quality related to (a) asphaltene and (b) sulfur content and (c) API gravity for the *e*-SDA processes at SOR value of 8 at 25°C and using *n*-heptane as a solvent.

[120, 122, 124, 126–129] and lowers the quantity of them present in the DAO. The sulfur content presents the same behavior and the explanation lays in the direct relation between asphaltene and sulfur content [82]. Additionally, Figure 8(c) shows that increasing nanoparticles dosage improved the °API values for the DAO. This result is also related to the reduction of DAO asphaltene content with the increment in nanoparticle dosage. Regarding the simulated distillation, results show that the distillable fractions for all DAO samples (at different nanoparticles dosage) were approximately 100% up to 750°C.

Figure 9 and Table 6 summarize the result of the rheological test carried out to the DAO obtained from *e*-SDA process with SiO₂ nanoparticles at dosages of 2.5 wt% and 10 wt%. Both DAO samples obtained with the 2.5 and 10 wt%

dosages exhibited a Newtonian behavior. For a dosage of 2.5 wt%, the n value is 1.001 and K value is 15802 cP·s ^{$n-1$} . The last parameter indicates a viscosity of 15802 cP. For a SiO₂ nanoparticles dosage of 10 wt% the DAO shows n value equal to 0.996 and K value of 9982 cP·s ^{$n-1$} , showing a viscosity of 9982 cP. It can be noticed that increasing nanoparticles dosage improves the rheological behavior of DAO considering these results and those obtained for a dosage of 5 wt%. Increasing the nanoparticles dosage from 2.5 to 5 wt% generates a viscosity reduction of 25% while raising the dosage from 5 to 10 wt% reduces the viscosity in 16%. Hence, a dosage of 5 wt% can be considered adequate because increasing in the DAO quality by rising nanoparticles dosage to 10 wt% is not as significant as that obtained when the dosage is increased from 2.5 to 5 wt%.

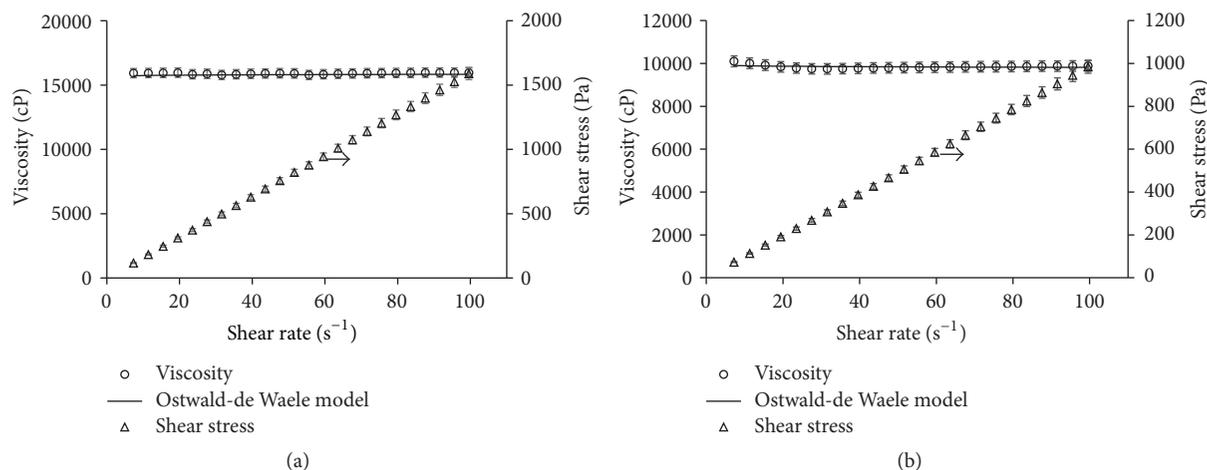


FIGURE 9: Viscosity and shear stress as a function of shear rate for SiO_2 nanoparticles dosages of (a) 2.5 and (b) 10 wt% at SOR = 8 at 25°C and using *n*-heptane as the solvent.

TABLE 6: Ostwald-de Waele estimated parameters for rheological experiments on DAO after *e*-SDA with SiO_2 nanoparticles dosage of 2.5 and 10 wt% at SOR = 8 at 25°C and using *n*-heptane as the solvent.

