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Effect of nanoparticles/nanofluids on the rheology of heavy crude oil and its mobility on porous media at reservoir conditions

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Esteban A. Taborda [a], Camilo A. Franco [a,b,*], Sergio H. Lopera [b], Vladimir Alvarado [c], Farid B. Cortés [a,b,*]

[a] Grupo de Investigación en Fenómenos de Superficie – Michael Polanyi, Facultad de Minas, Universidad Nacional de Colombia-Sede Medellín, Colombia
[b] Grupo de Investigación en Yacimientos de Hidrocarburos, Facultad de Minas, Universidad Nacional de Colombia-Sede Medellín, Colombia
[c] Department of Chemical Engineering, University of Wyoming, Dept. 3295, 1000 E. University Avenue, Laramie, WY 82071, United States

ABSTRACT

In this work, we evaluate the effect of nanoparticles and nanofluids as viscosity reducers for heavy crude oil (HO). The effect of alumina, silica and acidic silica nanoparticles was evaluated through n-C$_7$ asphaltene adsorption and aggregation tests using UV–vis spectrophotometry and dynamic light scattering. The nanoparticles of acidic silica were used to prepare a water-based nanofluid at different concentrations in distilled water, and also with the addition of 2.0 wt% of a non-ionic surfactant. The shear rheological response was obtained as function of nanoparticle concentration, temperature (from 298 to 323 K) and shear rate (ranging from 0 to 100 s^{-1}). Experimental results indicate that increasing the concentration of nanoparticles in the mixture, up to 10,000 ppm, leads to a viscosity reduction of approximately 90% in comparison with the nanoparticle-free crude oil. At higher concentration of nanoparticles, the effectiveness of the heavy-oil viscosity reduction diminishes. Rheological tests showed a non-Newtonian behavior for the mixtures tested at 298 K. However, as the temperature reaches 323 K the specimens behave in a Newtonian fashion. Coreflooding tests were conducted under typical reservoir conditions of pore and overburden pressures, i.e. 2600 and 3600 psi, respectively, and at 360 K. Results indicate that the addition of nanoparticles increases the heavy oil mobility and leads to an improvement in oil recovery of roughly 16%.

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1. Introduction

The world's reserves of crude oil amount to 30% in conventional and 70% in non-conventional reservoirs, respectively. Among the latter reservoir type, heavy oil (HO) and extra-heavy oil (EHO) represent approximately 25% and 45% of these resources, respectively [1,2]. Latin America possesses the largest reserves of HO and EHO worldwide, with Venezuela and Colombia having the first and fifth of largest reserves in the region [3,4]. However, the production, transport and refining of HO and EHO represent a considerable set of technological challenges [5–7]. The main challenging characteristics of these crude oils, namely their high specific gravity and high viscosity, complicate their production, transport and refining [5,6,8]. In the context of this research, a HO has an API gravity lower than 20° and the corresponding value for EHO is lower than 10° [5,7,9]. HO and EHO are also characterized by containing large concentrations of heavy metals and heteroatoms, and heavy compounds such as asphaltenes, as well as low H/C ratio [10], which directly influence the observed crude oil viscosity, typically higher than 100 cP at reservoir conditions [10].

Asphaltenes are refractory molecules with high molecular weight that can impact the different stages of the production system and refining streams [11]. Asphaltenes contain heteroatoms such as O, N and S and metals such as Ni, Fe and V. The presence of heteroatoms and their location in the structure make asphaltenes the most polar molecules present in crude oil, leading to their self-association and further formation of large asphaltic flocs. These flocs also cause an increase in the HO viscosity, which in some cases leads to formation damage [11–14] and precipitation/adsorption problems in production facilities [12,15,16]. At high concentration of asphaltene, namely >40,000 mg/L, the increase in viscosity is mostly due to the formation of a viscoelastic network of nanoaggregates [17,18]. In addition, sulfur can form strong C—S

and C=S bonds, which can also contribute to an increase in the crude oil viscosity [14,19].

