Extraction of Hydrocarbons from Bitumen and Bitumen-containing Process and Process Waste Streams using Supercritical Carbon Dioxide

by

Heidi Cossey

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science

in

Environmental Engineering

Department of Civil and Environmental Engineering
University of Alberta

Abstract

Extractions of hydrocarbons from bitumen and bitumen-containing process and process waste streams generated from surface mined oil sands were conducted using supercritical carbon dioxide (SC-CO_2). Dynamic extractions were performed on a bench-scale batch supercritical fluid extraction (SFE) system at a SC-CO_2 density of 0.78 g/mL. Initial dynamic extractions of bitumen tested the effects of two modifiers, toluene and methanol, at concentrations of 5, 10 and 15 mol% in SC-CO_2 on the extraction efficiency and the type of hydrocarbons extracted. Toluene extracted a higher, heavier mass percentage of hydrocarbons than an equivalent molar or mass concentration of methanol or SC-CO_2 alone. The condition of 15 mol% toluene in SC-CO_2 resulted in the highest extraction efficiency of 75.9 wt% and was then tested on the bitumen-containing process and process waste streams. At 15 mol% in SC-CO_2, toluene was capable of extracting 72.3 and 68.6 wt% of the hydrocarbons from the process and process waste streams, respectively. Dynamic extractions of process and process waste streams indicated that the presence of water can have a slightly positive effect on the extraction of hydrocarbons, and the presence of solids does not substantially impact the extraction.

Acknowledgements

I would first like to thank my supervisor, Dr. Selma Guigard. Selma, thank you for your support, expertise and consistently positive attitude. I am extremely grateful for all of the opportunities you have given me to present my research. A special thank you to Dr. Warren Stiver who provided endless support and insight, despite being so far away.

Thank you to all of the wonderful technicians in the Department of Civil and Environmental Engineering. A huge thank you to the SFE research group technician, Eleisha Underwood. Your expertise, humour and friendship have made this research project a very positive experience for me. Thank you to our summer student, William Wood, for your assistance and humorous eating habits. I would also like to thank my desk mate Dr. Maedeh Roodpeyma. Maedeh, I am so grateful for the kindness and advice you have given me.

Employees of Syncrude Canada Ltd., in particular Dr. Jennifer McMillan and Dr. Sujit Bhattacharya, have provided expertise and support during this project, for which I am greatly appreciative.

Lastly, to my family – I would not be where I am today without your love and support. Mom and dad, thank you for everything you have done, and continue to do, for me. Amber and Nicole, thank you for all of the laughter and friendship. I am so grateful to have you all in my life.

Table of Contents

List of Tables

List of Figures

List of Abbreviations

ASTM	American Society for Testing Materials
AFD	Atmospheric Fines Drying
CO_2	Carbon dioxide
CSS	Cyclic Steam Stimulation
DAO	Deasphalted oil
FID	Flame Ionization Detector
FT	Froth Treatment
FFT	Fluid fine tailings
GC	Gas Chromatography
HTSD	High Temperature Simulated Distillation
HWP	Hot Water Process
ISC	In-situ Combustion
MFT	Mature fine tailings
NA	Naphthenic acid
OSPW	Oil sands process-affected water
OTSG	Once Through Steam Generator
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
SAGD	Steam Assisted Gravity Drainage
SARA	Saturate, Aromatic, Resin and Asphaltene
SC-CO_2	Supercritical carbon dioxide
SCF	Supercritical fluid
SFE	Supercritical Fluid Extraction
THAI	Toe-to-Heel Air Injection
VAPEX	Vapor Extraction

List of Symbols

bbl	Barrels
bpd	Barrels per day
OD	Outer diameter
ρ_c	Critical density
P_c	Critical pressure
T_c	Critical temperature

CHAPTER 1 Introduction

1.1 Problem Scenario

Canada has the third largest oil reserve in the world, most of which is the unconventional oil found in Alberta's oil sands (Natural Resources Canada 2017). Unconventional oil refers to extra heavy oil, natural bitumen (oil sands) and oil shale (Mohr and Evans 2010). This viscous oil is contained within low permeability formations and thus cannot be extracted using the natural pressure differential created from drilling an oil well (Keystone Energy Tools 2017). Instead, this oil is extracted in one of two ways depending on the depth of the formation. Oil sands reserves that are within 75 m of the ground surface can be extracted through ex-situ recovery i.e. surface mining (Government of Alberta 2017a; Chalaturnyk et al. 2002). All other reserves are extracted using in-situ recovery methods. Once extracted, bitumen requires upgrading to improve its physical and chemical properties before being sent to conventional oil refineries (Hyndman and Luhning 1991).

The two most commonly used in-situ recovery methods in Alberta, Cyclic Steam Stimulation (CSS) and Steam Assisted Gravity Drainage (SAGD), are thermal recovery techniques (Oil Sands Magazine 2017a; Government of Alberta 2016). These methods require large surface facilities, significant amounts of water, with a water to oil ratio of 3:1 (Singhal et al. 1996), and require separation and treatment of a bitumen-water mixture after extraction from underground reserves (Ikebe et al. 2010). However, there are a number of emerging in-situ recovery technologies that could potentially overcome these issues (Upreti et al. 2007; Nasr and Ayodele 2005; Luhning et al. 2003).

Ex-situ recovery requires even more water than in-situ recovery – four to eight times more – to produce one barrel of synthetic crude oil (Government of Alberta 2017b). The high water usage is due to that fact that, once mined, the oil sands are subjected to a hot water process that uses caustic hot water to separate the bitumen from the rest of the oil sands (Chow et al. 2008; Chalaturnyk et al.

2002; Clark and Pasternack 1932). As a result, ex-situ recovery generates larger process waste streams than in-situ recovery (Kasperski and Mikula 2011).

Ex-situ process waste streams consist of aqueous slurries made up of varying amounts of minerals, process water and residual bitumen. These waste streams are currently stored on-site in tailings ponds. The residual bitumen in the waste streams either floats to the top of the ponds or remains trapped within the tailings (Syncrude Canada Ltd. 2017b; Romaniuk et al. 2015). Research and industry are focusing on dewatering the tailings ponds, and improving the recyclability and toxicity of the process water (Quinlan and Tam 2015; COSIA n.d.a). Based on 2015 data, the total liquid surface area of the tailings ponds is 98 km^2 and the total tailings area (including all tailings structures) is 246 km^2 (Alberta Environment and Parks 2018). Compared to in-situ recovery, ex-situ recovery also has a much larger footprint, due to the surface area required for both mining operations and tailings ponds (Oil Sands Magazine 2017a).

A novel approach to treating ex-situ process waste streams is using supercritical fluid extraction (SFE). SFE is a solvent extraction process that uses a supercritical fluid (SCF) to extract specific compounds from a matrix – for example to extract bitumen from a waste stream. A SCF is a fluid that has been heated and pressurized beyond its critical temperature and pressure, giving it properties of both liquids and gases (Akgerman 1997). These properties are advantageous because it means SCFs have densities similar to that of liquids and at the same time have excellent mass transfer capabilities (Akgerman 1997; Raynie 1997; Hawthorne 1990). Small changes to pressure and/or temperature can change the SCF's properties, thus influencing the extent to which the fluid extracts compounds from a matrix.

Common industrial applications of SFE include coffee and tea decaffeination, flavour and fragrance extraction for use in food and cosmetics, and active ingredient isolation for pharmaceuticals and cosmetics (Brunner 2005; Knox 2005; Perrut 2000; Phelps et al. 1996). Research has also been conducted into the use of SFE for various environmental applications such as for removing contaminants from soils and sediments (Herrero et al. 2010; Low and Duffy 1995) and for extracting hydrocarbons from bitumen and oil sands (La and Guigard 2015; Al-Sabawi et al. 2011; Subramanian and Hanson 1998).

In most cases, SFE is carried out in a batch system. This is particularly true when a solute is being extracted from a solid matrix, as solids are difficult to handle in a continuously pressurized system (Brunner 2005). In a batch system, a batch of the solute-containing mixture is placed in the vessel (Laitinen et al. 1994). The vessel is then pressurized and a continuous flow of the SCF is pumped through the vessel. After extraction of the solute is complete, the vessel is depressurized and the remainder of the mixture is removed.

Choosing which SCF to use is dependent on a number of factors including its toxicity, hazard, cost, availability, environmental friendliness and its affinity for the solute (Knox 2005). Carbon dioxide (CO_2) is the most preferred SCF, especially for food applications, because it is non-toxic, readily available, inexpensive and leaves behind little to no solvent residue (Brunner 2005; Knox 2005). Because CO_2 is non-polar, it is effective in extracting non-polar and slightly polar solutes (Brunner 2005; Phelps et al. 1996). A small amount of an additional solvent that has a greater affinity for the solute, called a modifier, may be added in order to extract more polar compounds (Knox 2005).

1.2 Research Objectives

Currently, the oil sands industry is looking for innovative techniques to remediate their process and process waste streams. SFE is one such technique that has the potential to not only clean these process and process waste streams, allowing them to be safely disposed of or even recycled, but also to recover residual bitumen, a valuable resource that would have otherwise been lost.

The purpose of this research is to investigate and improve the extraction of hydrocarbons from bitumen and bitumen-containing process and process waste streams generated from surface mined oil sands, using supercritical carbon dioxide (SC-CO_2). Specifically, the objectives of this research include the following:

1. Perform dynamic extractions on a bench-scale batch SFE system at a SC-CO_2 density of 0.78 g/mL (pressure and temperature conditions of 24 MPa and 60°C, respectively) to measure the extraction of hydrocarbons from bitumen. These bitumen dynamic extractions will be used to identify the most effective modifier type (toluene or methanol) and concentration (5, 10 and 15 mol% of SC-CO_2) to achieve the highest hydrocarbon extraction efficiency from bitumen.

2. Perform dynamic extractions on a bench-scale batch SFE system at a SC-CO_2 density of 0.78 g/mL to measure the extraction of hydrocarbons from bitumen-containing process and process waste streams, which consist of varying amounts of bitumen, water and solids. The effect of the most successful modifier type and concentration combination (as determined by previous bitumen dynamic extractions) on the hydrocarbon extraction efficiency from process and process waste streams will be determined.

3. Investigate the effect of SC-CO_2 and modifiers on the type of the hydrocarbons extracted from bitumen.

This research will demonstrate the ability of SC-CO_2 to extract hydrocarbons from bitumen and bitumen-containing process and process waste streams. Secondly, this research will improve the extraction of hydrocarbons from bitumen and bitumen-containing streams by identifying the most successful modifier parameters (type and concentration). The results will aid in the development and demonstration of an SFE process for residual bitumen recovery from oil sands process and process waste streams.

1.3 Thesis Organization

This thesis is divided into five chapters. Chapter 1 introduces the challenges associated with extracting bitumen from Alberta oil sands and oil sands waste streams and presents SFE as a potential solution. It also outlines the objectives of the research conducted for this thesis. Chapter 2 provides an in-depth literature review of the traditional methods of bitumen extraction, the technical and environmental challenges of these methods, and emerging technologies that address some of these challenges. Chapter 2 will also discuss

SFE and its potential application for bitumen recovery from surface mined oil sands and oil sands waste streams. Chapter 3 details the materials and procedures used to conduct this thesis research. Chapter 4 provides the results of a total of 35 dynamic extractions investigating the effect of modifier type and concentration on the extraction of hydrocarbons from bitumen, a bitumen-containing process stream and a bitumen-containing process waste stream. Chapter 4 includes both quantitative and qualitative analyses of the extracted hydrocarbons and a discussion of the potential sources of error throughout the experimental process. Chapter 5 summarizes key conclusions, as well as recommendations for future work in advancing SFE technology to a continuous, pilot-scale process for bitumen recovery from oil sands and oil sands process waste streams.

CHAPTER 2 Literature Review

This chapter details the traditional methods, both in-situ and ex-situ, of extracting bitumen from the Alberta oil sands. Emerging technologies that address some of the issues associated with the traditional extraction methods will be also identified. Because there are a number of emerging technologies that address issues associated with in-situ bitumen recovery, the focus of this research is improving bitumen recovery from surface mined oil sands and from associated process and process waste streams.

2.1 Alberta Oil Sands

Alberta has the third largest oil reserve in the world, following Venezuela and Saudi Arabia (Government of Alberta 2017a). Most of this oil is unconventional, contained within oil sands that consist of varying amounts of sand, clay, water and bitumen (Government of Alberta 2017a; Natural Resources Canada 2017). Unconventional oil (bitumen) production accounted for 84.4% of Alberta's oil production in December of 2017 (Government of Alberta 2018). In 2016, crude bitumen production in Alberta was approximately 2.5 x 10^6 bpd (Government of Alberta 2017a). Oil sands exist beneath approximately 142,200 km^2 of land in Alberta, resulting in an estimated 165.4 x 10^9 bbl of (remaining) recoverable oil reserves (Government of Alberta 2017a; Government of Canada 2013).

Figure 1 displays the oil sands deposits in three distinct regions in Alberta: Peace River, Athabasca and Cold Lake. The quality (up to 19 wt% bitumen) and thickness (50 - 825 m) of the oil sands deposits varies considerably both between and within these three regions (Chalaturnyk et al. 2002).

Figure 1. Alberta oil sands deposit map (taken from CAPP 2018 with permission).

The Athabasca oil sands deposits cover an estimated 93,000 km^2, and are the largest and most accessible of the three formations (Government of Alberta 2017a; Zhou et al. 2008). The Athabasca reserves exist largely in the McMurray Formation of the Lower Cretaceous Mannville Group and range from depths of 0 to 500 m below ground surface (Zhou et al. 2008). Reserves with an overburden thickness of < 50 to 75 m are surface mineable, and thus approximately 5% of the total area of the Athabasca deposits can be extracted using ex-situ recovery (Government of Alberta 2017a; Chow et al. 2008; Zhou et al. 2008; Chalaturnyk et al. 2002). However, the 18,000 km^2 Cold Lake deposit and the 29,000 km^2

Peace River deposit, which exist at depths of 985-1970 m and 550-700 m, respectively, and the remainder of the Athabasca formation require in-situ recovery techniques.

The Athabasca oil sands are a mixture of bitumen (averaging 12 wt%), water (3-6 wt%) and mineral matter (84-86%) (Chalaturnyk et al. 2002). As shown in Figure 2, the oil sands are essentially water-wet sand particles with bitumen filling the void spaces (as cited in Chalaturnyk et al. 2002). For example, a typical sand grain of 100 μm diameter is expected to have a 2 μm thick water film. Bitumen is a black, highly viscous mixture of low hydrogen-to-carbon ratio hydrocarbons, and many chemical impurities (Yoon et al. 2009). Fine clay particles may also be present in the water layer, however they typically exist instead in the form of thin discontinuous beds. In the Athabasca oil sands, clays are present in beds or bands ranging from 1 to 15 cm thick (Chalaturnyk et al. 2002).

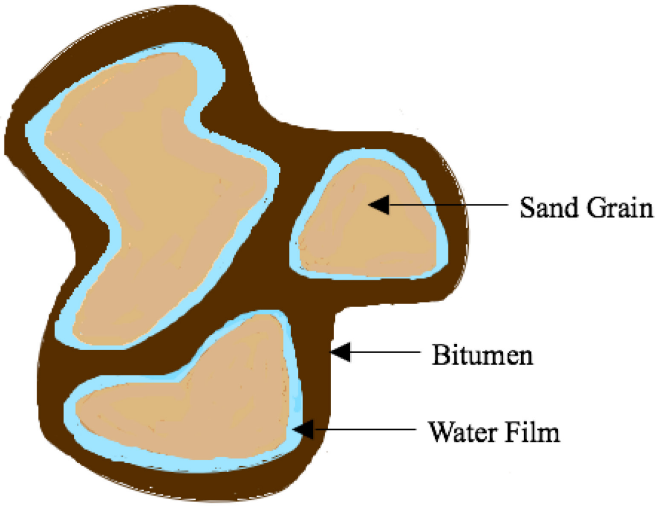


Figure 2. Components of an untreated oil sands matrix.

Properties of Athabasca bitumen are compared with those of synthetic crude (upgraded bitumen) and conventional crude in Table 1.

Table 1. Comparison of properties between Athabasca bitumen, and synthetic and conventional crude oil (adapted from Yoon et al. 2009; Hyndman and Luhning 1991).

Property	Athabasca Bitumen	Synthetic Crude	Conventional Crude
Viscosity (cSt* at 40°C)	3000	3.0	2.9
API (°)	8	32	41
Sulfur (wt%)	4.78	0.08	0.2
Nitrogen (wt%)	1.63	0.03	0.04
Vanadium (ppm)	174.00	<1	<1
Nickel (ppm)	68.50	<1	<1
H/C Ratio	1.5	n/a	n/a
Asphaltenes (wt%)	15.59	n/a	n/a
Saturate Aromatics (wt%)	67.97	n/a	n/a
Resin (wt%)	16.44	n/a	n/a

* cSt = centistokes

Bitumen can be fractionated into four different classes based on solubility and polarity: saturates (S), aromatics (A), resins (R) and asphaltenes (A) (Yoon et al. 2009; Speight 2006). Saturates and aromatics have the highest H/C ratios and the lowest molecular weights. Heteroatoms (sulfur, nitrogen and oxygen) tend to concentrate in the high molecular weight, polar fractions - resins and asphaltenes. Nickel and vanadium, which are the predominant metals found in bitumen, also tend to concentrate in the asphaltene fraction (Al-Sabawi et al. 2011). Asphaltenes are typically described as the n-pentane or n-heptane insoluble fractions of bitumen (Yoon et al. 2009; Speight 2006). Asphaltenes, which have a low H/C ratio of 1.18, contribute 15.6 wt% to Athabasca bitumen and as such, are primarily responsible for its high viscosity (Yoon et al. 2009; Abu-Khader and Speight 2007). Koots and Speight (1975) found that the asphaltic (asphaltenes plus resins) content of a given crude oil is proportional to the sulfur content and inversely proportional to the API gravity. As such, unconventional oil requires upgrading to improve its chemical and physical properties before being sent to conventional petroleum refineries (Hyndman and Luhning 1991). However, the heteroatoms, such as sulfur and nitrogen, and trace heavy metals, such as nickel and vanadium, found in Athabasca bitumen can negatively impact the upgrading process (Yoon et al. 2009; Abu-Khader and Speight 2007).

Depending on the depth of the oil sands deposits, the bitumen can be extracted either by in-situ or ex-situ recovery techniques. Figure 3 displays ex-situ (mining) and in-situ methods of extracting bitumen from Alberta oil sands (Government of Alberta 2016), all of which will be discussed in the following subsections. Approximately 20% of the total volume of recoverable bitumen reserves in Alberta are surface minable (Government of Alberta 2017a; Government of Canada 2013). The remainder of the deposits must be extracted using in-situ techniques.

2.2 *In-situ* Bitumen Recovery

Cyclic Steam Stimulation (CSS) and Steam Assisted Gravity Drainage (SAGD) are the two most commonly employed thermal in-situ techniques for extracting bitumen from Alberta oil sands deposits (Oil Sands Magazine 2017a; Government of Alberta 2016). CSS is a vertical, single-well process that involves an injection cycle, followed by a production cycle (Government of Alberta 2016; Vittoratos et al. 1990). During the injection cycle, which lasts for a period of several weeks, steam is injected into the well at pressures high enough to create hydraulic fractures in the reservoir. The steam condenses and spreads into the fractures, heating the bitumen and lowering its viscosity. The production cycle then begins, where bitumen and water are driven up the wellbore, initially due to the increased pressure in the reservoir. Later, bitumen moves to the well with the help of artificial lift technologies. The whole process is then repeated once production rates are no longer deemed efficient.