Nanoparticles dosage (wt%)	K ($\text{cP}\cdot\text{s}^{-n}$)	Parameter		
		n (dimensionless)	RSME%	χ^2
2.5	15802	1.001	0.58	0.19
10	9982	0.996	0.69	0.27

5. Conclusions

The efficiency of a typical SDA process was successfully increased at laboratory-scale conditions by the inclusion of nanoparticles in systems with different solvent to oil ratios, temperatures, types of solvent, and dosage. It was found that the use of nanoparticles reduces the DAO yield in comparison with the traditional SDA process, resulting in a higher quality product. The reason is the adsorption phenomena of the asphaltenes and the nanoparticles and how the former are transferred from the DAO fraction to the pitch fraction. Regarding the DAO quality, the *e*-SDA process was demonstrated to be a more suitable alternative regarding the asphaltene and sulfur contents, API gravity, and rheological properties. The improvement of the rheological properties is desirable because this leads to savings of energy and transportation efforts when the DAO has lower viscosities.

Finally, it is worth noting that this study was focused on DAO quality in the *e*-SDA process and there is importance in future investigations to assess the improvements of the catalytic thermal decomposition of the pitch when adding nanoparticles in the *e*-SDA process. This subject is important because of the energy costs involved in this process and its efficiency, considering that used solvent and nanoparticles can be recycled. It is expected that this knowledge will provide a suitable alternative for the enhancement of heavy and extra-heavy oil processing operations, particularly as related to the transportation process.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The authors would like to acknowledge COLCIENCIAS and Universidad Nacional de Colombia for logistical and financial support.

References

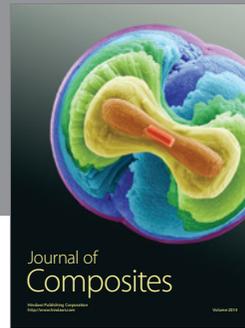
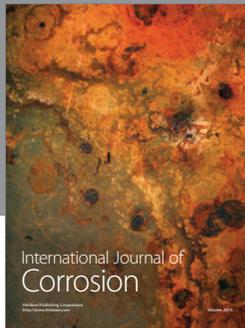
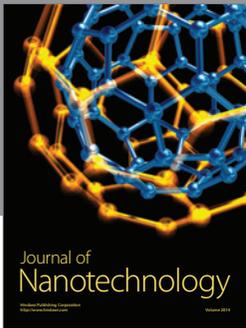
- [1] OPEC, *2015 World Oil Outlook*, OPEC Secretariat, Vienna, Austria, 2015.
- [2] H. Alboudwarej, J. J. Felix, S. Taylor et al., "La importancia del petróleo pesado," *Oilfield Review*, vol. 18, pp. 38–59, 2006.
- [3] IEA, *World Energy Outlook 2012*, International Energy Agency, Paris, France, 2012.
- [4] A.-Y. Huc, *Heavy Crude Oils: From Geology to Upgrading: An Overview*, Editions Technip, 2010.
- [5] J. G. Speight, *The Chemistry and Technology of Petroleum*, CRC Press, 4th edition, 2006.
- [6] J. G. Speight, *The Desulfurization of Heavy Oils and Residua*, CRC Press, Boca Raton, Fla, USA, 1999.
- [7] UPME, "Escenarios de Oferta y Demanda de Hidrocarburos en Colombia," 2012.
- [8] Campetrol, *Crudos Pesados: El Reto para Colombia*, 2015.
- [9] J. G. Speight, *Heavy and Extra-Heavy Oil Upgrading Technologies*, Gulf Professional Publishing, Houston, Tex, USA, 2013.

