PE01

Effect of Modifiers on Supercritical Carbon Dioxide Extraction of Bitumen

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ABSTRACT

Intensive operations are required to recover bitumen from oil sands and as a result, process waste streams containing bitumen are generated. Experiments have been conducted to determine the effects of modifiers on the extraction of bitumen using supercritical carbon dioxide (SC-CO_2). The data will aid the development and demonstration of a supercritical fluid extraction (SFE) process for bitumen recovery from oil sands process waste streams.

Two modifiers, toluene and methanol, have been tested in a bench-scale SFE system at a constant pressure of 24 MPa and temperature of 333 K. Bitumen was added to an extraction vessel and a dynamic extraction was initiated in the presence of a modifier at a concentration of 5, 10 or 15 mol%. Samples of extracted bitumen were collected in two separation vials in series every 5 to 15 minutes. The amount of bitumen extracted was determined from both the amount of bitumen collected in the separation vials and from the amount of bitumen remaining in the extraction vessel. The quality of the bitumen was also investigated by high temperature simulated distillation (HTSD).

Results show that, without the addition of a modifier, SC-CO_2 extracts 40 wt% of the original bitumen. Increasing the concentration of a modifier (to 5, 10 or 15 mol%) in SC-CO_2 results in an increase in the percentage of bitumen extracted for any given CO_2 to bitumen ratio. At 15 mol%, toluene is capable of extracting 76 wt% of the original bitumen, a 93% increase from SC-CO_2 alone. Compared to the same concentration of methanol, 5 mol% toluene extracts 9 wt% more bitumen. HTSD results show that toluene addition results in heavier bitumen extracts compared to an equivalent molar concentration of methanol or SC-CO_2 alone.

INTRODUCTION

Alberta has the third largest proven oil reserve in the world, equivalent to approximately 165.4 billion barrels, as of 2016 [1,2]. Of this volume, approximately 20% is within 75 m of the ground surface and is thus recoverable through surface mining. Extracting bitumen from these minable reserves results in process waste streams. Typically, waste streams from various stages in the extraction process are combined and stored on-site in tailings ponds. These waste streams exist as aqueous slurries and are made up of varying amounts of sand, water, clay, dissolved salts and residual bitumen [1-3]. A novel approach to recovering the residual bitumen, while simultaneously cleaning a process waste stream, is using supercritical fluid extraction (SFE).

Previous research has focused on bitumen recovery from oil sands, showing successful recovery using various supercritical fluids such as carbon dioxide, n-pentane and propane [4-7]. The addition of modifiers, commonly toluene, to the supercritical fluid has been shown to improve bitumen recovery [4,5,7]. It has been suggested that this increased recovery occurs because the addition of a modifier that is more polar than the supercritical fluid enhances the solubility of the polar components of bitumen [4,8,9]. However, increasing the concentration of a modifier from, for example, 5 to 10 mol% in a supercritical mixture has had conflicting results on recovery [5,10].

The objective of this research is therefore to investigate the extraction of bitumen using supercritical carbon dioxide (SC-CO_2) combined with one of two modifiers, toluene or methanol. The effects of increasing concentrations of a modifier (5, 10 and 15 mol%) on the quantity of bitumen extracted will also be explored. This research will provide preliminary results necessary for the development and optimization of a SFE process for bitumen recovery from bitumen-containing waste streams.

