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Heavy crude oil upgrading using nanoparticles by applying electromagnetic technique

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ABSTRACT

The upgrading of heavy oil is one of the most important processes in heavy oil recovery due to the low quality of these types of oil. In this study, the effects of nanomaterials of Fe, titanium oxide (TO) and super activated carbon (CA) as catalysts in the process of upgrading heavy oil from the Azadegan Oilfield in Southwest Iran using microwave (MW) radiation are investigated. Samples of heavy oil are exposed for 2, 4, 6, 8 and 10 min to MW radiation with 4 wt% of each nanoparticle in each step. The results of the experiments show that Fe and TO nanoparticles have no significant effect on MW absorption in the initial 2 and 4 min intervals, while the CA nanoparticle, due to its higher potential for absorbing these waves, causes the temperature of the heavy oil sample to rise from the earliest time intervals. The presence of nanoparticles in heavy oil leads to a greater reduction in viscosity at initial and even longer intervals. In fact, these nanoparticles, by absorbing MWs over longer periods of time, cause cracking of heavier compounds the effect of which exceeds that of the loss of lighter compounds from the heavy oil. The CA catalyst has the highest viscosity reduction during the 6-min period and viscosity varies from 882.37 mPa.s to 791.19 mPa.s. The results of the analysis of carbon compounds (C), hydrogen (H), sulfur (S) and nitrogen (N) indicate that the presence of nanoparticles results in a further reduction of S and N in heavy oil than with MW radiation alone. The highest CA desulfurization over a period of 8 min is a reduction by 30.5%, while the highest H/C ratio occurs in the presence of this nanoparticle at 6 min. On the other hand, the lowest amount of N in the heavy oil sample is observed in the presence of the Fe nanoparticle with a decrease of 0.65 wt% at 10 min. According to Fourier transform infrared (FTIR) spectra, the presence of nanoparticles along with MW radiation reduces the concentration of OH, S-H, alkyl groups, carbonyl, carboxylic acid or derivative groups and aromatic compounds in heavy oil. These changes are more evident with CA and Fe nanoparticles. In terms of deasphalting heavy oil, the Fe nanoparticle has the greatest effectiveness with the asphaltene content reduced from 12.75 wt% to 9.13 wt% in 4 min. However, other nanoparticles reduced asphaltene components compared to MW radiation alone and promoted the process of reducing asphaltene content over longer periods. From the results of this study, it can be concluded that the use of nanoparticles with a higher potential for MW absorption can be more suitable options for the process of upgrading heavy oils. Moreover, the optimal duration of MW radiation in the presence of nanoparticles is one of the key parameters that varies greatly depending on the type of catalyst and the type of heavy oil.

1. Introduction

Heavy oils, in addition to having high viscosity and density, have high levels of sulfur, nitrogen, oxygen and heavy metals. Although the production of these types of oil from reservoirs is very difficult and costly due to the poor quality of these oils, their refinement is also more complex. As a result, prices are lower than for light petroleum and there are fewer customers for heavy oils. Therefore, there is always a lot of interest in research studies to investigate the upgrading of heavy oils.

In the process of upgrading heavy oils, one of the main goals is the elimination of some compounds and the cracking of heavy compounds using additives and special techniques [1]. However, in using these techniques, in addition to obtaining the proper yields, an economical comparison should be made [2]. One of the methods that usually takes place in the upgrading process and is of more interest to researchers is hydrogen-donation, which usually includes adding various techniques and materials to increase its efficiency. The use of some materials [3], such as methane gases [4] and cyclohexane [5], are among these

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techniques. Supercritical fluids are also used in the process of upgrading heavy and extra heavy oil. In addition to decomposing asphaltene, supercritical methanol also significantly reduces the amount of coke in the process of upgrading heavy oils [6]. However, the use of supercritical water-oxygen fluid reduces the amount of asphaltene and resin fractions, which can be observed as a significant decrease in the products of vanadium and nickel [7]. Nanoparticle catalysts (nanoparticles) are among the new technologies that are being used today in upgrading and even increasing production from heavy oil reservoirs, focusing on viscosity reduction and wettability alteration [8]. Guo et al. (2018) used monodispersed nickel and cobalt nanoparticles in their studies to desulfurize heavy oil and improve oil quality [9]. Alaei et al. (2017) used an exfoliated MoS_2 nanoparticle in their studies and showed that this homogenous nanoparticle has superior activity compared to similar oil-soluble catalysts in upgrading and improving process conditions [10]. Nano oxides of metals can reduce the viscosity and increase the saturated hydrocarbons under certain temperature and pressure conditions, depending on the properties of the heavy oil [11]. Omajali et al. (2017) used dispersed bionanoparticles as one of the additives that can be used in conjunction with other catalysts in upgrading heavy oils [12]. Zhao et al. (2018) also introduced molybdenum-doped akaganeite nano-rods as a catalyst to reduce the viscosity of heavy oils [13].

