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Full Length Article

Rheological demonstration of alteration in the heavy crude oil fluid structure upon addition of nanoparticles

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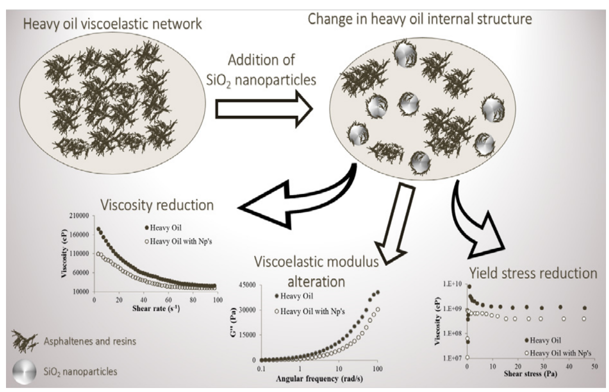
HIGHLIGHTS

- The addition of 1000 mg/L of SiO_2 nanoparticles simultaneously reduced both viscosity and yield stress of heavy oil.
- The nanoparticles interact directly with the asphaltenes and hence with the viscoelastic network.
- The presence of nanoparticles in the matrix of heavy oil generates a change in the internal structure of the fluid.
- The results obtained confirm that nanoparticles affect the internal structure of heavy oil, by modifying the viscoelastic network of asphaltenes.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanotechnology offers potentially disruptive methods to improve the mobility of heavy oil through viscosity reduction. In this sense, the objective of this work is to probe changes in the viscoelastic network of asphaltenes intrinsic to heavy oil structure upon addition of fumed SiO_2 nanoparticles, using dynamic rheological techniques. The effects of the addition of nanoparticle (100, 1000 and 10,000 mg/L) on heavy oil are patently reflected as a viscosity reduction (for shear rates between 0 and 100 s^{-1}) and a non-Newtonian shear thinning behavior. The best concentration of nanoparticles over the wide range evaluated is obtained at 1000 mg/L, which was evaluated at 288, 298 and 313 K. The viscosity reductions were found to range from 12 to 45% in the shear rate range 0–100 s^{-1}. The linear viscoelastic region (LVR) was determined by running an amplitude sweep test at 10 rad/s and 298 K. Viscoelastic moduli were measured in dynamic tests in a frequency range from 0.1 to 100 rad/s at a strain of 2% and at temperatures of 288, 298 and 313 K. For heavy crude oil without nanoparticles, the magnitude of the loss modulus G'' and its growing trend suggest the existence of a viscoelastic network of asphaltenes and auto-associative behavior. For all tests, the loss modulus, G'', is always greater than the storage modulus G', suggesting that the crude oil is more viscous than elastic, except at 313 K and at a frequency > 30 rad/s, where G' is greater than G''. By adding 1000 mg/L of nanoparticles, the magnitude of the viscoelastic moduli is reduced compared to values for crude oil without nanoparticles. The results conclusively prove that nanoparticles disrupt the viscoelastic network formed by asphaltenes aggregates in the presence of resins, and this causes the viscosity reduction in heavy crude oil. This conclusion is further supported by results obtained when nanoparticles were added to de-asphalted oil (DAO) and light oil with a low asphaltene content; in both cases the viscosity increases, suggesting that the nanoparticles interact

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directly with asphaltenes in crude oil. Effects are observed if asphaltenes are present at high enough concentration.

1. Introduction

At present, heavy (HO) and extra-heavy crude oils (EHO) represent a significant percentage of the current and future oil production, as their reserves duplicate those of light crudes [1,2]. Latin America represents a key player with the largest reserves worldwide [3,4]. However, the oil industry has several operational challenges related to the management and production of these crude oils due to their high viscosities and abundant fractions of heavy hydrocarbon components [5–7]. The most common techniques to optimize the conditions of transport and mobility of heavy oil at surface or reservoir conditions include oil de-asphalting [8–10], transport in the form of oil-in-water (O/W) emulsions [11–13], reducing the drag forces with annular flow [14–17], enhanced (EOR) or improved oil recovery (IOR) through thermal processes [18–22] and in-situ upgrading [23–26].

Since heavy and extra-heavy oils are highly viscous, the study of their rheology is vital for understanding and optimizing their production and transport. Rheology is part of the physics of continuum media that studies the deformation and flow of matter [27,28], and as such, it is essential for understanding the behavior of fluids in motion. Steady-state and dynamic oscillometry serve as rheological tools to analyze the viscoelastic behavior of heavy crude oils, which directly relates to the fluid internal composition and structure. Thus, many researchers [29–36] have used both the steady-state and transient rheology to characterize heavy and extra-heavy crude oils subjected to a variety of conditions with the objective of optimizing their mobility and transportation. One of the most commonly used techniques for reducing HO and EHO viscosities and hence increase oil production rate has been the dilution with solvents, light hydrocarbons [37–42], and some R=O bounds-based chemical compounds [43]. In this way, several authors have focused on studying diluted HO and EHO with different solvents [43–46] often evaluating the rheology behavior of the fluid mixture [30,31,44].

