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# Surface forces in unconventional oil processing

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### ABSTRACT

As the world population and energy demand grow every year, unconventional oil plays an increasingly more important role in satisfying our energy needs. At 3.2 trillion barrels of currently recoverable unconventional oil, and with in-place reserves putting Canadian oil sands alone at 1.7 trillion barrels, it is becoming increasingly important to find both economical and environmentally sound technologies to bring this resource to market. Characterized by its high density and high viscosity, many extraction methods that currently exist are expensive and/or provide low oil recovery. To develop new technologies, understanding fundamental surface science behind the two main steps of oil extraction – oil liberation from host rocks and separation of oil from water/oil and oil/water emulsions – is of critical importance. All the interactions between host rocks, oil, clays, asphaltenes, bubbles, and connate water are governed by surface forces. In this review, surface forces will be presented as a practical tool in understanding fundamental processes governing unconventional oil extraction. Following a thorough literature overview, the challenges, knowledge gaps and future research opportunities are discussed.

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#### 1. Introduction

This review examines the role surface forces play in unconventional oil processing and how understanding colloidal interactions could lead to improved understanding of various interactions that drive fundamental processes during oil processing. A thorough recent review regarding interfacial sciences in petroleum production by He et al. [1"] touched on surface forces, but only briefly, and a more detailed review on the topic is needed. The last review on surface forces in unconventional oil processing back in 2009 [2] focused only on the subject of atomic force microscopy. The current review encompasses several surface force measurement techniques, with a focus on the latest findings.

Unconventional oil simply refers to oil that cannot be extracted and processed using conventional methods. According to the International Energy Agency [3], unconventional oil includes kerogen shale, oil sands/tar sands, tight oil and oil derived from coal-to-liquids, gas-to-liquids and biomass-to-liquids. Alternatively, unconventional oil has been defined by its high viscosity, high density (below 20° API or above 934 kg/m<sup>3</sup>; "heavy oil") or the geological settling of the reservoir [3]. In this review, we will use the latter definition (high viscosity and high density), with bitumen as an example: density of 1003 kg/m<sup>3</sup> and viscosity of 250 Pa · s at 20 °C [4]. Predominately found in North America, Eastern Europe and Latin America, just over half of world oil reserves are unconventional oil at 3.2 trillion barrels [5] recoverable

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with current technologies. In-place reserves of unconventional oil are much larger, with Canadian oil sands alone representing 1.7 trillion barrels [1"] of bitumen. Improving extraction technologies is critical to fully harness this energy resource, with fundamental studies of surface forces governing unconventional oil extraction processes paving the way.

Currently, extraction technologies for unconventional oil fall into two categories: mining-extraction and in-situ production. For shallow deposits (less than about 70 m), open-pit mining can be used, while for deeper deposits in-situ techniques are employed [6]. The miningextraction method uses the Clark hot-water extraction process which typically involves crushing of mined ores and mixing of the crushed ores with warm water and process aids (e.g. NaOH) to form a slurry that is transported via a hydrotransport slurry pipeline. Under the favorable physicochemical condition, the turbulence in the pipeline causes heavy oil (bitumen) to detach from solid particles and become aerated with entrained air [4]. This slurry then enters a gravity separation vessel, where the aerated bitumen is collected as a bitumen froth consisting roughly of 60 wt.% bitumen, 30 wt.% water and 10 wt.% solids [7"]. Finally, bitumen is demulsified, separating bitumen from water and solids for subsequent upgrading to a synthetic crude oil (SCO). With in-situ production, many techniques [8] are used that can be broadly divided into thermal and non-thermal methods. Thermal methods use hot water and steam (such as cyclic steam stimulation (CSS) and steamassisted gravity drainage (SAGD)) to lower the viscosity of heavy oil and hence facilitate heavy oil migration to production well. Nonthermal methods rely on injections of miscible or immiscible fluids along with chemicals, aimed at lowering the interfacial tension and improving the mobility ratio [8]. Carbon dioxide and inert gases are

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popular for both miscible and immiscible injections, while chemical flooding with the addition of polymers, surfactants, alkaline and combinations thereof is less common due mainly to economic concerns.