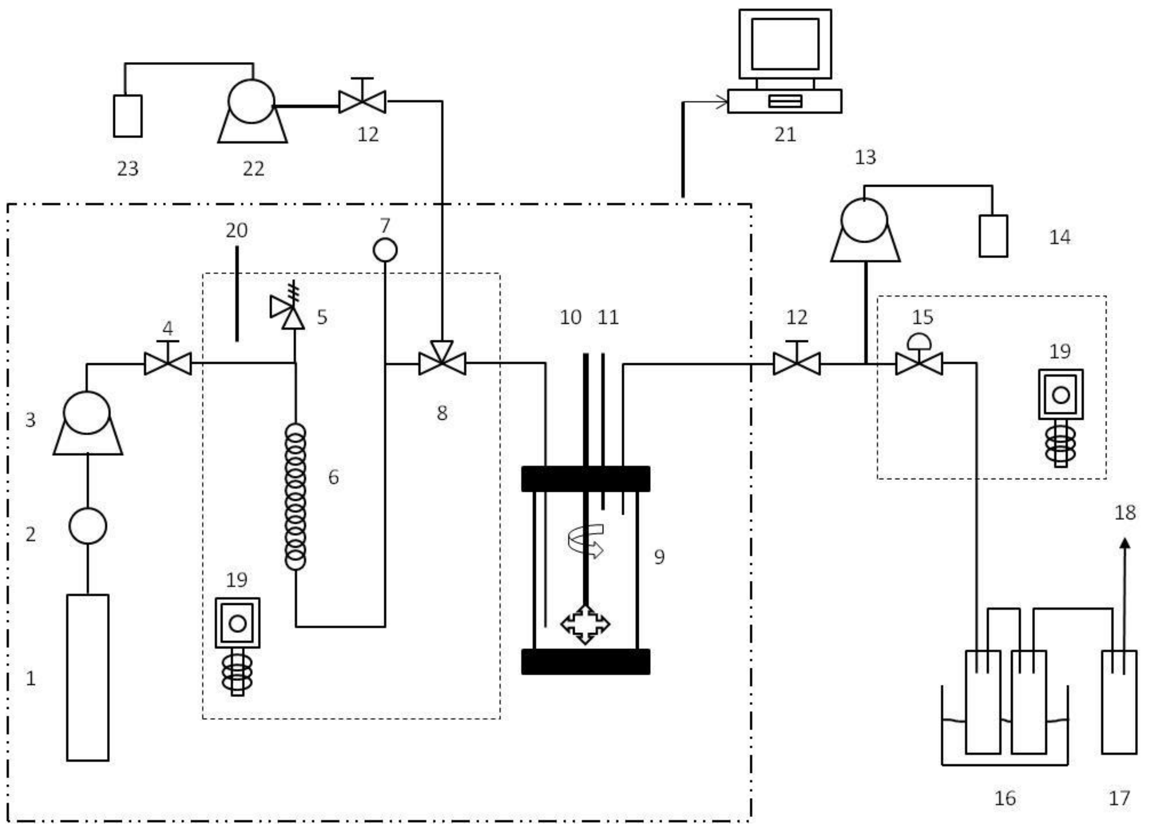
MATERIALS AND METHODS

A series of dynamic extractions were conducted in triplicate using a bench-scale batch SFE system shown in Figure 1 at a constant pressure of 24 MPa and temperature of 333 K. Approximately 10 g of bitumen (supplied by Syncrude Canada Ltd.) was added to a preheated 300 mL extraction vessel (Autoclave Engineers) and mixed at 250 rpm using a MagneDrive® mixer. SC-CO_2 (with or without a modifier) flowed through the extraction vessel at 20 g min^{-1}.

For experiments with modifier addition, toluene or methanol was added continuously using a Gilson 305 piston pump (Mandel Scientific). Toluene was added at concentrations of 5, 10 or 15 mol% of SC-CO_2 and methanol was added at 5 mol% of SC-CO_2. The exiting flow passed through three 40 mL collection vials or three 120 mL collection jars in series (labeled *a*, *b* and *c*). Vials (40 mL) were used for experiments with pure SC-CO_2 or SC-CO_2 in the presence of a modifier at a concentration of 5 mol%. Jars (120 mL) were used for the toluene experiments with a modifier concentration of 10 or 15 mol% to accommodate the larger volume of modifier exiting the system. Vials or jars labeled *a* and *b* were cooled in an acetone/dry ice bath to rapidly condense the extract, maximizing the collection of hydrocarbons. Vial/jar *a* contained glass beads, providing surface area for extract collection. Vial/jar *b* contained approximately 20 mL of toluene, acting as a solvent to trap the extract. Vial/jar *c* was maintained at ambient temperature and contained approximately 20 mL of toluene.