To improve production, transport and refining of HO and EHO, several techniques under reservoir and surface conditions have been used, namely: (i) emulsification of oil-in-water (O/W) emulsions [20–22] that can drastically reduce the fluid viscosity and hence improve the crude oil mobility; (ii) use of annular flow as a method for reducing the drag forces [23–26]; (iii) deasphalting oil using CO_2 [27–29], n-alkanes of low [30–32] and high molecular weight [33,34]; (iv) application of thermal processes based on heat injection through steam and other gases [35–39] to reduce oil viscosity; and (v) in-situ upgrading such as the various modes of air injection, e.g. in-situ combustion (ISC) [40,41], thermal cracking [14,42–44] and its catalytic variations [45–47].

One of the most frequently used techniques for reducing HO and EHO viscosities has been the dilution with solvents and light hydrocarbons such as naphtha [48–50], toluene [51], xylene [49], gasoline [52], diesel [53,54], light oil [51], or mixtures thereof [55] as well as some chemical compounds based on R = O (butanone type, among others) [55]. Several authors have reported on the dilution of HO and EHO [55–58] with different solvents and the changes to the rheological behavior of mixed fluids [56,59,60]. Recently, Mortazavi-Manesh and Shaw [61] studied the effect of toluene, n-heptane and a mixture 50/50 vol% of toluene and butanone on the rheological properties of Maya crude oil as a function of temperature. Their results showed that the mixture of toluene + butanone caused the largest viscosity reduction. Naphtha has been so far the most used diluent [57,62,63]. In some instances, mainly in Venezuela and Colombia, the quantity of naphtha used in the upgrading of these crude oil types can reach 20–40 vol% [58]. Adding naphtha can effectively reduce the viscosity and increase the API gravity of HO and EHO [56,59,61]. The excessive use of naphtha for diluting crude oil implies an increase in the operational costs [51], becoming an impractical technology [51]. Dilution with naphtha is an unfriendly technology for humans due to its lower boiling point, 100% volatiles content, and low explosive limits [51].

Nanoparticles have been used by the oil industry for formation damage inhibition [64–67], HO and EHO upgrading [68], enhanced (EOR) and improve oil recovery (IOR) processes [66,69], and wastewater remediation [70]. Due to their particle sizes, between 1 and 100 nm, large available surface area, high dispersibility and tunable physicochemical characteristics, nanoparticles are prone to selectively adsorb asphaltenes and inhibit their self-association [71]. In a previous study [66,69,72], our research group focused on using silica, γ-alumina and magnetite nanoparticles to inhibit the aggregation of asphaltenes under varying temperature, solvent ratios and asphaltene concentration [69]. Silica nanoparticles can induce significant reduction in the asphaltene mean aggregate size, which could prevent the formation of large viscoelastic networks and reduce the oil viscosity as a result. However, to the best of our knowledge, there are no studies reporting the rheological behavior of crude oil in the presence of nanoparticles and their impact on relative permeability curves and crude oil recovery (%) under flow conditions in porous media at typical reservoir temperature and pressure, based on "huff-n-puff" type stimulations. In this order, the aim of this paper is to evaluate the effect of nanoparticles on the rheological properties of a Colombian HO at varying conditions of temperature, shear rate and dosage of nanoparticles. The selection of the nanoparticles, optimized towards the adsorption and size reduction of asphaltenes, was achieved using adsorption isotherms and the growth kinetics of asphaltenes. In addition to rheological responses, coreflooding tests at reservoir conditions were also performed. The results in this paper are expected to open a wider landscape on the use of nanoparticles in IOR processes based mainly on "huff & puff" configurations.

