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Enhancing heavy oil liberation from solid surfaces using biodegradable demulsifiers

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ABSTRACT

Ethyl cellulose (EC) and EO/PO polymers are known as efficient demulsifiers for breaking oil–water emulsions, which are applied in this study as process aids to enhancing unconventional oil liberation from host rock surfaces. Their applicability in such a role was assessed by studying dynamic contact angle and liberation of bitumen from model solid surfaces. The addition of demulsifiers (EC and/or EO/PO blocked co-polymer, up to 300 ppm) into the solvent-diluted bitumen was found to significantly improve both bitumen liberation rate and ultimate degree of bitumen liberation (DBL) from glass surfaces. This finding suggests the potential combination of oil liberation and demulsification to develop more efficient process for recovering unconventional oils.

1. Introduction

As a major part (~70%) of petroleum fuels, unconventional oils (e.g., oil/tar sands, heavy oil, shale oil, etc.) are playing an increasingly important role in meeting the anticipated ever-increasing needs for energy [1]. However, characterized by their high viscosity (up to 10^6 mPa s) and density (up to 1050 kg/m^3) with the coexistence of complex mineral rock matrix, the traditional crude oil exploitation methods are often inefficient for the extraction of heavy oil from these unconventional oil reserves [2]. One of the widely accepted techniques for unlocking these unconventional oils is water-flooding, which involves two essential sub-steps of oil liberation from its host rock surfaces and subsequent oil–water separation [3]. Both of these two sub-processes are driven typically by interfacial forces for a given set of hydrodynamic conditions. They are often enhanced by application of certain functional chemicals such as solvents, inorganic salts, ionic liquids, nanoparticles, specialty surfactants and demulsifiers [3–5]. In practice, these two sub-steps are often accomplished in separate unit operations. As a result, the above chemicals are typically added into the tanks or reactors separately in different plants. For example, to enhance the liberation or recession of unconventional oils from the mineral surfaces, one would add a solvent into the ores while adding salts, ionic liquids, nanoparticles or surfactants into the processing medium such as water [3,4,6–8]. After the liberation, the oil droplets suspended in the aqueous solution in the form of emulsions are separated from the water by demulsification, during which the desired chemical demulsifiers are added into the water or oil externally [3]. Although these functional chemicals play vital roles in each process steps as designed, the multifunctionality of these chemicals is often overlooked, causing higher operating costs, due to repeated chemical additions in separate unit operations. An innovative idea was investigated in this study to evaluate whether the same functional chemicals such as demulsifiers would enhance both oil liberation and oil-water separation, as shown in Fig. 1. If this is the case, the production of heavy oil from unconventional oil resources would be made much more efficient and environmentally friendly.

Ethylene oxide and propylene oxide (EO–PO) copolymers and biodegradable ethyl cellulose (EC) are common demulsifiers used in oil recovery industries to break the oil–water emulsions [9–13]. Due to their special molecular architectures and highly surface active nature, these demulsifiers added to the emulsions are able to transfer to the oil–water interface and penetrate into the interfacial film by expelling the interfacial materials (e.g., asphaltenes) which are responsible for stabilizing emulsion droplets [3,9,11]. Such

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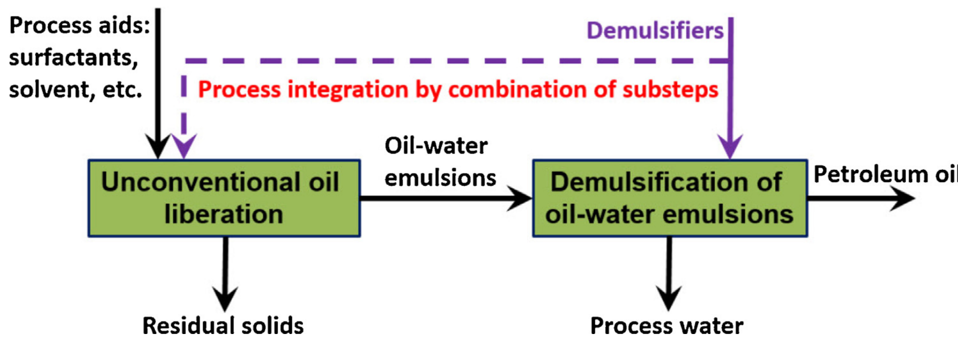

Fig. 1. Schematics of current process for unconventional oils production by water-flooding (the solid connections) and a hypothetical integrated process by combining the oil liberation with demulsification of oil–water emulsions (dotted connections). The demulsifiers currently used in the demulsification step are added up front in oil liberation step to reduce or even replace the addition of other external process aids.

