Reduction of heavy oil viscosity through ultrasound cavitation assisted by NiO nanocrystals-functionalized SiO₂ nanoparticles

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Abstract
The objective of this study is to reduce heavy oil viscosity through the catalytic decomposition of heavy fractions by ultrasound cavitation using metal oxide nanoparticles and water as a hydrogen donor, leading to the reduction of asphaltene content through its conversion into lighter components. NiO nanoparticles were synthesized over a 7 nm silica support using the incipient wetness technique. Emulsified heavy oil (HO) with 40%v/v of water and 13°API was used to evaluate the ultrasound cavitation process over different exposure times and nanoparticle dosages. The viscosity of the emulsified HO before and after ultrasound cavitation was measured with and without nanoparticles. Significant viscosity reduction was obtained, showing best results at 90 minutes of ultrasound exposure time with a nanoparticle dosage of 2000 mg/L, leading to a viscosity reduction at 10 s⁻¹ and 25°C, and an asphaltene content reduction of 44 and 16%, respectively.

Keywords: asphaltenes; heavy oil; nanoparticles; ultrasound cavitation; viscosity.

Reducción de la viscosidad de crudos pesados mediante cavitación por ultrasonido asistida por nanopartículas de SiO₂ funcionalizadas con nanocristales de NiO

Resumen
El objetivo de este estudio es la reducción de viscosidad de crudos extra-pesados mediante la descomposición catalítica de las fracciones pesadas del crudo y su conversión en sub-compuestos más livianos utilizando cavitación por ultrasonido asistida por nanopartículas. Nanopartículas de NiO fueron sintetizadas sobre sílice nanoparticulada de 7 nm usando la técnica de impregnación incipiente. Un crudo emulsionado con un contenido aproximado de 40%v/v de agua y 13°API fue usado para evaluar el proceso de cavitación aplicando distintos tiempos de exposición y dosificaciones de nanopartículas. La viscosidad del crudo a 10 s⁻¹ y 25°C fue medida antes y después del tratamiento en ausencia y presencia de nanopartículas. Los mejores resultados observados fueron a un tiempo de exposición de 90 minutos con una dosificación de nanopartículas de 2000 mg/L, generando reducciones de viscosidad y en el contenido de asfaltenos del 44 y 16%, respectivamente.

Palabras clave: asfaltenos; cavitación por ultrasonido; crudo pesado; nanopartículas; viscosidad.

1. Introduction

As the petroleum industry advanced over the last century, it encouraged many of the technological advances that developed over the same period, providing a cost-effective energy resource in almost all human social spheres [1].

However, as conventional crude oils have been exploited to satisfy world energy demands, HO (heavy oil) and EHO (extra-heavy oil) reserves have gained significant importance [2]. Nevertheless, exploiting HO and EHO carries appreciable technological challenges and issues for the petroleum industry in the different processes of production,

transport, and refining due to the fluid's properties, such as low API gravity, emulsifying tendencies, low gas/oil ratios, a high content of heavy components and high viscosities [3]. There is no direct relation between fluid density and viscosity in crude oils. However, it is common to find crude oils with low API gravity that have a high viscosity [4,5]. Oil mobility is a significant factor which accounts for fluid flow capacity through porous media and depends on relative permeability and fluid viscosity ratio, directly affecting recovery factors from a specified reservoir [6,7]. Also, at surface conditions, there are several standards for transporting fluids that include specific viscosity conditions [3]. HO and EHO high viscosity is caused by the large amount of organic compounds such as resins and asphaltenes that they contain [8,9]. Since HO and EHO have a high asphaltene and resin content, these compounds self-associate, leading to the formation of a complex viscoelastic network which is the main cause of high viscosity [10-13].

Several studies have been carried out to develop different kinds of treatments for increasing HO and EHO mobility at reservoir conditions (*in-situ*) and improving their properties for transport once brought to the surface. *In-situ* treatments include thermal enhanced oil recovery (EOR) [14-17], injection of solvents and light oils [18-20], deasphalting [21,22], and other treatments based on nanotechnology [7,23,24]. However, in many cases, these operations have been proven to promote distinct formation damage (FD) processes such as unwanted lithological changes related to mineral dissolution and transformation, wettability alterations, absolute permeability reductions due to the high complexity of the techniques and the completely unknown conditions in the reservoir which greatly encumber flow assurance [25].