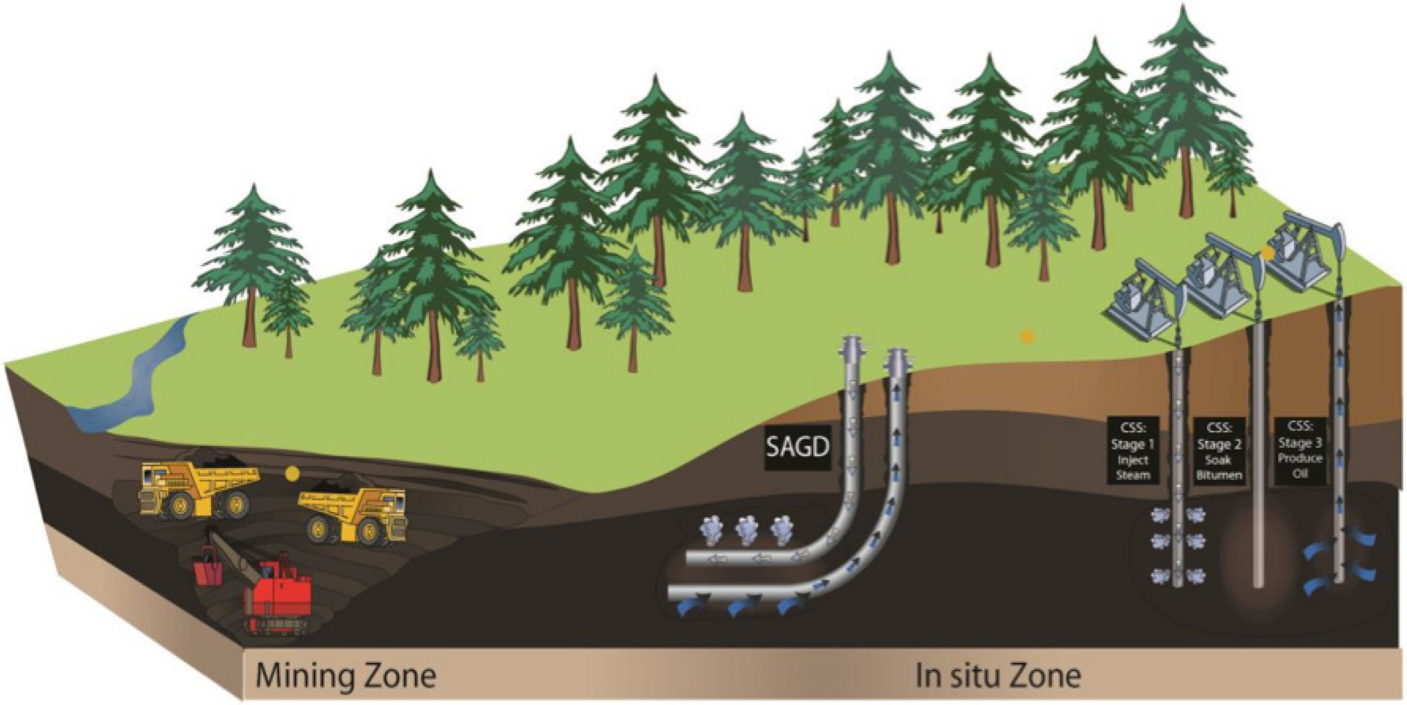


Figure 3. Ex-situ (mining) and in-situ methods of extracting bitumen from Alberta oil sands deposits (taken from Government of Alberta 2016).

The bitumen-water mixture recovered using CSS must then be separated. First, diluent is added to the mixture to reduce the bitumen viscosity, allowing the free water to be removed from the mixture using a free water knockout drum (Gray 2015). The oil remaining in the free water is removed using a skim tank, induced gas flotation and an oil removal filter (Husky Energy 2011; Ikebe et al. 2010). The water is then treated using a lime softener, followed by filtration and a weak acid cation softener, in order to reduce silica levels and water hardness, both of which are required for water reuse in a Once Through Steam Generator (OTSG) (Ikebe et al. 2010; Heins and Peterson 2006). Finally, the treated water can be recycled as boiler feed water in an OTSG.

CSS is a viable option for deep reservoirs that have thick, capping shale that is capable of maintaining high pressures. The main advantage of this process is its quick oil production, however, its recovery as a percentage of the oil in place (15-20%) is less than that of other thermal recovery processes (Nasr and Ayodele 2005). CSS is responsible for producing the most crude oil (247,656 bpd in 2014) in the Cold Lake region, which contains the deepest oil sands deposits in Alberta, with a compound annual growth rate of 4.0% between 2004 and 2014 (Government of Alberta 2016). In the Peace River region, CSS produces 4,010 bpd and has a compound growth rate of -6.8% due to SAGD's increasing use in this region. CSS is not used to extract bitumen from the Athabasca deposits.

SAGD is similar to CSS except it uses two parallel horizontal wells which are placed near the bottom of the formation, one to inject steam and the other to recover bitumen and water (Government of Alberta 2016; Nasr and Ayodele 2005). Initially, steam is circulated through both wells in order to establish a connection between them. The top well continues to inject steam, heating the reservoir and creating a steam chamber. Rising steam condenses on the boundary of the steam chamber and the heated, less viscous bitumen becomes entrained in the water. The bitumen and oil mixture flows to the production well below. Once again, initially the bitumen and water mixture travels up the production well due to increased reservoir pressures. Both the steam injection and bitumen recovery occur simultaneously and continuously once production has begun. The distance between the two wells typically varies between 2 and 10 m, depending on vertical permeability, thermal conductivity and viscosity (Nasr and Ayodele 2005).

SAGD is advantageous over CSS because it is a continuous process, has higher bitumen recovery and is more cost effective (Nasr and Ayodele 2005; Butler 1998). SAGD has the highest compound annual growth rate, 25.2%, (based on data from 2004 to 2014) of any oil sands recovery technology in Alberta (Government of Alberta 2016). In the Cold Lake region, the growth rate is 37.8%, with SAGD producing 19,592 bpd in this region in 2014. In the Athabasca region, SAGD is the most commonly used in-situ technology, producing 662,447 bpd in 2014. The Peace River region also started using SAGD in 2011.

A new approach to SAGD is Expanding Solvent SAGD (ES-SAGD) in which a hydrocarbon additive (for example hexane) that is capable of evaporating and condensing at the same conditions as the water phase is co-injected with the steam (Nasr and Ayodele 2005). The solvent then condenses at the boundary of the steam chamber, helping to entrain the bitumen and reduce its viscosity. Thus far, field tests indicate improved oil recovery rates, and lower energy and water requirements compared to SAGD. Pilot-scale projects have been conducted at the Burnt Lake, Firebag and Christina Lake oil sands developments in Alberta (McFarlane et al. 2012).

In-situ Combustion (ISC) is a process involving two vertical wells where air is injected into the first well, the injector, creating a combustion zone within the reservoir (Xia and Greaves 2006; Nasr and Ayodele 2005; Xia et al. 2003). Thermal cracking of the heavy hydrocarbons leads to the formation of coke – the fuel that exothermically reacts with the injected oxygen, producing the heat required to reduce the viscosity of the oil. The oil then moves toward the second well, the producer, as the combustion zone advances. This process is considered to be long-distance displacement because the distance between the mobile oil zone and the producer well can be hundreds of meters (Xia et al. 2003). This arrangement can cause oil saturation (oil banking) near the production well, leading to loss of air injectivity and thereby preventing the maintenance of the high temperatures required for oxidation. Conversely, if the air flux is too high it can cause gas overriding, leading to oxygen breakthrough at the producer well. This technology suffers from poor process control and because of its shortcomings, the ISC process is not commonly used. The last successful use of the ISC technology in Alberta was from 1980 to 1993 at the Morgan ISC Field Pilot (McFarlane et al. 2012).

To combat the problems associated with conventional ISC, the Toe-to-Heel Air Injection (THAI) process was developed. The mechanism of the THAI process is similar to that of ISC; however the pathway for oil displacement is different. The THAI process uses a horizontal producer well (instead of a vertical well as in ISC) and the toe of the horizontal producer well is within a few metres of the injection well – making this a short distance displacement process (not unlike SAGD) (Xia et al. 2003). The combustion zone propagates from the toe to the heel of the producer well. The combustion zone is upright, due to forced drainage of the mobilized oil into the horizontal producer well, and as such gas overriding is controlled. Air injectivity into the reservoir increases as the process continues due to depletion of the burned zone, enabling the maintenance of high temperatures for oxidation. The process also results in partially upgraded oil because the high temperatures promote thermal cracking of high molecular weight hydrocarbons (Xia et al. 2003; Greaves et al. 2001). While laboratory experiments conducted on Athabasca bitumen showed a promising 80% recovery of the oil in place and an average 8° increase in API gravity (Xia and Greaves 2006), Petrobank Energy and Resources Ltd., the company that developed the THAI process, was unable to demonstrate that THAI worked at a commercial-scale in the Alberta oil sands (Morgan 2016).

All of the in-situ technologies discussed thus far are thermal processes. While thermal technologies are the dominant method of in-situ recovery in Alberta (particularly CSS and SAGD), thermal processes, in general, have some disadvantages. Many of the processes cause large heat losses to the under- and overburden making it particularly inefficient to use these technologies in thin reservoirs (Mokrys and Butler 1993), require significant amounts of water (with a water to oil ratio of 3:1 for steam processes) (Singhal et al. 1996) and necessitate vast surface facilities (Upreti et al. 2007). Vapor Extraction (VAPEX), a chemical recovery process, overcomes some of these disadvantages (Singhal et al. 1996).

VAPEX is similar in design to SAGD except that it involves the injection of a vaporized hydrocarbon solvent such as propane (or a mixture of solvents) instead of steam (Upreti et al. 2007; Nasr and Ayodele 2005). Upon injection, the solvent diffuses, creating a vapor chamber in the reservoir (Upreti et al. 2007). Because a vaporized solvent will offer its maximum solubility near its dew point, the solvent is injected at pressures equal to or slightly less than its saturation vapor pressure at the given reservoir temperature. Further, injecting the solvent at pressures near its saturation vapor pressure can result in slightly upgraded oil through de-asphalting (Upreti et al. 2007; Nasr and Ayodele 2005).

Following extraction, the live oil (bitumen entrained with solvent) enters a flash tank where it experiences a pressure drop (El-Haj et al. 2009). This allows the live oil to separate into vaporized solvent and bitumen (now dead oil). Based on laboratory data, approximately 90% of the solvent can be retrieved and recycled during this process (Upreti et al. 2007).

VAPEX is more economical than conventional thermal technologies because it does not require extensive surface facilities (for steam generation or water processing), nor does it involve significant energy losses (Upreti et al. 2007; Luhning et al. 2003). Smaller energy losses also make this process more suitable for thin reservoirs compared to thermal processes such as SAGD. The major disadvantage of the VAPEX process is that its rate of oil production is very low compared to that of SAGD as a result of blockages caused by precipitated asphaltenes (Haghighat and Maini 2010; Nasr and Ayodele 2005). While several pilot-scale projects have been tested in Alberta, largely in the mid-2000s, such as the Primrose, Foster Creek and DOVAP VAPEX Pilot projects, the VAPEX technology is not yet commercial-scale (Jaremko 2017; Godin et al. 2009).

2.3 *Ex-situ* Bitumen Recovery

2.3.1 Extraction Process

Despite only being applicable to 20% of the total volume of bitumen from Alberta oil sands deposits, surface mining is the technology that produces the most crude oil (in terms of bpd) in Alberta, followed by SAGD and CSS (Government of Alberta 2016). Surface mining first requires removal of the vegetation, muskeg and overburden (which is characterized as having < 7% bitumen) that overlay the oil sands deposit (Oil Sands Magazine 2017b). The water table must also be lowered at this stage and maintained throughout the operation of the mine. Large mining shovels can then be used to excavate the oil sands ore, which is loaded into haul trucks for processing.

The current procedure used in Alberta for extracting bitumen from surface mined oil sands ore is still largely based on the Clark hot water process (HWP) patented by Dr. Karl Clark in 1929 (Chow et al. 2008; Chalaturnyk et al. 2002). The HWP uses caustic hot water to separate the oil sands ore such that the oil floats as froth on the surface of the water, while sand sinks to the bottom (Clark and Pasternack 1932). Over the years, the process has been refined for large-scale application and to improve operability and recovery, and to lower energy requirements (Hyndman and Luhning 1991), resulting in a current recovery rate of greater than 90% from high quality ore (> 10% bitumen) (Chow et al. 2008).

Figure 4 presents a schematic diagram of the process of extracting bitumen from surface mined oil sands ore.

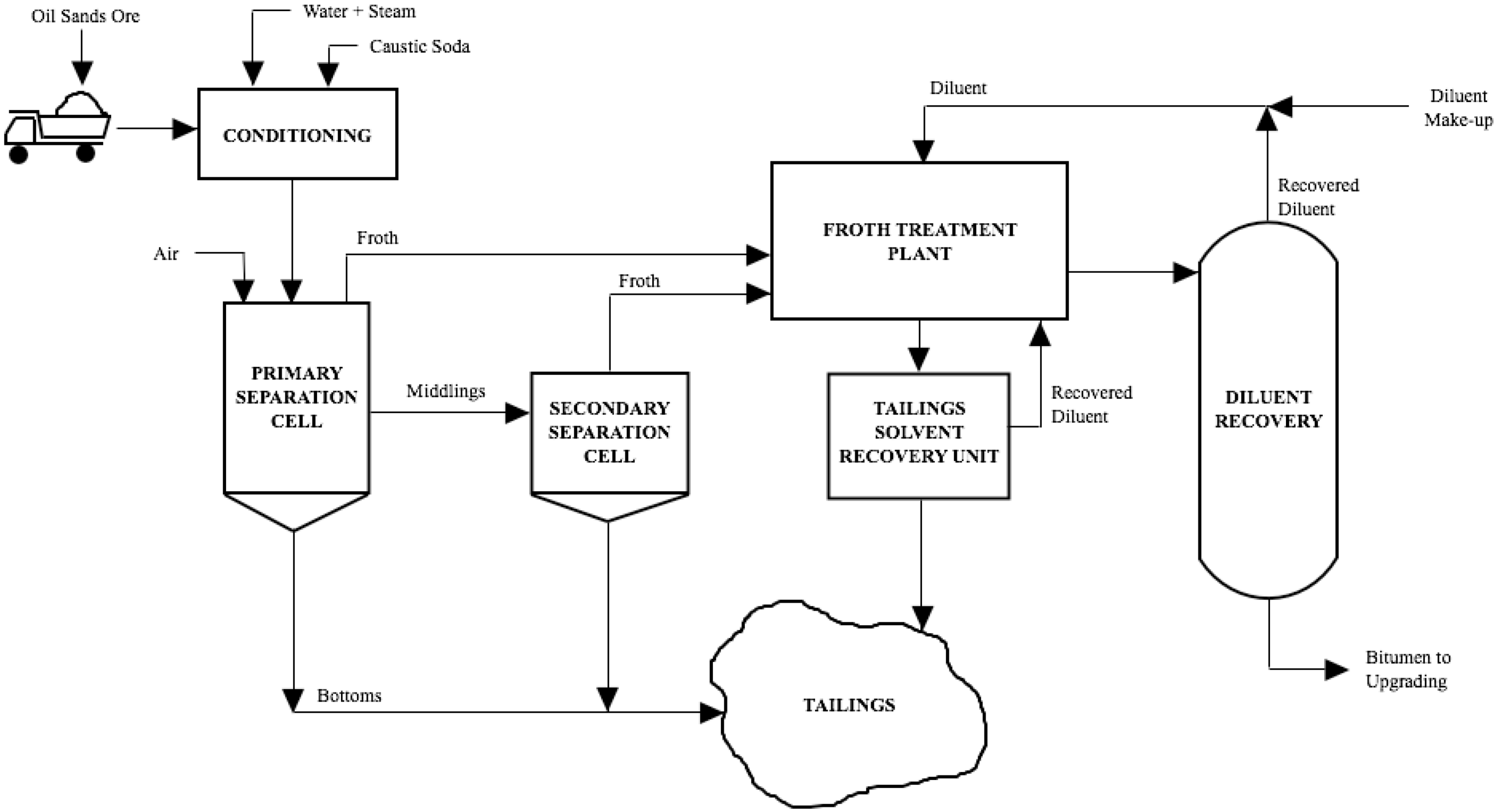


Figure 4. Illustration of the process of recovering bitumen from surface mined oil sands ore (adapted from Oil Sands Magazine 2017c; Chalaturnyk et al. 2002).

After mining the oil sands ore, the ore is crushed and fed to a rotary breaker where steam and water are added at a concentration of 50-60 wt% oil sand, creating a slurry. The oil sands industry currently performs conditioning and slurry transport processes simultaneously (Chow et al. 2008). Conditioning is the first step in extracting bitumen from the oil sands ore. Ideally, at the end of the conditioning process, the ore structure disintegrates and the bitumen cleanly separates from the sand grains producing solids-free bitumen droplets (Chow et al. 2008; Chalaturnyk et al. 2002). Caustic soda (NaOH) is added, causing the asphaltic acids present in bitumen to become water-soluble and act as surfactants, reducing surface and interfacial tensions, thereby disintegrating the ore structure and enhancing bitumen recovery (Chalaturnyk et al. 2002). A temperature between 41 - 53 °C, a velocity of 3.5 m/s and a residence time between 7 - 12 minutes are maintained as the slurry is transported to separation cells to ensure the destruction of the oil sands matrix (Chow et al. 2008).

The slurry is transported to a large cone bottom vessel, called the primary separation cell (Chow et al. 2008). Because the density of bitumen at the process temperatures used is similar to that of water, air must be added to promote bitumen flotation during the separation stage. Water is added again at this stage to make a 25 wt% oil sand in water slurry. The aerated bitumen (bitumen froth) floats to the top of the cell and is then skimmed off and pumped to a froth treatment plant. The coarse solids settle to the bottom and are withdrawn for further treatment to recover any entrapped bitumen before being discharged into tailings ponds. The middle phase (middlings) undergoes further treatment in a smaller vessel, the secondary separation cell, which typically involves air flotation (Syncrude Canada Ltd. 2017a; Chalaturnyk et al. 2002). Any residual bitumen trapped in the discharge from the secondary cell can be recovered in tailings oil recovery units, prior to discharge to tailings ponds (Chalaturnyk et al. 2002).

The bitumen froth collected from the separation process consists of water (25 wt%) and solids (10 wt%) in a bitumen suspension (Chow et al. 2008). The froth is heated and a solvent is added to decrease bitumen viscosity and enhance separation; typically naphtha has been used as the solvent at a 1:1 dilution rate.

Paraffinic froth treatment (PFT), which uses paraffinic solvents, is a newer process that is currently used in fewer commercial projects than naphthenic froth treatment (NFT) but is advantageous because it extracts bitumen with fewer contaminants (Rao and Liu 2013). However, NFT requires a lower solvent to bitumen ratio and produces a higher bitumen recovery than PFT because paraffinic solvents cannot dissolve asphaltenes and as such, most of the asphaltenes precipitate and are discharged with the froth treatment tailings. The mixture of bitumen froth and diluent is then pumped to inclined plate settlers and/or centrifuges to remove solids and water (Syncrude Canada Ltd. 2017a; Chow et al. 2008; Starr and Bulmer 1979). Greater than 99% of the diluent is then recovered through distillation and recycled, and the bitumen is sent for upgrading (Syncrude Canada Ltd. 2017a; Starr and Bulmer 1979). The froth treatment tailings from the froth treatment plant are pumped to a tailings solvent recovery unit to recover and recycle any additional diluent before being discharged into the tailings ponds (Rao and Liu 2013).

2.3.2 Process Waste Streams

The main advantage of extracting bitumen from surface mined ore is that the recovery is significantly greater than that of any in-situ method (Kasperski and Mikula 2011). However, surface mining is associated with greater land disturbance and larger process waste streams (Government of Alberta 2017b; Kasperski and Mikula 2011). Compared to in-situ recovery methods, which do not produce tailings ponds, ex-situ recovery requires four to eight times more water to produce one barrel of synthetic crude oil (Government of Alberta 2017b). Based on 2015 data, the total area occupied by tailings ponds in Alberta (including all tailings structures such as dykes, beaches and dedicated drying areas) is 246 km^2, with tailings pond water making up 98 km^2 of this area (Alberta Environment and Parks 2018).

As cited in Kasperski and Mikula (2011), approximately 12 volumes of wet sand, silt and clay suspensions are produced as process waste streams for every volume of bitumen recovered through ex-situ methods. There are three main waste streams produced as a result of bitumen extraction from surface mined ore: coarse tailings (minerals > 44 μm, mostly sand), fluid fine tailings (FFT) (minerals < 44 μm) and froth treatment tailings (Kasperski and Mikula 2011; Devenny 2009). All three streams are aqueous slurries made up of varying amounts of minerals, process water and residual bitumen. The coarse and fine tailings streams are combined before they enter the ponds, as seen in Figure 4. Froth treatment tailings are a relatively small stream that contains the most solvent and residual bitumen, and depending on the mine operation, may or may not be combined with the other tailings streams. As the process waste streams are discharged into tailings ponds, some of the bitumen will be released and float to the surface of the ponds, appearing as a slick on top of the water (Syncrude Canada Ltd. 2017b; Romaniuk et al. 2015). The remainder of the residual bitumen remains trapped in the tailings.