- [10] A. Hinkle and M. Batzle, "Heavy oils: a worldwide overview," *The Leading Edge*, vol. 25, no. 6, pp. 742–749, 2006.
- [11] R. Martínez-Palou, M. D. L. Mosqueira, B. Zapata-Rendón et al., "Transportation of heavy and extra-heavy crude oil by pipeline: a review," *Journal of Petroleum Science and Engineering*, vol. 75, no. 3–4, pp. 274–282, 2011.
- [12] S. Acevedo, A. Castro, J. G. Negrin et al., "Relations between asphaltene structures and their physical and chemical properties: the rosary-type structure," *Energy & Fuels*, vol. 21, no. 4, pp. 2165–2175, 2007.
- [13] H. Groenzin and O. C. Mullins, "Asphaltene molecular size and structure," *Journal of Physical Chemistry A*, vol. 103, no. 50, pp. 11237–11245, 1999.
- [14] O. C. Mullins, "The asphaltenes," *Annual Review of Analytical Chemistry*, vol. 4, pp. 393–418, 2011.
- [15] O. C. Mullins, H. Sabbah, J. L. Eyssautier et al., "Advances in asphaltene science and the Yen–Mullins model," *Energy & Fuels*, vol. 26, no. 7, pp. 3986–4003, 2012.
- [16] M. Ghanavati, M.-J. Shojaei, and S. A. Ahmad Ramazani, "Effects of asphaltene content and temperature on viscosity of Iranian heavy crude oil: experimental and modeling study," *Energy and Fuels*, vol. 27, no. 12, pp. 7217–7232, 2013.
- [17] K. J. Leontaritis, J. O. Amaefule, and R. E. Charles, "A systematic approach for the prevention and treatment of formation damage caused by asphaltene deposition," *SPE Production & Facilities*, vol. 9, no. 3, pp. 157–164, 1994.
- [18] J. R. Woods, J. Kung, D. Kingston, L. Kotlyar, B. Sparks, and T. McCracken, "Canadian crudes: a comparative study of SARA fractions from a modified HPLC separation technique," *Oil & Gas Science and Technology*, vol. 63, no. 1, pp. 151–163, 2008.
- [19] K. Akbarzadeh, H. Alboudwarej, W. Y. Svrcek, and H. W. Yarranton, "A generalized regular solution model for asphaltene precipitation from *n*-alkane diluted heavy oils and bitumens," *Fluid Phase Equilibria*, vol. 232, no. 1–2, pp. 159–170, 2005.
- [20] K. Akbarzadeh, A. Hammami, A. Kharrat et al., "Asphaltenes - problematic but rich in potential," *Oilfield Review*, vol. 19, no. 2, pp. 22–43, 2007.
- [21] R. R. Chianelli, M. Siadati, A. Mehta, J. Pople, L. C. Ortega, and L. Y. Chiang, "Self-assembly of asphaltene aggregates: synchrotron, simulation and chemical modeling techniques applied to problems in the structure and reactivity of asphaltenes," in *Asphaltenes, Heavy Oils, and Petroeconomics*, pp. 375–400, Springer, Berlin, Germany, 2007.
- [22] P. Luo and Y. Gu, "Effects of asphaltene content on the heavy oil viscosity at different temperatures," *Fuel*, vol. 86, no. 7–8, pp. 1069–1078, 2007.
- [23] I. Hénaut, L. Barré, J. Argillier, F. Brucy, and R. Bouchard, "Rheological and structural properties of heavy crude oils in relation with their asphaltenes content," in *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Society of Petroleum Engineers, Houston, Tex, USA, 2001.
- [24] C. Wu, G.-L. Lei, C.-J. Yao, P.-Y. Gai, Y.-B. Cao, and X.-N. Li, "Mechanism for reducing the viscosity of extra-heavy oil by aquathermolysis with an amphiphilic catalyst," *Journal of Fuel Chemistry and Technology*, vol. 38, no. 6, pp. 684–690, 2010.
- [25] S. Chavan, H. Kini, and R. Ghosal, "Process for sulfur reduction from high viscosity petroleum oils," *International Journal of Environmental Science and Development*, vol. 3, pp. 228–231, 2012.
- [26] R. Moore, C. Lareshen, S. Mehta et al., "A downhole catalytic upgrading process for heavy oil using in situ combustion," *Journal of Canadian Petroleum Technology*, vol. 38, p. 96, 1999.