At the surface, different techniques have been implemented, including heating [26,27], dilution [28], transport by oil-in-water (O/W) emulsions formation [29], partial upgrading [30], electromagnetic fields induction [31], and annular flow [32]. Nevertheless, these methods may have an adverse environmental impact [22,33] and could lead operations to be non-cost-effective due to high quantities of diluent, low perdurability, the possibility of formation damage due to the inestability of asphaltene in the presence of diluents such as naphta, enviromental impact due to low saturation pressure and high evaporation, or the additional costs of separation mainly in the emulsion formation [34].

Therefore, new and cost-effective technologies need to be developed to fulfill the production and transport requirements of HO and EHO. Hence, ultrasound application for the creation of cavitation bubbles has been proven to upgrade HO feedstock by breaking the heavy molecules followed by a hydrogenation process [35]. Cavitation has been proven to foment an increase in temperature and pressure as gas bubbles collapse within the working fluid [36,37]. It has been reported that the application of ultrasound cavitation along with surfactants can reduce the asphaltene content by 35% by converting the asphaltenes into gas oil and resins [36], using the water from an Oil-in-Water emulsion (O/W) as a hydrogen donor in order to generate termination reactions between asphaltene free radicals obtained by cracking reactions and the dissociated hydrogen radicals from the

water. Likewise, Kaushik *et al.* [38] employed ultrasound cavitation for vacuum residue upgrading, generating positive physicochemical changes in the feedstock.

Nowadays, nanoparticles are being used for multiple purposes in the oil and gas industry and may also be included in the cavitation system for improving the efficiency of the process [39]. Nanosized solid particles can selectively adsorb asphaltene and act as catalysts to break the structure of heavy molecules [40,41]. At the nano-scale, exceptional properties can be obtained, such as a high surface area to volume ratio and dispersibility, in addition to high thermal and chemical stability and dispersibility. The reactivity of particles with nanometric dimensions is significantly enhanced because the functional groups on the material's surface are hindered less as the size of the particle decreases. In other words, atoms on the surface of the nanomaterials are not surrounded by other atoms of the same material and can, therefore, interact with other compounds [42]. Also, due to their small size (1-100 nm), nanoparticles may be employed in both subsurface and surface conditions [43].

In this way, in the specialized literature only Askarian *et al.* [39] have evaluated nanoparticle usage in a cavitational cracking process. The authors employed iron oxide nanoparticles and used gasoline as a hydrogen donor, finding that the HO viscosity may be reduced by up to 20% and that the presence of nanoparticles lead to an increase in hydrogenation and/or cracking reactions. Nanoparticles of PdO and/or NiO supported on silica [44], alumina and titania [45], have been synthesized for the adsorption and subsequent catalytic decomposition of heavy compounds. Functionalized nanoparticles show enhanced adsorption capacity and high catalytic activity in the reduction of the decomposition temperature of refractory compounds of crude oil such as asphaltenes and resins. Different physicochemical properties of nanoparticles of the same chemical nature play a more critical role in the n-C_7 asphaltene adsorption than in catalytic cracking [41].

Nevertheless, functionalized nanoparticles have not been employed for improving the performance of the cavitation process. Therefore, the main objective of this work is to use NiO-functionalized silica nanoparticles for the enhancement of the cavitation process to reduce HO and EHO viscosity. NiO active sites on the surface of the silica nanoparticles lead to augmented adsorption of asphaltenes and contribute to cracking and their conversion into lighter compounds.

2. Methodology

2.2. Materials

NiO nanoparticles were synthesized over a 7 nm silica support (Sigma-Aldrich, St. Louis, MO) using a salt of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, Merk KGaG, Germany) as has been reported in previous studies [40].

A HO with approximately 40% emulsified water and 13 °API was used to evaluate ultrasound cavitation performance for viscosity reduction with and without nanoparticles in order to use the emulsified water as a hydrogen donor and evaluate droplets coalescence caused by cavitation and nanoparticle usage alongside viscoelastic network disruption as additional mechanisms in viscosity reduction.

The HO selected for the viscosity reduction tests was tested for saturates, aromatics, resins and asphaltene (SARA) content through a micro-deasphalting technique with n-heptane coupled to thin-layer chromatography following the IP 469 standard [46] using a TLC-FID/FPD Iatroscan MK6 (Iatron Labs Inc, Tokyo, Japan). SARA analyses were performed on HO samples before and after treatment. The contents of saturates, aromatics, resins and asphaltene were estimated at 18.23 wt%, 23.04 wt%, 41.71 wt%, and 17.02 wt%, respectively.

