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Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol

Asphaltene precipitation with partially oxidized asphaltene from water/heavy crude oil emulsion

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ARTICLE INFO

Article history:

Received 21 September 2015

Received in revised form

27 February 2016

Accepted 8 April 2016

Available online 9 April 2016

Keywords:

Solvent Deasphalting (SDA)

Oxidized asphaltene

Asphaltene precipitation

Paraffinic froth treatment

Bitumen

ABSTRACT

A novel asphaltene precipitation method of using partially oxidized asphaltene was proposed to reduce the amounts of asphaltene in heavy crude oil. Partially oxidized asphaltene enhanced the aggregation of asphaltene in oil, and the precipitation of asphaltene from heavy crude oil. By adding a small amount of partially oxidized asphaltene in water/diluted-crude-oil emulsion, a half of asphaltene and a quarter of resin in the feed stream were separated by a single cycle of centrifugation. The degree of oxidation of partially oxidized asphaltene may determine the selective dissolution between the oil phase and the water phase. The partially oxidized asphaltene, which has amphiphilic functional groups, is adsorbed on the interface between asphaltene and water, and can therefore facilitate the aggregation of asphaltene dissolved in the oil. The interfacial adsorption may be controlled by the hydrophilicity and aromaticity of surfactants and may contribute to the aggregation and separation of asphaltene. Therefore, it is believed that the pretreatment of partially oxidized asphaltene could significantly reduce the asphaltene load in a solvent deasphalting process.

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1. Introduction

Asphaltenes in heavy crude oil, bitumen, or tar sand can cause deposition onto transport pipeline and production facilities. Thus the pretreatment of upgrading process and oil recovery might enhance the efficiency of light oil recovery from bitumen, and extra heavy oil (Williams, 2003; Ma et al., 2009). Generally, asphaltenes are polar aromatic compounds that have the higher levels of sulfur, nitrogen, and heavy metals (Ni, V) (Long et al., 2011) and identified as the fraction which is insoluble in low-molecular-weight alkane solvents, but soluble in light aromatic hydrocarbon solvents (e.g., benzene, toluene) (Speight, 2014; Bouhadda et al., 2007). Though there has been a certain controversy on the molecular weight of asphaltene, it is currently considered to be in the range of 500–1000 Da, and large sizes of the upper bound may attribute the formation of aggregates (Mullins, 2007). Furthermore, heavy crude oil may easily cause the formation of cokes, catalyst deactivation, corrosion, and plugging/sedimentation in pipelines and in reactors (Reynolds et al., 1994; Boduszynski, 1987; Yen, 1974; Savastano, 1991).

Heavy crude oil would be analyzed according to the solubility

of solvent such as saturate, aromatic, resin, and asphaltene, also called as 'SARA'. The solvent deasphalting (SDA) process extracts light oils from residues of crude oil by adding low-molecular-weight-alkanes (C3–C7). The ROSE™ (Residuum Oil Supercritical Extraction) process developed by Kerr-McGee, for example, is a representative process for solvent deasphalting, whose importance has gradually increased in refinement technology (Du et al., 2012; Wilson et al., 1936; Subramanian et al. 1998; Rana et al., 2007). For an efficient solvent recovery, however, it is required to have the near-supercritical state of solvents and the amount of solvent required to be about four to ten times of the feed volume (Chen et al., 1994; Lee et al., 2014). Thus, it is an important issue to reduce the amount of solvent and operational costs, while obtaining the high efficiency of the SDA process (Long et al., 2011, 2013; Wang et al., 2012). Also, paraffinic froth treatment, which uses water and paraffin solvent for bitumen refinement, is employed to separate asphaltene and solid particles from bitumen (Rao and Liu, 2013). Partial deasphalting with paraffinic froth treatment can reduce the viscosity of oil as low as enough to be transported to far refinery (Moritis, 2010).

However, asphaltenes may not be easily separated from crude oil, since resins are strongly adsorbed on asphaltene dispersed in a form of reverse micelles, and asphaltene aggregates are dispersed

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in low alkanes and resins (Mansoori, 1996; Lhioreau et al., 1967). Therefore, the deposition of asphaltenes in process could be avoided by adding resins or oil soluble amphiphiles (González and Middea, 1991). On the other hand, if resins are removed, the dispersion of asphaltenes could be destabilized, forming aggregates and deposits. Naphthalenic acid could also disaggregate asphaltene clusters and reduce the size of asphaltene aggregates as a result of the acid-base interaction (Auflem et al., 2002). Taylor (2010) transferred asphaltene in heptane phase to water phase with non-ionic surfactant NPE8 (nonylphenol ethoxylate-8). Alkylphenol-ethoxylate surfactants are widely used as inhibitors in the transportation of crude oil to control dispersion of asphaltene (González and Middea, 1991; Leon et al., 1999; Chang and Fogler, 1994). Since an asphaltene molecule has many aromatic rings, they would interact with other aromatic rings through a π - π bond (Spiecker et al., 2003; Boukherissa et al., 2009). The proper hydrophilicity and aromaticity of asphaltenes in solvent or in oil may attribute the formation of micelle, the dispersion of aggregates (Goual et al., 2014), and the deposition or transfer of aggregates from oils.