- [27] I. Gates, N. Chakrabarty, R. Moore, S. Mehta, E. Zalewski, and P. Pereira, "In situ upgrading of Llançanelo heavy oil using in situ combustion and a downhole catalyst bed," *Journal of Canadian Petroleum Technology*, vol. 47, 2008.
- [28] W. R. Shu, "In-situ combustion method for recovery of heavy oil utilizing oxygen and carbon dioxide as initial oxidant," Google Patents, 1983.
- [29] R. Hashemi, N. N. Nassar, and P. Pereira Almaso, "Nanoparticle technology for heavy oil in-situ upgrading and recovery enhancement: opportunities and challenges," *Applied Energy*, vol. 133, pp. 374–387, 2014.
- [30] K. Guo, H. Li, and Z. Yu, "Metallic nanoparticles for enhanced heavy oil recovery: promises and challenges," *Energy Procedia*, vol. 75, pp. 2068–2073, 2015.
- [31] C. A. Franco, T. Montoya, N. N. Nassar, P. Pereira-Almaso, and F. B. Cortés, "Adsorption and subsequent oxidation of colombian asphaltenes onto nickel and/or palladium oxide supported on fumed silica nanoparticles," *Energy and Fuels*, vol. 27, no. 12, pp. 7336–7347, 2013.
- [32] C. A. Franco, L. Cardona, S. H. Lopera, J. M. Mejía, and F. B. Cortés, "Heavy oil upgrading and enhanced recovery in a continuous steam injection process assisted by nanoparticulated catalysts," in *Proceedings of the SPE Improved Oil Recovery Conference*, April 2016.
- [33] G. C. Wichert, N. E. Okazawa, R. G. Moore, and J. D. M. Belgrave, "In-situ upgrading of heavy oils by low-temperature oxidation in the presence of caustic additives," in *Proceedings of the International Heavy Oil Symposium*, pp. 529–536, Alberta, Canada, June 1995.
- [34] W. Li, J.-H. Zhu, and J.-H. Qi, "Application of nano-nickel catalyst in the viscosity reduction of Liaohe extra-heavy oil by aqua-thermolysis," *Journal of Fuel Chemistry and Technology*, vol. 35, no. 2, pp. 176–180, 2007.
- [35] P. Clark and J. Hyne, "Steam-oil chemical reactions: mechanisms for the aquathermolysis of heavy oils," *AOSTRA Journal of Research*, vol. 1, pp. 15–20, 1984.
- [36] A. Ambalae, N. Mahinpey, and N. Freitag, "Thermogravimetric studies on pyrolysis and combustion behavior of a heavy oil and its asphaltenes," *Energy and Fuels*, vol. 20, no. 2, pp. 560–565, 2006.
- [37] H. N. Woebecke, S. Narayanan, and A. R. Johnson, "Integrated heavy oil pyrolysis process," Google Patents, 1986.
- [38] A. Davletbaev, L. Kovaleva, and T. Babadagli, "Heavy oil production by electromagnetic heating in hydraulically fractured wells," *Energy & Fuels*, vol. 28, no. 9, pp. 5737–5744, 2014.
- [39] O. A. Alomair and A. S. Almusallam, "Heavy crude oil viscosity reduction and the impact of asphaltene precipitation," *Energy & Fuels*, vol. 27, no. 12, pp. 7267–7276, 2013.
- [40] J. L. García Zapata and A. De Klerk, "Viscosity changes during mild oxidation of oilsands-derived bitumen: solvent effects and selectivity," *Energy and Fuels*, vol. 28, no. 10, pp. 6242–6248, 2014.
- [41] D. Nguyen and V. Balsamo, "Emulsification of heavy oil in aqueous solutions of poly(vinyl alcohol): a method for reducing apparent viscosity of production fluids," *Energy & Fuels*, vol. 27, no. 4, pp. 1736–1747, 2013.
- [42] I. Md. Saaid, S. Q. A. Mahat, B. Lal, M. I. A. Mutalib, and K. M. Sabil, "Experimental investigation on the effectiveness of 1-butyl-3-methylimidazolium perchlorate ionic liquid as a reducing agent for heavy oil upgrading," *Industrial and Engineering Chemistry Research*, vol. 53, no. 19, pp. 8279–8284, 2014.