2.3. Experimental section

2.3.1. Synthesis of NiO-functionalized nanoparticles

NiO nanoparticles were synthesized in a 1 wt% dosage over 7 nm SiO_2 nanoparticles using the incipient wetness technique [47]. First, SiO_2 nanoparticles were dried for 2 hours at 120°C. A determined amount of the SiO_2 was placed in a thin layer on the bottom of a flat flask into which an aqueous solution of $Ni(NO_3)_2$ was dripped slowly to guarantee homogeneous impregnation. Finally, the material was dried at 120°C for 6 hours, and further calcined at 450°C for 6 hours to obtain the metal oxide nanoparticles [40]. The hybrid material in this study is named SiNi1, using the initials of the support substance, the symbol of the cation of the resulting metal oxide, and its weight percentage [40].

2.3.2. Nanoparticles characterization

The hydrodynamic diameter of the nanoparticles was measured using a dynamic light scattering technique (DLS) using a NanoPlus-3 (Micromeritics, USA) and X-ray diffraction (XRD) with an XPert PRO MPD X-ray diffractometer (PANalytical, Almelo, Netherlands). Surface area (S_{BET}) was determined using Brunauer–Emmett–Teller (BET) theory [48] through N_2 physisorption at -196°C using a surface area analyzer Gemini VII 2390r (Micromeritics, GA, USA) [49]. Characterization of the functional groups on the nanoparticles' surface was performed using Fourier transform infrared spectroscopy (FTIR) with an IRAffinity-1 FTIR (Shimadzu, Japan) spectrophotometer [50,51]. Additional information on the characterization of nanoparticles can be found in previous publications [40,52,53].

2.3.3. Emulsified heavy oil characterization

The emulsified heavy oil was characterized using droplet imaging through optic microscopy with a Motic BA310 microscope (Motic, Stockholm, Sweden). This process was carried out on the emulsified oil before and after treatment with and without SiNi1 nanoparticles in order to analyze the effect of cavitation and the addition of nanoparticles in the interfacial tension decrease observed through the droplets coalescence.

2.3.4. Cavitation treatment

An Elmasonic E60H sonicator (Elma Schmidbauer GmbH, Singen, Germany) was employed to provide the ultrasound cavitation treatment at 400 W of power and a frequency of 37 kHz. Sonication was applied, varying the samples' exposure time at 10, 30 and 90 minutes as well as the dosage of SiNi1 nanoparticles at 500, 1000 and 2000 mg/L. Experiments were conducted at atmospheric pressure and room temperature (25°C). Viscosity reduction caused by the addition of nanoparticles but with zero ultrasound cavitation exposition time was also evaluated. The effect of the nanoparticles supported on SiO_2 was also evaluated to find a base line. The sample was evaluated for remaining asphaltene content and better performance through micro-deasphalting with *n*-heptane.

2.3.5. Viscosity and rheology measurements

Viscosity and rheology measurements were performed in a Kinexus Pro+ rheometer using a GAP of 0.3 mm with serrated plate–plate geometry [13,24]. The viscosity of the samples was measured at a constant shear rate of 10 s^{-1}. The degree of viscosity reduction (DVR) was determined according to Eq. (1) [13,24,54]:

$$DVR = \left(\frac{\mu_{ref} - \mu_{treat}}{\mu_{ref}}\right) \times 100 \qquad (1)$$

where, μ_{ref} and μ_{treat} are the reference viscosity and viscosity after treatment, respectively. The effect of the shear rate of the HO was evaluated before and after cavitation treatment with nanoparticles ranging from 10 to 100 s^{-1}. All experiments were performed triplicate and the uncertainties are presented as error bars.