When the tailings waste streams are discharged into the ponds, the coarse sand settles quickly forming a beach as seen in Figure 5 (Kasperski and Mikula 2011; Chalaturnyk et al. 2002). This sand can be used to build containment dykes for the FFT and water, and the water released from the settling minerals can be recycled. Approximately 12 barrels of water are required to extract one barrel of bitumen, of which roughly 75% can be recovered and recycled (Kasperski and Mikula 2011). The remaining amount is trapped between settling minerals and must be replaced by fresh imports of water. The total volume of tailings (coarse sand and FFT) is approximately 1.4 times greater than the original volume of mined oil sands (Kasperski and Mikula 2011; Chalaturnyk et al. 2002).

Based on 2014 data, there are approximately 1075 x 10^6 m^3 of FFT in Alberta (Government of Alberta 2017c). After three to five years these FFT (originally 6-10 wt% solids) eventually settle to 30-40 wt% solids with a stable slurry structure (thought to be largely due to the behaviour of clay minerals) and 1-3 wt% hydrocarbons. At this point, the FFT is referred to as mature fine tailings (MFT) (Kasperski and Mikula 2011; Thomas 2011; Chalaturnyk et al. 2002). The stability of this clay slurry is thought to be due to the addition of NaOH during the conditioning stage of the extraction process (Powter et al. 2011; Chalaturnyk et al. 2002). NaOH causes asphaltic acids in bitumen to become water-soluble surfactants, thereby acting as clay dispersants, inhibiting settling and consolidation. Because of their extremely slow consolidation rate, MFT remain in this fluid state for decades (Kasperski and Mikula 2011; Chalaturnyk et al. 2002). Figure 5 depicts a typical tailings pond after the FFT have settled into a more stable layer of MFT.

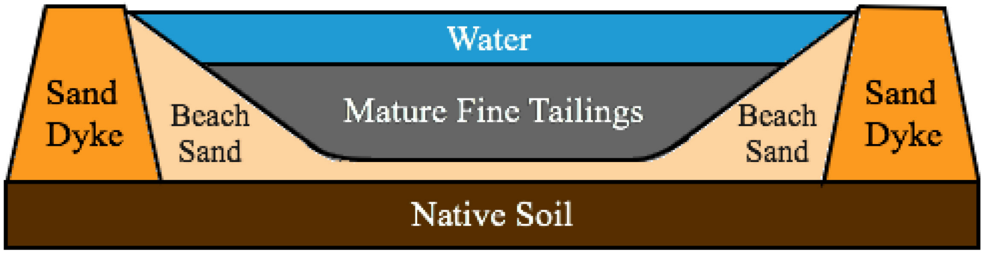


Figure 5. Illustration of a typical tailings pond after three to five years of settling (adapted from Syncrude Canada Ltd. 2017b; Devenny 2009).

2.3.2.1 Tailings Ponds Remediation and Reclamation

Dewatering the tailings is critical because if left unmanaged, MFT could take centuries to naturally dewater to a point where they could be reclaimed (Suncor Energy Inc. 2018). Suncor Energy Inc. (2017) is testing the use of a petroleum coke cap in accelerating the dewatering process. The coke cap layer floats on the surface of the pond and is strong enough that large trucks and equipment are able to drive over the pond’s surface - allowing Suncor to install vertical drains in the pond. These vertical drains allow water to escape the ponds more quickly. A few years after completion of the capping project, the deposit will have settled enough and will continue to settle at a slow enough rate that the area can be reclaimed.

Shell Canada launched an Atmospheric Fines Drying (AFD) commercial-scale field demonstration in 2010 to accelerate the drying of MFT and now has AFD projects at two of their mines (COSIA n.d.b). AFD involves collecting MFT from the ponds, mixing it with a flocculant and placing it on a sloped drying surface (The Engineer 2010). Water from the MFT flocculant mixture is released and runs down the slope to a collection area where it can be reused in the extraction process and the dried tailings material can then be reclaimed (The Engineer 2010; COSIA n.d.b).

Canadian Natural is adding carbon dioxide (CO_2) to its tailings lines, before the waste streams are discharged into the tailings pond, at its Horizon facility (COSIA n.d.c). The addition of CO_2 decreases the pH of the tailings, allowing the solids to consolidate and settle more quickly, thereby increasing the release of water from the tailings (Zhu et al. 2011; COSIA n.d.c). The water can then by recycled and reused in the extraction process.

Centrifugation is a process whereby MFT is treated with a coagulant and/or flocculant and is separated into water and solids streams using centrifuges (Kasperski and Mikula 2011; COSIA n.d.d). The process produces a solid cake that dries rapidly and does not need containment, and recovered water (centrate) that is returned to the ponds and ultimately, recycled to the extraction process. Both Syncrude and Shell Canada have commercial centrifuge facilities in operation (COSIA n.d.d).

Research has also focused on improving the recyclability and reducing the toxicity of the oil sands process-affected water (OSPW) contained within the tailings ponds (Quinlan and Tam 2015). OSPW is a mixture of suspended solids, salts and other dissolved organic compounds including naphthenic acids (NAs) (Shu et al. 2014). NAs are a broad family of saturated aliphatic and alicyclic carboxylic acids that are released from bitumen into the aqueous phase during the caustic hot water process (Quinlan and Tam 2015; Scott et al. 2005). NAs corrode process equipment and are acutely toxic to a number of aquatic organisms (Quinlan and Tam 2015). Shu et al. (2014) investigated the use of solar UV/chlorine treatment for remediating OSPW and found that after laboratory-scale UV/chlorine treatment with OCl^-, the NAs and fluorophore organic compounds in OSPW were effectively degraded.

Clemente et al. (2004) assessed the biodegradation of two commercial NA mixtures using microorganisms native to the tailings ponds. After 10 days of incubation in aerobic conditions and an abundant supply of inorganic nutrients, the concentration of NAs declined by approximately 90%. However they noted that in a real industrial process, the rate of biodegradation would likely be reduced due to a limited supply of nutrients. Scott et al. (2005) further noted that the NAs present in OSPW are less biodegradable than commercial NAs.

Additional research on OSPW remediation technologies has included advanced oxidation, coagulation/flocculation, membrane filtration and adsorption (Quinlan and Tam 2015; Pérez-Estrada et al. 2011; Pourrezaei et al. 2011; Mohamed et al. 2008; Peng et al. 2004).

2.3.2.2 Residual Bitumen Recovery

Bitumen that is entrained in process waste streams may be the result of: i) incomplete extraction from slurry due to the formation of stable bitumen-in-water emulsions; ii) rejection of asphaltenes during froth treatment; and iii) incomplete separation of bitumen froth due to the formation of a stable layer of oil, water and solids (a rag layer) (Romaniuk et al. 2015). Once discharged, residual bitumen from the process waste streams will either float on the top of the tailings ponds, or will remain trapped within the tailings (Syncrude Canada Ltd. 2017b; Romaniuk et al. 2015). Residual bitumen is a potential hazard for aquatic biota, and its biodegradation in the tailings ponds could be an additional source of NAs (Allen 2008; Quagraine et al. 2005). There is little information available on the recovery of bitumen floating on the top of the ponds, though there is some research being conducted on its removal from MFT in conjunction with treating the tailings. Theoretically, bitumen could be recovered from the centrate as part of the centrifugation process for tailings treatment, though the focus of this process is primarily on dewatering MFT (Kasperski and Mikula 2011).

A bench-scale study conducted by Romaniuk et al. (2015) investigated the effects of adding lime (CaO) to MFT in an attempt to remove the residual bitumen before further remediation as it can hinder the dewatering process by interfering with the performance of coagulants and polymers. They found that CaO increased the pH of the mixture, thereby destabilizing bitumen-clay interactions and releasing the residual bitumen, allowing it to float to the surface. The bitumen was then recovered using air flotation. Romaniuk et al. concluded that recovery of residual bitumen from MFT using CaO should improve the effectiveness of subsequent MFT remediation processes, such as dewatering MFT using centrifugation.

2.2 Supercritical Fluid Extraction

2.2.1 Supercritical Fluids and Their Use in Extraction Processes

A supercritical fluid (SCF) is a fluid that has been heated and pressurized beyond its critical temperature (T_c) and pressure (P_c), also called the critical point. As temperature and pressure approach this critical point, the thermodynamic properties of the liquid and gas phases of the substance begin to merge until the critical point is surpassed and a single continuous phase exists, as seen in Figure 6 (Knox 2005; Phelps et al. 1996). Because the physical properties of the substance are evolving as conditions approach the critical point, there is no sudden change in these properties once the critical point is reached, unlike with other phase changes (Brunner 2005).

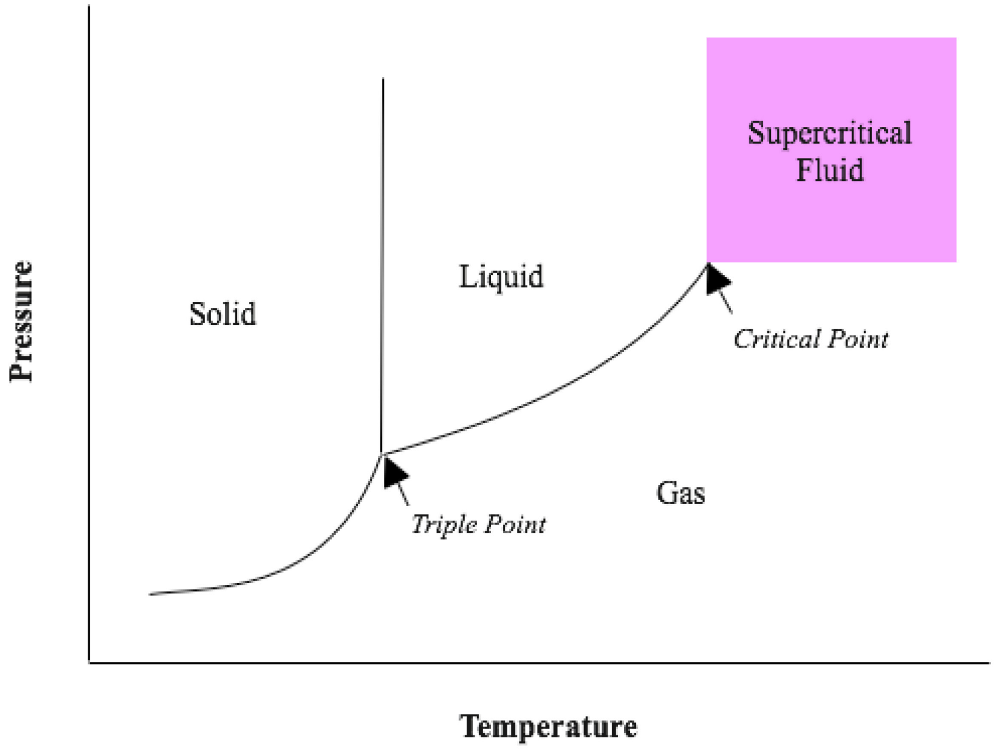


Figure 6. Phase diagram for a pure substance (modified from Knox 2005).

SCFs are unique in that they exhibit both liquid-like and gas-like properties (Akgerman 1997). As seen in Table 2, SCFs have densities close to that of a liquid, and diffusivities and viscosities between that of a liquid and a gas. Similar to a gas, SCFs have near zero surface tension, allowing them to easily penetrate porous matrices (Akgerman 1997; Raynie 1997). Due to rapid diffusion, low viscosity and the absence of surface tension, SCFs have excellent mass transfer capabilities (Raynie 1997; Hawthorne 1990). A significant advantage of SCFs is that they have solvating power similar to (though less than) that of a liquid meanwhile having diffusion rates one to two orders of magnitude greater than a liquid (Akgerman 1997; Raynie 1997; Brunner 2005; Hawthorne 1990). Because SCFs have the benefit of liquid-like solvating characteristics, meanwhile having efficient gas-like transport properties, they are attractive for use in extraction processes over conventional liquid solvents (Hawthorne 1990).

Table 2. Physical property comparison between a gas, a supercritical fluid and a liquid (modified from Raynie 1997).

	Density ($g\ mL^{-1}$)	**Diffusivity** ($cm^2\ s^{-1}$)	**Viscosity** ($g\ cm^{-1}\ s^{-1}$)
Gas	$0.6\text{-}2 \times 10^{-3}$	0.1-0.4	$1\text{-}3 \times 10^{-4}$
Supercritical Fluid	0.2-1.0	$2\text{-}7 \times 10^{-4}$	$1\text{-}9 \times 10^{-4}$
Liquid	0.6-1.6	$0.2\text{-}2 \times 10^{-5}$	$0.2\text{-}3 \times 10^{-2}$

Supercritical fluid extraction (SFE) is a solvent extraction process that uses a SCF to selectively remove compounds from a matrix, for example to remove bitumen from a waste stream. Making small adjustments to temperature and/or pressure can substantially alter the extent to which a compound dissolves in a SCF (Akgerman 1997; Raynie 1997). As such, SFE can be used to preferentially dissolve and extract specific compounds, and the process can be easily manipulated through changes to the system's temperature and/or pressure. For example, near the critical point, increasing the pressure of a SCF will increase its density, in turn increasing its solvating power and allowing it to selectively extract a compound from its matrix (Laitinen et al. 1994; McHugh and Krukonis 1994). Upon depressurization of a SCF that contains a dissolved compound, the density and thereby solubility of the SCF decreases, allowing the extracted compound to precipitate out of solution. This sequence of pressurization followed by depressurization forms the basis for the operation of a SFE system (Brunner 2005).

2.2.2 Supercritical Carbon Dioxide

Most SFE processes use CO_2 as the fluid because it possesses the following characteristics (Brunner 2005; Knox 2005; Phelps et al. 1996; Laitinen et al. 1994):

- Non-flammable
- Non-toxic
- Chemically inert
- Safe to handle
- Readily available at high purity
- Relatively inexpensive
- Leaves behind little or no solvent residues

Because CO_2 can be easily separated from the extracted compound after the extraction process is complete, almost all of the CO_2 can be recovered and recycled, preventing its contribution to the greenhouse gas effect (Brunner 2005; Laitinen et al. 1994). CO_2 is an inert gas and as such, it is viewed as more environmentally friendly than the organic solvents used in traditional extraction processes (Brunner 2005; Phelps et al. 1996).

In addition, CO_2 has a relatively easily achievable critical point (Al-Marzouqi et al. 2007). Table 3 compares the critical temperatures, pressures and densities of four solvents commonly used in heavy oil applications: CO_2, ethane, propane and pentane. All four solvents are non-polar given that they are used to extract primarily non-polar compounds. Even though some of the organic solvents may have greater solvating powers than CO_2 (Rose et al. 2000), it has the lowest T_c of the four solvents and thus, with the exception of ethane, CO_2 typically requires the least amount of energy to reach supercritical conditions. In addition,

CO_2 is safer to handle than highly flammable and potentially explosive solvents like ethane, propane and pentane.

Table 3. Commonly used supercritical fluids for hydrocarbon and oil recovery from oil sands and similar matrices (data obtained from NIST 2017).

Chemical	**T_c** (°C)	**P_c** (MPa)	**ρ_c *** (g mL^{-1})
CO_2	31.0	7.4	0.47
C_2H_6	32.2	4.9	0.21
C_3H_8	96.7	4.3	0.22
C_5H_{12}	196.6	3.4	0.23

* ρ_c = critical density

As supercritical CO_2 (SC-CO_2) is a non-polar solvent, it is effective in extracting non-polar and slightly polar solutes such as alkanes, terpenes, aldehydes, esters, alcohols and fats (Brunner 2005; Phelps et al. 1996). Solutes with higher vapour pressures are more soluble in SC-CO_2 and thus SC-CO_2 is successful in extracting volatile hydrocarbons (Laitinen et al. 1994). Low molecular weight solutes experience a high solubility in SC-CO_2 and solubility decreases with increasing molecular weight (Brunner 2005). In order to solubilize and extract polar compounds, the polarity of SC-CO_2 can be increased through the addition of more polar modifiers such as water or short-chain alcohols (Phelps et al. 1996; Laitinen et al. 1994). The addition of organic compounds as modifiers can negatively impact the notion that SFE is an environmentally friendly process, however the volume of modifier used is usually relatively low (Płotka-Wasylka et al. 2017).

2.2.3 Applications of Supercritical Fluid Extraction

The first commercial-scale applications of SFE using SC-CO_2 were developed in Germany in the late 1970's and early 1980's in the food industry, namely coffee decaffeination and hops extraction (Perrut 2000; Phelps et al. 1996). The motivation for using SC-CO_2 was to reduce the use of organic solvents in extraction processes, especially those producing consumer goods (Phelps et al. 1996). The application of SFE began to expand, within and outside of the food industry, to include tea decaffeination; denicotinization of tobacco; de-alcoholization of beverages; fat removal from various foods; dyeing textiles; bone delipidation for use in grafts; fragrance and flavour extraction for use in the food and cosmetics industries; as well as various applications within the pharmaceutical, cleaning and materials processing industries (Brunner 2005; Knox 2005; Perrut 2000; Teja and Eckert 2000; Phelps et al. 1996). While these applications generate high quality products by taking advantage of the high diffusivities and/or solubilities associated with SCFs, SFE is generally more expensive than traditional organic solvent extraction processes and as such, its use is less widespread (Knox 2005; Perrut 2000). However, SFE is advantageous over other extraction processes because it uses significantly smaller volumes of solvent, the extracted compound can be easily recovered, the solvent can be reused and the extraction occurs at a faster rate (Płotka-Wasylka et al. 2017; Avila-Chavez et al. 2007).

SFE also has a number of environmental applications. Extensive research has been conducted on the use of SFE for removing contaminants from soil. SFE has been shown to successfully remove polychlorinated biphenyls (PCBs), pesticides, insecticides, phenols, polycyclic aromatic hydrocarbons (PAHs), dioxins and heavy metals from various soils, sands and sediments (Herrero et al. 2010; Zúñiga et al. 2009; Miyawaki et al. 2008; Mmualefe et al. 2008; Elshani et al. 2001; Burk et al. 1990; Lopez-Avila et al. 1990; Brady et al. 1987). The use of SFE is also being investigated for heavy metals removal from spent automobile catalytic converters and treated wood (Faisal et al. 2008; Wang and Chiu 2008).

Research has also focused on using SFE for extracting hydrocarbons from soil, oil sands, bitumen and other crude oils, showing successful laboratory-scale extraction using various SCFs, including CO_2 (La and Guigard 2015; Rudyk and Spirov 2014; Geranmayeh et al. 2012; Al-Sabawi et al 2011; Al-Marzouqi et al. 2007; Avila-Chavez et al. 2007; Nagpal and Guigard 2005; Rose et al. 2000; Morselli et al. 1999; Subramanian and Hanson 1998; Low and Duffy 1995; Deo et al. 1992). However, there are currently no reports of a commercial-scale SFE process for extracting hydrocarbons from these types of materials.

2.2.4 Solubility in Supercritical Fluids

The solubility of a substance in a SCF represents the upper limit at which the solute can be present in the SCF phase under a given set of conditions, and is thereby related to the maximum obtainable extraction efficiency. A discussion of the solubility of bitumen and similar hydrocarbons in SC-CO_2 is provided below.

2.2.4.1 Solubility of Hydrocarbons in Supercritical Carbon Dioxide

Previous literature has primarily focused on the solubility of CO_2 in bitumen, with bitumen solubility in CO_2 assumed to be negligible in many cases (Eastick et al. 1992), partly because it is more difficult to measure accurately (Yu et al. 1989). However, Huang and Radosz (1990) and Yu et al. (1989) measured mutual solubilities of bitumen-rich and CO_2-rich phases using bitumen and three bitumen fractions or 'cuts' at a variety of pressures and temperatures. The results of the experiments conducted at 16 MPa and two select temperatures, 323 and 373 K, are displayed in Table 4. Bitumen cuts were made by distillation of Cold Lake bitumen (Huang and Radosz 1990). The original bitumen, from which five cuts were made, had a molecular weight of approximately 568 g/mol (calculated based on boiling point) but only the three lightest cuts were measured for solubility. The three lightest cuts had molecular weights of 201, 304, and 572 g/mol for cuts 1, 2 and 3, respectively. As shown in Table 4, both CO_2 and bitumen solubility decreased as the molecular weight of the cut increased. Both Yu et al. (1989) and Huang and Radosz (1990) reported good reproducibility for the bitumen-rich phases, but less accurate results for the CO2-rich phases.

