PE02

The Effect of Temperature, Pressure and Modifier on the Initial Solubility of Waste Stream Bitumen in Supercritical Carbon Dioxide

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ABSTRACT

Oil sands operations produce various process waste streams, many of which contain residual bitumen and other process hydrocarbons. Bitumen and hydrocarbon recovery from these waste streams may be possible using supercritical carbon dioxide (SC CO_2). In this work, initial solubility experiments were performed, with and without modifiers. The initial solubility of a mixture (akin to an initial boiling point) is the equilibrium concentration reached in a small quantity of SC CO_2 in contact with a large quantity of the mixture. Initial solubility data and composition is fundamental to process design, development and scale up.

Experiments were carried out on a bench-scale supercritical fluid extraction system at varying conditions of temperature and pressure. Two mixtures were used: (i) bitumen only and (ii) a waste stream composed of water, solids and residual bitumen. Experiments consisted of a 60 minute static period, followed by a 25 minute dynamic period at a low flow rate. For experiments with modifier, the modifier was added prior to the static period and then continuously during the dynamic period. The initial solubility was measured gravimetrically from the collected samples and presented as gram of bitumen per gram of CO_2.

Maximum initial solubility for both the bitumen and the waste stream, without modifier, was seen at the tested temperature and pressure conditions that resulted in the highest density of SC CO_2 (314 K and 24 MPa), with bitumen having an initial solubility of 1.22×10^{-2} g bitumen/g CO_2 and the waste stream having an initial solubility of 1.57×10^{-2} g bitumen/g CO_2. The lowest initial solubility was seen at conditions that resulted in the lowest SC CO_2 density. Modifier addition increased solubility. At 333K and 24 MPa, the initial solubility of the bitumen mixture was 1.14×10^{-2} g bitumen/g CO_2. With the addition of methanol as a modifier, the solubility increased to 1.31×10^{-2} g bitumen/g CO_2, while with toluene, it increased to 2.19×10^{-2} g bitumen/g CO_2 (at the same temperature and pressure). At 333K and 24 MPa, the waste stream had an initial solubility of 1.26×10^{-2} g bitumen/g CO_2 without modifier, 1.74×10^{-2} g bitumen/g CO_2 with methanol as a modifier and 2.38×10^{-2} g bitumen/g CO_2 with toluene as a modifier.

INTRODUCTION

Oil sands deposits located in Alberta, Canada contain the 3rd largest oil reserves in the world, distributed over 3 major regions in northern Alberta [1]. Development of these reserves is integral to the province's economy, where bitumen revenue totaled 47.9% of the non-renewable resource revenue in 2016-17 [1]. In 2016, mined and in situ bitumen production was 403.3 thousand cubic metres per day (10^3 m^3/d), and is forecasted to increase to 602.5 thousand cubic metres per day (10^3 m^3/d) [2]. This production creates wastes streams, some of which contain residual bitumen and hydrocarbons left over from processing. The residual bitumen and hydrocarbons are valuable and it would be beneficial to recover them. In addition, these waste streams have an environmental impact, as they are currently being stored in large tailings ponds, whose liquid surface area covers 88 km^2[1]. Tailings are required by Alberta Energy Regulator to be "treated and progressively reclaimed during the life of the project" [9]. New technologies such as supercritical fluid extraction can be useful in both recovering valuable bitumen and hydrocarbons from newly generated waste streams prior to deposition in tailings ponds and treating already established tailings.

Previous supercritical fluid extraction work has shown that SC CO_2 is capable of extracting bitumen and that increasing solvent density increases the extraction yield [3,4]. When added to SC CO_2, modifiers have been shown to improve extraction yields [5,7]. While SC CO_2 is a non-polar solvent with polarities similar to that of n-hexane [8], the addition of modifiers of higher polarity such as toluene and methanol can increase the polarity of the fluid [5,7] and allow for increased extraction of more polar species.

One parameter that is important in understanding the extraction of bitumen from different mixtures is the initial solubility. Bitumen itself is a mixture of many components. While solubility work is historically performed on a single pure substance dissolved in a solvent, previous phase behaviour work has studied the solubility in SC CO_2 and bitumen systems [10,11].