3. Rheological modeling

In order to carry out a phenomenological explanation of the ultrasound cavitation effect on viscosity reduction alongside additional mechanisms involving viscoelastic network disruption and droplets coalescence, different rheological models, namely those proposed by Cross and Carreau, have been used to describe the rheological behavior of the untreated and treated samples, as in previous studies these have been proven to have a good fit [23]. The equations corresponding to these models are shown below:

$$\mu = \mu_{\infty,\dot{\gamma}} + \frac{\mu_{0,\dot{\gamma}} - \mu_{\infty,\dot{\gamma}}}{1 + (\alpha_c \dot{\gamma})^m} \qquad (2)$$

Eq. (2) describes the Cross model where, μ (cP) is viscosity, α_c (s) characteristic relaxation time, $\dot{\gamma}$ (s^{-1}) shear rate, m constant, $\mu_{\infty,\dot{\gamma}}$ (cP) viscosity at infinite shear rate and $\mu_{0,\dot{\gamma}}$ (cP) viscosity at zero shear rate.

$$\mu = \mu_{\infty,\dot{\gamma}} + \frac{\mu_{0,\dot{\gamma}} - \mu_{\infty,\dot{\gamma}}}{(1 + (\lambda_c \dot{\gamma})^2)^N} \qquad (3)$$

Eq. (3) accounts for the Carreau model, where λ_c (s) is characteristic relaxation time, and N a constant.

4. Results and discussion

4.1. Nanoparticles characterization

Table 1 shows the properties of the SiO_2 and SiNi1 nanoparticles. It is observed that after the functionalization
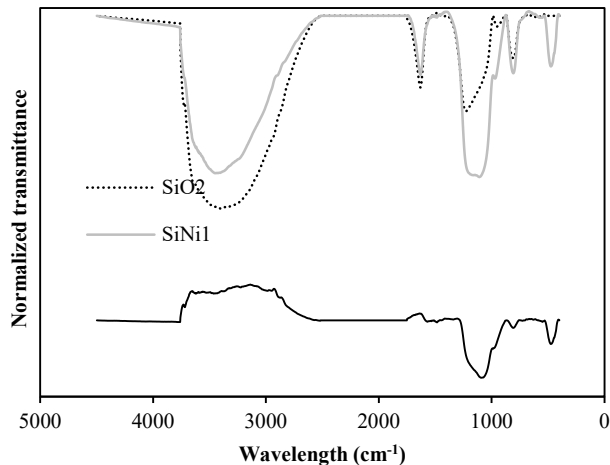
Figure 1. FTIR spectra for SiO₂ and SiNi1 nanoparticles.
Source: The authors.

Table 1
Surface area and mean particle size of SiO₂ and SiNi1 nanoparticles.

Material	S_{BET} (± 0.1 m²/g)	dp SiO₂ (± 0.2 nm)	dp NiO (± 0.2 nm)
SiO₂	389.00	7.1	-
SiNi1	290.31	7.1	1.9

Source: The authors.

process, the surface area of the nanoparticles is reduced and this could be due to the blockage of some pore space in the support. The mean particle size of NiO nanoparticles over the SiO₂ surface was estimated to be 1.9 nm. Fig. 1 shows the FTIR spectrum of SiO₂ and SiNi1 nanoparticles, as well as the difference spectrum of both materials. The SiO₂ FTIR spectrum shows silica bands assigned to different vibrations in the solid structure. Silanol (Si-OH) groups are observed in the band located at 3780-2470 cm⁻¹ along with an overlapping O-H bond, corresponding to the water molecules [55]. Moreover, a band centered at 1630 cm⁻¹ could correspond to deformation vibrations created by adsorbed water molecules, while the band between 1000 and 1300 cm⁻¹ shows the Si-O covalent bond vibrations. Furthermore, siloxane (O-Si-O) symmetric vibrations appear at about 808 cm⁻¹ [56]. The SiNi1 nanoparticles FTIR spectrum shows significant changes due to the calcination process during SiO₂ functionalization. An increase in siloxane groups is observed, this is due to oxidation caused by calcination, as well as a decrease in silanol groups and water adsorbed, generated by the same process [57]. In addition, the increase in the absorption band near 430 cm⁻¹ confirms the presence of NiO nanoparticles in the system as this is related to Ni–O bond vibration [58, 59]. Furthermore, when looking at the difference spectrum, it can be observed that the main bands related to the SiO₂ support are subtracted and that bands corresponding to the NiO are exposed.

