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Demulsifying water-in-oil emulsions by ethyl cellulose demulsifiers studied using focused beam reflectance measurement

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HIGHLIGHTS

- Quantitative on-line monitor of water-in-oil emulsion size distributions using FBRM.
- Evaluation on demulsification dynamics by on line droplet size distribution measurement.
- Quantification of factors influencing size distribution of emulsified water droplets by ethyl cellulose demulsifiers.
- Demonstration of more rapid flocculation process than coalescence by polymeric chemical demulsifiers.
- Phenomenological model of demulsifying water in diluted bitumen emulsions by ethyl cellulose demulsifiers.

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ABSTRACT

Removal of residual water droplets from produced fluids of petroleum is a challenging task because the emulsified water droplets with size of a few micrometers are extremely stable. A focused beam reflectance measurement (FBRM) was used for on-line monitoring of emulsified water droplet size distribution in petroleum emulsion systems and chemical demulsification process. After establishing the feasibility of using FBRM to measure droplet size distributions in petroleum emulsions, factors influencing the average size of water droplets were investigated to evaluate the demulsification dynamics by ethyl cellulose demulsifiers. The FBRM is proven to be a valuable tool for monitoring demulsification process in situ in real time to understand demulsification mechanisms, which sheds the lights on improving the current technology of demulsifying water-in-oil emulsions of petroleum industry.

1. Introduction

Emulsification plays a critical role in a wide range of industrial processes such as food processing, pharmaceutical formulation, material coating, manufacture of cosmetics, engineering drug delivery mechanisms and petroleum processing (Gutierrez et al., 2008). Emulsion is a dispersion system formed from two or more immiscible liquids under mechanical forces. Due to the presence of large liquid–liquid interfaces of finite interfacial energies to create the interface, emulsions in general are inherently unstable. As a result, surfactants are added to make emulsions more stable by reducing the interfacial tension and creating steric repulsion between the dispersed liquid droplets. Emulsions are often formed during petroleum production. For example, in oil sands engineering bitumen is liberated by hot water from sand grains, attaches to air bubbles and forms bitumen froth upon flotation. Bitumen froth typically contains 60% bitumen, 30% water and 10% solids by weight (Zhang et al., 2003). Most of the water in bitumen froth can be removed by solvent-based bitumen froth cleaning. However, 2–4 wt% water remains in the naphtha-diluted bitumen product in the form of stable emulsified water droplets of several micrometers in size (Long et al., 2004; Masliyah and Xu, 2003). The presence of this water is highly undesirable, because the chloride ions in the water could cause severe damage to downstream upgrading equipment by corrosion (Feng et al., 2010). Its presence also undermines the commercial value of the crude and the operation of refining equipment. For these reasons, dewatering of stable water-in-diluted bitumen emulsion is a continuous challenge to the petroleum industry (Feng et al., 2009).

The high stability of water-in-diluted bitumen emulsions is generally attributed to the presence in the petroleum of amphiphilic substances, e.g., asphaltenes, resins and natural surfactants (Teklebrhan et al., 2012, 2014). These substances act as lipophilic

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emulsifiers (Stanford et al., 2007a, 2007b; Spiecker and Kilpatrick, 2004; Fan et al., 2009). The stability of water droplets in diluted bitumen is believed to be enhanced by the presence of bi-wettable fine solids, which occupy oil–water interfaces and confer stability against phase separation (Spiecker et al., 2003; Czarnecki and Moran, 2005; Angle et al., 2007; Gafonova and Yarranton, 2001) Methods currently available for demulsifying petroleum emulsions can be broadly classified as chemical, electrical and mechanical. Chemical demulsification is induced by chemical additives to destabilize the protective interfacial films and hence accelerate the emulsion breaking process. Chemical demulsification is the most economical and commonly used method in dewatering of crude oils (Pena et al., 2005; Xu et al., 2005). Several studies suggest that the demulsifier molecules, most of which are surfactants, can penetrate into the protective rigid oil–water interfacial films and modify the compressibility and rheological properties of the films that stabilize the emulsion. The presence of the demulsifier molecules at the oil–water interface favors the drainage of the thin liquid films between the approaching emulsified water drops. On the other hand, demulsifiers could also bridge water droplets and therefore lead to flocculation of the emulsified water droplets, enhancing coalescence and phase separation (Kumar et al., 2001; Liu et al., 2003; Rondon et al., 2008).

Monitoring the size distribution of water droplets on-line is highly desirable to evaluate the efficiency of demulsifying water-in-oil emulsions by chemical demulsifiers. Moreover, in the design and study of demulsification process, knowledge on factors governing the average size of water droplets would provide valuable information on designing separation vessels and/or controlling the operating conditions. Such knowledge could also offer further insights into the molecular mechanism of demulsification. Size distribution can be investigated by sampling for emulsions followed by microscopic visualization (Feng et al., 2009, 2010; Angle et al., 2006). However this method is not an on-line, neither real time analysis. Offline sampling and imaging require the original samples to be diluted and/or stable, prior to their measurements. Sampling techniques does not guarantee maintaining the size distribution of the sampled droplets from further coalescence during the sampling and imaging. Also only a selected area of emulsions instead of the entire emulsion that can be observed by microscopy techniques. Thus novel technologies that realize in-situ analysis of water drop size distribution in real time during demulsification process in petroleum industry are highly desirable.