In this work, we investigated the initial solubility of two mixtures under a series of conditions of pressure, temperature and modifier type. The first mixture was raw bitumen and the second was a waste stream containing bitumen (similar but not identical to the raw bitumen), water and solids. The objective was to provide initial data on the magnitude of the initial solubility values in addition to identifying the sensitivity of the initial solubility to the mixture composition, pressure, temperature and presence of modifier. With respect to mixture composition in particular, the objective of this work was to determine if the presence of water and solids that are commonly found with most waste streams significantly impacts initial solubility values. The initial solubility is the concentration of a mixture dissolved in an infinitely small droplet of solvent. Practically, the amount of solvent is small enough to be a reliable measure if the dissolution into the solvent does not noticeably or significantly alter the composition of the mixture. The initial solubility of a mixture is a thermodynamic limit for a supercritical fluid extraction process and thus it is an important factor in process design and development.

MATERIALS AND METHODS

Initial solubility experiments were conducted on two mixtures: raw bitumen and a waste stream containing, on average, 44.3 wt% bitumen, 54.2 wt% water and 1.5 wt% solids. According to the high temperature simulated distillation (HTSD) analysis (ASTM 7169) of the bitumen in both mixtures (Figure 1), the bitumen in the waste stream mixture is an overall lighter mixture (from a distillation perspective) than the raw bitumen.

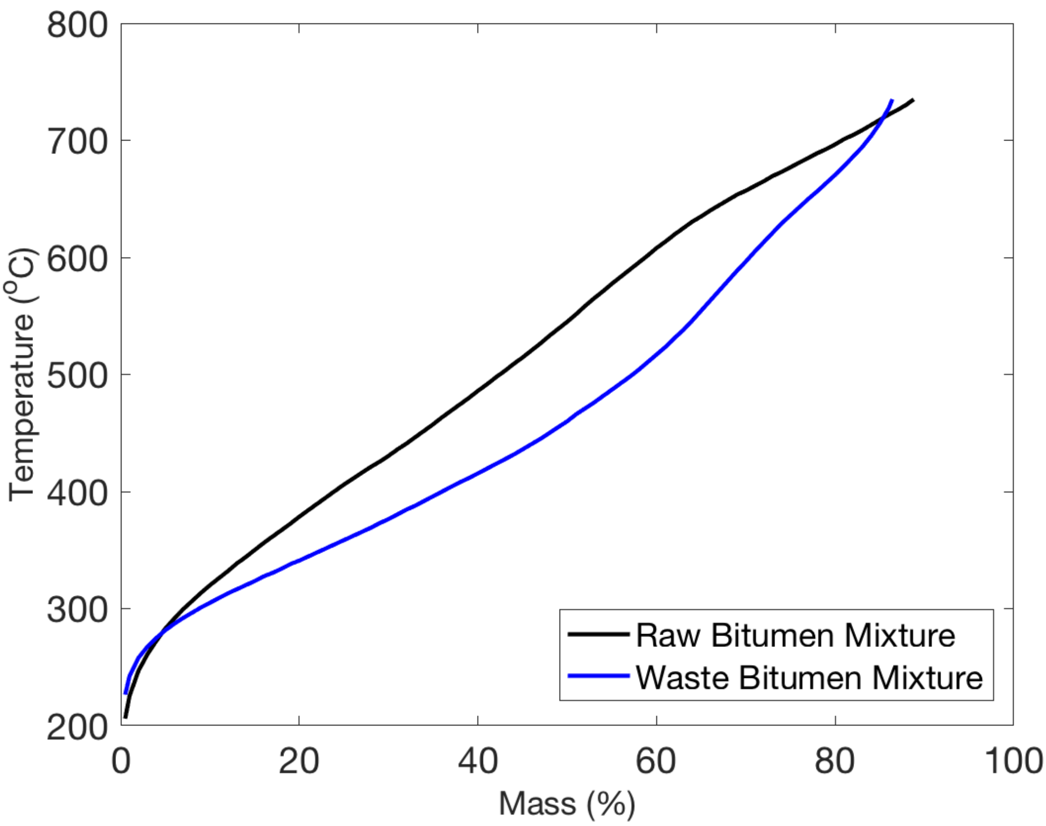
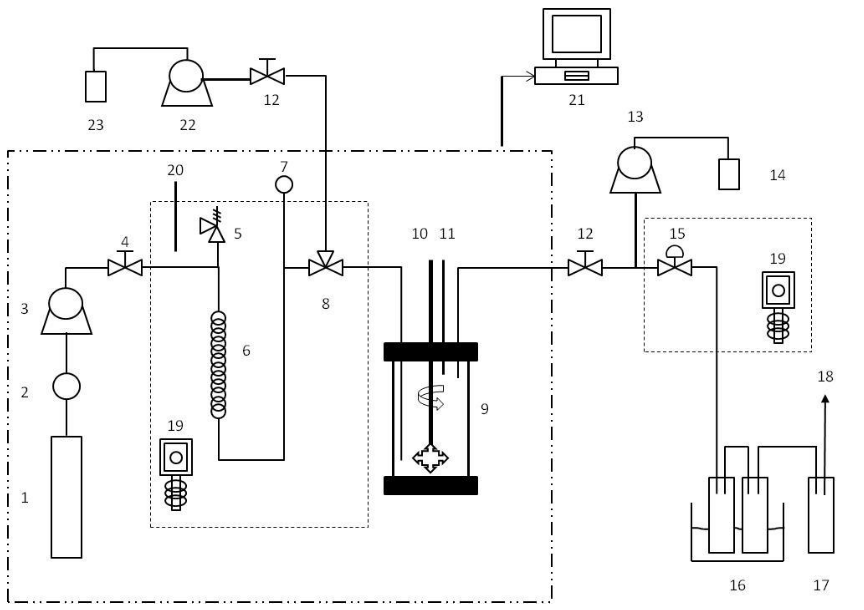