- [43] K. Sharma, V. Saxena, A. Kumar et al., "Pipeline transportation of heavy/viscous crude oil as water continuous emulsion," in *Proceedings of the SPE India Oil and Gas Conference and Exhibition*, New Delhi, India, 1998.
- [44] H. L. Alfonso and Y. D. Drubey, "Propiedades reológicas de emulsiones de petróleo pesado en agua," *Ingeniare. Revista Chilena de Ingeniería*, vol. 16, no. 1, pp. 244–249, 2008.
- [45] J. Colyar, "Has the time for partial upgrading of heavy oil and bitumen arrived?" *Petroleum Technology Quarterly*, vol. 14, no. 5, pp. 43–56, 2009.
- [46] M. Motaghi, P. Saxena, and R. Ravi, "Partial upgrading of heavy oil reserves," *Petroleum Technology Quarterly*, vol. 15, pp. 55–64, 2010.
- [47] R. Luhning, A. Anand, T. Blackmore, and D. Lawson, "Pipeline transportation of emerging partially upgraded bitumen," in *Proceedings of the Canadian International Petroleum Conference*, Alberta, Canada, 2002.
- [48] R. V. A. Oliemans, G. Ooms, H. L. Wu, and A. Duijvestijn, "Core-annular oil/water flow: the turbulent-lubricating-film model and measurements in a 5 cm pipe loop," *International Journal of Multiphase Flow*, vol. 13, no. 1, pp. 23–31, 1987.
- [49] P. Poesio and D. Strazza, "Experiments on start-up of an oil-water core annular flow through a horizontal or nearly horizontal pipe," in *Proceedings of the 13th International Conference on Multiphase Production Technology*, Edinburgh, UK, June 2007.
- [50] S. Ghosh, T. K. Mandal, G. Das, and P. K. Das, "Review of oil water core annular flow," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 8, pp. 1957–1965, 2009.
- [51] E. Bobok, D. Magyari, and G. Udvardi, "Heavy oil transport through lubricated pipeline," in *Proceedings of the European Petroleum Conference*, pp. 239–244, Milan, Italy, October 1996.
- [52] R. Tao and X. Xu, "Reducing the viscosity of crude oil by pulsed electric or magnetic field," *Energy & Fuels*, vol. 20, no. 5, pp. 2046–2051, 2006.
- [53] J. J. Taber, F. D. Martin, and R. Seright, "EOR screening criteria revisited," in *Proceedings of the Symposium on Improved Oil Recovery*, pp. 387–415, April 1996.
- [54] J. J. Taber, F. D. Martin, and R. S. Seright, "EOR screening criteria revisited—part 2: applications and impact of oil prices," *SPE Reservoir Engineering*, vol. 12, no. 3, pp. 199–206, 1997.
- [55] J. J. Taber, F. Martin, and R. Seright, "EOR screening criteria revisited-part 1: Introduction to screening criteria and enhanced recovery field projects," *SPE Reservoir Engineering*, vol. 12, no. 3, pp. 189–198, 1997.
- [56] T. Nasr, G. Beaulieu, H. Golbeck, and G. Heck, "Novel expanding solvent-SAGD process 'ES-SAGD,'" *Journal of Canadian Petroleum Technology*, vol. 42, no. 1, 2003.
- [57] R. Butler, "SAGD comes of age!," *Journal of Canadian Petroleum Technology*, vol. 37, no. 7, pp. 9–12, 1998.
- [58] S. Thomas, "Enhanced oil recovery—an overview," *Oil and Gas Science and Technology*, vol. 63, no. 1, pp. 9–19, 2008.
- [59] T. Babadagli, "Evaluation of EOR methods for heavy—oil recovery in naturally fractured reservoirs," *Journal of Petroleum Science and Engineering*, vol. 37, no. 1-2, pp. 25–37, 2003.
- [60] K. E. Kisman and K. C. Yeung, "Numerical study of the SAGD process in the burnt lake oil sands lease," in *Proceedings of the International Heavy Oil Symposium*, pp. 275–286, Alberta, Canada, June 1995.