The use of microwave (MW) technology in the process of upgrading heavy and extra heavy oil is one of the new processes that are being considered. As the heating rate in terms of time can be very important in the conventional upgrade process [14], in this technology the process time is one of the key points [15]. Jackson (2002) examined the effect of various MW frequencies on the process of upgrading heavy oil [16]. Based on the results presented by Jackson, each type of catalyst produces different reactions at different frequencies. However, when using MW radiation it is important to note that because of the high potential of asphaltene compounds to absorb MWs, they can affect their amounts in heavy oil [17]. On the other hand, due to the time interval of the radiation of these waves, viscosity is reduced and the structure and composition of asphaltenes in heavy oils are changed [18]. Heating time is a critical factor in microwave heating, because unlike under conventional heating the trend of changes in heavy crude is clear and predictable [19]. The rate of cracking of heavy components was continuously greater than the rate of light components leaving the sample at early time intervals; ultimately, this resulted in an upgraded heavy oil. In some cases, despite cracking of large-chain molecules and creation of light components, the output values of light components were higher [20]. Asphaltene particles have the potential for high absorption of microwave. Asphaltene flocks break down by high absorption of microwave [21–24]. Wax and asphaltene particles are more susceptible to the effects of microwave radiation, which alters the levels at which they are present in crude oil. Microwave reduce the dispersion of the parameters related to the size and shape of crystals (circular diameter, roundness, and aspect ratio) relative to the crude oil; in other words, the microwave radiation effects on the wax appearance temperature [25–27]. This study examines the process of upgrading a heavy oil sample from Iran using Fe, titanium oxide (TO) and super activated carbon (CA) nanoparticles in the presence of MW radiation. The results of the experiments show that the presence of nanoparticles has an important influence on the upgrading process that is a function of the MW radiation time.

2. Experiment

2.1. Materials

In the experiments, the Azadegan oil sample from Southwest Iran has been used. The specifications of this oil sample are given in Table 1. We performed a set of experiments to determine saturations, aromatics, resins (ASTM D-4124) and asphaltenes (IP-143), referred to as SARA experiments. The viscometer SVM 3000 was also used to measure viscosity. We utilized a Vario Max-CHNS elementer to determine values of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) (ASTM D5291–ASTM D4294). The nanomaterial specification used in the experiments is presented in Fig. 1. In these experiments, nanoparticles of iron (Fe), titanium oxide (TO) and super activated carbon (CA) have been used as catalysts.

Table 1
Specifications of heavy oil used in experiments.

Saturates (wt%)	8.13
Aromatics (wt%)	58.44
Resin (wt%)	20.68
Asphaltene (wt%)	12.75
API Gravity	17.19
Viscosity (mPa.s) (@ 22 °C)	882.37
C content (wt%)	85.15
H content (wt%)	10.11
S content (wt%)	3.21
N content (wt%)	1.53

2.2. Fourier transform infrared (FTIR) spectrum

The FTIR spectra of the samples for all bands were obtained from the FT-IR VERTX70 device.

2.3. Experimental setup and procedure

150 g of the Azadegan oil sample from an oilfield in Southwest Iran was exposed to MW radiation under the Fischer Assay apparatus. A schematic of the Fischer Assay extended to microwave radiation can be seen in Fig. 2. MW heating was carried out at 2450 MHz frequency and 600 W power. First, all parts of the device were filled with helium gas so that the heating was carried out without the presence of oxygen and other gases. The oil sample, with 4 wt% of nanoparticle, was heated inside the Fischer Assay at time intervals of 2, 4, 6, 8 and 10 min. The gas extracted by heating the sample of oil was stored inside the gas meter. The output condensate from the oil sample was collected by heating after cooling by a condenser inside the receiving flask. The condenser used cold-water flow for cooling. The heated oil sample was cooled for 1 day at the ambient temperature to reach stability. Because intervals of 2 min were selected, there was no significant change between the steps in the 1-min intervals. The heating interval was chosen to extend up to 10 min because the variations were almost constant after that time. After the MW radiation, the oil sample and the nanoparticles were centrifuged for 20 min at 6000 rpm to remove the upgraded oil from the nanoparticles.

3. Results and discussion

3.1. Temperature

The temperature variation diagram of the oil sample with microwave radiation alone as well as with nanoparticles is shown in Fig. 3.

Energy absorption varies depending upon sample composition and dielectric properties. MW heating is based on the ability of materials such as oil to absorb MW energy and effectively convert the electromagnetic energy to heat (kinetic energy). Because MW heating is dependent on the dipole moment of a molecule, it is logical that components with greater polarity convert MW irradiation into heat more effectively compared to nonpolar components. The radiation passes through transparent material, like hydrocarbons, with little or no absorption. However, the electromagnetic field generated by the MWs stimulates vibrational modes of molecules such as activated carbon [28]. As the MW energy radiates through the oil components three different interaction scenarios occur which lead to the vibration and