2. Experimentation

2.1. Materials and reagents

n-Heptane (99%, Sigma-Aldrich, St. Louis, MO), and Toluene (99.5%, Merck KGaA, Germany) were used as received. A Colombian heavy crude oil of 13°API and a viscosity of 1.2×10^5 cP at 298 K was used as source of asphaltenes. n-C_7 asphaltenes were extracted following a standard procedure as described in previous works [65,66,68]. The elemental analysis of asphaltenes shows a C: 81.4 wt%, H: 7.5 wt%, O: 8.8 wt%, N: 2.3 wt%. A non-ionic surfactant, Tween 80 (Sigma-Aldrich, St. Louis, MO), was used for dispersing the nanoparticles in the water-based nanofluid. The nanofluid was prepared using distilled water with a conductivity of 3 μS/cm. Three kinds of nanoparticles were evaluated: (1) unmodified synthesized silica (SiO_2), (2) silica NP with a modified acid surface (SiO_2A) and (3) NPs of commercial alumina (Al_2O_3). Al_2O_3 nanoparticles were purchased from Sigma-Aldrich (St. Louis, MO). SiO_2 nanoparticles were synthesized with tetraethyl orthosilicate, TEOS (>99%, Sigma Aldrich, United States), ethanol (99.9%, Panreac, Spain), NH_4OH (30%, J.T. Baker, United States) and deionized water [73]. For SiO_2 nanoparticles surface modification, H_2SO_4 (95–97%, Merck KGaA, Germany) was used.

2.2. Synthesis and characterizations of nanoparticles/nanofluids

SiO_2 nanoparticles were synthesized according to the sol-gel method as described in previous works [73,74]. In summary, a solution with tetraethylorthosilicate (TEOS) as the precursor of silicon, ethanol and NH_4OH, is prepared and the mixture is manually stirred, in a process that continues for 1 h and finally dried at 80 °C for 24 h to remove any remaining water fraction. The molar ratio of TEOS:H_2O:NH_4OH was 1:1.1:0.2. The procedure for acidification of the surface of SiO_2 nanoparticles consisted of mixing nanoparticles and sulfuric acid at 0.3 wt% to obtain a solution at pH = 4. A Horiba Navih pH meter was used for pH measurements. The solution was sonicated for 2 h at room temperature, then further stirred magnetically at 100 rpm for 12 h and subsequently centrifuged at 4500 rpm for 15 min. The nanoparticles were dried at 393 K for 4 h. In this work, nanoparticles without modification and acidified nanoparticles are referred to as SiO_2 and SiO_2A, respectively. The carrier fluid used was composed of a mixture of distilled water and 2 wt% surfactant. The procedure followed for the preparation of the nanofluid is described elsewhere [75,76]. In brief, the nanoparticles and the carrier fluid are stirred at 500 rpm for 20 min at room temperature, then subject to ultrasound for 12 h at 298 K. The nanofluid has a viscosity of 8.2 cP, a density of 0.96 g/cm³ and a pH = 7.3.

The mean particle size of the nanoparticles (dp) was measured using dynamic light scattering (DLS) with the help of a nanoplus-3 from Micromeritics (Norcross,GA) at 298 K and equipped with a 0.9 mL glass cell [69]. The BET surface area (S_{BET}) of the nanoparticles was measured through nitrogen physisorption at 77 K using an Autosorb-1 from Quantacrome BET, after outgassing samples overnight at 413 K under high vacuum (10^{-6} mbar).

Total acidity of the nanoparticles surface was determined via a NH_3-Temperature programmed desorption. The NH_3 desorption, previously adsorbed on the surface of the nanoparticles, is a direct measure of the degree of acidity of the materials evaluated. We used a ChemBet TPR/TPD (Quantachrome Instruments, USA) to this end. The procedure involves drying the sample at 470 K in an inert atmosphere. Then, the sample is cooled down to 370 K in the presence of NH_3 to promote the adsorptive process. Subsequently, the physisorbed amount is removed by flowing He for 1 h. Finally, the specimen is heated at a constant heating rate of up to 1170 K for