- [61] S. Larter, J. Adams, I. D. Gates, B. Bennett, and H. Huang, "The origin, prediction and impact of oil viscosity heterogeneity on the production characteristics of tar sand and heavy oil reservoirs," *Journal of Canadian Petroleum Technology*, vol. 47, no. 1, pp. 52–61, 2008.
- [62] M. S. Picha, "Enhanced oil recovery by hot CO₂ flooding," in *Proceedings of the SPE Middle East Oil and Gas Show and Conference*, Society of Petroleum Engineers, 2007.
- [63] M. Islam, B. Erno, and D. Davis, "Hot gas and waterflood equivalence of in situ combustion," *Journal of Canadian Petroleum Technology*, vol. 31, 1992.
- [64] P. L. McGuire, R. Okuno, T. L. Gould, and L. W. Lake, "Ethane-based EOR: an innovative and profitable EOR opportunity for a low price environment," in *Proceedings of the SPE Improved Oil Recovery Conference*, Tulsa, Okla, USA, April 2016.
- [65] S. Ghedan, "Global laboratory experience of CO₂-EOR flooding," in *Proceedings of the SPE/EAGE Reservoir Characterization and Simulation Conference 2009*, pp. 883–897, Abu Dhabi, UAE, October 2009.
- [66] F. Gozalpour, S. R. Ren, and B. Tohidi, "CO₂ EOR and storage in oil reservoir," *Oil & Gas Science and Technology*, vol. 60, no. 3, pp. 537–546, 2005.
- [67] G. R. P. Oskui, M. A. Jumaa, E. G. Folad, A. Rashed, and S. Patil, "Systematic approach for prevention and remediation of asphaltene problems during CO₂/hydrocarbon injection project," in *Proceedings of the 21st International Offshore and Polar Engineering Conference (ISOPE '11)*, pp. 50–57, Maui, Hawaii, USA, June 2011.
- [68] S. Gharfeh, A. Yen, S. Asomaning, and D. Blumer, "Asphaltene flocculation onset determinations for heavy crude oil and its implications," *Petroleum Science and Technology*, vol. 22, no. 7-8, pp. 1055–1072, 2004.
- [69] R. S. H. Al-Maamari and J. S. Buckley, "Asphaltene precipitation and alteration of wetting: the potential for wettability changes during oil production," *SPE Reservoir Evaluation and Engineering*, vol. 6, no. 4, pp. 210–214, 2003.
- [70] J. M. Lee, S. Shin, S. Ahn et al., "Separation of solvent and deasphalted oil for solvent deasphalting process," *Fuel Processing Technology*, vol. 119, pp. 204–210, 2014.
- [71] W. H. Richard, "Process of distilling petroleum oil," Google Patents, 1928.
- [72] R. R. Rosenbaum, "Process for separating hydrocarbons," Google Patents, 1918.
- [73] C. S. Hsu and P. Robinson, *Practical Advances in Petroleum Processing*, Springer, 2007.
- [74] G. Gester Jr., *Solvent Extraction in the Petroleum Industry*, ACS Publications, 1951.
- [75] G. H. Weber, "Modern Petroleum Processes," in *Proceedings of the 3rd World Petroleum Congress*, 1951.
- [76] E. W. Funk, "Behavior of tar sand bitumen with paraffinic solvents and its application to separations for athabasca tar sands," *The Canadian Journal of Chemical Engineering*, vol. 57, no. 3, pp. 333–341, 1979.
- [77] D. L. Mitchell and J. G. Speight, "The solubility of asphaltenes in hydrocarbon solvents," *Fuel*, vol. 52, no. 2, pp. 149–152, 1973.
- [78] G. Brons and J. M. Yu, "Solvent deasphalting effects on whole cold lake bitumen," *Energy & Fuels*, vol. 9, no. 4, pp. 641–647, 1995.
- [79] E. Buenrostro-Gonzalez, C. Lira-Galeana, A. Gil-Villegas, and J. Wu, "Asphaltene precipitation in crude oils: theory and experiments," *AIChE Journal*, vol. 50, no. 10, pp. 2552–2570, 2004.
- [80] D. Hartmann, H. E. Lopes, C. L. S. Teixeira et al., "Alkanes induced asphaltene precipitation studies at high pressure and

