Fuel 180 (2016) 538–550

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Formation of extremely fine water droplets in sheared, concentrated bitumen solutions via surfactant-mediated tip streaming

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HIGHLIGHTS

- Microfluidic setup to study drop breakup dynamics in concentrated bitumen solutions.
- Extremely fine water droplets produced via tip streaming under industrial conditions.
- Naphthenic acids, not asphaltenes, are responsible for tip streaming.

ARTICLE INFO

Article history:
Received 18 December 2015
Received in revised form 28 March 2016
Accepted 11 April 2016
Available online 23 April 2016

Keywords:
Froth treatment
Diluted bitumen
Water-in-bitumen emulsions
Drop breakup
Tip streaming
Asphaltenes
Naphthenic acid

ABSTRACT

After extraction via surface mining, bitumen froth is purified by reducing its particle and water content in the naphthenic froth treatment section. The ineffectiveness of this treatment in reducing water content below 2 wt% is, however, known only too well, and arises primarily due to the exceedingly small sizes of the emulsified water droplets. Using a flow-focusing microfluidic device, we demonstrate a possible mechanism for the formation of fine water droplets – surfactant-mediated tip streaming. Via this mechanism, a drop, when sheared in a flow, can produce droplets that can be more than two orders of magnitude smaller than the parent drop. The capillary number, which represents the strength of flow-induced drop stretching forces relative to shape-restoring interfacial tension forces, was found to range between 0.35 and 0.9 to observe tip streaming. It was discovered that naphthenic acids, and not asphaltenes, are the primary interfacially-active species responsible for tip streaming. Higher bitumen dilutions, which reduce viscosity contrast, and higher basic pH, which amplifies interfacial concentrations and decreases interfacial tension gradients, were found to suppress tip streaming. It was also demonstrated that even a mere second of exposure of water droplets to flow conditions conducive to tip streaming is capable of producing a volume fraction of micron/sub-micron water droplets comparable to the residual water fraction in bitumen after froth treatment.

1. Introduction

The bitumen froth recovered after the Clark Hot Water Extraction (CHWE) process [8] typically consists of 60 wt% bitumen, 30 wt% water and 10 wt% mineral solids [37,38]. However, the extraction product is not suitable to be sent directly to the bitumen processing plants to produce synthetic crude oil, and requires further treatment. The naphthenic froth treatment process is commonly used to supply high quality diluted-bitumen to the bitumen processing plants, while minimizing hydrocarbon losses in the tailings. The naphthenic treatment begins with the dilution of the bitumen–water–solids mixture with a solvent such as naphtha, that reduces the hydrocarbon viscosity and density, thus making the particles and water droplets more amenable to mechanical separation. The diluted froth is then pumped through a series of inclined plate settlers and centrifuges to maximize the separation of water and solids from the oil. Unfortunately, the bitumen product thus obtained still contains, on an average, 2–5 wt% water and 0.5–1 wt% solids [37,47]. The residual water, in particular, has highly deleterious effects in the downstream processing of bitumen. The recovery and reuse of process water leads to accumulation of chloride salts. Upon upgradation by H_2, these salts transform into hydrochloric acid, which corrodes equipment [10]. The salts also poison the reactor catalysts. The losses incurred in the maintenance of pipeline and reactor catalysts, and in downtime, often run into millions of dollars. Thus, the efficiency of froth treatment in removing water to produce dry bitumen product critically impacts the longevity of the downstream operations.

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http://dx.doi.org/10.1016/j.fuel.2016.04.053
0016-2361/

The ineffectiveness of the froth treatment process in meeting the required diluted bitumen quality target is a result of the small size (<10 μm) of the emulsified water droplets [47]. These fine droplets are extremely hard to eliminate using the current separation processes [43]. While the research in the field has focused primarily on emulsion stability, unfortunately, a discussion of the mechanisms of formation of extremely fine, emulsified water droplet is still missing in the literature. The work presented in this paper attempts to fill this void by exploring hydrodynamic drop breakup mechanisms leading to such small drops.

Drops suspended in a flowing fluid can experience shear-induced deformation and breakup [57,58]. It has been shown through stretching-relaxation experiments [23,56] and boundary-integral simulations [46,56] that drops stretch into thread-like structures under the influence of hydrodynamic stresses. These threads can eventually fracture into daughter droplets due to capillary instability or end-pinching effects. The size of the primary daughter droplets formed by the drop/thread fracture is typically of the same order of magnitude as the parent drop. For small drops, at low Reynolds numbers, the breakup dynamics can be adequately described in terms of a dimensionless parameter called the capillary number. The capillary number describes the ratio of viscous forces deforming the interface, to the interfacial forces resisting the deformation. The viscous stresses, τ, for an isolated drop scale as $\mu_c G$, and the interfacial stresses scale as σ/R, where μ_c is the continuous phase viscosity, G is the strain rate, R is drop radius and σ is the interfacial tension [35]. The capillary number can thus be defined as

$$Ca = \frac{\mu_c G R}{\sigma}. \quad (1)$$

Below a critical value of Ca, the drop attains a steady deformed shape, while above this value, it undergoes continuous stretching and fracture [56,59]. Assuming drop fracture to be the mechanism for sub-micron water droplet formation during bitumen processing, we can deduce the shear rate required for this event. Considering that the critical value, Ca_{cr}, for drop fracture has a lower bound of the order of unity [21], with $\mu_c \approx 15$ cP for S/B (Solvent to Bitumen ratio by weight) = 0.7, $R = 1$ μm and $\sigma \approx 12$ mN/m, the required shear rate for drop fracture is on the order of 10^6 s^{-1}. Such high shear rate zones are extremely unlikely in any of the froth treatment unit operations. Thus, fine droplet formation via primary drop fracture appears to be improbable.