Vials or jars labelled *a* and *b* were replaced every 5 minutes for the first 15 minutes of the first dynamic extraction period. During the next 30 minutes, vials/jars *a* and *b* were replaced every 15 minutes for a total sampling time of 45 minutes. Vial/jar *c* was replaced after the first sampling period was complete. This first sampling period was followed by a 60-minute static period and then a second sampling period of 75 minutes. During the second sampling period, vials/jars *a* and *b* were replaced every 15 minutes. The first sampling period generated Samples 1 through 6 while the second sampling period generated Samples 8 through 13. A toluene rinse of the outlet line was conducted after each sampling period and collected in vials or jars labeled Samples 7 and 14. After each experiment was completed, the bitumen/modifier mixture remaining in the vessel (vessel residue) was quantified and analysed.

The mass of bitumen extracted was determined gravimetrically after 48 hours of drying to evaporate the toluene and/or methanol. Select extract samples and a sample of the vessel residue were analyzed by high temperature simulated distillation gas chromatography (HTSD) (ASTM 7169).



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 or jars in acetone/dry ice bath
17. Separator vial or jar 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 1. Supercritical Fluid Extraction (SFE) bench-scale dynamic extraction system.

RESULTS

Table 1 displays the cumulative mass percent of bitumen extracted using pure SC-CO_2, as well as SC-CO_2 in the presence of a modifier at a concentration of 5, 10 or 15 mol%.

Table 1. Effect of modifiers on the cumulative mass percent of bitumen extracted.

Modifier	Modifier Concentration (mol%)	Mass Extracted (wt%)	
		Average	SD*
None (CO_2 only)	0	39.5	0.41
Toluene	5	54.3	3.2
	10	66.0	2.9
	15	76.2	1.2
Methanol	5	45.8	1.4

* SD - standard deviation (n=3)

Pure SC-CO_2 extracts 39.5 wt% of the original bitumen at supercritical conditions of 24 MPa and 333 K. At a concentration of 15 mol%, toluene is capable of extracting 76.2 wt% of the original bitumen, a 93% increase from pure SC-CO_2 alone. Figure 1 displays the effects of increasing concentrations of toluene on the cumulative mass percent of bitumen extracted. The addition of toluene to SC-CO_2 increases the percentage of bitumen extracted for any given CO_2 to bitumen ratio. Increasing the concentration of toluene enhances the concentration of bitumen in SC-CO_2. This is reflected in the initial slopes of the cumulative mass extraction curves; as the concentration of toluene increases, the initial slope of the extraction curves steepens.