- temperature in the presence of argon," *Energy & Fuels*, vol. 30, no. 5, pp. 3693–3706, 2016.
- [81] S. L. Kokal, J. Najman, S. G. Sayegh, and A. E. George, "Measurement and correlation of asphaltene precipitation from heavy oils by gas injection," *Journal of Canadian Petroleum Technology*, vol. 31, no. 4, p. 24, 1992.
- [82] S. H. Ng, "Nonconventional residuum upgrading by solvent deasphalting and fluid catalytic cracking," *Energy and Fuels*, vol. 11, no. 6, pp. 1127–1136, 1997.
- [83] L. M. Arciniegas and T. Babadagli, "Quantitative and visual characterization of asphaltenic components of heavy-oil after solvent interaction at different temperatures and pressures," *Fluid Phase Equilibria*, vol. 366, pp. 74–87, 2014.
- [84] P. Luo, X. Wang, and Y. Gu, "Characterization of asphaltenes precipitated with three light alkanes under different experimental conditions," *Fluid Phase Equilibria*, vol. 291, no. 2, pp. 103–110, 2010.
- [85] S. Ng, E. Castellanos, and B. Farnand, "Deasphalting of non-conventional residues," 2016, http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/37_3_WASHINGTON%20DC_08-92_1506.pdf.
- [86] F. I. Samedova, A. M. Kasumova, S. Y. Rashidova, and V. M. Alieva, "A new method for isolation of asphaltenes from petroleum and its heavy residues," *Petroleum Chemistry*, vol. 47, no. 6, pp. 399–401, 2007.
- [87] L. Lodi, V. O. Cárdenas Concha, R. A. Souza, L. C. Medina, R. M. Filho, and M. R. Wolf Maciel, "An experimental study of a pilot plant deasphalting process in subcritical and supercritical conditions," *Petroleum Science and Technology*, vol. 32, no. 22, pp. 2659–2665, 2014.
- [88] L. Lodi, V. O. C. Concha, L. C. Medina, R. M. Filho, and M. R. W. Maciel, "An experimental study of a pilot plant deasphalting process in CO₂ supercritical," *Petroleum Science and Technology*, vol. 33, no. 4, pp. 481–486, 2015.
- [89] Z. M. Liu, G. Y. Yang, Y. Lu, B. X. Han, and H. K. Yan, "Phase equilibria of the CO₂-Jiangsu crude oil system and precipitation of heavy components induced by supercritical CO₂," *Journal of Supercritical Fluids*, vol. 16, no. 1, pp. 27–31, 1999.
- [90] H. Edward and J. J. M. Michael, "When solvent deasphalting is the most appropriate technology for upgrading residue," in *Proceedings of the International Downstream Technology & Strategy Conference (IDTC '06)*, pp. 1–11, London, UK, 2006.
- [91] F. Cao, D. Jiang, W. Li, P. Du, G. Yang, and W. Ying, "Process analysis of the extract unit of vacuum residue through mixed C4 solvent for deasphalting," *Chemical Engineering and Processing: Process Intensification*, vol. 49, no. 1, pp. 91–96, 2010.
- [92] L. S. Moreno and T. Babadagli, "Quantitative and visual characterization of asphaltenic components of heavy-oil and bitumen samples after solvent interaction at different temperatures and pressures," in *Proceedings of the SPE International Symposium on Oilfield Chemistry*, Society of Petroleum Engineers, The Woodlands, Tex, USA, 2013.
- [93] P. Luo and Y. Gu, "Characterization of a heavy oil-propane system in the presence or absence of asphaltene precipitation," *Fluid Phase Equilibria*, vol. 277, no. 1, pp. 1–8, 2009.
- [94] A. Hirschberg, L. DeJong, B. Schipper, and J. Meijer, "Influence of temperature and pressure on asphaltene flocculation," *Society of Petroleum Engineers Journal*, vol. 24, pp. 283–293, 1984.
- [95] F. Chung, P. Sarathi, and R. Jones, *Modeling of Asphaltene and Wax Precipitation*, National Institute for Petroleum and Energy Research, Bartlesville, Okla, USA, 1991.
- [96] H. Rassamdana, B. Dabir, M. Nematy, M. Farhani, and M. Sahimi, "Asphalt flocculation and deposition: I. The onset of precipitation," *AIChE Journal*, vol. 42, no. 1, pp. 10–22, 1996.
- [97] J. Long, B.-X. Shen, H. Ling, J.-G. Zhao, and J.-C. Lu, "Improving the solvent deasphalting process by the co-treating of residue and coal," *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, vol. 35, no. 20, pp. 1956–1963, 2013.
- [98] J. Long, B. Shen, H. Ling, J. Zhao, and J. Lu, "Novel solvent deasphalting process by vacuum residue blending with coal tar," *Industrial and Engineering Chemistry Research*, vol. 50, no. 19, pp. 11259–11269, 2011.
- [99] O. R. Koseoglu, "Enhanced solvent deasphalting process for heavy hydrocarbon feedstocks utilizing solid adsorbent," Google Patents, 2009.
- [100] O. R. Koseoglu, "Process for upgrading hydrocarbon feedstocks using solid adsorbent and membrane separation of treated product stream," Google Patents, 2012.
- [101] M. Ikematsu, I. Honzuo, and K. Sakai, "Process for the solvent deasphalting of asphaltene-containing hydrocarbons," Google Patents, 1985.
- [102] N. N. Nassar, A. Hassan, L. Carbognani, F. Lopez-Linares, and P. Pereira-Almao, "Iron oxide nanoparticles for rapid adsorption and enhanced catalytic oxidation of thermally cracked asphaltenes," *Fuel*, vol. 95, pp. 257–262, 2012.
- [103] N. N. Nassar, A. Hassan, and P. Pereira-Almao, "Comparative oxidation of adsorbed asphaltenes onto transition metal oxide nanoparticles," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 384, no. 1-3, pp. 145–149, 2011.
- [104] N. N. Nassar, A. Hassan, and P. Pereira-Almao, "Metal oxide nanoparticles for asphaltene adsorption and oxidation," *Energy and Fuels*, vol. 25, no. 3, pp. 1017–1023, 2011.
- [105] N. N. Nassar, "Asphaltene adsorption onto alumina nanoparticles: kinetics and thermodynamic studies," *Energy and Fuels*, vol. 24, no. 8, pp. 4116–4122, 2010.
- [106] F. B. Cortés, J. M. Mejía, M. A. Ruiz, P. Benjumea, and D. B. Riffel, "Sorption of asphaltenes onto nanoparticles of nickel oxide supported on nanoparticulated silica gel," *Energy and Fuels*, vol. 26, no. 3, pp. 1725–1730, 2012.
- [107] C. A. Franco, N. N. Nassar, M. A. Ruiz, P. Pereira-Almao, and F. B. Cortés, "Nanoparticles for inhibition of asphaltenes damage: Adsorption Study and Displacement Test on Porous Media," *Energy & Fuels*, vol. 27, no. 6, pp. 2899–2907, 2013.
- [108] N. N. Nassar, A. Hassan, and G. Vitale, "Comparing kinetics and mechanism of adsorption and thermo-oxidative decomposition of Athabasca asphaltenes onto TiO₂, ZrO₂, and CeO₂ nanoparticles," *Applied Catalysis A: General*, vol. 484, pp. 161–171, 2014.
- [109] C. A. Franco, M. M. Lozano, S. Acevedo, N. N. Nassar, and F. B. Cortés, "Effects of resin I on Asphaltene adsorption onto nanoparticles: a novel method for obtaining asphaltenes/resin isotherms," *Energy and Fuels*, vol. 30, no. 1, pp. 264–272, 2016.
- [110] ASTM, "Standard test method for sulfur in automotive, heating, and jet fuels by monochromatic energy dispersive X-ray fluorescence spectrometry," ASTM D7220-12, 2012.
- [111] ASTM, "D1298-12b Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method," 2012.
- [112] ASTM, "D7169-11 Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography," 2011.