Figure 1: HTSD curve for bitumen and waste stream mixtures

Initial solubility experiments were performed on a bench scale apparatus shown in Figure 2. Approximately 50 g of bitumen or waste stream mixture (provided by Syncrude Canada Ltd.) was placed in a pre-heated 300 mL extraction vessel (205 mL working volume) and mixed using a MagneDrive® mixer. SC CO_2 with and without modifier flowed into the bottom of the vessel and exited the top of the vessel. An initial 1-hour static period allowed for system equilibration. During this static period, there was slow mixing of 50 rpm for bitumen experiments and 20 rpm for waste stream experiments.

A series of 3 glass vials (*a*, *b* and *c*) were used to collect the hydrocarbons after depressurization of the CO_2. They were attached to the outlet with the first two vials (vials *a* and *b*) sitting in a dry ice-acetone bath and the third (vial *c*) sitting at ambient temperature. Vial *a* contained glass beads and vials *b* and *c* contained approximately 20 mL of toluene. At the end of the static period, the mixer was stopped and CO_2 flowed through the 3 collection vials at a rate of 2-4 mL/min, as measured at pump conditions. Samples were collected in 3 sets over 25 minutes for each set. During each set, vials *a* and *b* were changed every 5 minutes and vial *c* was changed at the end of each 25-minute set. The metering valve and the lines downstream were rinsed at the end of each set to collect any hydrocarbon remaining in the metering valve or lines.

Initial solubility, represented as the mass of hydrocarbons collected divided by the mass of CO_2 flowed through the system, was determined gravimetrically after a drying period (2 days for bitumen experiments and 5 days for waste stream experiments). The mass collected in vial *c* and any mass collected from the rinse was also considered in the initial solubility calculation and was distributed evenly across the mass collected from vials *a* and *b* over an entire set (5 sub-sets of 5 minute collection periods).



1. CO_2 cylinder
2. Filter
3. ISCO syringe pump
4. Check valve
5. Pressure relief valve
6. Preheating coil
7. Pressure transducer
8. Three-way ball valve
9. Extraction vessel
10. MagneDrive® mixer
11. Thermocouple
12. Two way ball valve
13. Microlab® pump for toluene rinse
14. Toluene reservoir
15. Heated metering valve
16. Separator vials in acetone/ dry ice bath
17. Separator vial at ambient conditions
18. CO_2 vent to fumehood
19. Circulating water bath
20. Thermometer
21. Data acquisition system
22. Pump for modifier addition
23. Modifier reservoir

Figure 2. Supercritical Fluid Extraction (SFE) bench-scale dynamic extraction system

RESULTS

Table 1 provides the initial solubility data from both the raw bitumen and the waste stream as a function of temperature and pressure. For all conditions tested, the initial solubility values are on the order of 1 wt% for both the raw bitumen and the waste stream. This solubility value is encouraging given the proportion of mid- and high-molecular weight compounds that are prevalent in bitumen.