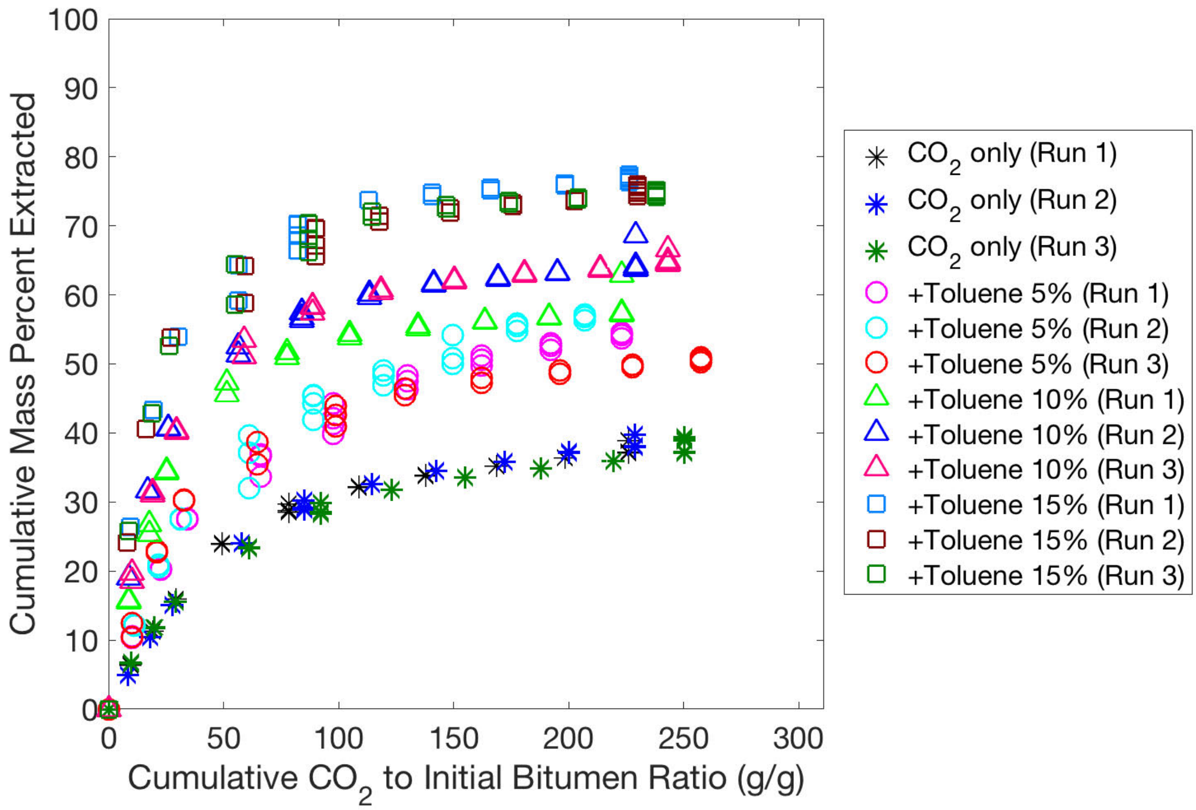


Figure 1. Effect of toluene concentration (5, 10 and 15 mol%) on the cumulative mass percent of bitumen extracted.

The effects of 5 mol% toluene versus 5 mol% methanol addition on the cumulative mass percent of bitumen extracted are compared in Figure 2. At a concentration of 5 mol%, methanol extracts 45.8 wt% bitumen compared to the same concentration of toluene which extracts 54.3 wt%. The addition of methanol to SC-CO_2 increases the percentage of bitumen extracted for any given CO_2 to bitumen ratio as compared to SC-CO_2 alone, but to a lesser extent than toluene. These results are consistent with the findings of Hwang and Ortiz [8] who noted that toluene is a particularly effective solvent for heavy bitumen components, more so than methanol.