4.2. Viscosity reduction evaluation

4.2.1. Effect of exposure time

Ultrasound cavitation exposure time was evaluated for 0, 10, 30, and 90 minutes to identify the time range in which

DVR is higher. It is worth mentioning that HO without nanoparticles was stirred by hand for 15 minutes, as was the HO with different nanoparticles added. Panels a and b from Fig. 2 show the a) viscosity and b) degree of viscosity reduction for HO before and after the cavitation process with a fixed concentration of 1000 mg/L of SiNi1 nanoparticles for different exposure times. Fig. 2 shows that the viscosity of the sample decreases as the exposure time increases, and this could be due to that fact that as time increases, a higher number of bubbles would be involved in the cavitation process. For the sample that includes SiNi1 nanoparticles, a DVR of 12% is observed when only the nanomaterial is added. This DVR is similar to that of the sample without nanoparticles with an exposure time of between 30 and 90 min. The highest reduction in viscosity (42%) was obtained for the system with nanoparticles and 90 min of exposure time. All experiments were performed in triplicate and the uncertainties are presented as error bars with values < 2%.

4.2.2. Effect of support and nanoparticles dosage

An exposure time of 90 min was selected for evaluating the effect of the SiO₂ support and the effect of the nanoparticle concentration. Furthermore, SiNi1 nanoparticle
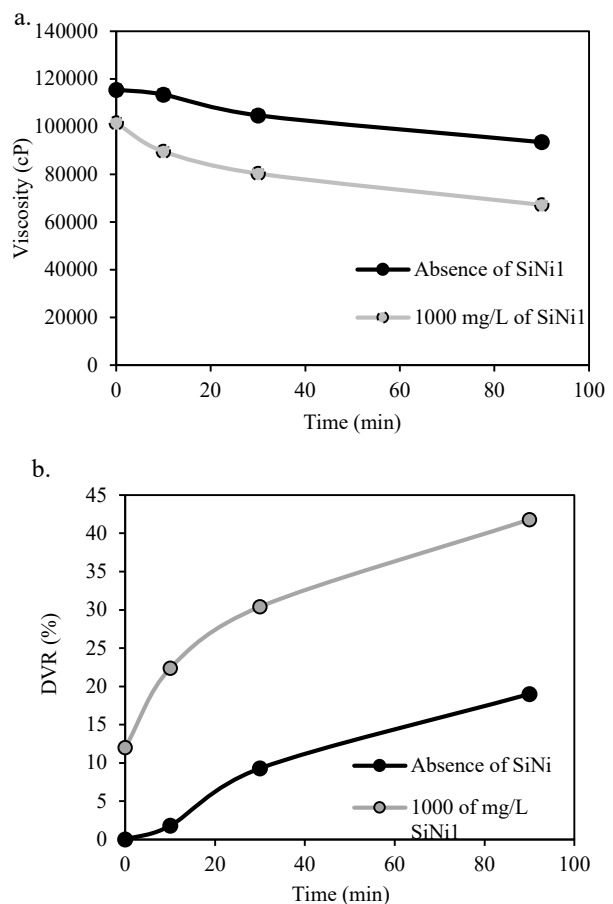

Figure 2. a) Viscosity and b) viscosity reduction degree for HO before and after cavitation process with 1000 mg/L of SiNi1 nanoparticles for different exposure times of 0, 10, 30 and 90 min. Temperature = 25 °C and 10 s⁻¹.
Source: The authors.

concentrations of 500 and 2000 mg/L were evaluated. Fig. 3 shows the degree of viscosity reduction for a) no ultrasound treatment, b) ultrasound exposure evaluating the effect of nanoparticle dosage and SiO_2 support on the HO viscosity reduction. It can be observed in Fig. 3a that a higher viscosity reduction is obtained for the samples that include nanoparticles. These results can be explained due to the adsorption of asphaltenes, a process which disrupts the asphaltene viscoelastic network favoring HO flow capacity [13]. Additionally, it is observed that the higher DVR (20%) was obtained from a 1000 mg/L dosage of SiNi1 nanoparticles. However, when comparing dosages of 1000 and 2000 mg/L in Fig. 3b, the viscosity reduction is 2% higher for the highest dosage, indicating that a concentration of 1000 mg/L could be enough. It is observed that the role of SiO_2 role in viscosity reduction is lower than that of the SiNi1 nanoparticles and this is mainly due to the fact that adsorptive capacity and catalytic activity are better in the functionalized material [60].

