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Towards the design of unit operations to remove colloidal particles from hydrocarbons and fuels through aggregation and sedimentation

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ABSTRACT

The presence of fine (submicron) particles in hydrocarbon streams is problematic due to their undesirable impact on product quality and their gradual deposition and fouling effects on equipment. By forming large aggregates that are subject to gravity settling, these particles can be removed. However, the particles are often coated with carbonaceous matter that may negatively influence their aggregation. In this study, submicron silica particles were coated with a layer of hydrocarbon materials, and then suspended in different types of organic solvent to examine their settling rates. The experiments showed that the coating caused quite different settling regimes in different types of solvent. A mathematical model was proposed to study the kinetics of the settling process. The results were used to evaluate the performance of current settling units. A specific modification was suggested to improve the efficiency of particle separation.

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1. Introduction

A suspension of unwanted fine solid particles in a hydrocarbon medium is commonly encountered in many industrial applications. For example, the fuels derived from shale oil have been characterized with some levels of solid contents (Akash, 2003). Similarly, in the process of obtaining oil from the Canadian oil sands, an oil-rich product, called bitumen froth is obtained. This viscous heavy oil, which is diluted with organic solvents for further processing, contains ultrafine solid particles (Romanova et al., 2006; Sparks et al., 2003). Even a low concentration of these fine solids limits the direct use of these streams as a substitute for petroleum-derived fuels, and limits any further processing because the solids in the fuel gradually deposit in storage tanks and engines. If the products are sent for further processing, the solids cause fouling in downstream equipment such as heat exchangers, and cause higher rates of cavitation in pumps. The presence of fine particles in the liquid streams in packed bed reactors can plug the catalyst bed and increase the pressure drop (Narayan et al., 1997). Solid catalyst particles can also remain in product streams in refining operations (Argyle and Bartholomew, 2015). The conventional crude oil industry faces a similar challenge when colloidal particles stabilize the petroleum emulsions, resulting in the entrapment of water droplets (Aveyard et al., 2003; Binks, 2002; Hannisdal et al., 2006). Thus, removal of such solids by a non-complicated procedure is of great importance.

Large solid particles can be removed by sedimentation, filtration, or centrifugal separation; however, these methods are often expensive or impractical to remove colloidal particles (Bensebaa et al., 2000). In a colloidal suspension, submicron particles are susceptible to thermal agitation due to their small size and thus can be suspended in the fluid indefinitely (forming an equilibrium concentration profile); even when the particles are larger than $\sim 1\,\mu m$, the settling velocity is so slow that the particles are effectively "neutrally buoyant" on the time scale of the separation process. In these cases, the remedy is the aggregation of particles.

Aggregation is a process in which two or more particles associate to form a larger entity, which is not prone to Brownian motion and will settle much faster than the unassociated particles. Aggregation of fine particles is an important process in many fields, and extensive studies can be found in the literature regarding this phenomenon (Elimelech et al., 1995; Friedlander, 2000). The rate of particle aggregation depends on interparticle surface forces (Israelachvili, 2011); if strong repulsion exists between the particles, aggregation will occur very slowly, if at all. These particles are usually coated with a layer of organic matter such as heavy oil or bituminous material that may change the interparticle surface forces and thus the rate of aggregation.

There is a vast literature on particle aggregation, but studies of the role of coating in aggregation and sedimentation of particles in nonaqueous media are scarce. Researchers in the 1970s studied the separation of mineral matter from coal-derived liquids in a solvent (Henry et al., 1979; Vaidyanathan et al., 1979). There are also a few studies reported the solid content of a solvent diluted bitumen extracted from Canadian oil sands after a given settling time or upon centrifugation (Nikakhtari et al., 2014; Pal et al., 2015). Others examined the settling behaviour of fine particles coated with a layer of bituminous material (Hooshiar et al., 2012; Long et al., 2002; Sui et al., 2016; Zahabi et al., 2010). All these studies pertained to particular situations in which the suspending medium contained substances such as asphaltene or water that influenced the settling mechanism (as an example, it was shown that the asphaltene might precipitate and thus enhance the settling rates significantly through a network formation (Madge and Garner, 2007)). Also, in these settling experiments the solid content in the suspension was high enough to cause hindered settling, while the concentration of colloidal particles in many processed products is lower than the amount required for hindered settling to occur. Due to all these issues, the effect of surface coating on the removal of fine solids through sedimentation has not yet been properly investigated. In the present study, the goal was to design experiments that would exclude interfering factors. Therefore, the settling experiments were carried out in pure solvents and the solid concentration was intentionally low.