- [113] H. A. Barnes, J. F. Hutton, and K. Walters, *An Introduction to Rheology*, Elsevier, 1989.
- [114] M. A. Rao, "Flow and functional models for rheological properties of fluid foods," in *Rheology of Fluid, Semisolid, and Solid Foods*, Food Engineering Series, pp. 27–61, Springer, Boston, MA, USA, 2014.
- [115] D. C. Montgomery and G. C. Runger, *Applied Statistics and Probability for Engineers*, John Wiley & Sons, 2010.
- [116] J. Murgich, M. Jesús Rodríguez, and Y. Aray, "Molecular recognition and molecular mechanics of micelles of some model asphaltenes and resins," *Energy & Fuels*, vol. 10, no. 1, pp. 68–76, 1996.
- [117] S. I. Andersen and J. G. Speight, "Petroleum resins: separation, character, and role in petroleum," *Petroleum Science and Technology*, vol. 19, no. 1-2, pp. 1–34, 2001.
- [118] J. G. Speight, "Petroleum asphaltenes—part 1: asphaltenes, resins and the structure of petroleum," *Oil & Gas Science and Technology*, vol. 59, no. 5, pp. 467–477, 2004.
- [119] J. J. Adams, "Asphaltene adsorption, a literature review," *Energy & Fuels*, vol. 28, no. 5, pp. 2831–2856, 2014.
- [120] N. N. Nassar, T. Montoya, C. A. Franco, F. B. Cortés, and P. Pereira-Almao, "A new model for describing the adsorption of asphaltenes on porous media at a high pressure and temperature under flow conditions," *Energy & Fuels*, vol. 29, no. 7, pp. 4210–4221, 2015.
- [121] S. Betancur, J. C. Carmona, N. N. Nassar, C. A. Franco, and F. B. Cortés, "Role of particle size and surface acidity of silica gel nanoparticles in inhibition of formation damage by asphaltene in oil reservoirs," *Industrial & Engineering Chemistry Research*, vol. 55, no. 21, pp. 6122–6132, 2016.
- [122] C. A. Franco, N. N. Nassar, T. Montoya, M. A. Ruíz, and F. B. Cortés, "Influence of asphaltene aggregation on the adsorption and catalytic behavior of nanoparticles," *Energy and Fuels*, vol. 29, no. 3, pp. 1610–1621, 2015.
- [123] R. Zabala, C. Franco, and F. Cortés, "Application of nanofluids for improving oil mobility in heavy oil and extra-heavy oil: a field test," in *Proceedings of the SPE Improved Oil Recovery Conference, Society of Petroleum Engineers*, April 2016.
- [124] E. A. Taborda, C. A. Franco, S. H. Lopera, V. Alvarado, and F. B. Cortés, "Effect of nanoparticles/nanofluids on the rheology of heavy crude oil and its mobility on porous media at reservoir conditions," *Fuel*, vol. 184, pp. 222–232, 2016.
- [125] S.-Y. Yang, G. J. Hirasaki, S. Basu, and R. Vaidya, "Statistical analysis on parameters that affect wetting for the crude oil/brine/mica system," *Journal of Petroleum Science and Engineering*, vol. 33, no. 1–3, pp. 203–215, 2002.
- [126] T. Montoya, D. Coral, C. A. Franco, N. N. Nassar, and F. B. Cortés, "A novel solid-liquid equilibrium model for describing the adsorption of associating asphaltene molecules onto solid surfaces based on the 'chemical theory'," *Energy & Fuels*, vol. 28, no. 8, pp. 4963–4975, 2014.
- [127] N. N. Nassar, S. Betancur, S. Acevedo, C. A. Franco, and F. B. Cortés, "Development of a population balance model to describe the influence of shear and nanoparticles on the aggregation and fragmentation of asphaltene aggregates," *Industrial and Engineering Chemistry Research*, vol. 54, no. 33, pp. 8201–8211, 2015.
- [128] T. Montoya, B. L. Argel, N. N. Nassar, C. A. Franco, and F. B. Cortés, "Kinetics and mechanisms of the catalytic thermal cracking of asphaltenes adsorbed on supported nanoparticles," *Petroleum Science*, vol. 13, no. 3, pp. 561–571, 2016.
- [129] J. D. Guzmán, S. Betancur, F. Carrasco-Marín, C. A. Franco, N. N. Nassar, and F. B. Cortés, "Importance of the adsorption method used for obtaining the nanoparticle dosage for asphaltene-related treatments," *Energy & Fuels*, vol. 30, no. 3, pp. 2052–2059, 2016.



Hindawi

Submit your manuscripts at
<https://www.hindawi.com>

