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Extraction of hydrocarbons from Athabasca oil sand slurry using supercritical carbon dioxide

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ABSTRACT

The oil sands industry is seeking innovative technologies to address the water intensity and the high-energy consumption associated with current oil sands processing technologies. This research therefore investigates the use of supercritical fluid extraction (SFE) as an alternative to the current water-based extraction technology. Bitumen, a complex mixture of hydrocarbons, was extracted from an Athabasca oil sand slurry using supercritical carbon dioxide (SC-CO_2). Preliminary experiments revealed the importance of a higher mixing speed and a longer static time on hydrocarbon yields. In a second set of experiments, when toluene was introduced as a modifier, a higher SC-CO_2 density (i.e. high pressure, low temperature) led to higher extraction yields. In the absence of toluene, higher temperature conditions (i.e. lower SC-CO_2 density) provided higher extraction yields—suggesting desorption resistant hydrocarbon components in the oil sand matrix slurry are released as a result of increasing temperature. Using gas chromatography-flame ionization detector (GC–FID), the experiment that produced the highest cumulative hydrocarbon extraction yield was analyzed for product quality and the extracted hydrocarbons were observed to center on C_{25}.

1. Introduction

Canada's oil sands reserves, often regarded as the third major petroleum reserve after Venezuela and Saudi Arabia [1], are primarily concentrated in the province of Alberta and are distributed in three deposits: Peace River, Cold Lake and Athabasca [2]. The depth of the oil sand reserves dictates the method of bitumen recovery: surface mining is used for deposits less than 50 to 75 m in depth [3,4] and in-situ methods are used for deeper deposits. Approximately 20% of the oil sand reserves can be recovered by surface mining extraction methods and the remaining 80% is recovered by in-situ methods [2]. Open-pit mining is the most common surface mining method and steam assisted gravity drainage (SAGD) is the most common in-situ technology.

The oil sands industry currently faces challenges with the high water intensity and the high energy intensity of current technologies used for the extraction and upgrading of bitumen. Recently, efforts have been placed on developing extraction methods that make more efficient use of resources and are less energy intensive. Examples include effective water-recycling processes [5] and lower temperature extraction methods [6,7] for surface mining operations; and non-aqueous methods for in-situ recovery of bitumen, such as toe-to-heel air injection (THAI) [8,9] and vapor extraction (Vapex) [3].

Supercritical fluid extraction (SFE) is being considered as an alternative to water-based extraction methods for surface mined oil sands. Supercritical fluids (SCFs) provide an added advantage of possessing tunable features that can be controlled by selective adjustments to operating conditions and permits the quality of the extracted product to be varied and moderated. Upon reaching supercritical state, the density, diffusivity, and viscosity of an SCF exhibits properties of both a gas and a liquid [10]. Once in the supercritical phase, a small adjustment to temperature and/or pressure near the critical point can result in a drastic change in density; therefore, the extraction of a particular compound can be regulated by increasing the pressure. which in turn increases the SCF density. If both temperature and pressure are increased together, it is possible that a corresponding increase in solute vapor pressure will result in a parallel enhancement in solute dissolution in the SCF. These attributes allow the SCF to possess a density and solvation power similar to those of a liquid and mass transfer properties and compressibilities similar to those of a gas—including

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exhibiting near zero surface tension for enhanced diffusivity into a porous matrix [11–13].

Supercritical carbon dioxide (SC-CO_2) is often the solvent of choice for SFE research and industrial application [12,14] due to the relatively low critical temperature (31 °C) and critical pressure (7.4 MPa), as compared to other solvents. SC-CO_2 is also seen as an environmentally acceptable solvent and is increasingly being considered as a replacement solvent in heavy oil production applications including as a primary solvent for Vapex [15], as a diluent substitute (also known as carbit) [16], and as an alternative injection fluid to supplement or replace steam in SAGD operations [17]. On the other hand, SC-CO_2 has a preference to extract nonpolar components, especially low molecular weight *n*-alkanes [18], while leaving polar components behind. The potential application of SC-CO_2 on bitumen extraction from oil sands can lead to lower operating costs and material handling [19] as the extracted product is a naturally deasphalted oil [20,21] that contains little to no heavy molecular weight asphaltenes that are the precursor to coke formation during conventional upgrading processes. SFE has been used to deasphalt heavy oil by the ROSE^{TM} (residuum oil supercritical extraction) process, developed in the 1970s and uses butane or propane to deasphalt under sub-critical conditions followed by supercritical conditions for solvent recovery [22]. The solvation power of SC-CO_2 has been compared to *n*-hexane [23,24], which is a solvent that may be used to precipitate asphaltenes from bitumen. However, the solubility of both polar and nonpolar components in SCFs can be increased upon the addition of polar and nonpolar miscible fluids in small quantities of ≤5% volume, while adding additional benefits such as decreasing the extraction time, lowering the operating pressure [18,25], and increasing the extraction efficiencies [26–29].