unique characteristics of chemical demulsifiers could provide a practically feasible opportunity as multipurpose specialty chemicals for enhanced oil recovery. However, to the best of our knowledge, little work has been done to demonstrate this multifunction of chemical demulsifiers on enhancing liberation of unconventional oil from their host rocks/sands. The expected benefits are to greatly reduce chemical usage and hence the operating cost, and mitigate negative environmental impact of oil production from unconventional oil resources. It is the purpose of this study to explore such opportunity by investigating the role of these two types of demulsifiers in unconventional oil liberation from solid surfaces.

2. Materials and methods

2.1. Samples and water

Bitumen of extra high viscosity and density was used in this study to represent the extreme case of heavy oil. It was extracted from Athabasca oil sands and contained 17.7 wt% asphaltenes with a viscosity of 127 Pa s at room temperature. To simplify the operation, the bitumen used in the following tests was diluted with naphtha at the dosage of 30 wt% of bitumen. Naphtha, a typical petroleum byproduct, was purchased from Fisher Scientific Inc. Ethyl Cellulose (EC4, MW: ~46,000 Da from Sigma–Aldrich) and EO/PO copolymer of 1:1 ethylene oxide/propylene oxide molar ratio (MW: ~12,000 Da from Baker Hughes) were used as received. They were first dissolved in the naphtha by shaking for 24 h. A precisely measured amount of demulsifier-in-naphtha solution was added into the bitumen by a pipette. The concentration of demulsifiers in the bitumen was set at 200 ppm and 300 ppm by weight of bitumen.

The pH and surface tension of the oil sands processing water (provided by Syncrude) used in this study were measured to be 8.0 ± 0.3 and 68 ± 2 mN/m, respectively. The process water contained 23–25 ppm K^+, 653–659 ppm Na^+, 15–17 ppm Mg^{2+}, 25–27 ppm Ca^{2+}, 602–724 ppm Cl^-, 128 ppm SO_4^{2-}, 556–659 ppm HCO_3^-, and 7 ppm NO_3^-.

2.2. Contact angle measurement

The contact angle of bitumen on a glass slide in the process water was measured to investigate the effect of demulsifier addition on bitumen liberation. To simplify the analysis, glass plates were used as model solids to mimic host rocks or sand grains. The smooth and homogeneous glass plates were cleaned using piranha (a mixture of concentrated sulfuric acid (H_2SO_4 96 wt%) with hydrogen peroxide (H_2O_2 30 wt%) at volume ratio of 3:1) and thoroughly rinsed with deionized water to remove any impurities from the glass surface. The cleaned glass plate was dried by filtrated air stream in a clean fume hood. A diluted bitumen drop of ~0.45 μL volume was then placed on the glass surface by a micropipette. After spreading to an equilibrium state of mirror-like smoothness of bitumen layer on the glass surface, the plate was immersed into the process water quickly to avoid any aging effect on the wettability of the bitumen/solid surfaces, which is known to have a great impact on the wettability of solid surfaces and hence affect the results. The entire recession process of bitumen on the glass plate was recorded by a drop shape analyzer (DSA). The angle between bitumen-water and solid–water interfaces at the solid-bitumen-water three-phase contact point was determined on both left and right hand sides of the bitumen droplets as shown in Fig. 2. All of the measurements were conducted at pH 8.0 and ambient conditions. In this study, the average value of the angles on the

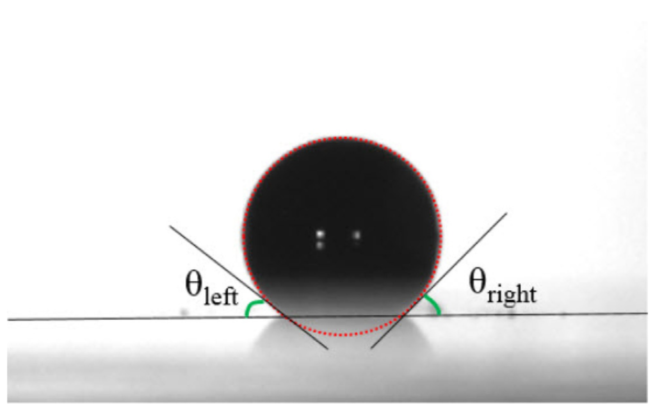

Fig. 2. Measurement of contact angle (θ) of bitumen droplet on glass surface in the water.