Focused Beam Reflectance Measurement (FBRM) is the only tool that will give a real-time, in situ indication of particle/drop size distribution over a wide range of particle concentrations in even opaque liquids. In FBRM, a focused laser is scanned at a fixed high velocity across the sapphire window of the instrument. When the laser beam scans across a particle that flows across the window, the probe measures the duration of the reflected laser beam from the particle, which allows determination of the chord length by the duration of the reflected light pulse times the speed of laser scan. By translating the backscattered response into a chord length of individual pulses during the measurement, several thousand chord lengths are measured per second and a droplet size distribution in a wide range of the fluids under agitation is obtained as a statistical representation of droplet/particle size distribution of the sample. In liquid–liquid dispersions such as oil-in-water emulsion, FBRM can also be utilized to determine drop size distribution by taking the advantage of the difference in the reflectance between the organic and aqueous phases. It should be noted however that the measured droplet size distribution does not depend on the magnitude of the difference in reflectance between the dispersed and continuous phases so long as the difference is sufficient to distinguish the two phases as in our systems. A large community of users have successfully applied FBRM technology for monitoring dynamic solid–liquid or gas–liquid processes, such as particle flocculation (Thapa et al., 2009; Kirwan, 2009; Owen et al., 2007), ice and hydrate formation (Greaves et al., 2008), crystal growth under antisolvent addition or cooling (Hermanto et al., 2012; Li et al., 2013, 2014; Zhao et al., 2012), biomass concentration in a number of biological systems (Whelan et al., 2012), etc. FBRM has also been applied to liquid–liquid emulsion systems (Dowding et al., 2001; Maass et al., 2011), and previous results already showed FBRM to be a very practical tool in studying emulsion stability (Cobbledick et al., 2014). Sloan and co-workers monitored droplet size distributions of water suspended in a crude oil at multiple shear rates in four crude oils of variable surface tensions and viscosities. Based on FBRM data in their study, a correlation was developed to predict the size distribution of water droplets (Turner et al., 2009). Cameirao et al. reported chord length distributions measured by FBRM in a water-in-oil emulsion on both a laboratory and pilot scale flow loop (Leba et al., 2010). The data were used to describe the physical properties of aggregates. Recently water droplet size distributions in crude oil emulsions were measured using a particle video microscope (PVM) probe and FBRM probe (Boxall et al., 2010). The mean droplet size values obtained using FBRM were found to be lower than the values from PVM measurement, but could be related to the size obtained using PVM by an empirical quadratic relationship with an average error of less than 20%. The droplet size distribution was found to follow a log-normal distribution with a good agreement between the measured and predicted mean droplet sizes. FBRM has also been compared with other methods such as two-dimensional optical reflectance measurement, a fiber optical FBR sensor and a photo-based endoscope technique (Maass et al., 2011). Fawell and coworkers summarized the results carried out using FBRM and alternative particle sizing techniques for a variety of sizes and materials of particles. They concluded that the FRBM oversized small particles ($<150\ \mu m$) and undersized larger particles ($>500\ \mu m$) (Heath et al., 2002). Although great efforts have been made to study liquid–liquid emulsions by FBRM, to the best of our knowledge, comprehensive research to evaluate demulsification process using FBRM has not been explored.

In this paper, size distributions of water-in-diluted bitumen emulsions were measured on line in real time using FBRM. Flocculation and coalescence dynamics of emulsion water droplets with the addition of polymer demulsifiers were comprehensively studied. Factors influencing the demulsification of water-in-diluted bitumen emulsions were investigated by comparing size distributions of water droplets in diluted bitumen. Meanwhile microscopic images were analyzed to further understand the underpinning mechanism of emulsified water droplet flocculation and coalescence. The results from this study will provide further guidance on optimizing the current operation parameters of heavy oil production and further understanding the demulsification mechanisms of petroleum emulsions.

2. Experimental section

2.1. Materials

Vacuum distillation feed bitumen was provided by Syncrude Canada Ltd. Industrial-grade naphtha and heavy naphtha were supplied by Champion Technologies, Inc. and used as received. Ethanol (AR), hydrochloric acid (37 wt%), sodium bicarbonate and toluene (AR) were purchased from Fisher Chemicals. Two types of silica (Silica-15 and Silica-40) were purchased from U.S. Silica Company. Silica-15 has 98 wt% of particles finer than 15 μm and a mean size of 4.12 μm, while Silica-40 has 98.5 wt% of particles