Table 1: Initial solubility of bitumen and waste stream mixtures in supercritical CO_2

P	T	Density[a]	Initial Solubility (g/g)		
(MPa)	(K)	(g/mL)	average	range	n
Bitumen Mixture					
24	313.5	0.8709	1.22×10^{-2}	2.75×10^{-3}	3
24	333.9	0.7723	1.14×10^{-2}	4.56×10^{-3}	6
16	334.7	0.6236	4.53×10^{-3}	1.79×10^{-3}	3
Waste Stream Mixture					
24	314.3	0.8672	1.57×10^{-2}	2.80×10^{-3}	2
24	333.2	0.7758	1.26×10^{-2}	1.59×10^{-3}	2
16	334.5	0.6254	7.07×10^{-3}	2.31×10^{-4}	2

[a]density values have been calculated based on Span and Wagner [12]; n = number of experimental values

The average range is 23% of the average initial solubility measured, with a maximum range of 63%. Given the complexity of bitumen, this level of experimental consistency is excellent.

Also, the mass of sample collected in vials *b* and *c* represent less than 2% of the mass collected in vial *a* which provides an indication that the sample collection system worked effectively.

The temperature and pressure conditions were chosen to cover a range of densities of the SC CO_2. Initial solubility increases with increasing SC CO_2 density in both the bitumen and waste stream mixtures. Initial solubility is greatest at conditions of highest pressure and lowest temperature. This is expected as the increased density at these conditions increases solvation power of the SC CO_2 [3].

The initial solubility is consistently higher for the waste stream mixture relative to the raw bitumen mixture at all three conditions. This is most likely due to the bitumen in the waste stream mixture having a lighter hydrocarbon profile than the bitumen mixture. It is also an indication that the presence of the water and solids in the waste stream does not appear to have a severe negative impact on the initial solubility.

Table 2 provides initial solubility data for bitumen and waste stream mixtures with and without modifier. The addition of modifier (5 mol%) increases the initial solubility in all cases relative to the initial solubility with SC CO_2. Methanol's solubility enhancement was less than that of toluene for both mixtures. Methanol's increase is likely associated with the increasing the polarity of the solvent. Toluene is known to completely dissolve all bitumen components including asphaltenes which drives its effectiveness as a modifier.

Table 2: Initial solubility of waste stream and bitumen mixtures in supercritical CO_2 at 333K and 24MPa

Sample type	Modifier	Solubility (g/g)		
		average	range	n
Bitumen Mixture	None	1.14×10^{-2}	4.56×10^{-3}	6
	Methanol (5% mol)	1.31×10^{-2}	8.29×10^{-3}	3
	Toluene (5% mol)	2.19×10^{-2}	5.28×10^{-3}	3
Waste Stream Mixture	None	1.26×10^{-2}	1.59×10^{-3}	2
	Methanol (5% mol)	1.74×10^{-2}	4.20×10^{-4}	2
	Toluene (5% mol)	2.38×10^{-2}	3.80×10^{-4}	2

Methanol's solubility enhancement was more pronounced for the waste stream (38% increase) than it was for bitumen (15% increase) but it is uncertain why. It may be that the waste stream mixture has a slightly higher fraction of polar compounds in addition to being slightly lighter. Another factor to consider is that the range for the methanol modifier experiments with bitumen is distinctly larger than observed for all other cases, so the enhancement difference may be an artifact of the variability in the results. Further data and analysis is necessary to understand this difference.

Toluene's solubility enhancement is nearly a factor of 2 for both the bitumen and waste stream mixtures. This level of solubility enhancement, at just 5 mol%, indicates that the use of toluene in processing warrants further exploration.

CONCLUSION

The initial solubility of the bitumen mixture in pure SC CO_2 was observed to be 1.22 $x10^{-2}$ g/g at 24 MPa and 313 K. For the limited number of conditions studied, this initial solubility was observed to be a function of density. Methanol, as a modifier, had a modest solubility enhancement of 15% whereas toluene's solubility enhancement was a factor of 1.9.

The initial solubility of the waste stream mixture in pure SC CO_2 was 1.57 $x10^{-2}$ g/g at 24 MPa and 313 K. The slightly lighter bitumen in the waste stream mixture, relative to the bitumen only mixture, likely caused this increased solubility. The presence of water and solids does not appear to significantly negatively impact the initial solubility. Methanol had a modest solubility enhancement of 38% whereas toluene's solubility enhancement was a factor of 1.9.

ACKNOWLEDGEMENTS

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