4.2.3. Effect of droplets coalescence

Figure 4 shows the mean droplet size of emulsified heavy oil before and after the cavitation process during 90 minutes with and without 1000 mg/L of SiNi1 nanoparticles. When
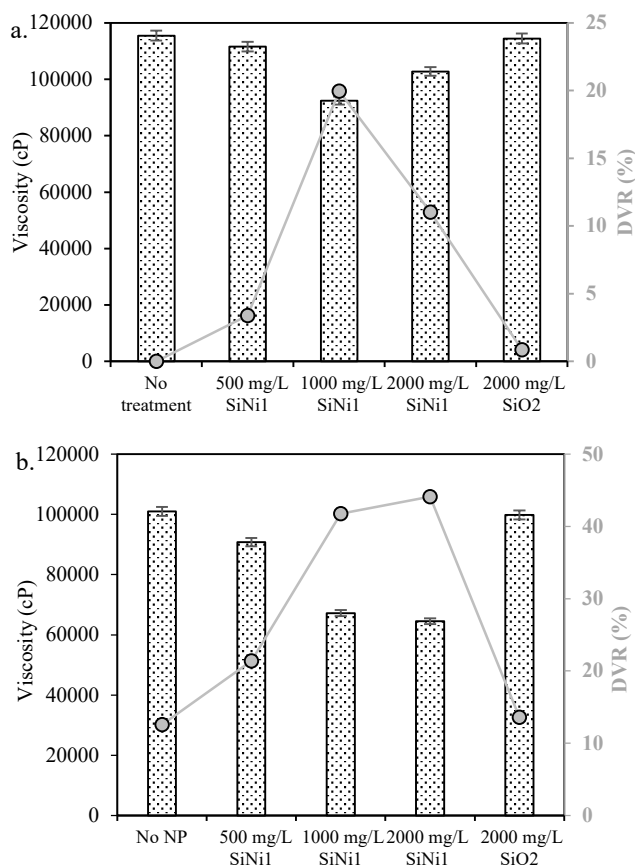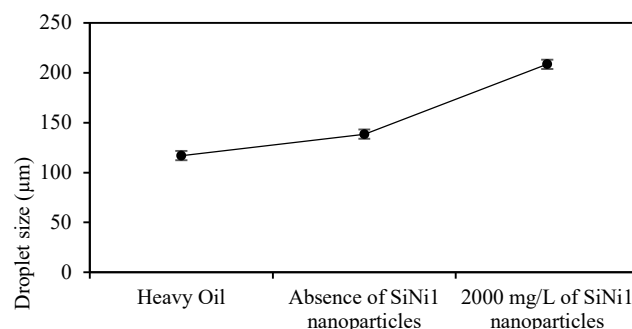

Figure 4. Mean droplet size of emulsified heavy oil before and after cavitation process with and without 1000 mg/L of SiNi1 nanoparticles. Exposure time = 90 minutes; Temperature = 25 °C.
Source: The authors.

only the ultrasound cavitation treatment is applied the effect on droplets coalescense is minimal, which minimizes the effect of viscosity reduction from either the demulsifying process or the hydrogenation of free radicals obtained by cracking reactions. However, with the addition of nanoparticles to the system, an appreciable droplets calescence effect was obtained which can be identified by the increase in the size of the droplets, allowing the dissociated hydrogen to freely interact with the HO and futher generating termination reactions with the free radicals obtained from the asphaltenes [36]. Mean droplet size measurements also showed almost negligible errors of less than 5%.

4.2.4. Rheological behavior

The effect of the shear rate on rheological behavior is shown in Fig. 5 for the untreated sample and HO after the cavitation process with 1000 mg/L of SiNi1 nanoparticles. As expected, as shear rate increases, viscosity decreases dramatically, with both fluids exhibiting a pseudoplastic behavior. Additionally, it can be seen that the viscosity of the treated sample is lower than that of the untreated one, corroborating the performance of the catalytic decomposition reaction produced by the ultrasound cavitation treatment alongside the viscoelastic network disruption mechanism.

A phenomenological approach to the experimental data was carried out using rheological modeling based on the Cross and Carreau models which in previous studies have proved to be a good fit for the rheological behavior of crude oils.

The rheological model illustrates that the parameters have a logical tendency in which both $\mu_{\infty,\dot{\gamma}}$ and $\mu_{0,\dot{\gamma}}$ have lower values than the sample submitted to ultrasound cavitation with 2000 mg/L of SiNi1. Furthermore, a better fit was achieved using the Cross model which can be seen in the lower root-square-mean error values. A decrease in the m constant for the Cross model was observed for the treated sample, which indicates that this fluid showed a more Newtonian behavior, while the α_c is similar for both samples, which indicates a similar internal structure recovery time after being subjected to disturbance.