In the literature, SFE has been suggested for the extraction of bitumen from oil sands. For example, a patent by Poska [30] proposed a process by which oil sands and a SCF (aromatic hydrocarbons, alicyclic hydrocarbons and others) are contacted countercurrently in a vertical extractor. Operating conditions ranged from 180 to 500 °C for temperature and up to 35 MPa for pressure. Poska [30] suggested that a major advantage of a supercritical fluid process is that there is minimum entrainment of fine solids from the oil sands with the extracted bitumen. Subramanian and Hanson [31] investigated the extraction of four different types of bitumen using supercritical propane. They successfully extracted bitumen without extracting metals and asphaltenes, indicating the potential for some upgrading using SFE [31]. Rose et al. [32,33] investigated the extraction of bitumen from a bitumen-sand mixture using supercritical ethane and CO_2 and found that, for both solvents, the amount of bitumen extracted increased with increasing pressure and decreasing temperature. The bitumen extracted at low temperature/high pressure conditions was heavier and for both supercritical solvents, the bitumen extracted during an experiment was heavier as the extraction proceeded [33], indicating the potential for upgrading as part of the extraction process. Recently, McGrady and co-workers [19,34] proposed a supercritical process for the extraction and upgrading of bitumen from oil sand. They successfully extracted bitumen from oil sands using SC-CO_2 with toluene as a modifier and then upgraded the extracted bitumen to synthetic oil in the SCF in the presence of hydrogen and a catalyst. Rudyk et al. [18,21,29,35] have investigated the use of polar modifiers such as methanol, ethanol, propanol, acetone, and kirasol with SC-CO_2 for the extraction of crude oil and for the extraction of bitumen from Nigerian oil sands. The results showed that ethanol was the better modifier for recovering hydrocarbons because of its better hydrogen bonding potential as compared to the other polar modifiers tested. It was suggested that, although the use of methanol as a modifier resulted in a higher amount of total hydrocarbons being extracted, there was a tendency for more lighter-end hydrocarbons to be extracted especially at lower pressures when methanol was used. In the experiments with Nigerian oil sands, Rudyk and Spirov [21] found that the addition of salty water to the oil sands led to a higher hydrocarbon recovery than when tap water or no water was added to the oil sands prior to extraction with SC-CO_2 alone. However, temperatures in excess of 100 °C were necessary for successful extractions of bitumen from Nigerian oil sands—Rudyk and Spirov [21] suggest that higher temperatures are needed so that the oil sands are in a melted state and that only then can sufficient hydrocarbon recovery occur using SC-CO_2.

Previous work by Fang [36] investigated the use of SC-CO_2 to extract hydrocarbons from oil sands (low and medium grade) by exploring the effects of temperature, pressure, mixing speed, premixing, static and dynamic extraction times on extraction efficiencies using a laboratory-scale batch reactor. As a follow-up to the work by Fang [36], the work described herein will focus on using SC-CO_2 to extract hydrocarbons from an oil sand–water slurry. As the surface mined oil sands are currently hydrotransported to extraction, if a SC-CO_2 process is to be used for the extraction of bitumen from surface mined oil sands, it is important to look at the influence of water on the SFE process. In particular, the objectives of this research are to:

- examine the effect of temperature and pressure (and thus SC-CO_2 density) at temperatures of 31 °C and 60 °C and at pressures of 13.8 MPa and 24.1 MPa on hydrocarbon extraction efficiencies from a 1:1 Athabasca oil sand–water slurry,
- investigate the effect of the addition of toluene as a modifier on hydrocarbon extraction efficiencies and,
- analyze the product quality of the extracted hydrocarbons obtained at the experimental conditions providing the highest yield.

2. Materials and experimental procedure

2.1. Materials

Medium grade oil sand samples from the Athabasca formation in northern Alberta, Canada were purchased from the Alberta Innovates Technology Futures' oil sands sample bank (Edmonton, Alberta, Canada). The oil sand was stored in a 20 L pail and kept in a −5 °C walk-in freezer in the Department of Civil & Environmental Engineering at the University of Alberta. Subsamples were transferred into 1 L jars for the primary experiments and stored in a separate freezer. The oil sand was characterized in our lab using Dean Stark extraction and asphaltene precipitation as outlined in [37]. The oil sand composition was found to be 10.7 ± 0.73 wt% bitumen, 88.2 ± 0.95 wt% solids, and 1.1 ± 0.41 wt% water. The asphaltenes content of the bitumen was found to be 15.3 ± 1.55 wt%. Oil sand composition and asphaltenes content analyses were based on three replicates each.

Toluene (HPLC grade) and *n*-pentane (98%) used for Dean–Stark extractions, asphaltene precipitation, and experiments were purchased from Fisher Scientific (Fair Lawn, NJ, USA).

2.2. SFE bench-scale batch system description

A laboratory bench-scale batch SFE apparatus was used for experiments on the 1:1 oil sand–water slurry. Fig. 1 provides a schematic of the extraction apparatus. A liquid CO_2 cylinder (Grade 3, bone dry, from Praxair, Mississauga, ON, Canada) supplies CO_2 for the extraction experiments. Two cooled (−2 °C) ISCO syringe pumps (Model 500D, Teledyne ISCO, Lincoln, NE, USA) operate in tandem to ensure a continuous supply of compressed CO_2 for the extraction process at the desired experimental pressure. The