Eastick et al. (1992) measured the solubility of CO_2 in five cuts of bitumen over a range of temperatures and pressures, many of which were beyond the critical point of CO_2. Solubility was found to be highest in the first two cuts, which presented as clear liquids. The boiling point ranges of cuts 1 and 2 were < 343 °C and 343 to 510 °C, respectively. Cut 5, which was comprised of 50 wt% asphaltenes, had the lowest CO_2 solubility. These results reflect the findings of Yu et al. (1989) and Huang and Radosz (1990), with the solubility of CO_2 in bitumen decreasing as the molecular weight of the bitumen fraction increases. Yu et al. (1989) and Huang and Radosz (1990) further concluded that SC-CO_2 solubility in bitumen increased with increasing pressures and decreased with increasing temperatures – this was not always the case for bitumen solubility in SC-CO_2.

Table 4. Mutual solubilities of SC-CO_2 and Cold Lake bitumen at 16 MPa (developed from Huang and Radosz 1990; Yu et al. 1989).

		Temperature (K)	
		323	373
Total Bitumen	CO_2 in Bitumen (Weight Fraction)	0.136	0.120
	Bitumen in CO_2 (Weight Fraction)	0.019	0.0044
	CO_2-to-Bitumen (Weight Ratio in Feed)	3.68	3.15
Cut 1	CO_2 in Cut 1 (Weight Fraction)	0.409	0.265
	Cut 1 in CO_2 (Weight Fraction)	0.123	0.0205
	CO_2-to-Cut 1 (Weight Ratio in Feed)	3.13	3.83
Cut 2	CO_2 in Cut 2 (Weight Fraction)	0.208	0.17
	Cut 2 in CO_2 (Weight Fraction)	0.021	0.0032
	CO_2-to-Cut 2 (Weight Ratio in Feed)	3.54	2.46
Cut 3	CO_2 in Cut 3 (Weight Fraction)	0.137	0.118
	Cut 3 in CO_2 (Weight Fraction)	0.001	0.0002
	CO_2-to-Cut 3 (Weight Ratio in Feed)	2.5	3.59

Hwang and Ortiz (1998) collected oil samples from the McElroy Field in Texas, which was undergoing a pilot CO_2 flood project. CO_2 was believed to be in the supercritical state in the reservoir, based on the injection pressure and reservoir temperature. Hydrocarbon solubility in CO_2 was shown to decrease as the carbon number increased and thus, heavier hydrocarbons ($> C_{25}$) were not as readily soluble in CO_2 compared to lighter hydrocarbons; a finding that is consistent with that of Yu et al. (1989) and Huang and Radosz. (1990). Hwang and Ortiz (1998) further reported that the saturate, aromatic and resin content of oil samples taken during the CO_2 flood remained relatively unchanged from oil samples taken before the flood. However, due to precipitation, the asphaltene content of the oil decreased by 50%. This illustrates the anti-solvent effect of SC-CO_2 toward asphaltenes, which are, in general terms, high molecular weight, aromatic, polar compounds (Abu-Khader and Speight 2007; Zaki et al. 2003; Hwang and Ortiz 1998). Zaki et al. (2003) investigated the fraction of asphaltenes that were insoluble in CO_2 and found that, compared to the total asphaltenes, they were more polar, had a higher molecular weight, and contained greater amounts of the elements oxygen, sulfur, nitrogen, vanadium, nickel and iron. Some authors have suggested that as CO_2 dissolves into crude oil, it destabilizes aromatic-resin-asphaltene colloidal structures, causing asphaltene molecules to agglomerate and precipitate out of solution as lighter hydrocarbons are preferentially extracted (Speight 2004; Hwang and Ortiz 1998; Koots and Speight 1975).

The addition of a small amount of volatile modifier to a SCF can considerably increase the solubility of the solute in the SCF (Cansell and Rey 1998). Unfortunately there is limited literature available on the effects of modifiers on hydrocarbon solubility in SCFs.

2.2.5 Supercritical Fluid Extraction Parameters

2.2.5.1 Pressure, Temperature and Density

A high solvent density, associated with increasing pressures and/or decreasing temperatures, enhances the extraction of hydrocarbons. Several authors who have examined the extraction of hydrocarbons from bitumen and matrices similar to that of oil sands reported achieving their highest extraction efficiency at the highest solvent density tested (Avila-Chavez et al. 2007; Nagpal and Guigard 2005; Rose et al. 2000; Subramanian and Hanson 1998). These results are expected because as the density of SC-CO_2 increases (which is typically achieved by increasing the extraction pressure), so does its solubilisation strength. This enhanced solvating power increases the solubility of hydrocarbons in SC-CO_2, resulting in higher extraction efficiencies (La and Guigard 2015; Geranmayeh et al. 2012; Al-Marzouqi et al. 2009; Cansell and Rey 1998; Phelps et al. 1996). Al-Marzouqi et al. (2009) suggested that a decrease in the interfacial tension between CO_2 and oil as a result of high pressures, and thus densities, may also be partly responsible for the increased extraction efficiencies associated with high pressures.

While high pressures are known to be advantageous, largely because of the associated increase in density, high temperatures have also been shown to improve extraction efficiencies. La and Guigard (2015) found that the highest temperature and pressure conditions tested (60 °C and 24 MPa) produced two of the three highest hydrocarbon extraction efficiencies from a 1:1 oil sands slurry. They suggested that high temperatures may increase hydrocarbon vapour pressure and therefore solubility in SC-CO_2, may increase the exposure of hydrocarbons to CO_2 by releasing desorption resistant hydrocarbons, and/or may increase mass transfer rates (diffusion) overcoming any shielding effects of the matrix. Similarly, Jaffé et al. (1998) found that hydrocarbon extraction from shale samples was temperature dependent – desorption resistant, ‘trapped’ fractions required high temperatures in order to induce thermal restructuring of the organic matrix, allowing the ‘trapped’ fractions be extracted. Geranmayeh et al. (2012) reported that at high pressures, increases in temperature resulted in increased concentrations of pollutants in SC-CO_2. Allawzi et al. (2011) suggested that increasing temperatures enhanced the extraction of oil from shale deposits due to increased volatility, enhanced diffusion rates and weakened intermolecular forces. This suggests that extraction efficiency is not solely based on SC-CO_2 density.

For a given pressure, an increase in extraction temperature coincides with a decrease in solvent density and therefore a decrease in solvation power. However, if both temperature and pressure are increased together, the increase in vapour pressure, and thereby volatility, of the solute may be enough to offset the decrease in solvent density (La and Guigard 2015; Geranmayeh et al. 2012; Low and Duffy 1995). This concept is illustrated by Al-Marzouqi et al. (2007) who found that at conditions of 10 MPa and 40 °C and a density of 0.629 g mL^{-1}, 46.5 wt% of hydrocarbons were extracted from an oil-saturated soil. However, they found that by increasing the pressure and temperature to 30 MPa and 100 °C, resulting in a density of 0.662 g mL^{-1}, the mass of hydrocarbons extracted increased to 72.4 wt%.

Table 5 displays select extraction efficiencies that illustrate the various effects of pressure, temperature and density on the SCF extraction of hydrocarbons from heavy oil and other feed streams with matrices similar to oil sands.

Changing pressures and temperatures also impact the type of the extracted hydrocarbons. Al-Marzouqi et al. (2007) investigated the capacity of SC-CO_2 to extract hydrocarbons from an oil-saturated soil and found that the amount of heavy hydrocarbons extracted increased with pressure. At a temperature of 120 °C, SC-CO_2 extracted hydrocarbons up to C_{25} at 20 MPa and up to C_{31} at 30 MPa. Rose et al. (2000) also found that as operating pressures increased, extracts became slightly heavier. Furthermore, Allawzi et al. (2011) extracted oil from shale deposits using SC-CO_2 and reported that increasing the extraction temperature produced more low-molecular weight compounds.

Table 5. Effects of pressure, temperature and density on the supercritical fluid extraction of hydrocarbons from various feed streams.

Feed	**SCF**	**Pressure** (MPa)	**Temperature** (K)	**Density** (g mL^{-1})	**Extraction Efficiency** (wt%)	**Reference**
Crude oil	CO_2	10.3	311	0.684	40	Deo et al. 1992 [1]
		17.2	311	0.823	50	
Bitumen and sand mixture	CO_2	10	307	0.728	8.8	Rose et al. 2000 [1]
		15	307	0.823	10.5	
		12.2	320	0.642	8.4	
		12.2	328	0.522	3.5	
Oil-saturated soil	CO_2	10	313	0.629	46.5	Al-Marzouqi et al. 2007
		10	333	0.290	7.6	
		20	373	0.481	41.3	
		30	373	0.662	72.4	
Bitumen	Propane	5.6	380	0.296	20	Subramanian and Hanson 1998
		10.4	339	0.460	40	
		10.4	422	0.281	24	
		17.3	380	0.427	48	
Crude oil tank bottom sludge	Ethane	10	308	0.362	48.6	Avila-Chavez et al. 2007
		10	338	0.264	40.8	
		17.2	308	0.400	58.5	
		17.2	338	0.348	54.9	

[1] Estimated extraction effiiciency values based on figures.

2.2.5.2 Modifiers

Because solubilities in typical SCFs, such as CO_2 or ethane, are generally lower than that of liquid solvents (particularly for polar compounds), there is interest in adding modifiers to enhance the solubility and selectively for various groups of solutes (Stubbs and Siepmann 2004). The choice of an appropriate modifier is dependent on a number of factors such as the target compounds and the affinity of the solute for the modifier (Płotka-Wasylka et al. 2017). It has been shown that hydrocarbon extraction using SCFs can be enhanced through the addition of a modifier, most commonly toluene (Rudyk et al. 2017; La and Guigard 2015; Al-Sabawi et al. 2011). The addition of a modifier that is more polar than the SCF is thought to enhance the solubility of the polar hydrocarbons, thus resulting in increased extraction efficiencies (La and Guigard 2015; Al-Marzouqi et al. 2009; Hwang and Ortiz 2000).

Table 6 displays select extraction efficiencies that illustrate the effects of modifier type and concentration on the SCF extraction of hydrocarbons from heavy oil and other feed streams similar to oil sands. All of the studies indicate that modifier addition improves the extraction of hydrocarbons, with the exception of 3 g isopropanol addition to SC-CO_2 (Rudyk et al. 2017) and 20 mol% methanol addition to SC-CO_2 (Al-Sabawi et al. 2011). Toluene consistently outperforms other modifiers for a variety of matrices, though one study by Magomedov et al. (2017) found that 20 wt% o-xylene yielded 10.6 wt% more extract than an equivalent mass concentration of toluene. These results are consistent with the notion that toluene is an excellent solvent for asphaltics (asphaltenes, nitrogen, sulfur and oxygen) (Hwang and Ortiz 2000).

As of yet there are a limited number of studies that have investigated the effect of increasing modifier concentrations on the extraction of hydrocarbons. Magomedov et al. (2017) reported that increasing the concentration of a toluene in SC-CO_2 from 15 to 30 wt% led to a fivefold increase in vacuum residue extraction efficiency (from 9.9 to 52.4 wt%). Al-Sabawi et al. (2011) found that increasing the concentration of acetone, toluene or ethyl acetate from 5 to 20 mol% in supercritical n-pentane increased the mass of hydrocarbons extracted from bitumen. However they found that increasing the concentration of methanol above 5 mol% in n-pentane decreased the extraction efficiency. Morselli et al. (1999) found that 5% (v/v) of acetone increased extraction of the aromatic fraction of crude oil but at a higher concentration of 10% (v/v), the extraction of aromatics and saturates (non-polar compounds) decreased.

While toluene addition often results in the highest hydrocarbon extraction efficiency, Al-Sabawi et al. (2011) found that it also produces the poorest quality extract. They studied the effects of modifiers on the extraction of Athabasca bitumen using supercritical n-pentane and found that the addition of a modifier such as toluene, ethyl acetate or methanol, was associated with increased impurities in the extract due to decreased asphaltene precipitation. Extracts collected with toluene had the highest concentration of impurities such as nickel, vanadium, and nitrogen, though this was anticipated given that asphaltenes (which contain these elements) are often defined as toluene soluble components of bitumen. Increasing the concentration of either toluene or ethyl acetate further increased the impurities in the extract. According to Hwang and Ortiz (2000), the low polarity of SC-CO_2 causes asphaltenes to precipitate, allowing for a more upgraded product compared to SC-CO_2-modifier mixtures.

Hwang and Ortiz (2000) extracted crude oil from spiked samples of dolomite rock and found that chemically modified CO_2 was able to extract a wider range of hydrocarbons and greater amounts of intermediate and heavy hydrocarbons compared to CO_2 alone. CO_2 at 31 °C and 80 atm was able to effectively extract hydrocarbons up to C_{12} but little or no hydrocarbons heavier than C_{22} were extracted. With the addition of 10% methanol, the CO_2 – methanol mixture was capable of extracting hydrocarbons up to C_{30}. Furthermore, Rudyk et al. (2013) reported that methanol-modified CO_2 extracted lighter hydrocarbons compared to ethanol-modified CO_2, and that ethanol extracted heavier hydrocarbons faster. These results illustrate that modifier addition affects both the quantity and type of hydrocarbons extracted using SCFs.

Table 6. Effect of modifier type and concentration on the supercritical fluid extraction of hydrocarbons from various feed streams.

Feed	SCF	Modifier	Concentration	Extraction Efficiency (wt%)	Reference
Limestone rock and soil spiked with crude oil	CO_2	None	-	4.20	Al-Marzouqi et al. 2009
		Heptane	5 v/v %	49.85	
		Toluene	5 v/v %	91.52	
Towels soaked with crude oil	CO_2	None	-	54	Rudyk et al. 2014 [1]
		Acetone	5 g	63	
		Propanol	5 g	65	
		Methanol	5 g	66	
		Ethanol	5 g	71	
Oil sands slurry	CO_2	None	-	27.9	La and Guigard 2015
		Toluene	9.1 wt%	33.7	
Oil sands	CO_2	None	-	15.38	Rudyk et al. 2017
		Isopropanol	3 g	12.05	
		Ethanol	3 g	24.50	

[1] Estimated extraction efficiency values based on figures.

[2] Extraction efficiency measures deasphalted oil yields only.

Table 6. Effect of modifier type and concentration on the supercritical fluid extraction of hydrocarbons from various feed streams (continued**).**

Feed	**SCF**	**Modifier**	**Concentration**	**Extraction Efficiency** (wt%)	**Reference**
Vacuum residue (heavy petroleum feedstock)	CO_2	Methanol	20 wt%	6.3	Magomedov et al. 2017
		Ethanol	20 wt%	7.9	
		Acetone	20 wt%	12.0	
		n-heptane	20 wt%	21.9	
		o-xylene	20 wt%	34.9	
		Toluene	15 wt%	9.9	
			20 wt%	24.3	
			30 wt%	52.4	
Bitumen	n-pentane	None	-	80	Al-Sabawi et al. 2011 [1,2]
		Acetone	5 mol%	81	
			20 mol%	83	
		Methanol	5 mol%	85	
			20 mol%	80	
		Ethyl Acetate	5 mol%	83	
			20 mol%	85	
		Toluene	5 mol%	86	
			20 mol%	92	

[1] Estimated extraction efficiency values based on figures.

[2] Extraction efficiency measures deasphalted oil yields only.

2.2.5.3 Matrix

If a solute is contained within a matrix, the water content and physicochemical properties of the solids will also affect the extraction capacity of SC-CO_2 (Al-Marzouqi et al. 2009). Similar to chemical modifiers, water can act as a polar modifier, enhancing hydrocarbon extraction. Al-Marzouqi et al. (2009) assessed the extraction of oil from soil and rocks using SC-CO_2 and found that small amounts of water (<10 wt%) increased the extraction of oil but the addition of >10 wt% water resulted in decreased extraction efficiencies. Rudyk and Spirov (2014) found that the addition of 10 mL of fresh or salty water enhanced hydrocarbon extraction from Nigerian tar sands whereas La and Guigard (2015) determined that excess water (50 mL) in a 1:1 oil sands slurry hindered extractions. Thus small amounts of water may increase the extraction of hydrocarbons from oil sands and similar matrices by increasing the capacity of CO_2 to extract polar compounds (Al-Marzouqi et al. 2009). However because bitumen is also made up of non-polar compounds, the presence of highly polar molecules (such as water) in large amounts may decrease the extraction of hydrocarbons. Excess water may also act as a physical barrier, shielding bitumen in the oil sands or soil matrix from CO_2 (La and Guigard 2015; Al-Marzouqi et al. 2009; Low and Duffy 1995; Camel et al. 1993). Further, high concentrations of water may hinder the diffusion of hydrocarbons out of the matrix (La and Guigard 2015), and may suppress the volatility of hydrocarbons in the matrix (Low and Duffy 1995). As such, excess water may cause mass transfer limitations that hinder the extraction of hydrocarbons (La and Guigard 2015). To counteract this, La and Guigard (2015) found that high mixing speeds could decrease water shielding effects and decrease mass transfer limitations experienced by oil sands slurries.

Water may also influence the action of a chemical modifier (Camel et al. 1993). Roop et al. (1989) reported that the addition of methanol to SC-CO_2 increased the extraction of phenol from a dry soil, due to the increased polarity of the mixture. However, in the case of wetted soil, methanol addition had no effect. This is likely a result of the dissolution of methanol in the water and thus in this instance, adding methanol did not increase the polarity of the mixture. However, benzene, which is virtually insoluble in water, favoured the supercritical phase over the wetted soil phase, thus increasing the extraction of phenol from wetted soil.

Solid substrates in the matrix can also impact the extraction. For example, pollutants in a soil sample may be associated with inorganic (for example, alumina and silica) and/or organic (for example, humic and fulvic) active sites and thus may be resistant to desorption (Laitinen et al. 1994; Hawthorne et al. 1993). They may also be inhibited by physical barriers such as being located in micropores or being coated with water. Extractions from clays are typically less efficient because of their small particle size and high adsorption capacity (Laitinen et al. 1994).

Low et al. (1995) found that SFE of petroleum hydrocarbons from silica beads was limited by the solubility of the hydrocarbons in SC-CO_2 and they reported complete recovery of the surface area and pore volume after the extraction. However, the removal of hydrocarbons from activated carbon was much more difficult. Initially hydrocarbons were extracted from the large pores, and as the extraction proceeded, hydrocarbons were released from smaller pores. A significant amount of the hydrocarbons were permanently trapped in micropores. After 75% of the hydrocarbons were extracted, the remaining 25% occupied 40% of the total surface area. Al-Marzouqi et al. (2009) reported higher extraction efficiencies of oil from soil matrices than from limestone. Despite a larger surface area and smaller porosity, the higher permeability of soil is likely the reason for these higher extraction efficiencies. In addition, Al-Marzouqi et al. found that medium and large limestone particles had extraction efficiencies 15% greater than that of small limestone particles – likely due to the larger surface area of the small particles.

2.3 Summary

Unconventional oil, or oil sands bitumen, production constitutes the vast majority of oil production in Alberta. In-situ or ex-situ methods are used to recover the bitumen, depending on the depth of the oil sands deposits. While ex-situ recovery, or surface mining, produces the most crude oil, it also requires the largest footprint and generates the largest process waste streams. These waste streams consist of large volumes of water, sand, silt, clay and residual bitumen, for which there is currently no effective recovery method.

SFE is a novel approach to recovering the residual bitumen from the current inventory of ex-situ process waste streams. Furthermore, SFE could also be used as an alternative to the current ex-situ hot water extraction process – preventing the generation of these large volumes of process waste and thus eliminating the need for tailings ponds.

SFE with CO_2 is considered to be an environmentally friendly process because the CO_2, an inert gas, can be almost entirely recovered and recycled. In addition, CO_2 is relatively inexpensive and has an easily achievable critical point. Using SFE as an ex-situ oil sands bitumen extraction technique would reduce or eliminate the need for water in the extraction process. This would not only reduce the volume of process waste, but could potentially eliminate the need for tailings ponds. SFE could also be used to treat the current volume of tailings by extracting the residual bitumen, a valuable resource that would have otherwise been lost.