Regardless of the production method, there are two essential steps involved in unconventional oil extraction: oil liberation from host rocks or reservoir solids (Fig. 1:a-b) and the separation of water (either connate or added as extraction aid) and oil (Fig. 1:c-d). Oil liberation can be subdivided into two sub-processes: bitumen recession and bitumen/ solid detachment (Fig. 1-a). The most important interaction is between heavy oil and host rock/sand in processing fluids. There are two methods of oil-water separation: i) flotation through oil-air bubble attachment and ii) creaming/sedimentation of dispersed oil/water droplets through flocculation/coalescence. Numerous interactions are involved in oilwater separation, as shown in Fig. 1-b and c, respectively. In flotation, attractions between air bubbles and oil droplets are essential while interactions between air bubbles and solids and/or between solids and oil would interfere with the separation. The oil-oil interaction also plays an important role in flotation due to extreme difficulties in attachment of small oil droplets to flotation size bubbles. In oil-water separation by creaming or sedimentation, demulsification of water-in-oil (W/O) and oil-in-water (O/W) emulsions (Fig. 1-c) is essential, where oil-oil, water-water and asphaltene-solvent interactions are important in determining the success of the demulsification process. Oil-in-water (O/W) emulsions are most commonly observed during water-flooding and hydrotransport, while water-in-oil (W/O) emulsions are found further along the extraction route, including bitumen froth treatment, crude oil transportation and oil desalting [9]. While thermodynamically unstable, these emulsions have remarkable kinetic stability often attributed to surface active species, such as asphaltenes (Fig. 1-c, orange inset) and small mineral solids (fines, Fig. 1-b)) that migrate to the water-oil interface. Asphaltenes are a solubility class, defined as soluble in toluene but insoluble in *n*-alkanes. Clays can make up 15–30 wt.% of solids in the mined oil sands, predominantly kaolinite and illite [4]. More details regarding asphaltenes and clays in unconventional petroleum can be found elsewhere [10<sup>•</sup>]. Destabilization of such emulsions is largely determined by the properties and stability of interfacial thin films between approaching droplets. Many factors can influence all of these interactions, including the presence of electrolytes, endogenous surface-active species and fines (e.g. clays), along with process parameters such as temperature, pH, weathering and the addition of potential processing aids, to name a few. All these interactions that determine the success of unconventional oil production are governed by surface forces. Better understanding of surface forces will lead to more economical and environmentally-sound unconventional oil extraction techniques.

#### 2. Experimental techniques

Background information regarding Atomic Force Microscope (AFM), Surface Force Apparatus (SFA), Thin Liquid Film (TLF) techniques (SI2) and Surface Forces in general (SI1) can be found in Supporting Information. The Integrated Thin Film Drainage Apparatus (ITFDA) is a new, custom designed instrument and for this reason will be discussed in this review. Table 1 on the next page summarizes the major findings for interactions shown in Fig. 1, sorted by experimental technique.

The ITFDA, developed by Wang et al. [11<sup>•</sup>] and shown in Fig. 2-a [11<sup>•</sup>], has some added benefits to the simpler TLF technique. The ITFDA allows the direct and simultaneous measurement of numerous parameters, including: interaction forces and thin film drainage dynamics over a wide range of hydrodynamic conditions. Specifically, it covers interactions in the intermediate Reynolds number regime (between 0.01 and 100) that cannot be studied by any of the previously listed instruments while often encountered in unconventional oil production. Briefly, a droplet (or bubble) is generated inside a glass capillary via an air-tight syringe. A motorized actuator coupled with a speaker diaphragm allows for precisely controlled vertical approach of the droplet at a wide range of speeds (0.01–50 mm/s) [11<sup>•</sup>]. The lower surface (a glass sphere in Fig. 2-a) is attached to the free end of a piezoelectric bimorph [12] (shown in Fig. 2-b) that allows the direct measurement of interaction forces with a sensitivity of up to 0.1 µN. The ITFDA can be used to measure interaction forces between air bubbles and solids, liquid droplets or another air bubble, between two liquid droplets, and between droplets and solids in a fluid, as encountered in unconventional oil recovery process outlined in Fig. 1. The instrument has recently been modified in our group to replace the glass sphere in Fig. 2-a to a transparent silica window that allows for better overlap control and film thickness monitoring via interference fringes.

#### 3. Surface forces in unconventional oil liberation (oil/water/sand)

Heavy oil is typically found impregnated in host rocks or solid minerals. The rock/mineral composition varies by location, and typically consists of carbonate rocks (e.g.: calcite, dolomite, etc.), sands (e.g.: silica, kaolinite or aluminum silicate), clays and heavy minerals [1<sup>\*\*</sup>]. The size of solids varies widely, from a micron-sized clay platelet to a rock



Fig. 1. Schematic illustration of unconventional oil recovery steps: (a-b) liberation of unconventional oil from host solids/sands and aeration of liberated oil to air bubbles, and (c-d) separation of unconventional oil from water via demulsification of water-in-oil and oil-in-water emulsions. Important interactions for each step are circled and labeled in red.

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