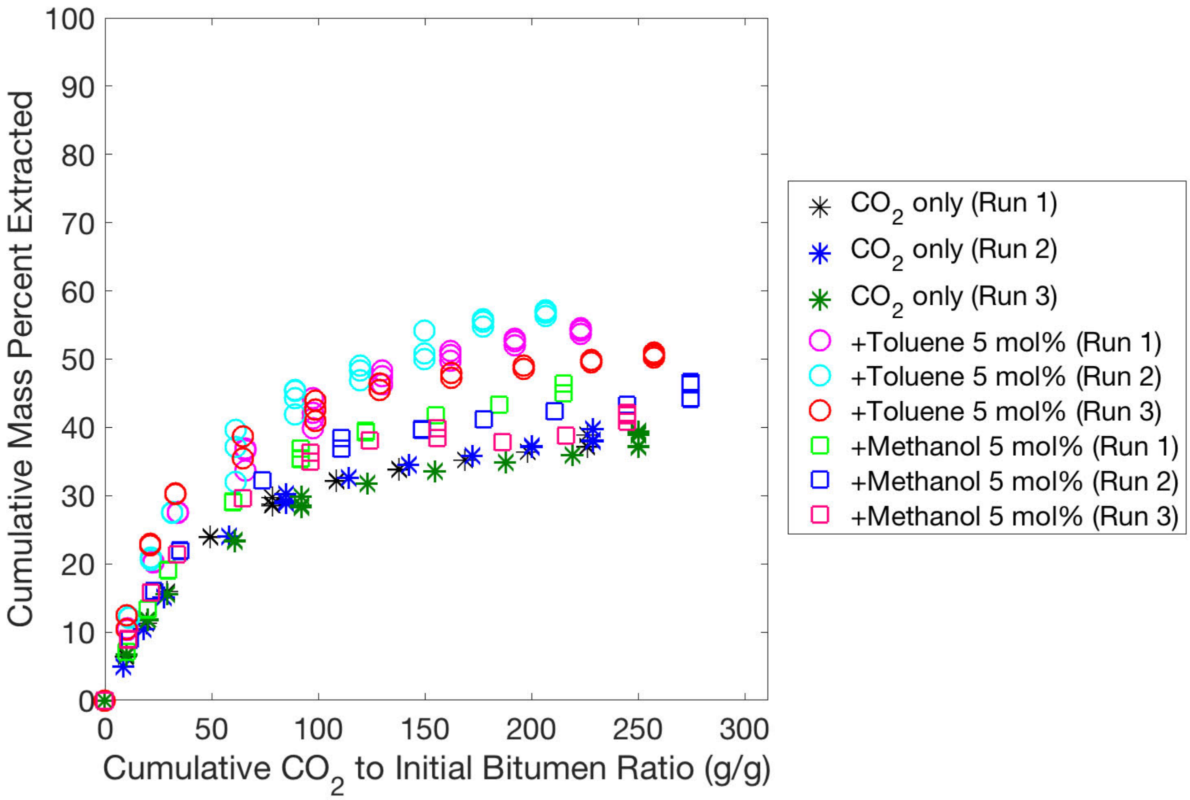


Figure 2. Effect of toluene versus methanol on the cumulative mass percent of bitumen extracted.

Figure 3 provides the HTSD curves for the initial bitumen, the extracts (from vial or jar *a* at each sampling time) and the vessel residue from an extraction conducted using SC-CO_2 alone. These HTSD curves provide the mass percent of extract or residue collected as a function of increasing distillation temperature. Higher distillation temperatures indicate a heavier extract or residue. The initial bitumen begins distilling at 200 °C and by 735 °C, 89 wt% of the bitumen is distilled. The remaining 11 wt% are heavier hydrocarbons that have boiling points higher than what can be achieved by the instrumentation, and thus do not distil before 735 °C. Sample 1*a*, collected during the first 5 minutes of the dynamic extraction, is composed primarily of the lighter hydrocarbons from the initial bitumen. As the dynamic extraction proceeds, slightly heavier hydrocarbons are extracted. The vessel residue contains little material that distills below 500 °C. Thus SC-CO_2 readily extracts the fraction of bitumen that distils at less than 500 °C and a portion of the bitumen that distils between 500 °C and 700 °C.