The use of CO_2 in the SFE process can result in a slightly upgraded extract through the precipitation of asphaltenes. However the addition of a modifier, such as toluene, can substantially increase the quantity of hydrocarbons extracted compared to SC-CO_2 alone. Modifiers are capable of extracting a wider range of hydrocarbons and greater amounts of intermediate and heavy hydrocarbons, though impurities, such as heavy metals and heteroatoms, are typically associated with these greater extraction efficiencies. In addition, chemical modifiers may reduce the environmentally friendly image of SFE and increase the cost of the process, and would likely require separation, from both the extracted bitumen and the residue, after completion of the SFE process.

CHAPTER 3 Materials and Methods

This chapter details the materials used in the dynamic extractions, and then provide a description of the SFE system used for in this thesis research. The experimental conditions and procedures associated with the dynamic extractions, Dean-Stark extractions and high temperature simulated distillation (HTSD) are then detailed. Lastly, the method of calculating hydrocarbon extraction efficiency, based on the results of dynamic extractions and Dean-Stark extractions, will be presented.

3.1 Summary of Experiments

In this thesis research, dynamic extractions were performed on three feed materials: bitumen, a bitumen-containing process stream (Froth Treatment Froth or FT Froth) and a bitumen-containing process waste stream (Pond Froth). Table 7 provides a summary of the dynamic extractions performed as part of this thesis research.

Table 7. Summary of SC-CO_2 dynamic extractions conducted for thesis research.

Feed Material	**Modifier**	**Modifier Concentration** (mol %)
Bitumen	None (CO_2 only)	-
	Toluene	5
		10
		15
	Methanol	5
		10
		15
		33.7
FT Froth (Process stream)	None (CO_2 only)	-
	Toluene	15
	Methanol	33.7
Pond Froth (Process waste stream)	None (CO_2 only)	-
	Toluene	15
	Methanol	33.7

All dynamic extractions were conducted at a fixed pressure and temperature of 24 MPa (3480 psi) and 333 K (60°C), resulting in a SC-CO_2 density of 0.78 g/mL (NIST 2017).

The principle result from these dynamic extractions was the hydrocarbon extraction efficiency (the cumulative mass of hydrocarbons extracted), calculated from both the mass of hydrocarbons extracted and the mass of hydrocarbons remaining in the residue after extraction.

The type of hydrocarbons extracted during the dynamic extractions and the type of hydrocarbons remaining in the residue after the dynamic extraction were determined using HTSD.

3.2 Materials

This section describes the feed materials and chemicals used in this research. Three feed materials were used: bitumen, Froth Treatment Froth (FT Froth) and Pond Froth. All feed materials were provided by Syncrude Canada Ltd. (hereafter referred to as Syncrude).

3.2.1 Bitumen

Bitumen was provided by Syncrude in 1 L glass jars and stored in a refrigerator (0 – 4 °C) in the Supercritical Fluid Extraction Lab of the Natural Resources Engineering Facility at the University of Alberta. The bitumen was extracted from FT Froth, which is the feed material for Syncrude's Froth Treatment Plant. The FT Froth was sampled from Syncrude's Froth Treatment Plant on an unknown date and Dean-Stark extraction was used to separate the bitumen from the froth mixture in November 2014. This bitumen originates from oil sands from the Athabasca formation and it is referred to as 'virgin bitumen' since it has not been exposed to any solvents (such as naphtha) during the oil sands extraction process. The bitumen was subsampled by Syncrude on January 7, 2015 and was then sent to the University of Alberta. At room temperature, the bitumen is viscous and dark brown to black in color. Appendix A1 provides additional properties of the virgin bitumen.

3.2.2 Process and Process Waste Streams

Two bitumen-containing streams were provided by Syncrude: FT Froth and Pond Froth. FT Froth is a process stream and is the feed material into Syncrude's Froth Treatment Plant. FT Froth is generated during the extraction of bitumen from surface mined oil sands from the Athabasca formation; (see Figure 4). Pond Froth is a process waste stream and is made up of the residual bitumen that floats to the surface of tailings ponds, forming a slick layer on top of the water.

Fifty gram samples of FT Froth were provided by Syncrude in 120 mL glass jars and stored in a refrigerator (0 – 4 °C) in the Supercritical Fluid Extraction Lab of the Natural Resources Engineering Facility at the University of Alberta. FT Froth was sampled from Syncrude's Froth Treatment Plant on November 8, 2011 and was stored in 1 gallon paint cans until it was subsampled by Syncrude on February 21, 2018. At room temperature, the FT Froth samples consist of a mixture of dark brown to black bitumen and fine solids, with cloudy water pockets (water entrained with solids) surrounding the bitumen-solids mixture.

Fifty gram samples of Pond Froth were provided by Syncrude in 120 mL glass jars and stored in a refrigerator (0 – 4 °C) in the Supercritical Fluid Extraction Lab of the Natural Resources Engineering Facility at the University of Alberta. Pond Froth was collected on site on July 13, 2017 and was stored in 20 L pails until subsampling on February 27, 2018. At room temperature the Pond Froth samples are a medium to dark brown homogenous, highly viscous mixture of bitumen, solids and water.

Syncrude performed the subsampling on both FT Froth and Pond Froth using the following procedure. The process or process waste stream sample (contained in either cans or pails) was heated to 86°C in a water bath and was then poured into an 8.25" diameter mixing tank that was also kept at 86 °C using a water jacket. The sample was then mixed at 1000 rpm for 10 minutes and subsampled into 120 mL jars (with approximately 50 g of sample in each 120 mL jar).

In addition to the 20 subsamples of each of FT Froth and Pond Froth that were sent to the University of Alberta, a total of nine subsamples of each of the two materials were collected and analyzed by Syncrude for bitumen, water and solids content and for solids particle size distribution. Table 8 displays the mass percentages of bitumen, water and solids for both FT Froth and Pond Froth, based on Dean-Stark extraction of applicable subsamples. As can be seen in Table 8, compared to Pond Froth, FT Froth contains a higher mass percentage of bitumen and solids, and a lower mass percentage of water.

Table 8. Composition of FT Froth and Pond Froth (data provided by Syncrude).

	FT Froth[1] (wt%)	**FT Froth**[2] (wt%)	**Pond Froth**[3] (wt%)	**Pond Froth**[4] (wt%)
Bitumen	60.56	61.32	51.05	51.56
Water	27.38	27.90	44.35	43.75
Solids	12.06	10.77	4.60	4.69

[1] Applicable to FT Froth Jars 1 to 5 (used in dynamic extractions on March 9, 13 and 19; May 24 and 28, 2018).

[2] Applicable to FT Froth Jars 6 and 7 (used in dynamic extractions on May 30 and July 9, 2018).

[3] Applicable to Pond Froth Jars 2 to 5 (used in dynamic extractions on June 20, 25, 27 and 29, 2018).

[4] Applicable to Pond Froth Jar 6 (used in a dynamic extraction on July 5, 2018).

The bitumen extracted from both the FT Froth and Pond Froth subsamples underwent HTSD analysis. Figure 7 provides a typical HTSD curve for each of the virgin bitumen, FT Froth bitumen and Pond Froth bitumen. HTSD curves illustrate the temperature by which a portion of the sample is distilled, with a higher distillation temperature indicating heavier hydrocarbons in the sample. From Figure 7, it is evident that the virgin bitumen contains lighter hydrocarbons than both FT Froth bitumen and Pond Froth bitumen, and that both the FT Froth bitumen and Pond Froth bitumen are composed of hydrocarbons of similar weights.

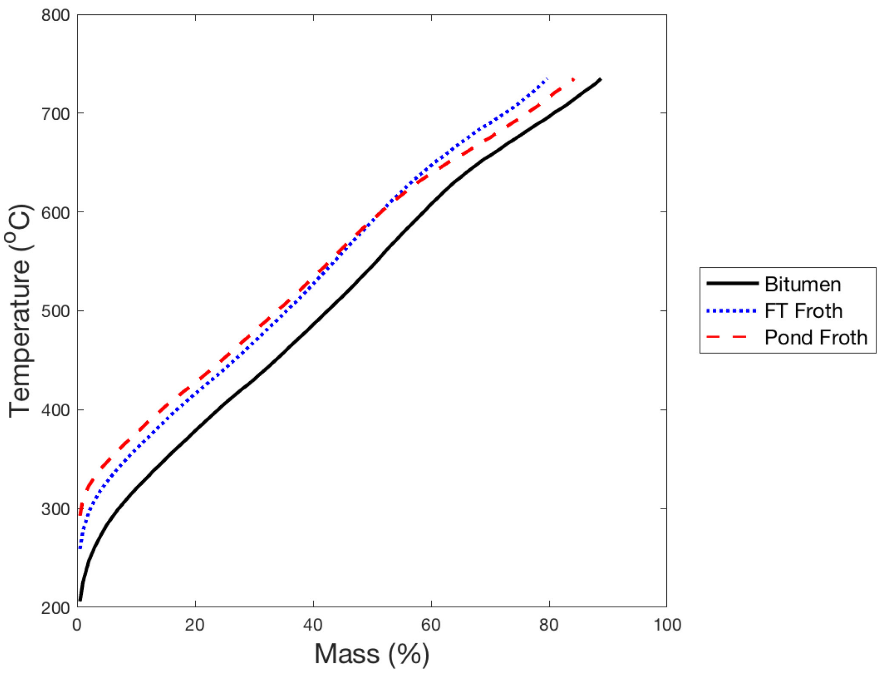


Figure 7. Comparison of hydrocarbons in virgin bitumen, FT Froth bitumen and Pond Froth bitumen samples.

Appendices A2 and A3 contain particle size distributions for solids from FT Froth and Pond Froth, respectively. FT Froth and Pond Froth have similar particle size distributions. However, FT Froth solids are slightly larger; 80% of FT Froth solids are ≤ 100 µm, whereas 80% of Pond Froth solids are ≤ 60 µm. Based on the Unified Soil Classification System (American Society of Testing Materials (ASTM) D2487), the majority of the solids in both feed materials are fines (≤ 75 µm), with some sand (ASTM International 2017).

3.2.3 Chemicals

Table 9 provides a list of chemicals used in the dynamic extractions, their purpose, and the supplier.

Table 9. List of chemicals, purpose of usage, and supplier.

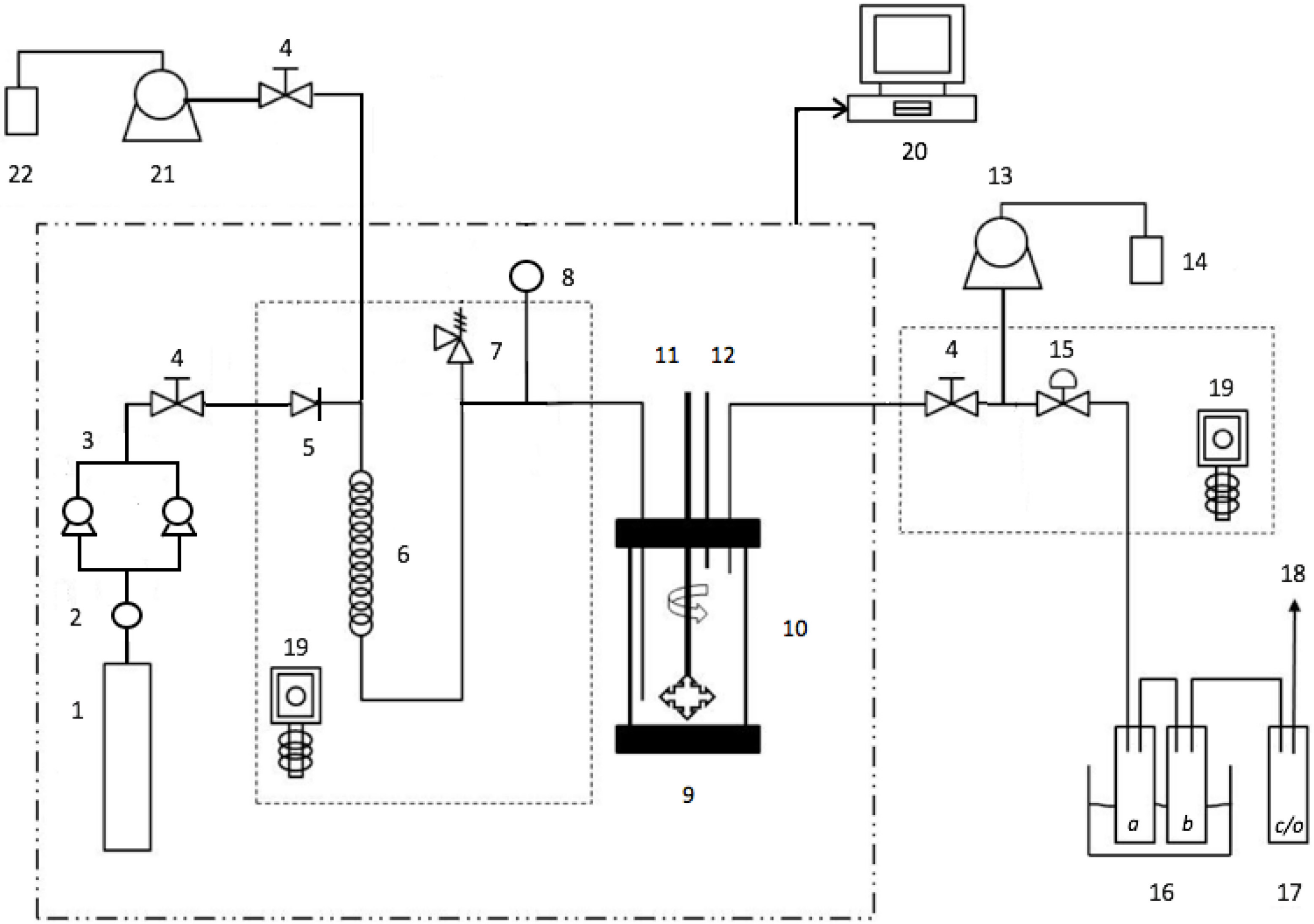
Chemical	Use	Supplier
Carbon Dioxide (liquid, grade 3 bone dry)	Supercritical solvent	Praxair (Edmonton, AB)
Toluene (ACS grade)	Modifier and cleaning solvent	Fisher Scientific (Fair Lawn, NJ)
Methanol (ACS/HPLC grade)	Modifier and cleaning solvent	Fisher Scientific (Fair Lawn, NJ)
Acetone (ACS/HPLC grade)	Acetone/dry ice bath	Fisher Scientific (Fair Lawn, NJ)

3.3 Supercritical Fluid Extraction System

Each dynamic extraction was performed using the bench-scale batch SFE system shown in Figure 8. A photo of this SFE system is presented in Figure 9. The suppliers and pressure specifications (if applicable) of the major system components are provided in Table 10**.**

A liquid CO_2 cylinder (labelled 1 in Figure 8) supplies CO_2 for the dynamic extractions. The CO_2 passes through a filter (2) to remove any particulate matter before entering two ISCO syringe pumps (3). The syringe pumps operate in tandem to provide a continuous supply of pressurized CO_2 to the extraction system. Pump A, the primary pump, pressurizes the CO_2 until it needs to be refilled. While Pump A refills, drawing more CO_2 from the cylinder, the secondary pump (Pump B) pressurizes the CO_2. As soon as Pump A is refilled, it again takes over for Pump B. Each of the syringe pumps has a cooling jacket that is fed with a chilled mixture of anti-freeze and water by means of a refrigerated circulator set to 2 °C (not shown), ensuring that the CO_2 remains in a liquid state. Pressurized CO_2 then passes through the inlet valve (4) and a check valve (5; which prevents backflow from the extraction vessel to the pumps) before entering a preheating coil (6) submerged in a circulating water bath (19) set to the desired experimental temperature. A pressure relief valve (7) set to a pressure of approximately 27.6 MPa is situated at a union tee after the preheating coils.

Pressurized CO_2 then enters a 300 mL stainless steel extraction vessel (9). The vessel is equipped with a heating jacket, connected to the circulating water bath (19) in order to maintain the desired experimental temperature. Mixing inside the vessel is conducted by a helical impeller (10) operated by a MagneDrive® motor (11) and controller. The pressure and temperature of the system are measured using a pressure transducer (8) connected to the system just prior to the vessel, and a thermistor probe (12) contained within a stainless steel thermowell in the vessel lid. The pressure and temperature of the system, as well as the pressure of the pumps and flow rate of CO_2 exiting the pumps, are recorded using LabVIEW™ data acquisition software (20).



1. CO$_2$ cylinder
2. Filter
3. ISCO syringe pumps
4. Two way ball valve
5. Check valve
6. Preheating coil
7. Pressure relief valve
8. Pressure transducer
9. Extraction vessel
10. Helical impeller
11. MagneDrive® mixer
12. Thermistor probe
13. Microlab® pump for toluene rinse
14. Toluene reservoir
15. Metering valve
16. Collection vials/jars *a* and *b* in acetone/dry ice bath
17. Carryover (c/o) vial/jar at ambient conditions
18. CO$_2$ vent to fumehood
19. Circulating/hot water bath
20. Data acquisition system
21. Gilson pump for modifier addition
22. Modifier reservoir

Figure 8. Bench-scale supercritical fluid extraction system.

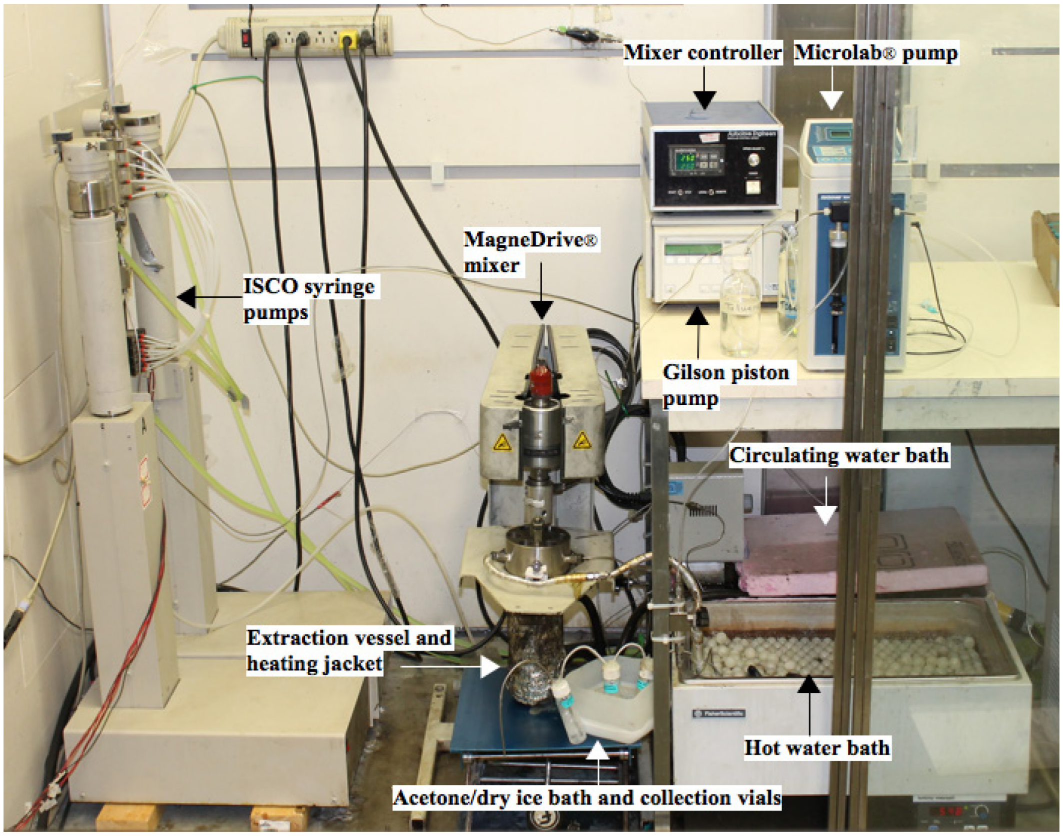


Figure 9. Laboratory bench-scale supercritical fluid extraction system.

The CO_2 flow exiting the extraction vessel is manually controlled using a metering valve (15) submerged in a second hot water bath (19) set to 60 °C. A Microlab® pump (13) is connected to the system in order to rinse the outlet lines with toluene (14). The rinse line is connected to the system at a union tee between the outlet valve (4) and heated metering valve.

For dynamic extractions with modified CO_2, a Gilson piston pump (21) is used to continuously add the modifier (22) into the pressurized CO_2 at a union tee just prior to the preheating coil.

Stainless steel tubing with an outer diameter (OD) of 1/16” is used for all of the lines up to and shortly after the pressure transducer union tee, and all lines thereafter use tubing with an OD of 1/8”.

