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Green phenolic amphiphile as a viscosity modifier and asphaltenes dispersant for heavy and extra-heavy oil

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ABSTRACT

The production and transportation of highly viscous heavy and extra-heavy crude oils are two of the paramount concerns in the oil and gas industry due to logistical difficulties and costs. Viscosity is highly sensitive to asphaltenes content of heavy oils and bitumen. Asphaltenes, which are the most polar and aromatic components of heavy oil, have high propensity toward self-association, thus increasing viscosity significantly. The present work proposes a new type of plant-based solvent that contains functionalized molecules that can interact with asphaltenes at the molecular level and modify viscosity. Effects of solvent on the viscosity of tested crude oil and functional groups of asphaltenes were evaluated both qualitatively and quantitatively by viscosity measurements and Fourier Transform Infrared (FTIR) analysis. Sensitivity of asphaltenes aromaticity and stacking to solvent were evaluated by curve deconvolution and fitting routines of X-ray diffraction (XRD) patterns of solid asphaltenes. The proposed solvent is a plant-based, non-hazardous substitute to the conventional hazardous solvents, e.g., toluene, that provides efficient viscosity reduction. Asphaltenes critical concentration in the heavy oil was delayed by adding the solvent, requiring more precipitating agent to separate asphaltenes from oil. Furthermore, asphaltenes aromaticity decreased by the addition of solvent. Its application also increases asphaltenes solubility in the oil and decreases asphaltenes precipitation and deposition.

1. Introduction

Increasing global demand for oil, coupled with gradual depletion rates of conventional oil resources, make the exploitation and production of unconventional oil resources necessary. Heavy and extra-heavy oil have been investigated for two decades as potentially productive unconventional resources. This type of crude oil, which is characterized by high viscosity and low API gravity, is abundant in Canada (mainly Alberta), Venezuela (in the Orinoco Belt), and China (Liaohe oil field, Xinjiang oil field, Shengli oil field, and Henan oil field). The amount of heavy oil resources has been estimated to be around six trillion barrels, and one to two trillion barrels of that can be retrieved economically [1].

The high viscosity and low API gravity of heavy crude oil engender some difficulties in its production and transportation processes. Flow resistance, both in the reservoir and in the production well tubing, occurrence of multiphase flow, high pressure drops, and clogged pipes are the main problems associated with heavy oils. Due to these difficulties, special treatments should be applied to production and transportation of these kinds of reservoirs [2,3].

A comprehensive understanding of the origin and nature of high

viscosity in crude oil leads to a more efficient production design approach for these reservoirs. Rheological behavior of heavy oil is highly dependent on the chemical and phase composition, the degree of dispersion, and the strength of the intermolecular and interparticle interactions. High viscosity of heavy and extra-heavy crudes is associated with existence of asphaltenes and resins that are the most polar and heaviest portions of crude oil [4–6].

Asphaltenes are solubility class compounds that contain most polar with the highest molecular weight components of crude oil. Due to the extreme complexity of these structures, asphaltenes are defined as a part of the oil that is soluble in aromatic solvents and insoluble in aliphatic solvents. The structure of asphaltenes contain polynuclear aromatic core with 4–10 aromatic rings and peripheral aliphatic chains with a length of 3–7 carbons [7–9].

Molecular arrangement of various parts of asphaltenes structure has been a paramount issue, especially regarding the size of aromatic groups and the way that they are linked to other groups. There are two accepted models for describing the aromatic moieties of asphaltenes molecules. The first model includes a highly condensed aromatic core that contains at least seven fused rings that are bonded covalently to

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peripheral aliphatic chains. Stacking interactions of aromatic cores lead to formation of densely packed aggregates. Based on computational studies, favorable substitution on the periphery of aromatic rings is conducive to aggregation as well. The archipelago model is the second explanation that consists of aromatic and cycloalkyl groups connected by alkyl carbon bridges [10–12].

The presence of asphaltenes in oil may cause severe problems within the formation itself, e.g., plugging a porous formation via flocculation and precipitation, altering wettability from water-wet to oil-wet, and forming of stable emulsions. Based on the literature, two distinct approaches can explain asphaltenes behavior in crude oil: solution theory and the steric-colloidal approach. The former approach assumes that asphaltenes are molecular entities dissolved in crude oil, while in the latter approach, it is assumed that asphaltenes and resins have the ability to form aggregates that are dispersed in maltenes [13,14].

Due to the existence of aromatic and polar functional groups, asphaltenes tend to associate and form nanoaggregates. Several studies have been done to investigate this process, including defining the concentration at which nanoaggregation initiates and characterizing the nanoaggregates with various methods such as static light scattering, nuclear magnetic resonance, centrifugation measurements, and DC conductivity. Cluster formation can be observed following nanoaggregation if the concentration of asphaltenes increases in the crude oil. This concentration can be interpreted as the critical micelle concentration (CMC) of surfactants, the point at which viscosity elevation starts to occur. Perturbation of crude oil composition and environment can further aggravate the flocculation and precipitation of asphaltenes [15,16].