In present paper, we propose partially oxidized asphaltenes to be a dispersion controlling agent that plays the role of resin, asphaltenic acid, or amphiphilic additives. Partially oxidized asphaltenes may have higher hydrophilicity and aromaticity than other additives, and form a hydrophilic core in oil phase. Asphaltenes could be oxidized with various oxidants, such as, ozone, hydroperoxide, and potassium permanganate (Moschopedis and Speight, 1971a, 1971b, 1978; Erdman and Ramsey, 1961; Antonishin et al., 1977; Desando et al., 1999) but no attempts so far reported to facilitate the precipitation of asphaltenes from oils by using oxidized asphaltenes. In present research, we partially oxidized asphaltenes with potassium permanganate (Siddiqui, 2003). Here, a phase transfer agent was added to disperse the ions of potassium permanganate in the organic phase, leading to a fast reaction rate (Herriott, 1975; Starks, 1971; Herriott and Picker, 1975; Makosza, 2000). Therefore, it is our proposal to use partially oxidized asphaltene to remove asphaltene from W/O type emulsion of bitumen and crude oils.

2. Experimental section

2.1. Materials and chemicals

Bitumen was obtained from Alberta, Canada. Table 1 shows the chemical and physical properties of the bitumen used in present study. The chemicals in the experiments (heptane, Adogen 464, Tergitol NP7, NP-40S, Triton X-100, Brij 30, Brij 58, and Brij 76) were purchased from Sigma-Aldrich. H_2SO_4 (99%, extra pure), dichloromethane, $KMnO_4$, and H_2O_2 (35% in water) were obtained from Junsei Chemical Co., Ltd.. Water was deionized to eliminate

Table 1
Property of bitumen recovered from oilsand in Alberta, Canada.

| Analysis | Result |
|----------------------------|---|
| Higher heating value | 9950 kcal/kg |
| Boiling point distribution | 206–745 °C |
| MCR content | 14.48% |
| Heavy metal content | Ni: 105 ppm V: 195 ppm |
| Absolute viscosity | 240~46,400 mPa s (35–100 °C) |
| API gravity | 8.18 API |
| SARA composition | Saturate: 21.7% Aromatic: 22.1% Resin: 35.8% Asphaltene: 20.4% |

the effect of salinity.

2.2. Asphaltene separation

Asphaltene was precipitated through the addition of an excess volume of heptane. Excessive n-heptane was added with a ratio of 100 mL per 1 g of sample. The solution was heated to 60 °C and stirred for 15 min with a magnetic stirrer. After mixing, the solution was cooled and filtered with a 0.45 μ m membrane filter. Then, the asphaltene filter cake was dried in oven at 107 °C for 20 min.

2.3. Asphaltene oxidation

0.5 g of asphaltene, 1 g of Adogen 464, 40 mL of dichloromethane, and 20 mL H_2SO_4 were put into a 250 mL beaker with magnetic stirring in ice bath. Then, 2 g of $KMnO_4$ were slowly added. After addition of $KMnO_4$, the beaker was maintained at 30 °C during the reaction. The product was washed with H_2O_2 and water. Then, it was strained with a membrane filter. After drying the filter cake in desiccator at room temperature, oxidized asphaltene was obtained.

2.4. Asphaltene precipitation in water/oil solution

10 mL of DI water, 10 mL of heptane, and 40 mg of surfactant (or oxidized asphaltene) were put in a 30 mL vial. Then 1 g of bitumen was added with vigorous shaking in a vortex shaker, following settlement for precipitation of asphaltene. Asphaltene precipitate was separated and was completely dried in oven at 70 °C for 5 h.

2.5. Instrument and measurement

CHONS composition element analysis was performed using FlashEA 1112 (Thermo Finnigan, Italy) and FLASH 2000 series (Thermo Scientific). X-ray photoelectron spectroscopy (XPS) was obtained using Sigma Probe (Thermo VG Scientific) with energy resolution of 0.47 eV FWHM to obtain the chemical state of the sample. The functional groups of the products were analyzed using FT-IR spectroscopy (Alpha, Bruker, Germany), and the SARA result was obtained using a TLC/FID Analyzer (IATROSCAN MK-6s Mitsubishi Kagaku Iatron, Japan). Metal content was measured using XRF (X-Supreme 8000, Oxford Instruments).

3. Results and discussion

3.1. Asphaltene precipitation with surfactant in water/oil emulsion

In aromatic solvents, asphaltene forms reverse micelles or aggregates of micelles (Rogacheva et al., 1980). In paraffin oil, however, asphaltene precipitates to form aggregates as a colloidal dispersion. The aryl groups in solvents or surfactants has an important role in the interaction with asphaltene by forming π - π complex. In water-in-oil emulsion, it is interesting to see that asphaltene molecules tends to be adsorbed on the interface of oil and water, but nano-aggregates and clusters of asphaltene do not adsorb (Rane et al., 2013). When surfactants are added to the emulsion, surfactant molecules will attach on an asphaltene molecule by polar and π - π interactions. Then, the asphaltene-surfactant globules get bigger, and the surfactant molecules will adhere on globules with hydrophilic or aromatic group toward asphaltenes. The addition of the surfactant may increase the polarity and aromaticity of the globules as if they were resins, and the hydrophobicity of the chains of surfactants with a pendant group of asphaltene also increases.

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