Further details on some specific components of the SFE system are provided in the following sub-sections.

Table 10. SFE system components, their suppliers and pressure ratings (if applicable).

SFE Components	Supplier	Pressure Rating (MPa)
CO_2 cylinder	Praxair (Edmonton, AB)	-
Filter	Swagelok (Edmonton, AB)	-
ISCO syringe pumps (Model 500D) with controller	Teledyne ISCO (Lincoln, NE)	25.9
Isotemp 3013 refrigerated circulator	Fisher Scientific (Fair Lawn, NJ)	-
Stainless steel tubing, 1/16" OD and 0.020" wall thickness	Swagelok (Edmonton, AB)	82.7
Two-way ball valve (SS-4SKPS4)	Swagelok (Edmonton, AB)	41.4
Check valve (SS-CHS2-1/3)	Swagelok (Edmonton, AB)	41.4
305 Gilson Piston pump (25-SC pump head)	Mandel Scientific Company Inc. (Guelph, ON)	28
Pressure relief valve (Model SS-4R3A with spring R3A-F)	Swagelok (Edmonton, AB)	27.6
Pressure Transducer (Custom)	Omegadyne Inc. (Sunbury, OH)	34.5
Stainless steel tubing, 1/8" OD and 0.028" wall thickness	Swagelok (Edmonton, AB)	58.6
Stainless steel extraction vessel, 300 mL	Autoclave Engineers (Erie, PA)	37.9
MagneDrive® mixer (II, Series 0.75)	Autoclave Engineers (Erie, PA)	37.9
Helical Impeller	Custom-made	-
Thermistor probe (YSI 406)	Labcor Technical Sales Inc. (Anjou, QC)	-
Needle metering valve (Model SS-31RS4)	Swagelok (Edmonton, AB)	34.4
Isotemp 2100 immersion circulator (circulating water bath)	Fisher Scientific (Fair Lawn, NJ)	-
Isotemp hot water bath	Fisher Scientific (Fair Lawn, NJ)	-
Microlab® 500 series pump	Hamilton (Reno, NV)	-

3.3.1 Extraction Vessel, MagneDrive® Mixer and Helical Impeller

The stainless steel extraction vessel has a maximum volume of 300 mL. However once the stainless steel sleeve is placed inside the vessel to protect the inlet line from the helical impeller, the available volume of the vessel decreases to approximately 205 mL. Figure 10 shows a cross-section of the vessel (without the sleeve). The heating jacket that surrounds to vessel in order to maintain the desired extraction temperature is also not shown.

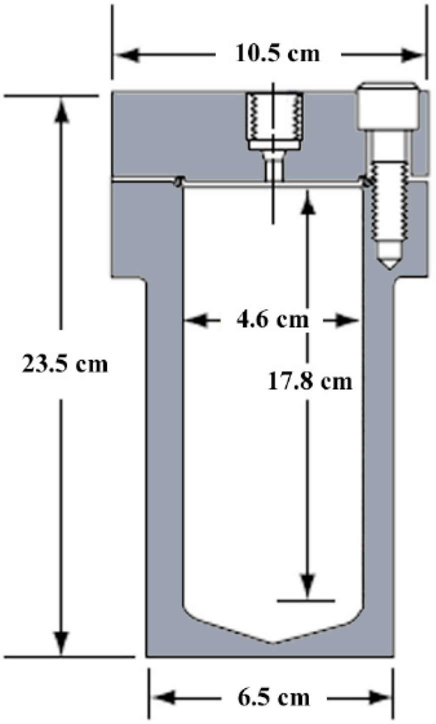


Figure 10. Cross-sectional view of the 300 mL extraction vessel (modified from Autoclave Engineers 2002).

A top view of the vessel lid is shown in Figure 11. In order to create a pressure seal between the vessel and the lid, a Teflon o-ring is placed around the opening of the vessel. The vessel and lid are then bolted together using a maximum torque of 50 ft-lb. The vessel lid contains a thermowell for the thermistor probe, and ports for the inlet and outlet lines. Other connections are also available, however they are not used in these SFE experiments and thus they have been sealed off.

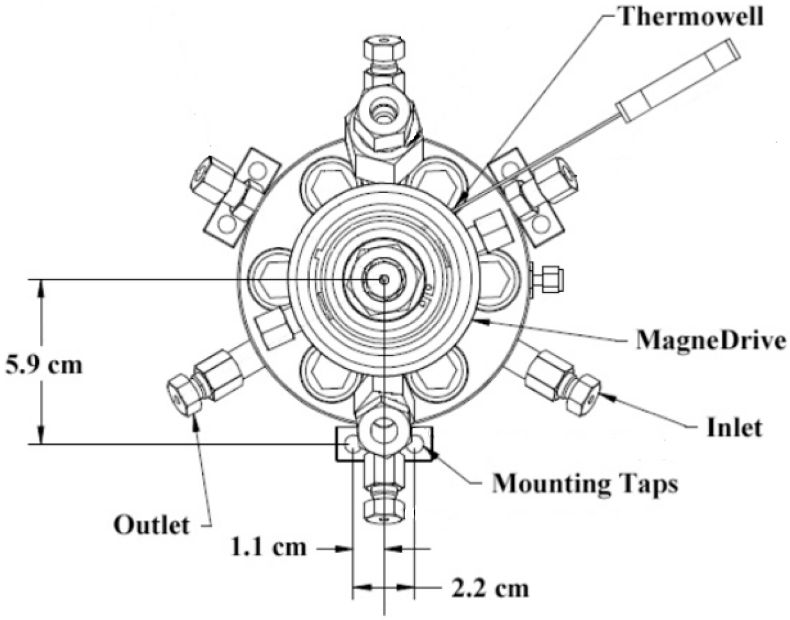


Figure 11. Top view of the extraction vessel lid depicting various parts and connections including the thermowell, and the inlet and outlet ports (modified from Autoclave Engineers 2002).

A stainless steel helical impeller (Figure 12) is used to thoroughly mix the viscous feed material with the SC-CO_2. A controller operates a MagneDrive® motor connected to a rubber chain. The rubber chain drives two rotating magnets contained within a shaft, which in turn drive the impeller. The rotating magnets are external to the vessel in order to maintain the pressure seal between the vessel and the vessel lid. The extraction vessel assembly, including the vessel, the vessel lid and MagneDrive® mixer, is shown in Figure 13.

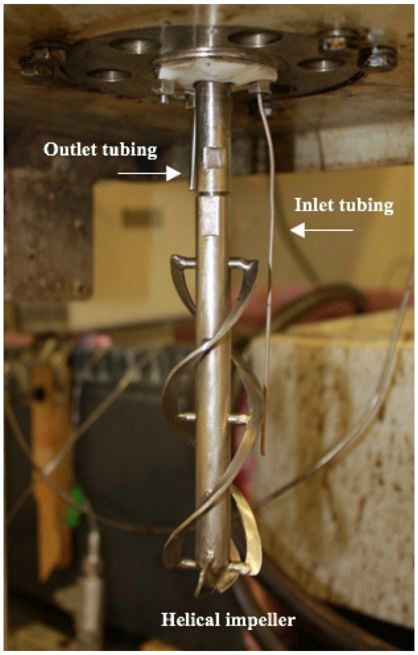


Figure 12. The helical impeller, and SC-CO_2/modifier inlet and outlet tubing.

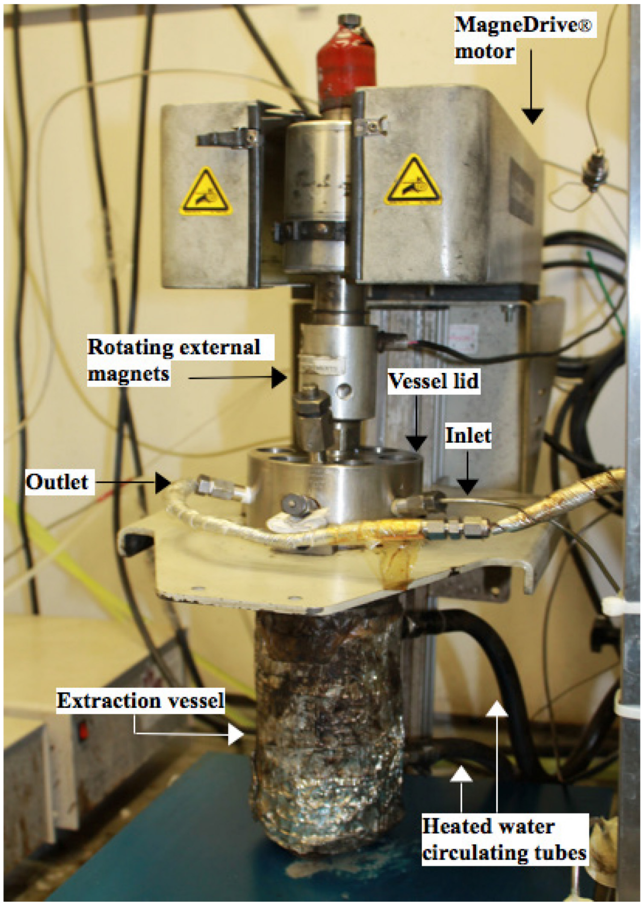


Figure 13. The extraction vessel and lid, and the MagneDrive® mixer.

3.3.2 Modifier Addition Apparatus

A 305 Gilson piston pump and 25-SC pump head are used for modifier addition. When the pump is operating, the modifier, contained within a sealed glass jar, is fed through Teflon tubing into the pump head inlet. After passing through the pump head outlet, the modifier enters the SFE system via 1/16" OD stainless steel tubing. The pump head has inlet and outlet check valves capable of handling a backpressure of up to 28 MPa, in case of CO_2 backflow from the SFE system.

Figure 14 shows a front view of the 305 Gilson piston pump and the 25-SC pump head, as well as the modifier feed jar. The required modifier flow rate is set using the keypad located on the front panel of the piston pump. The flow of the modifier is then controlled using the *Run* or *Stop* buttons under the front panel display.

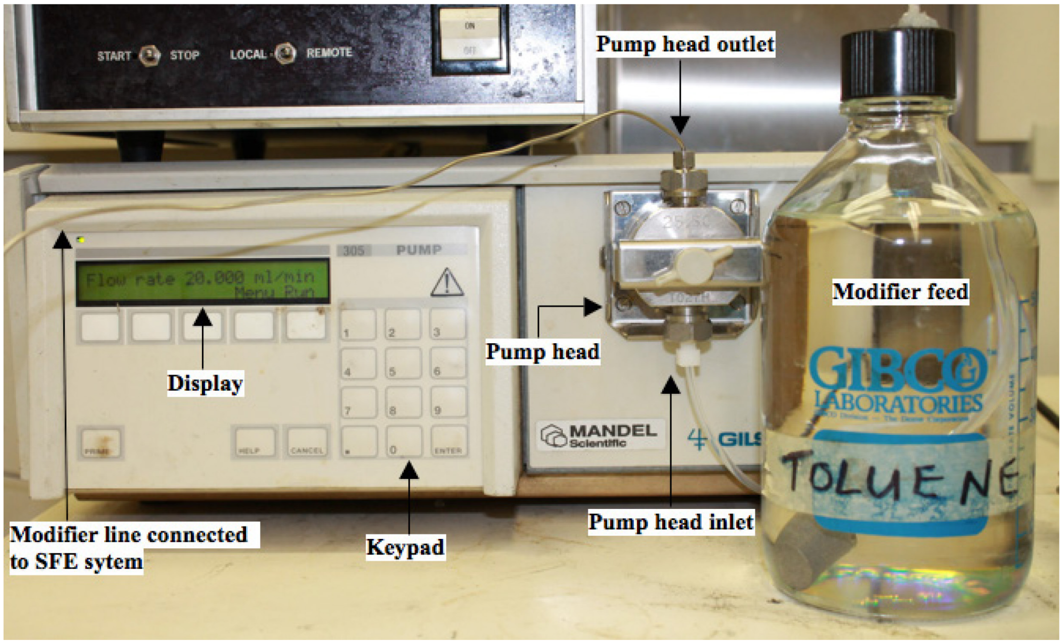
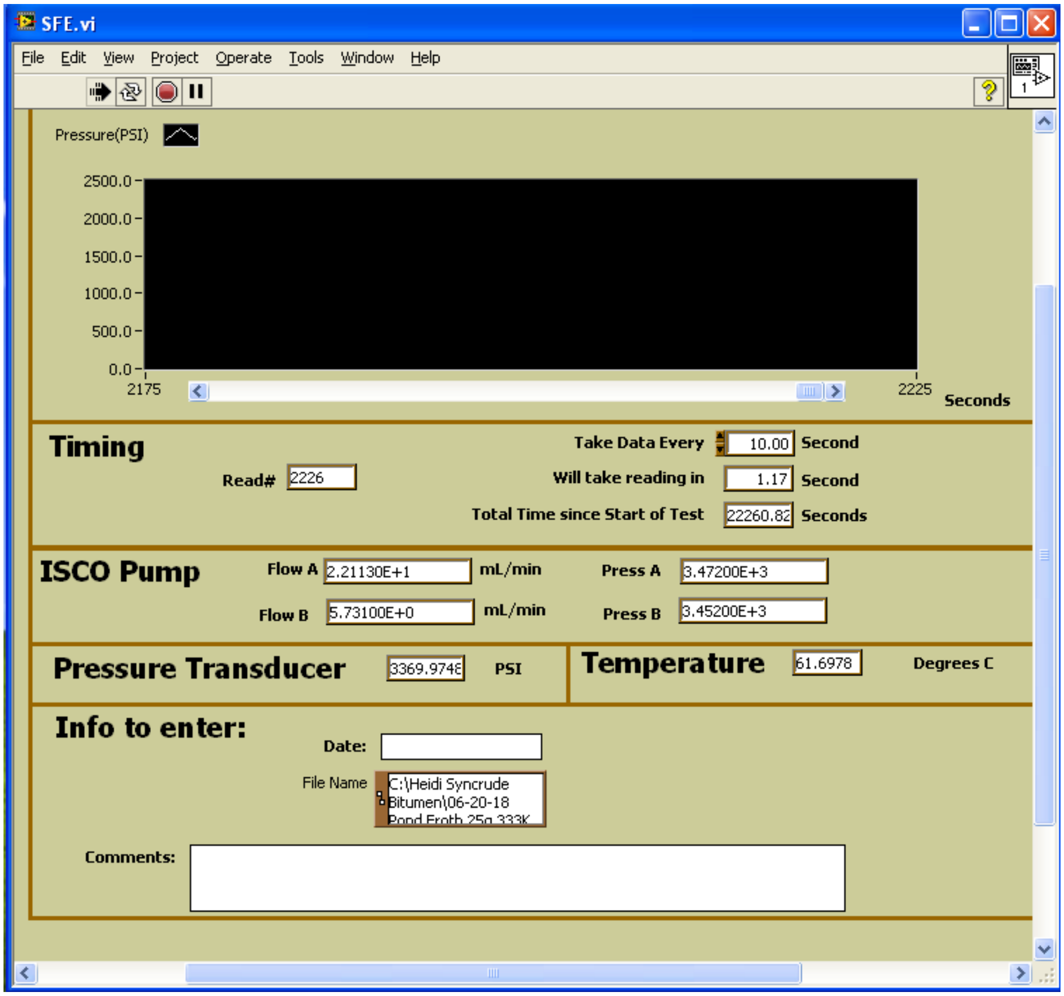


Figure 14. Front view of the 305 Gilson piston pump and 25-SC pump head.

3.3.3 LabVIEW™ Data Collection

Throughout the extraction, LabVIEW™ software is used to record the experimental pressure and temperature as measured by the pressure transducer and thermistor probe, respectively. LabVIEW™ also records the syringe pumps' pressures and the CO_2 flow rate from the pumps (as measured by the ISCO pump controller). An example of the LabVIEW™ computer display is shown in Figure 15. A sample of the LabVIEW™ output data is provided in Appendix B.



Timing

Read# 2226

Take Data Every 10.00 Second

Will take reading in 1.17 Second

Total Time since Start of Test 22260.82 Seconds

ISCO Pump

Flow A 2.21130E+1 mL/min

Press A 3.47200E+3

Flow B 5.73100E+0 mL/min

Press B 3.45200E+3

Pressure Transducer 3369.9748 PSI

Temperature 61.6978 Degrees C

Info to enter:

Date:

File Name C:\Heidi Syncrude Bitumen\06-20-18 Pond Froth 25g 333K

Comments:

Figure 15. LabVIEW™ computer display showing pressure, temperature and flow rate of the extraction.

3.4 Experimental Conditions and Procedures

3.4.1 Dynamic Extraction Conditions

Several dynamic extraction conditions were selected based on previous work. A CO_2 flow rate of 20 mL/min (measured at the pump conditions; experimental pressure of 24 MPa and approximately 2 °C or 275 K) and a total dynamic extraction time of 120 minutes were selected for all dynamic extractions, both of which were based on previous bitumen dynamic extractions performed by the SFE research group, some of which is published (Guigard et al. 2017).

A pressure of 24 MPa (3480 psi), the highest pressure rating of the SFE system, and a temperature of 333 K (60 °C) were also chosen based on the work of Fang (2010), La (2011) and other unpublished data. These previous works demonstrated that these high pressure and high temperature conditions produced high (if not the highest) hydrocarbon extraction efficiencies and initial solubilities of hydrocarbons in SC-CO_2, despite a lower SC-CO_2 density than similar high pressure and low temperature conditions. All dynamic extractions were therefore conducted at fixed pressure and temperature conditions of 24 MPa (3480 psi) and 333 K (60 °C), and thus a SC-CO_2 density of 0.78 g/mL (NIST 2017).

Based on the work of La (2011), a mixing speed of 250 rpm was used for the dynamics extractions. La (2011) investigated mixing speeds of 50, 150 and 250 rpm on hydrocarbon extraction from 1:1 oil sands slurries and found that a mixing speed of 250 rpm contributed most significantly to higher hydrocarbon extraction efficiencies.

Static periods, prior to dynamic extraction periods, allow time for mixing and time for hydrocarbons to dissolve into the SC-CO_2. The duration of these static periods was selected based on the work of Fang (2010). Fang examined the effects of two static periods: 60 versus 90 minutes, on the extraction of hydrocarbons from oil sands and found that the 90-minute static period did not improve extraction efficiencies. Thus, 60-minute static periods were chosen for this work.

Toluene and methanol were chosen as modifiers based on their success in improving hydrocarbon solubility in SC-CO_2 (unpublished data). Further, toluene has been found to be highly effective in improving the extraction of hydrocarbons from bitumen and similar matrices (Guigard et al. 2017; Magomedov et al. 2017; Rudyk et al. 2017; La and Guigard 2015; Al-Sabawi et al. 2011; Al-Marzouqi et al. 2009). Methanol was chosen because of its high polarity and because it has been also shown to improve the extraction of hydrocarbons from bitumen and similar matrices (Rudyk et al. 2014; Rudyk et al. 2013; Al-Sabawi et al. 2011; Hwang and Ortiz 2000).

3.4.2 Dynamic Extractions of Bitumen

Bitumen dynamic extractions were conducted using 10 g of bitumen to test eight extraction conditions:

- SC-CO_2 only
- Toluene addition (at 5, 10 and 15 mol% of SC-CO_2)
- Methanol addition (at 5, 10, 15 and 33.7 mol% of SC-CO_2)

The purpose of these extractions was to determine the effects of modifier type and concentration on hydrocarbon extraction efficiency and the type of hydrocarbons extracted. The additional condition, 33.7 mol% methanol, was tested in duplicate to determine if the distinction between mole and mass percent when expressing modifier concentration was important when comparing the effects of toluene versus methanol. The addition of 33.7 mol% (or 26.98 wt%) methanol is equivalent to 15 mol% toluene in terms of mass percent in SC-CO_2. All conditions, except for 33.7 mol% methanol, were tested in triplicate which resulted in a total of 23 dynamic extractions with bitumen as the feed material.