There are, however, some secondary drop breakup mechanisms that can form droplets that are orders of magnitude smaller than the parent drop. It has been observed that the fracture of stretched drops is often accompanied by production of several generations of smaller, satellite drops in cascading steps [56,60]. The tendency to form satellite drops increases for systems with low drop to suspending fluid viscosity ratios. The typical viscosity ratio, $\lambda = \mu_d/\mu_c$, for the water–bitumen system is less than unity, and hence favorable for satellite drop formation. The subscripts d and c represent the dispersed phase – process water, and the continuous phase – bitumen solution, respectively.

Another secondary breakup mechanism, first observed by Taylor [58], is surfactant-mediated tip streaming. Tip streaming is a phenomenon whereby large drops in a shear or extensional flow stretch and form pointed tips that subsequently generate fine droplets about 100 times smaller than the parent drop [13,14]. After careful experimentation, De Bruijn [13] proposed the following mechanism for tip streaming. The adsorbed surfactants under the imposed extensional flow are convected along the interface from the equator to the pole of the drop (see Fig. 1), leading to surfactant accumulation there. The local increase in surfactant concentration at the pole strongly reduces the interfacial tension, and the interface locally assumes a high-curvature, pointed shape

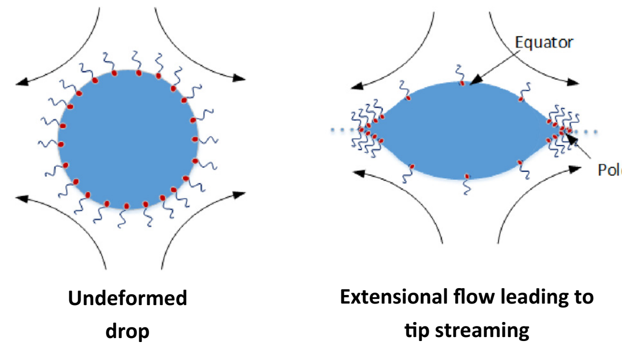

Fig. 1. Schematic describing the tip streaming mechanism for a surfactant-laden drop in an unbounded flow.

to balance the normal stresses. The viscous stresses then pull a fine thread from the tip, which eventually breaks due to capillary instability. de Bruijn also reported that the capillary number for observing this phenomenon was approximately 0.5.

While the occurrence of both secondary breakup mechanisms is plausible, in this study, we will concentrate on tip streaming as the primary source of fine water droplet generation in bitumen solutions. There are several arguments to support this choice of mechanism: (a) Shear conditions required for tip streaming ($Ca \sim 0.5$) are weaker than those needed for satellite drop formation ($Ca \sim 1$) during drop fracture. This implies that sub-micron droplets can be produced via tip streaming even if the flow is not strong enough to cause drop fracture. (b) A model developed by Cristini et. al. [9] estimated that small satellite drops (2 orders of magnitude smaller than the critical drop size) account for mere 0.1% of the volume of the parent drop. As we will estimate later in this paper, tip streaming is capable of generating much larger volumes of fine droplets than satellite droplet formation. (c) Recently, crude oil drops suspended in water containing dispersants, were shown to form microthreads and microdroplets under turbulent shearing via mechanisms suggestive of tip streaming, eventually producing fine droplets [20].

The presence of surfactants in the fluid system is a necessary condition for tip streaming [13,14,42]. Bitumen has a variety of species known for high interfacial activity at the water–bitumen interface: asphaltenes and resins (e.g. naphthenic acids) [11,15,18,27,31,37,38,44,64,65]. But, the presence of surfactants alone is not sufficient to initiate this mechanism. Establishing an interfacial concentration gradient of surfactants and hence, interfacial tension gradient, is critical [14,42]. Therefore, it needs to be demonstrated that the bitumen–water interface is susceptible to tip streaming. It is also critical that this demonstration be done for conditions similar to those found in industrial operation. A major hindrance to the real-time optical study of the water–bitumen emulsion dynamics (formation and stability) has been the opacity of concentrated bitumen solutions which limits the experimental dilution level to far below the industrial operating range [11,12,16,40,65,66]. In the current study, we present an experimental protocol to successfully operate at high concentrations of bitumen. We *visually demonstrate* the tip streaming of process water in solvent-diluted bitumen solutions using a microfluidic flow-focusing geometry [3,30,63], and map out the effect of industrially-relevant operating parameters such as bitumen dilution, process water pH, solvent aromaticity and surfactant concentration, on tip streaming.

2. Material and methods

2.1. Materials

Coker-feed bitumen containing ~20.3 wt% C5-insoluble asphaltenes [from SARA (Saturates, Aromatics, Resins and