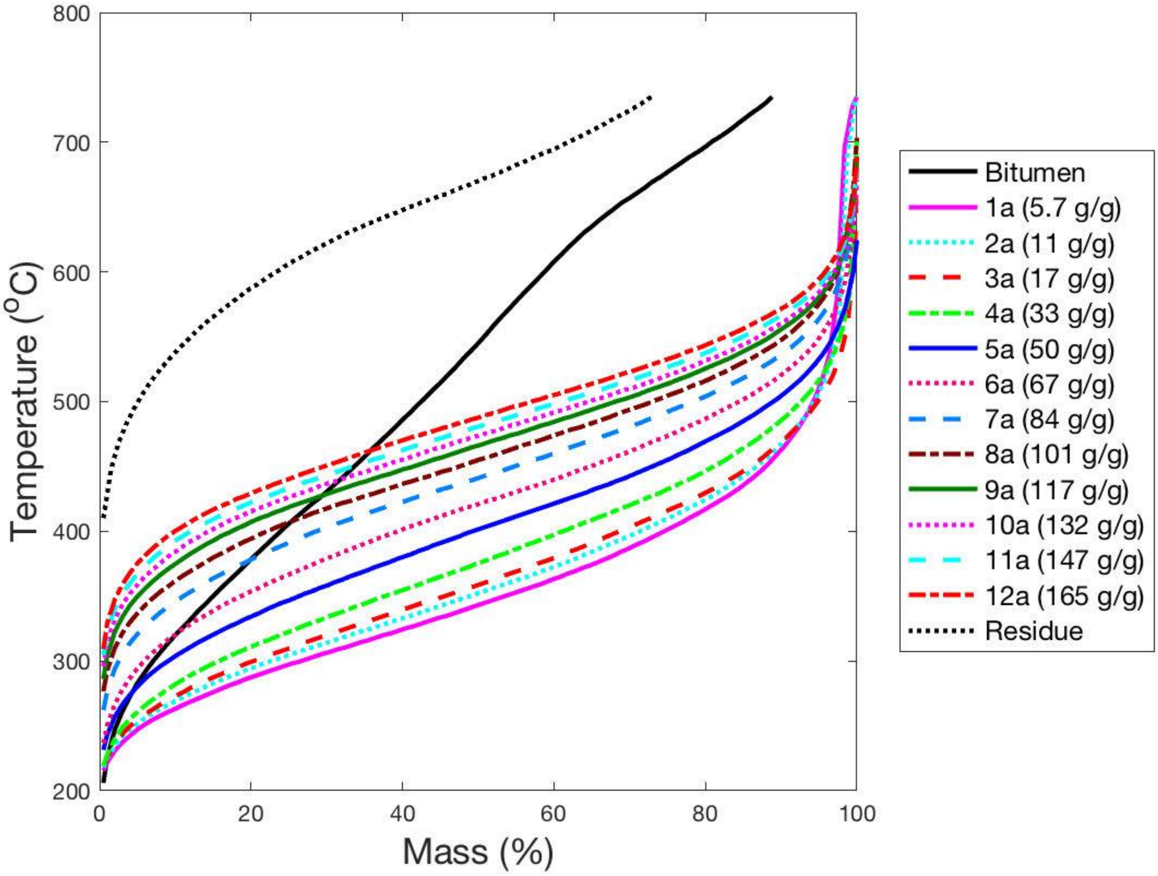


Figure 3. HTSD curves for bitumen extracts and residue from SC-CO_2 experiment. HTSD curve for initial bitumen provided for comparison.

Figure 4 displays HTSD curves for select extract samples and vessel residue from three extractions: SC-CO_2 alone, SC-CO_2 with 5 mol% toluene and SC-CO_2 with 5 mol% methanol. In all three cases, as the dynamic extraction progresses, slightly heavier hydrocarbons are extracted. However, comparing samples with cumulative CO_2 to initial bitumen ratios of 10 or 11 g/g in Figure 4, it can be seen that the slope of the toluene and methanol curves are steeper than that of SC-CO_2 alone. This indicates that the addition of a modifier not only extracts more bitumen than SC-CO_2 alone, it yields heavier bitumen components as well.

Compared to the addition of an equivalent molar concentration of toluene, methanol is not as effective at extracting heavier bitumen components and overall extracts a lighter, lower mass percentage of bitumen. This is evident in Figure 4 when comparing samples with cumulative CO_2 to initial bitumen ratios of 98 g/g for toluene addition and 92 g/g for methanol; toluene addition yields extracts that distil at higher temperatures, and are thus heavier than those obtained when extracting with methanol. The extraction of heavier bitumen components with the addition of toluene is also apparent when comparing HTSD curves for the vessel residues. With the addition of 5 mol% toluene, 9 wt% of the vessel residue distils below 600 °C whereas with the addition of 5 mol% methanol, lighter bitumen components still remain in the vessel after extraction and 20 wt% of the residue is distilled by 600 °C. The major difference between toluene and methanol addition is that not only does toluene extract a greater mass percentage of bitumen, it has the most distinct effect on heavier bitumen components, resulting in consistently heavier extracts as the dynamic extraction progresses.