3.4.3 Dynamic Extractions of FT Froth and Pond Froth

A second set of dynamic extractions was conducted on FT Froth and Pond Froth to determine the effects of matrix components (water and solids) on hydrocarbon extraction efficiency. Both feed materials were tested at three extraction conditions:

- SC-CO_2 only
- Toluene addition (15 mol% of SC-CO_2)
- Methanol addition (33.7 mol% of SC-CO_2)

Given the success of the bitumen dynamic extractions, it was decided that triplicate runs were not necessary. All conditions were tested in duplicate, except for 33.7 mol% methanol which was tested only once on each of the two feed materials. Toluene addition at 15 mol% was chosen because it was the most successful condition from the bitumen dynamic extractions. Initially, 50 g of FT Froth was added to the vessel. However, to avoid sample carryover and to allow for comparison to bitumen dynamic extractions based on the cumulative CO_2 to initial bitumen ratio, 25 g of feed material was added in all subsequent FT Froth and Pond Froth dynamic extractions (and the two 50 g FT Froth dynamic extractions were repeated using 25 g of feed material).

The additional condition, 33.7 mol% methanol in SC-CO_2, was tested on both FT Froth and Pond Froth to determine the effects of methanol on the extraction of hydrocarbons from these two feed materials. Given that toluene was the more successful modifier in dynamic extractions of bitumen, these experiments were performed only once. A total of 12 dynamic extractions were conducted on FT Froth (seven) and Pond Froth (five).

3.4.4 Dynamic Extraction Procedure

Appendix C details the dynamic extraction procedure using SC-CO_2 alone and modified SC-CO_2. A brief description of the procedure is provided here. Sample spreadsheets illustrating the results of a bitumen dynamic extraction and an FT Froth dynamic extraction are provided in Appendices D1 and D2, respectively.

The refrigerated circulator (set to 2°C) was turned on, and the circulating water bath and hot water bath were set to 66 and 60 °C, respectively. Setting the circulating water bath to 66 °C ensured the vessel would reach 60 °C (due to heat transfer loss between the bath and vessel). The temperature of the circulating water bath was adjusted as necessary throughout the duration of the dynamic extraction to ensure the vessel remained at 60°C. A 10, 25 or 50 g sample of feed material was weighed on an analytical balance (Mettler Toledo AX205 DeltaRange®) and placed in the extraction vessel. A time zero sample (approximately 10 g for bitumen and 25 g for FT Froth and Pond Froth) of the initial feed material was also collected. The Teflon o-ring was put in place on top of the vessel and the vessel was then bolted closed according to the manufacturer's suggested procedure.

As soon as the vessel reached 45 °C, the ISCO syringe pumps (set to 24 MPa or 3480 psi) were turned on (in continuous constant pressure mode) and the inlet valve was opened to pressurize the vessel. For extractions with modified SC-CO_2, the Gilson piston pump valve (a two-way ball valve) was immediately opened and the piston pump was run for one minute to allow a predetermined volume of modifier to enter the vessel while it pressurized. The volume of modifier added during pressurization for each extraction condition is displayed in Table 11. After the required volume of modifier had been added, the Gilson piston pump valve was closed. The MagneDrive® mixer was then turned on and set to 250 rpm and the stopwatch was started for the 60-minute static period.

Table 11. Volume and flow rate of modifier required for each extraction condition.

Feed Material	**Modifier**	**Concentration** (mol %)	**Volume of modifier added during pressurization** (mL)	**Flow rate of modifier during extraction** (mL/min)
Bitumen	Toluene	5	19.3	2.61
		10	33.6	5.52
		15	48.6	8.76
	Methanol	5	14.4	2.10
		10	21.9	3.34
		15	7.35	0.99
		33.7	52.0	9.62
FT Froth	Toluene	15	45.0	8.76
	Methanol	33.7	48.2	9.62
Pond Froth	Toluene	15	44.9	8.76
	Methanol	33.7	48.1	9.62

After the static period, three pre-weighed collection vials or jars were secured to the system: a primary vial/jar (denoted as *a*), a secondary vial/jar (denoted as *b*) and a carryover vial/jar (denoted as *c/o*). Vials (40 mL) were used for all dynamic extractions with SC-CO_2 only or 5 mol% modifier addition to SC-CO_2. Jars (120 mL) were used for all dynamic extractions with 10, 15 or 33.7 mol% modifier addition to SC-CO_2, to accommodate the larger volume of hydrocarbons and modifier exiting the system. The vials/jars *a* and *b* were immersed in an acetone/dry ice bath in order to rapidly condense the extracted hydrocarbons, minimizing the volatilization of hydrocarbon compounds. Vial/jar *a* contained glass beads, providing surface area for hydrocarbon collection. Vial/jar *b* contained approximately 20 mL of toluene, acting as a solvent to trap the extracted hydrocarbons. The vial/jar *c/o*, served as a carryover vial/jar to trap any hydrocarbon still entrained in the CO_2 gas. Vial/jar *c/o* was maintained at ambient temperature and contained approximately 20 mL of toluene.

Once the vials/jars were in place, the dynamic extraction was initiated. The flow of CO_2 began by opening the outlet valve and carefully setting the metering valve to 20 ± 3 mL/min as measured by the ISCO syringe pumps. For extractions with modified SC-CO_2, the Gilson pump valve was opened and the required continuous flow of modifier into the vessel was started. The flow rate of modifier entering the vessel for each extraction condition is displayed in Table 11. SC-CO_2 (or modified SC-CO_2) continuously entered the extraction vessel through an inlet tube near the bottom of the vessel. The CO_2-hydrocarbon mixture (or CO_2-hydrocarbon-modifier mixture) exited the extraction vessel through an outlet at the top of the vessel. Upon exiting the metering valve, rapid cooling and depressurization occurred, causing the CO_2 to vaporize. The rapid cooling and depressurization allowed the hydrocarbons to separate from the CO_2 and collect in one of the three collection vials/jars. Any modifier exiting the system was also collected in the collection vials/jars. CO_2 gas exiting the system was vented to the fumehood.

The *a* and *b* vials/jars were changed every 5 minutes for the first 15 minutes of the dynamic extraction, and then every 15 minutes for the last 30 minutes of Set 1. Set 1 was a total of 45 minutes. At the end of each 5 or 15 minute period, the outlet valve was shut, the Gilson piston pump was stopped (for modified SC-CO_2) and the vials/jars were exchanged. To begin the next 5 or 15 minute period, the outlet valve was opened and the Gilson piston pump was started (for chemically modified SC-CO_2). After the completion of Set 1, the outlet, metering and Gilson piston pump valves (for chemically modified SC-

CO_2) were closed and the collection vials/jars were detached from the SFE system. The Microlab® pump valve was opened and toluene was rinsed through the outlet line to clean it. The Microlab® pump valve was then closed and a second 60-minute static period was initiated.

After the second static period was complete, Set 2 was started. The procedure for Set 2 was identical to Set 1 except that the vials/jars were exchanged every 15 minutes for a total of 75 minutes. At the end of Set 2 and after the toluene rinse, the inlet valve was closed, the ISCO syringe pumps and MagneDrive® mixer were turned off, and the vessel was slowly depressurized overnight. Following depressurization, the vessel was unbolted and the residue remaining in the vessel (vessel residue) was collected by rinsing it into a 250 mL jar with toluene, at which point it was referred to as vessel residue solution.

After the extraction, the collection vials/jars were dried in a fumehood using a drying apparatus to evaporate any extracted water, toluene and any other modifier collected in the vials/jars along with the hydrocarbon extracts. The drying apparatus blew a stream of air into the top of each vial or jar, speeding up the evaporation process. Extracts from dynamic extractions of bitumen were dried for two days – sufficient time to evaporate both toluene and methanol. Extracts from dynamic extractions of FT Froth and Pond Froth were dried for five days – sufficient time to evaporate any water (and toluene and methanol) collected along with the hydrocarbons.

Drying times were determined based on preliminary tests that measured the masses of extracts from dynamic extractions of waste streams. The masses of the extracts were measured every day for seven days during drying. It was found that the masses plateaued after five days and thus, this was considered sufficient time to evaporate any water that was collected along with the extract.

The cumulative mass of hydrocarbons extracted was obtained using the mass of hydrocarbon extract remaining in the vials/jars after two or five days of drying, depending on the type of feed material.

3.4.5 Dean-Stark Extraction

Dean-Stark extractions were performed by Syncrude and the results were used to determine the mass of hydrocarbons, water and solids in the vessel residue after each dynamic extraction. This data was used as a second measure of the hydrocarbon extraction efficiency and was used to perform an overall mass balance check on the recovery of hydrocarbons. Dean-Stark extractions were conducted using a modified version of the procedure described in Syncrude Analytical Method 2.9: *"Determination of Bitumen, Water and Solids Content of Froth (Classical)"* (Starr and Bulmer 1979), summarized below. A more detailed description of the Dean-Stark extraction process is available in Appendix E.

Three Kimwipes® (Kimberly-Clark) were placed in a 43 x 123 mm Whatman® cellulose thimble and dried for one hour at 120 °C in a weighing bottle. After recording the weight of the weighing bottle and its contents, the Kimwipes® were removed. The thimble was placed in its wire support basket and mounted in the neck of the kettle. The contents of the vessel residue solution jar were poured into the thimble, and the jar was rinsed with toluene and wiped clean with the three Kimwipes®. The Kimwipes® were then placed in the thimble. The kettle was filled with toluene to a final volume of approximately 200 mL and the solvent distribution screen was placed on top of the thimble for even distribution of toluene during the extraction. The rest of the apparatus (adapter, water trap and condenser) was then assembled.

Heat was applied to the system and the extraction process commenced. Reflux was continued for 30 minutes after no water was visible in the apparatus (except the water trap) and the toluene dripping from the thimble was colorless. To determine the water content of the original solution, the water trap and its contents were cooled to room temperature and the volume of water in the trap was estimated to the nearest 0.05 mL. The apparatus was then disassembled, and the thimble was removed from its wire support basket and returned it to its original weighing jar. After drying the weighing jar and its contents for three hours at 120 °C, the final solids content of the original solution could be determined through subtraction. To determine the hydrocarbon content, the bitumen/toluene solution in the kettle was separated using a Rotary Evaporator (Rotavap). The empty evaporation flask was weighed before the contents of the kettle were poured into the flask. The flask was then placed in the water bath, allowing the toluene to evaporate and separate into the receiving flask. The final mass of the evaporation flask and its contents (hydrocarbons) were weighed and the hydrocarbon content of the original vessel residue solution was determined through subtraction.

3.4.6 High Temperature Simulated Distillation

For each dynamic extraction, air-dried hydrocarbon extracts collected in vials/jars *a*, time zero samples of the initial feed materials and vessel residue hydrocarbons (obtained using Dean-Stark extraction) were analyzed using HTSD to indicate the type of hydrocarbons extracted. HTSD analyses of samples were performed by Syncrude and were used to determine the mass percent of hydrocarbon extract or residue that distilled at or below a given temperature. Higher distillation temperatures indicated a heavier extract or residue. HTSD was conducted using a method equivalent to ASTM D7169: *Standard Test Method for Boiling Point Distribution of Samples with Residues Such as Crude Oils and Atmospheric and Vacuum Residues by High Temperature Gas Chromatography* (ASTM International 2011), summarized below. A more detailed description of the HTSD process is provided in Appendix F.

The HTSD process used a Gas Chromatograph (GC) with a Flame Ionization Detector (FID). The MXT-1HT SimDist column (Restek, Bellefonte, PA) in the GC had an inner diameter of 0.5 mm that was coated with a 100% bonded polydimethylsiloxane film (stationary phase), 0.09 to 0.17 μm in thickness. Helium was used as the carrier gas. The FID converted the mass of the compounds leaving the column to an electrical signal. A data acquisition system operating in slice mode (with a time interval of 0.1 s) and chromatography software were used to accumulate the electronic signal.

Carbon disulfide, CS_2, was used as the solvent and was injected into the system to establish a blank (baseline) signal, which was later subtracted from the response factor and sample chromatograms. A retention calibration mixture made up of Polywax and paraffins was used to develop a boiling point versus retention time curve. Using the mixture of Polywax and paraffins, the system was calibrated for C_5 to C_{110} and could therefore analyze samples with a boiling point range from 40 to 735 °C. A solution of Reference Oil 5010, which fully eluted from the column under these conditions, was used to determine the response factor.

A 2 mL aliquot of sample solution was then injected into the GC and, using the response factor and area from the sample chromatograph, the percent of sample recovered was calculated for each time interval. The retention time corresponding to 0.5, 1, 2 … % recovery was determined and then converted to a boiling point using the boiling point versus retention time curve. This process was repeated for each sample. HTSD curves were obtained by graphing the cumulative percent recoveries against the corresponding boiling points for each sample.

3.5 Determination of Hydrocarbon Extraction Efficiency

The hydrocarbon extraction efficiency refers to the cumulative mass percentage of hydrocarbons extracted from the bitumen. Extraction efficiency can be calculated in one of two ways: using the mass of air-dried hydrocarbon extracts collected in the collection vials/jars during the dynamic extraction periods (Equation 1) or using the mass of hydrocarbons in the vessel residue as determined by Dean-Stark extraction (Equation 2).

$$Extraction\ efficiency = \frac{\Sigma_{vials/jars}(M_{sample\ collected})}{M_{bitumen\ in\ vessel}}\ x\ 100\% \qquad (1)$$

$$Extraction\ efficiency = \frac{M_{bitumen\ in\ vessel} - M_{hydrocarbons\ in\ vessel\ residue}}{M_{bitumen\ in\ vessel}}\ x\ 100\% \qquad (2)$$

Both equations use the mass of bitumen originally placed in the vessel (ie. $M_{\text{bitumen in vessel}}$). For FT Froth and Pond Froth dynamic extractions, this value was calculated using mass of feed material placed in the vessel and the applicable bitumen content reported in Table 8. For each dynamic extraction, the numerator in equation 1 was calculated by summing the values in the ‘Mass of sample collected' column (as shown in Tables D1b and D2b in Appendices D1 and D2) for vials/jars $1a$ to 14. The 'Mass of sample collected' is the difference between the mass of the air-dried hydrocarbons in the vial/jar and the initial mass of the vial/jar.

A mass balance check was also performed on the hydrocarbons from each dynamic extraction, as shown in Equation 3.

$$Mass\ balance = \frac{\Sigma_{vials/jars}(M_{sample\ collected}) + M_{hydrocarbons\ in\ vessel\ residue}}{M_{bitumen\ in\ vessel}}\ x\ 100\% \qquad (3)$$

The numerator in equation 3 was calculated by summing the values in the 'Mass of sample collected' column (as shown in Tables D1b and D2b in Appendices D1 and D2) for vials/jars $1a$ to 18 and the mass of hydrocarbons in the vessel residue.

CHAPTER 4 Results and Discussion

This chapter details the results of 35 dynamic extractions performed as part of this thesis research. The results of bitumen dynamic extractions are first discussed in Section 4.1 – both the extraction efficiencies and the types of hydrocarbons extracted are presented and discussed. The extraction efficiencies from the dynamic extractions of FT Froth and Pond Froth are discussed in Section 4.2. The HTSD results for FT Froth and Pond Froth extractions were not available at the time this thesis was submitted and thus the results and discussion of the type of hydrocarbons extracted from these two feed materials is not included.

4.1 Dynamic Extractions of Bitumen

Dynamic extractions of bitumen were conducted in order to determine the effects of modifier addition on the extraction of hydrocarbons. The effects of two modifiers (toluene and methanol) at concentrations of 5, 10 and 15 mol% in SC-CO_2 were examined. The effects of methanol were also examined at a concentration of 33.7 mol% in SC-CO_2. All dynamic extractions were conducted at 24 MPa and 333 K, and at a CO_2 flow rate of 20 mL/min (measured at pump conditions of 24 MPa and 275 K).

4.1.1 Dynamic Extractions with SC-CO_2 only

4.1.1.1 Hydrocarbon Extraction Efficiencies

Dynamic extractions using SC-CO_2 were conducted in triplicate in order to develop a baseline for the extraction of hydrocarbons from bitumen. Table 12 displays the extraction efficiencies and mass balance results for these three dynamic extractions. A discussion of the mass balance results is provided in Section 4.1.4.

Table 12. Extraction efficiencies and mass balance results for dynamic extractions of bitumen using SC-CO_2.

Date	*Initial bitumen in vessel* (g)	*Cumulative mass of hydrocarbon extracts* (g)	*Mass of hydrocarbons in vessel residue* (g)	**Extraction Efficiency** (wt%)						**Mass Balance** [3] (wt%)
				Based on extracts [1]			*Based on residue* [2]			
				Replicate	*Average*	*SD* [4]	*Replicate*	*Average*	*SD* [4]	
04-15-16 [5]	10.367	4.040	4.8992	39.0	39.2	0.445	52.7	47.6	4.82	86.5
05-02-16 [5]	10.856	4.313	5.7568	39.7			47.0			93.0
11-29-17	10.168	3.960	5.7774	39.0			43.2			96.2

[1] Calculated using Equation 1

[2] Calculated using Equation 2

[3] Calculated using Equation 3

[4] SD - standard deviation (n=3)

[5] Dynamic extraction conducted by Eleisha Underwood, a Research Associate in the SFE group

As described in Section 3.5, extraction efficiency can be calculated using the mass of hydrocarbon extracts collected during the dynamic extractions, or using the mass of hydrocarbons remaining in the vessel residue. Extraction efficiencies based on hydrocarbon extracts may be biased low, due to loss of light end hydrocarbons during the dynamic extraction and/or the drying period. They may also be biased high if the extracts still contain toluene after the drying period. Extraction efficiencies calculated using the hydrocarbon mass in the vessel residue may biased high due to loss of hydrocarbons during vessel residue collection and handling. It is difficult to completely recover all of the hydrocarbons remaining in the vessel after an extraction; some hydrocarbons adhere to the vessel walls and lid, as well as the helical impeller, and can be difficult to remove with toluene.

It can be seen in Table 12 that the standard deviation for extraction efficiencies calculated based on hydrocarbon extracts is smaller (0.445 wt%) than the standard deviation for extraction efficiencies calculated based on vessel residue (4.82 wt%). Vessel residue undergoes more handling and analyses than hydrocarbon extracts and as a result, the extraction efficiencies calculated based on vessel residue have more variability. All further discussions of the three SC-CO_2 only dynamic extractions will be based on the extraction efficiencies calculated using the hydrocarbon extracts collected in the vials.

SC-CO_2 is capable of extracting an average of 39.2 wt% of the bitumen at conditions of 24 MPa and 333 K. All three extraction efficiencies are in good agreement, with a low standard deviation of 0.445 wt%. However, it is likely that in all of the dynamic extractions, some of the light end hydrocarbons were lost as they exited the heated outlet tubing (though collection vials were submerged in an acetone/dry ice bath to prevent this) and/or during the two day drying period. If this were the case, the extraction efficiencies based on hydrocarbon extracts would be slightly underestimated.

Figure 16 illustrates the cumulative mass percent of hydrocarbons extracted as a function of the cumulative CO_2 to initial bitumen ratio for these three SC-CO_2 dynamic extractions. The cumulative CO_2 to initial bitumen ratio was calculated using the volume of CO_2 entering the SFE system (as recorded in LabVIEW™) during the 5 and 15 minute intervals of the dynamic extraction periods, the density of the CO_2 at the pump conditions and the initial mass of bitumen placed in the extraction vessel. Examples of the volumes of CO_2 entering the SFE system during the 5 and 15 minute extraction intervals can be seen in Tables D1b and D2b in Appendices D1 and D2, respectively.