Recently, Mortazavi-Manesh and Shaw [47] studied the effect of different types of chemical compounds on the rheological properties of Maya crude oil at various temperatures. The compounds used in their study were toluene, *n*-heptane and a 50/50 vol% mixture of toluene and butanone. The rheological evaluation was performed using steady-state methods at share rates 0–200 s^{-1}; as expected, dilution and temperature increase reduced oil viscosity. These mixtures exhibit a characteristic non-Newtonian shear-thinning behavior, but with increasing temperature, the Newtonian behavior becomes dominant. Solvents in decreasing viscosity reduction effectiveness for the entire range evaluated are a mixture of toluene-butanone > toluene > *n*-heptane. Earlier, Mortazavi-Manesh and Shaw [48] characterized Maya crude oil to investigate its thixotropic characteristics as a function of temperature to determine the influence of time on viscosity measurements. The authors demonstrated that the thixotropic behavior of this oil increases as temperature decreases. Authors performed thixotropy measurements based on three tools widely used: hysteresis loops, step-wise change in shear rate and start-up experiments. The results are useful to optimize pipeline transport conditions, mainly in processes where pressure is required to restart fluid flow. Pierre et al. [30] evaluated the effect of asphaltenes on the viscosity of a Venezuelan heavy crude oil. First, they determined the influence of asphaltenes and resins on oil viscosity by extraction with *n*-pentane and *n*-nonane and the subsequent dissolution in xylene. For all experiments, the authors demonstrated that with increments of the asphaltene content, the viscosity increases significantly. Additionally, the authors characterized the heavy oil using a dynamic oscillometric method and examined the influence of asphaltenes on the crude oil viscoelastic behavior. The results showed the presence of an internal network of colloids formed by asphaltenes. Behzadfar and Hatzikiriakos [49] studied the viscoelastic properties of bitumen from the Athabasca oil sands by oscillometry at different temperatures; also, they proposed a constitutive equation based on the K-BKZ model, widely used in the rheology of polymer melts. The results indicate that the constitutive equation predicts reasonably well the linear viscoelastic response of the bitumen, for the range of temperatures evaluated. To describe the rheological behavior one should obtain the parameters to feed the K-BKZ equation, and for this reason, the authors used the generalized Maxwell model that fits the linear response of the bitumen under dynamic flow corresponding to the small amplitude shear oscillator. Abivin et al. [50] studied the viscoelastic behavior of 13 different heavy crude oils from Asia and America, in a temperature range between −50 and 50 °C. The article presents comparative results of the viscoelastic properties such as phase angle, viscoelastic moduli and relaxation times, among crude oils with similar rheological behavior (Newtonian and non-Newtonian). The authors concluded that for some crude oils, the viscoelastic nature related to the presence of waxy paraffinic crystals. However, for another group of crude oils, the viscoelastic behavior related to the high content of asphaltenes, present in a high percentage, which produces a macroscopic behavior similar to a weak gel, due to the auto-associative tendency of asphaltenes to create an elastic network in the oil.

Recently, nanotechnology has been shown to enable viscosity reduction of heavy oil in experiments where nanoparticles were incorporated into the oil. These particles interact with the heavier fractions of the fluid and thereby alter the viscoelastic components of heavy crude oil. Due to their exceptional characteristics, such as small particle size (1–100 nm), large available surface area, high dispersibility and tunable physicochemical characteristics, nanoparticles are prone to selectively adsorb asphaltenes and inhibit their self-association [51–53]. Our research group has pioneered this novel topic of research [52,54,55] and has demonstrated the ability of nanoparticles to reduce viscosity and increase the mobility of heavy oil at reservoir conditions as tested at both laboratory [56] and field scales [57]. It has been observed that SiO_2 nanoparticles are able to reduce the viscosity of heavy oil to a greater degree than other nanomaterials, which has been mainly attributed to high adsorptive capacities of asphaltenes that lead to the reduction of its mean aggregate size and consequently to the perturbation of the viscoelastic network formed [56]. Also, results of coreflooding tests at reservoir conditions showed that SiO_2 nanoparticles are able to increase heavy-oil mobility and therefore oil recovery [56]. When evaluated in the field [57], it was found that by forcing an average amount of 175 bbl of nanofluid within a radius of penetration of ~3 ft, the oil rate can be increased approximately 56 and 63% for a HO and a EHO with API gravities of 12° and 8°, respectively. Although several papers in the specialized literature report viscosity reduction using nanoparticles, these mainly relate to high-temperature processes in thermal enhanced oil recovery. Research involving viscosity