The role of aggregation has not been thoroughly studied in previous research because it is possible to track only a limited number of empirical observables in experiments done on a macroscopic scale. Frequently used observables such as "mud line" level (Sui et al., 2016; Vanderhasselt, 2000), turbidity (Balastre et al., 2002), and settling time (Gonzalez and Hill, 1998) do not provide the microscopic information that is essential to study the effect of aggregation. To reconcile these few observables with the fundamental mechanisms of aggregation and sedimentation, a "full blown" simulation of the sedimentation process appears inevitable. After a detailed calculation from the massive amount of information produced through simulation, one may then extract the few observables that are accessible to empirical studies. The result of this exercise would be clearer insight into the underlying mechanisms of simultaneous aggregation and sedimentation. Therefore, the experimental work here is followed by a modeling study to uncover the fundamental mechanisms behind the aggregation and sedimentation process. Such information is crucial in efforts to remove fine particles more efficiently from hydrocarbon streams.

This paper is organized as follows. The experimental methods and a sedimentation test are described in Section 2. Model development and the theory pertaining to our experimental procedures can be found in Section 3. The results are presented and discussed Section 4, and conclusions are presented in Section 5.

2. Materials and methods

2.1. Materials

Silica beads of diameter 0.25 μm were purchased from Fiber Optic Center Inc. (Massachusetts, USA). HPLC grade organic solvents (toluene, n-heptane, cyclohexane) were purchased from Fisher Scientific (Ottawa, Canada). A sample of bitumen, a type of heavy oil extracted from the Canadian oil sands was obtained from Syncrude Canada Ltd.

The silica beads used in this study were either clean or coated with a layer of bituminous material. The silica beads as received were first heated at 400 °C for 30 min to eliminate surface contamination. Surface-coated silica beads were prepared as follows: 5 g of clean silica beads were dispersed in 100 mL toluene-diluted bitumen solution at 1:1 weight ratio, then gently stirred at 1000 rpm for 2 h to allow adsorption of bitumen materials onto the silica surfaces. Next, the silica beads were washed multiple times (i.e., repeated centrifugation and decantation) in toluene until the washing liquid was

clear; this ensured that the only bituminous materials that remained on the beads were irreversibly adsorbed onto the bead surfaces.

2.2. Sedimentation test

Clean or treated silica beads were dispersed in three different types of solvent—toluene, n-heptane, and cyclohexane—at 0.524 vol%. These solvents were chosen to represent the three types of low molecular weight hydrocarbons—aromatics, alkanes and cycloalkanes—present in industrial applications. The mixtures were agitated vigorously by sonication for 20 min. At time t = 0, the agitation ceased and the particles were allowed to settle. A series of 0.5 mL samples were drawn from a fixed location (1 cm from the free surface) in each mixture at specific times. The silica was isolated from each sample (by vaporizing all organic matter in an oven) and its mass m was determined using a microbalance (Mettler Toledo, model MX5). A plot of m vs. t served as an empirical representation of the sedimentation process. A minimum of three runs was made for each system. The described test can be used to quantify sedimentation rates in the event that the suspending liquid is completely opaque (e.g., crude oil).

3. Model development

The aggregation and sedimentation of particles were modelled numerically. Individual particle trajectories were not followed (as done in granular/particle dynamics); instead, the number concentrations of particles and aggregates were treated as continuous functions of position and time. For simplicity, only gradients in the vertical direction were considered.

Although by no means straightforward, in principle it was possible to predict the detailed dynamics of sedimentation. The results of such a calculation, which contains the full information of a sedimentation process, can be summarized as follows:

$$n_k = n_k(z, t); \quad k = 1, 2, 3 \cdots, \tag{1}$$

where n_k is the number density of aggregates containing k primary particles (also called "k-aggregates"), z is the depth in a quiescent fluid (often measured from the free surface), and t is the time (with t = 0 marking the beginning of aggregation). To date, there has been no theoretical or numerical study that provides the level of detail expressed in Eq. (1).

3.1. Particle aggregation

Particle aggregation can be divided into two steps: transport, in which two particles are brought into close contact, followed by attachment, in which the particles adhere to each other via short-range colloidal forces. In general, suspended particles can come into contact (i.e., collide) by three mechanisms of transport: perikinetics, orthokinetics, and differential settling (Elimelech et al., 1995; Friedlander, 2000; Gregory and O'Melia, 1989). Perikinetics refers to the encounter of two objects that are undergoing Brownian motion. This process is driven by thermal energy and is prominent in the submicron region. In orthokinetics, the fluid is subjected to some form of shear flow. Particles, especially large particles, carried along by this flow have an enhanced rate of collision. Differential settling refers to the fact that larger particles/aggregates settle more rapidly than smaller particles. Due to this velocity difference, large