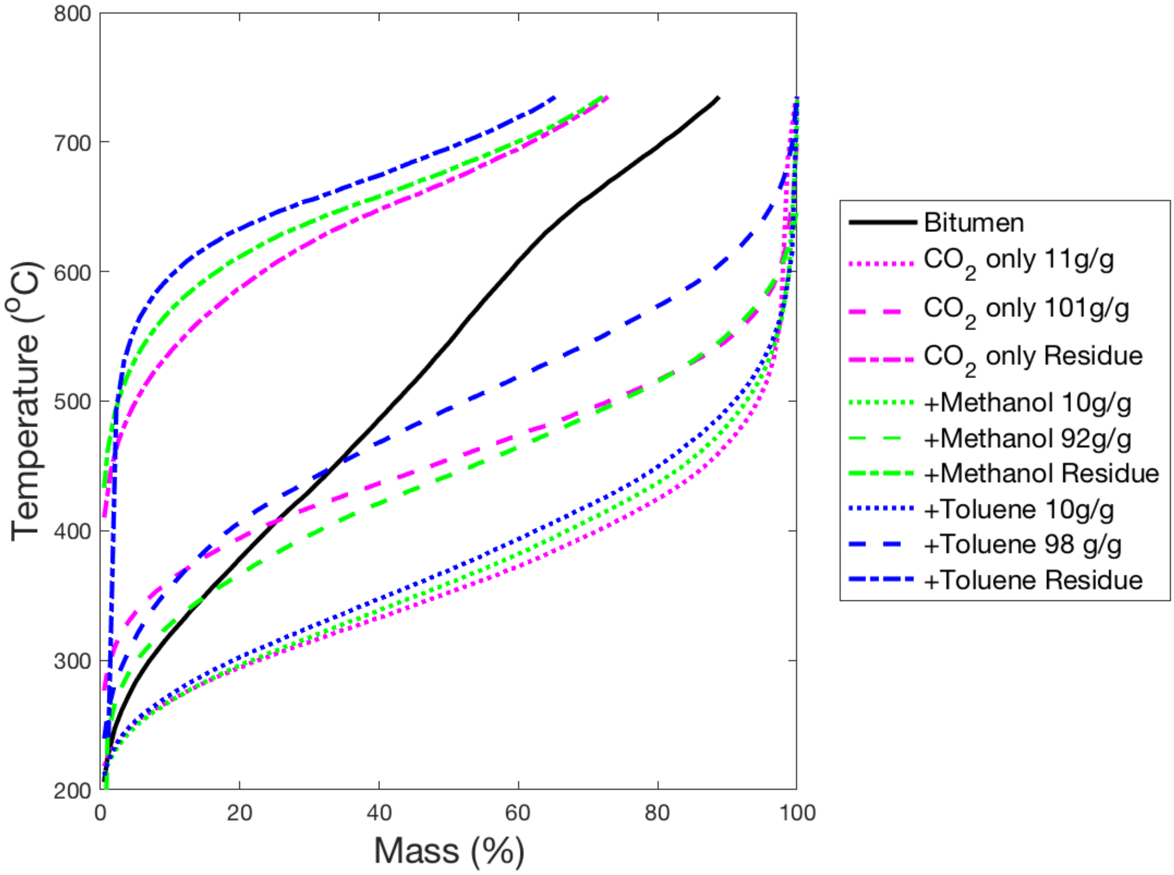


Figure 4. HTSD curves comparing bitumen extracts and residue from three experiments: SC-CO_2, SC-CO_2 with 5 mol% toluene and SC-CO_2 with 5 mol% methanol.

CONCLUSION

The addition of either toluene or methanol as a modifier to SC-CO_2 can enhance bitumen extraction. Toluene extracts a heavier, higher mass percentage of bitumen compared to an equivalent molar concentration of methanol. Increasing the concentration of toluene results in an increase in the percentage of bitumen extracted for any given carbon dioxide to bitumen ratio. At a concentration of 15 mol%, toluene is capable of extracting 76 wt% of the original bitumen at supercritical conditions of 24 MPa and 333 K.

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