The main approach to facilitate the production of heavy oil is to reduce its viscosity to a value such that it can be produced and transported easily using existing facilities. This technique also improves its displacement efficiency. Common methods to reduce heavy oil viscosity can be classified into two main categories: (1) increasing the fluid temperature (thermal methods) and (2) adding chemicals. The method ultimately applied is chosen based on the reservoir geology, reservoir thickness, and heavy oil composition and viscosity.

Chemical treatments are shown to be promising methods to modify heavy oil rheological properties by affecting asphaltenes structural characteristics. The main concept originated from the peptization effect of resin on asphaltenes particles. Asphaltense micelles are stabilized by resin, the other polar constituent of oil that is soluble in aliphatic solvents, by the peptization process in which the aliphatic part of asphaltense is stretched by attachment of the resin polar part, resulting in the formation of a steric-stabilization layer around the asphaltene. However, the quantitative analysis of resin-asphaltenes interactions cannot be done because of the existence of the same polar functional groups in both species, as well as their complex structures [17].

Effects of four aromatic polyisobutylene succinimides as asphaltenes dispersant and viscosity reduction agent of heavy oil were evaluated by Chavez-Miyauchi et al. (2013) [18]. The selection of these compounds were based on their ability to interact with asphaltenes particles viastacking, hydrogen-bond formation, and acid-base interactions. They concluded that the viscosity improvement is mainly related to asphaltenes disaggregation ability of added chemical rather that dispersionaggregate hindrance ability. Yang et al. (2014) [19] evaluated the influence of dodecyl benzene sulfonic acid and lauric amine on the viscosity of heavy oil through differential scanning calorimetry analysis and electrical conductivity measurement. They showed that viscosity of the oil system has an inverse relationship with the size of asphaltenes particles. Further, their results indicated that efficiency of amphiphiles is related to the ratio of resin to asphaltenes as well. Application of ionic liquids in viscosity treatment of heavy oil was assessed by Subramanian et al. (2015) [20]. They observed ionic liquids with higher tail length have more efficient viscosity reduction ability. Based on this study, anion charge density and cation head groups are other important factors in the efficiency of viscosity modifiers.

Table 1

Gliaracteristics	01	crude	on	sample.	

Specific	Viscosity at	Saturates	Aromatics	Resins	Asphaltenes
gravity	75°F	(wt%)	(wt%)	(wt%)	(wt%)
0.95	68470	20.6	34.5	19.1	25.8

In the current study, the effects of a proposed solvent (ACC) on the rheological properties of a tested heavy crude oil, and aggregation behavior of its extracted asphaltene, are investigated by conducting viscosity measurements, X-ray powder diffraction, UV-vis spectroscopy and microscopic analysis. Furthermore, the mechanism of viscosity reduction and asphaltenes inhibition by the proposed solvent are studied by means of Fourier transform infrared spectroscopy (FTIR). Acquiring fundamental knowledge of the chemistry and technology corresponded to this green chemical as a viscosity modifier and asphaltenes inhibitor additive, and its prospective application in petroleum industry is the main objective of the present study.

2. Materials and methods

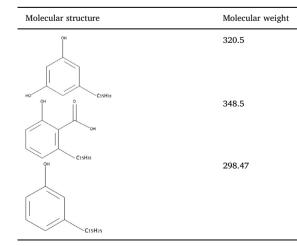
2.1. Materials

Mexican heavy oil sample with characteristics shown in Table 1 was studied in the present work. The main constituents of the proposed solvent, that is referred to as ACC throughout the paper, are anacardic acid, cardanol, and cardol that exist in cashew nut shell liquid (Table 2). All these compounds consist of an unsaturated phenolic head with unsaturated long-chain alkyl groups with molecular weight in the range of 311–350 Da [21]. Toluene, carbon tetrachloride, and n-heptane with purity grades of 99.3 and 99.0 wt%, respectively, were obtained from Sigma-Aldrich.

2.2. Methods

Asphaltenes were extracted using the American Society for Testing and Materials (ASTM) D3279-12 norm; a sample of crude oil was first poured in an excess of n-heptane (1 g of oil and 100 mL of heptane), then stirred for 25–30 min at 122° F, and allowed to rest at ambient temperature for two hours to facilitate asphaltenes precipitation. The precipitated asphaltenes fraction was filtered; the residue was washed with three portions of heptane of about 10 mL each. Next, the solid fraction of asphaltenes was dried at 212° F and then grinded. After that, the asphaltenes was mixed with toluene (5000 ppm), sonicated for 15 min and then centrifuged at 3500 rpm for 5 min. The amount of

Table 2
Chemical structures of Anacardic acid, cardanol, and cardol.



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