Figure 3. Effect of SiNi1 nanoparticle dosage (0, 500, 1000, and 2000 mg/L) and SiO_2 support (2000 mg/L) on the HO viscosity reduction for a) no ultrasound treatment, b) after ultrasound exposure. Exposure time = 90 minutes; Temperature = 25 °C and 10 s^{-1}.
Source: The authors.

Table 2.
Estimated parameters of the Cross and Carreau rheological models for the untreated sample and the crude oil after ultrasound cavitation with 2000 mg/L of SiNi1.

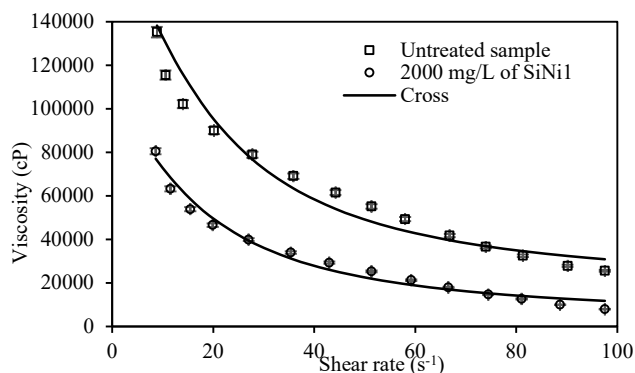| Model	Parameter	Untreated sample	2000 mg/L of SiNi1
	α_c (s)	0.051	0.047
	m	1.48	1.39
Cross	$\mu_{\infty,\dot\gamma}$ (cP)	17351.89	3104.78
	$\mu_{0,\dot\gamma}$ (cP)	175141.70	103288.46
	RSME (%)	0.54	0.88
	λ_c (s)	0.07	0.07
	N	0.61	0.62
Carreau	$\mu_{\infty,\dot\gamma}$ (cP)	17414.67	2957.83
	$\mu_{0,\dot\gamma}$ (cP)	170811.52	93772.71
	RSME (%)	0.69	0.96

Source: The authors.

Figure 5. Heavy oil before and after the cavitation process with and without 1000 mg/L of SiNi1 nanoparticles. Exposure time = 90 minutes; Temperature = 25 °C.
Source: The authors.

4.2.5. Asphaltene content reduction

The micro deasphalting technique was carried out on the HO before and after treatment to corroborate the catalytic decomposition of the heavy fraction of crude oil. For these experiments, the sample that had obtained better results in viscosity reduction was selected. A decrease in asphaltene content from 17.02 to 14.30 wt% was observed, showing a reduction of 16%. Results indicate that nanoparticles can enhance the decomposition of asphaltenes during the cavitation process. These results coincide with previous studies in which NiO-functionalized nanoparticles have been able to reduce the effective activation energy for asphaltene decomposition, leading to the obtention of lighter compounds and the upgrading of heavy oil [40,44,61,62].

5. Conclusions

This study evaluated heavy oil viscosity reduction through a decrease in its asphaltene content. Its conversion into lighter compounds was achieved through a catalytic decomposition reaction propitiated by an ultrasound cavitation treatment, assisted by NiO nanoparticles. The exposure time, nanoparticle dosage and incidence of emulsified water were studied for their effect on changes in viscosity. Results showed that nanoparticles could reduce viscosity in heavy oils by disrupting the asphaltene viscoelastic network, and by the catalytic decomposition of the heavy fraction after ultrasound cavitation treatment with a dosage of 1000 mg/L. The Cross model described the rheological behavior of the crude oil before and after treatment well. The parameters of the Cross model indicated that after ultrasound cavitation with SiNi1 nanoparticles, the crude oil shows a more Newtonian behavior. Reduction of asphaltene content corroborated that the presence of SiNi1 nanoparticles during the ultrasound cavitation treatment lead to catalytic decomposition of the heavy fraction. The scaling up of this technology can be performed at both surface or sub-surface conditions according to the needs of the oil well and/or oilfield. Further studies should include the effect of other metal oxide and nanoparticle supports, as well as the inclusion of a carrier fluid. This study aims to widen the scope for the application of nanofluids and nanoparticles in the oil and gas industry.

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