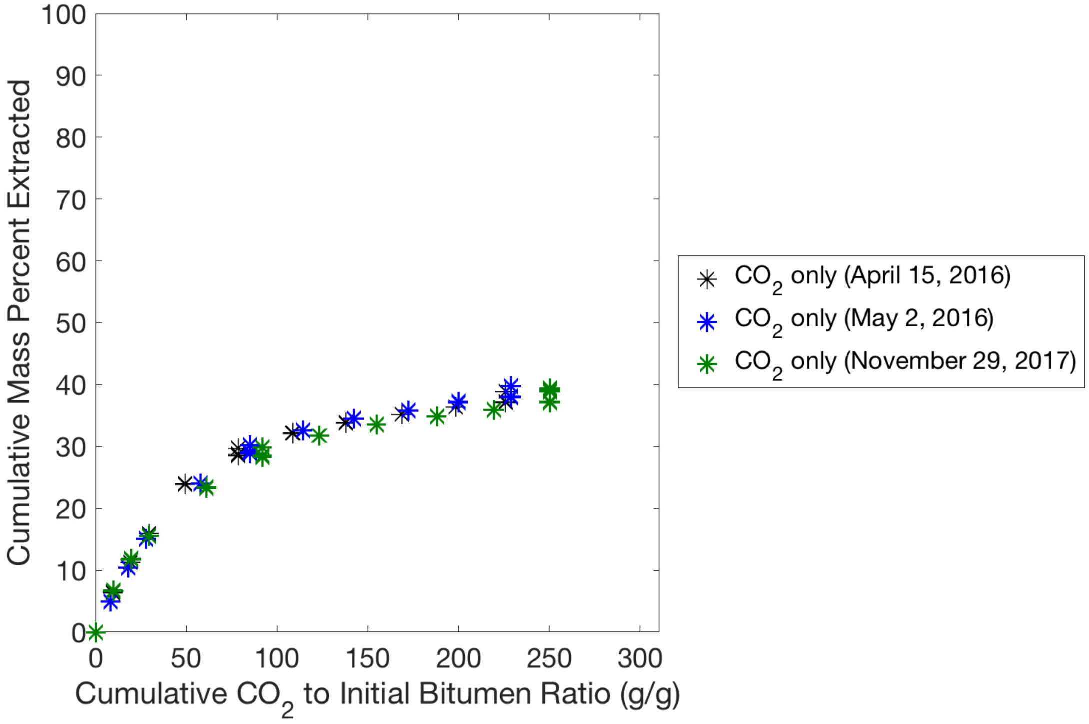


Figure 16. Cumulative mass percent of hydrocarbons extracted using SC-CO_2 at 333K, 24 MPa and a CO_2 flow rate of 20 mL/min.

Each of the extraction curves presented in this thesis were developed by plotting the cumulative mass of hydrocarbons collected in each of vials *a* and *b*, as well as the carryover and rinse vials from each of Sets 1 and 2. Because *b* vials typically contain very little mass, the data points representing the cumulative mass of hydrocarbons collected in vials *a* and *b* for a given CO_2 to initial bitumen ratio often overlap. Data points for the mass collected in the carryover (*c/o*) and rinse vials for each of the two sets were added to the cumulative mass of hydrocarbons extracted at the cumulative CO_2 to initial bitumen ratios corresponding to the end of each of Set 1 and Set 2. Thus the *c/o* and rinse vials from Set 1 (a total 45 minutes) are included in the cumulative mass of hydrocarbons extracted at a cumulative CO_2 to initial bitumen ratio of approximately 90 g/g, and the *c/o* and rinse vials from Set 2 (a total of 75 minutes) are included in the cumulative mass percent of hydrocarbons extracted at a ratio of approximately 250 g/g.

As the extraction proceeds, the cumulative mass percent of hydrocarbons extracted increases. At a cumulative CO_2 to initial bitumen ratio of approximately 250 g/g, 39 wt% of the initial bitumen has been extracted using SC-CO_2. At the end of Set 1 of the dynamic extraction (45 minutes, equivalent to a cumulative CO_2 to initial bitumen ratio of approximately 90 g/g), approximately 30 wt% of the hydrocarbons from the original bitumen are extracted, while the remaining 9 wt% of the hydrocarbons are extracted during Set 2 (75 minutes).

As illustrated in Figure 16, initially the slope of the curve is steep, and then it decreases, and remains relatively constant after a cumulative CO_2 to initial bitumen ratio of 100 g/g. The shape of the curve is dependent on a number of factors including mass transfer and solubility. During the first five to ten minutes of the dynamic extraction, as hydrocarbons are dissolving into the CO_2 rich phase and CO_2 is dissolving into the hydrocarbon rich phase, mass transfer likely controls the extraction of hydrocarbons. This assumption could be verified by collecting extracts for shorter time intervals during the first five to ten minutes of the dynamic extraction (as opposed to collecting extracts for five minute intervals). If shorter initial time intervals have an effect on the shape of the extraction curve, this would indicate that mass transfer is initially controlling the extraction.

Once time and contact are sufficient and mass transfer limitations are overcome, solubility controls the extraction. As the extraction proceeds, the solubility of the hydrocarbon mixture in SC-CO_2 is changing. Deo et al. (1993) found that supercritical propane initially extracted the lighter (more soluble) hydrocarbons, such as saturates, and progressively heavier (less soluble) hydrocarbons were extracted as the experiment continued – it is likely that this is also happening when SC-CO_2 is used as the solvent. The decreasing solubility of the remaining hydrocarbons in SC-CO_2 is reflected in the decreasing slope of the extraction curve as the extraction progresses. After the second static period, which occurs after a CO_2 to initial bitumen ratio of approximately 90 g/g, neither the mass of hydrocarbons extracted nor the slope abruptly increase – this is consistent with the system operating near equilibrium during this period. A significant increase in the mass of hydrocarbons extracted or the slope after the second static period would indicate that the system is operating far from equilibrium.

The slope of curve is low towards the end of the extraction. Though it does not appear that an exhaustive extraction was reached, it is unlikely that increasing the extraction time beyond 120 minutes would substantially increase the mass of hydrocarbons extracted. At this point in the extraction, the solubility of the remaining hydrocarbons is low and so it is unlikely that increasing the extraction time would substantially increase the extraction of these hydrocarbons.

The first two dynamic extractions were conducted in 2016 by Eleisha Underwood, a Research Associate in the SFE group. Unlike the dynamic extraction conducted in 2017, the two dynamic extractions conducted in 2016 did not have an initial 60-minute static period before the dynamic extraction – they only had a 60-minute static period between Sets 1 and 2 of the extraction. Despite this, the extraction efficiencies for all three dynamic extractions are similar, as are the shapes of the three extraction curves. This indicates that the system is able to quickly approach equilibrium with or without an initial static mixing period, suggesting that mass transfer limitations at the beginning of each dynamic extraction are likely minor.

4.1.1.2 Type of Hydrocarbons Extracted

After the dynamic extractions, select extract samples and the vessel residue were sent to Syncrude for HTSD analysis. Of the three SC-CO_2 dynamic extractions, only the November 29, 2017 extracts were sent to Syncrude for HTSD analysis. Figure 17 displays HTSD curves for the initial bitumen sample (time zero), the hydrocarbon extracts collected in *a* vials and the vessel residue from the November 29, 2017 extraction.

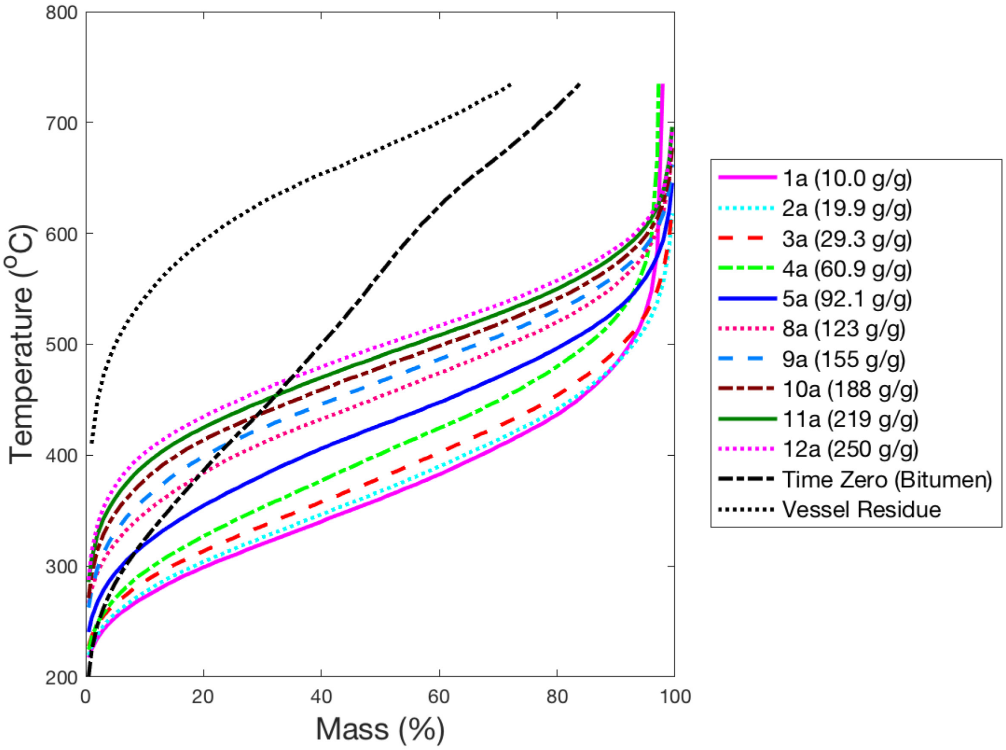


Figure 17. HTSD curves for hydrocarbon extracts and residue from dynamic extraction of bitumen with SC-CO_2 at 333K, 24 MPa and a CO_2 flow rate of 20 mL/min.

HTSD curves illustrate the mass percent of hydrocarbons extracted as a function of increasing distillation temperature – a higher distillation temperature indicates a heavier extract or residue. The initial bitumen sample (time zero sample) begins distilling at 200 °C and by 735 °C, approximately 81 wt% of the original bitumen has been distilled. The remaining 19 wt% of hydrocarbons have boiling points higher than 735 °C, the maximum temperature that can be achieved by the instrumentation. Sample 1*a*, collected during the first five minutes of the dynamic extraction, is primarily composed of the lightest hydrocarbons from the initial bitumen. As the extraction proceeds, slightly heavier hydrocarbons are extracted with sample 12*a* distilling between 300 and 700 °C. Less than 10 wt% of the vessel residue hydrocarbons distil below 500 °C and approximately 70 wt% of the residue distils before 735 °C. This indicates that the heaviest hydrocarbons are not extracted and are thus left behind in the vessel residue. SC-CO_2 alone readily extracts hydrocarbons that distil below 500 °C and a portion of the hydrocarbons that distil between 500 and 600 °C

In Figure 17, it appears that samples 1*a* and 4*a* are also composed of some heavy hydrocarbons that do not distil before 735 °C. This is likely an error as sample 12*a*, the heaviest sample, is completely distilled before 700 °C. Errors could be due to residue on the GC inlet or column from a previous analysis, contaminated carbon disulfide (CS_2) solvent, contamination during sample preparation, or carryover in the extraction vessel from a previous SFE experiment.

Figure 18 shows the extracts collected in the *a* vials from the May 2, 2016 dynamic extraction with SC-CO_2. Set 1 vials were collected during the first 45 minutes of the dynamic extraction, and following a static period, Set 2 vials were collected over a 75 minute period. The extracted hydrocarbons are light yellow in color, which is in contrast to the dark brown to black color of the bitumen placed in the vessel. Furthermore, the extracted hydrocarbons are less viscous than the original bitumen.

Figure 19 displays the vessel residue remaining on the helical impeller after the May 2, 2016 dynamic extraction with SC-CO_2. Some of the vessel residue is stuck to the impeller and the vessel lid. The vessel residue is dark brown to black in color, and is sticky and viscous.

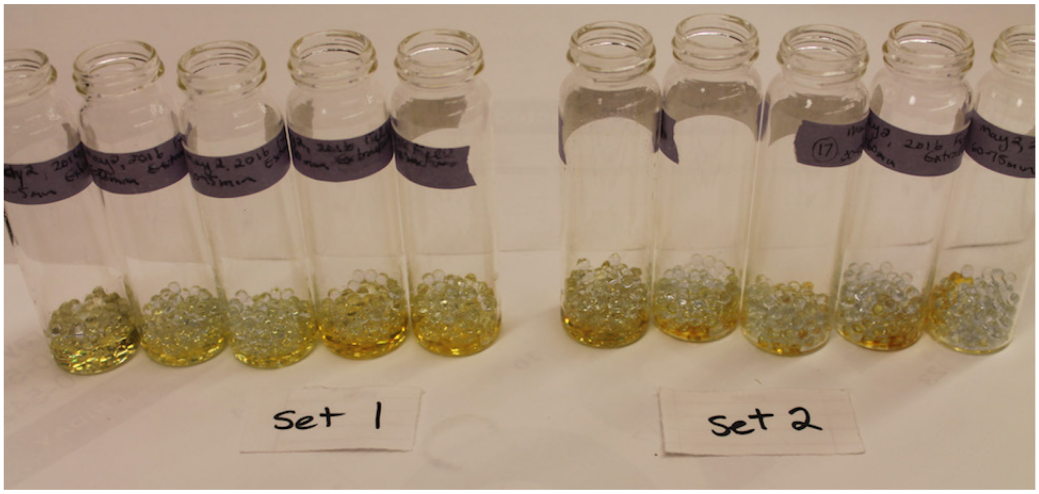


Figure 18. Extracts collected in *a* vials from a dynamic extraction of bitumen with SC-CO_2 (May 2, 2016 extraction).

Figure 19. Helical impeller after a dynamic extraction of bitumen with SC-CO_2 (May 2, 2016 extraction).

By comparing Figure 18 and Figure 19, it can be seen that the extract collected in the vials is lighter in color than the vessel residue (and the original bitumen). Based on HTSD analysis, the extracts collected using SC-CO_2 distil at lower temperatures compared to the vessel residue and the original bitumen, indicating that the hydrocarbons extracted using SC-CO_2 are upgraded compared to the original bitumen. This is consistent with the findings of Rudyk and Spirov (2014) who noted the bitumen upgrading potential of SC-CO_2. Rudyk and Spirov (2014) found that after SFE of bitumen with SC-CO_2, the extracted oil was upgraded compared to the original bitumen in that it did not contain solids or asphaltenes. According to Hwang and Ortiz (2000), the low polarity of SC-CO_2 limits the solubility of heavier bitumen components like asphaltenes in SC-CO_2

and therefore these heavier components are not extracted. The extracted oil is therefore partially upgraded. Saturate, Aromatic, Resin and Asphaltene (SARA) analysis of Syncrude bitumen (see Appendix A1) indicates that it is made up of 17.5 wt% asphaltenes. Though SARA analysis was not performed on the vessel residue, it is likely that the asphaltene content of the residue is substantially higher than 17.5 wt% (Deo et al. 1993) and that most, if not all, of the asphaltenes are contained within the vessel residue. Bitumen upgrading has also been noted in several other studies using supercritical propane, ethane and n-pentane (Al-Sabawi et al. 2011; Rose et al. 2001; Subramanian and Hanson 1998; Deo et al. 1993).

4.1.2 Effect of Modifier Addition to SC-CO_2

4.1.2.1 Hydrocarbon Extraction Efficiencies

To determine the effects of modifier addition on the extraction of hydrocarbons, two modifiers, toluene and methanol, were tested. Initially these modifiers were each tested (in triplicate) at a concentration of 5 mol% in SC-CO_2. The extraction efficiencies and mass balance results for these six dynamic extractions are presented in Table 13. The mass balance results are discussed in Section 4.1.4.

Toluene was selected as a modifier because it has been shown to be highly effective in improving the extraction of hydrocarbons from crude oil and similar matrices (Magomedov et al. 2017; Rudyk et al. 2017; La and Guigard 2015; Al-Sabawi et al. 2011; Al-Marzouqi et al. 2009). Toluene is known to be a particularly effective solvent for heavy bitumen components (Hwang and Oritz 2000); however toluene also extracts impurities, such as sulfur and nitrogen, associated with these heavier fractions (Al-Sabawi et al. 2011). The heavy fractions and sulfur content of the extracted oil would have to be reduced through upgrading before the oil could be sent to a conventional refinery, as they are only designed for light, sweet (sulfur-free) feedstock (Oil Sands Magazine 2017d).

Methanol was chosen as a second modifier because it is highly polar, with a polarity index of 5.1 (LSU n.d.). The addition of a modifier that is more polar than the SCF is thought to enhance the solubility of polar hydrocarbons (La and Guigard 2015; Al-Marzouqi et al. 2009; Hwang and Ortiz 2000). While toluene is more polar than CO_2, it has a polarity index of 2.4, which is much lower than that of methanol (LSU n.d.). Additionally, methanol is less expensive than an equivalent volume of toluene (Fisher Scientific n.d.).

For the extraction conditions used in this work, it is assumed that during dynamic extractions with modified SC-CO_2, the CO_2/modifier mixture acts as a single homogenous phase into which hydrocarbons dissolve. This is based on estimated critical points for binary mixtures of CO_2 and toluene reported in Wu et al. (2006) and Ziegler et al. (1995), and on estimated critical points for binary mixtures of CO_2 and methanol reported in Yeo et al. (2000).

As seen in Table 13, for bitumen dynamic extractions with 5 mol% toluene, extraction efficiencies calculated using hydrocarbon extracts have a slightly smaller standard deviation (3.16 wt%) than extraction efficiencies calculated using vessel residue (3.85 wt%). Using the extraction efficiency calculated based on hydrocarbon extracts, SC-CO_2 with 5 mol% toluene is capable of extracting an average of 54.1 wt% of the original bitumen. For bitumen dynamic extractions with 5 mol% methanol, extraction efficiencies calculated using hydrocarbon extracts have a smaller standard deviation (1.42 wt%) compared to that of extraction efficiencies calculated using vessel residue (15.5 wt%). Based on extraction efficiencies calculated using hydrocarbon extracts, SC-CO_2 with 5 mol% methanol is capable of extracting an average of 45.5 wt% of the original bitumen, 8.6 wt% less than an equivalent molar concentration of toluene.

Table 13. Extraction efficiencies and mass balance results for dynamic extractions of bitumen using 5 mol% toluene or methanol in SC-CO_2.

Date	**Modifier**	*Initial bitumen* (g)	*Mass of extracts* (g)	*Mass of hydrocarbons in residue* (g)	**Extraction Efficiency** (wt%)						**Mass Balance**[3] (wt%)
					Based on extracts[1]			*Based on residue*[2]			
					Replicate	*Average*	*SD*[4]	*Replicate*	*Average*	*SD*[4]	
06-01-16[5]	5 mol% toluene	9.966	5.419	4.3775	54.4	54.1	3.16	56.1	59.6	3.85	95.6
06-08-16[5]		10.488	5.989	3.8050	57.1			63.7			93.6
10-03-17		10.223	5.194	4.1850	50.8			59.1			91.9
07-20-16[5]	5 mol% methanol	10.408	4.816	7.6295	46.3	45.5	1.42	26.7	44.6	15.5	119.9
09-25-17		9.148	4.242	4.2150	46.4			53.9			105.6
09-28-17		10.391	4.557	4.87	43.9			53.1			101.0

[1] Calculated using Equation 1

[2] Calculated using Equation 2

[3] Calculated using Equation 3

[4] SD - standard deviation (n=3)

[5] Dynamic extraction conducted by Eleisha Underwood, a Research Associate in the SFE group

There is some variation in the toluene extraction efficiency results. During the June 8, 2016 dynamic extraction, the volume of toluene added to the vessel during pressurization was 23.6 mL instead of 19.3 mL. This is equivalent to adding 6 mol% toluene initially instead of 5 mol% (during the remainder of the June 8, 2016 extraction, the flow of toluene into the vessel was equivalent to 5 mol%). This additional 4 mL of toluene may account for the higher extraction efficiencies for the June 8, 2016 dynamic extraction. Further, for extractions with modified SC-CO_2, extract may have been lost due to leakage of extract from the silicone seals on the collection vial lids. This is especially true when toluene was used as the modifier as toluene is an excellent solvent for silicone. If extract leaked from the silicone seals on the vial lids, it would be unaccounted for in the extraction efficiency calculated based on hydrocarbon extracts. This may explain why in most dynamic extractions presented in Table 13, the extraction efficiency calculated based on hydrocarbon extracts is less than the extraction efficiency calculated based on vessel residue.

There is some variability in the extraction efficiencies calculated based on hydrocarbon extracts for dynamic extractions with 5 mol% methanol. This is primarily due to the lower extraction efficiency for the September 28, 2017 dynamic extraction. For the September 28, 2017 extraction, the difference between the original and final mass of vial 10*a* was negative – likely an indication that a glass bead was lost from the vial during the dynamic extraction, which would have impacted the cumulative mass of hydrocarbons extracted, and thus the extraction efficiency. For the July 20, 2016 dynamic extraction with 5 mol% methanol, the low extraction efficiency of 26.7 wt% (based on vessel residue) resulted in a high standard deviation of 15.5 wt% and may be due errors in vessel residue collection and handling.

There is less variability in the extraction efficiencies calculated based on hydrocarbon extracts and as such, all further discussions of dynamic extractions with 5 mol% toluene and 5 mol% methanol will use extraction efficiencies based on hydrocarbon extracts.

Figure 20 illustrates the effects of 5 mol% toluene versus 5 mol% methanol addition to SC-CO_2 on the cumulative mass percent of hydrocarbons extracted. The CO_2 only curves (from Figure 16) are provided in Figure 20 for comparison purposes.

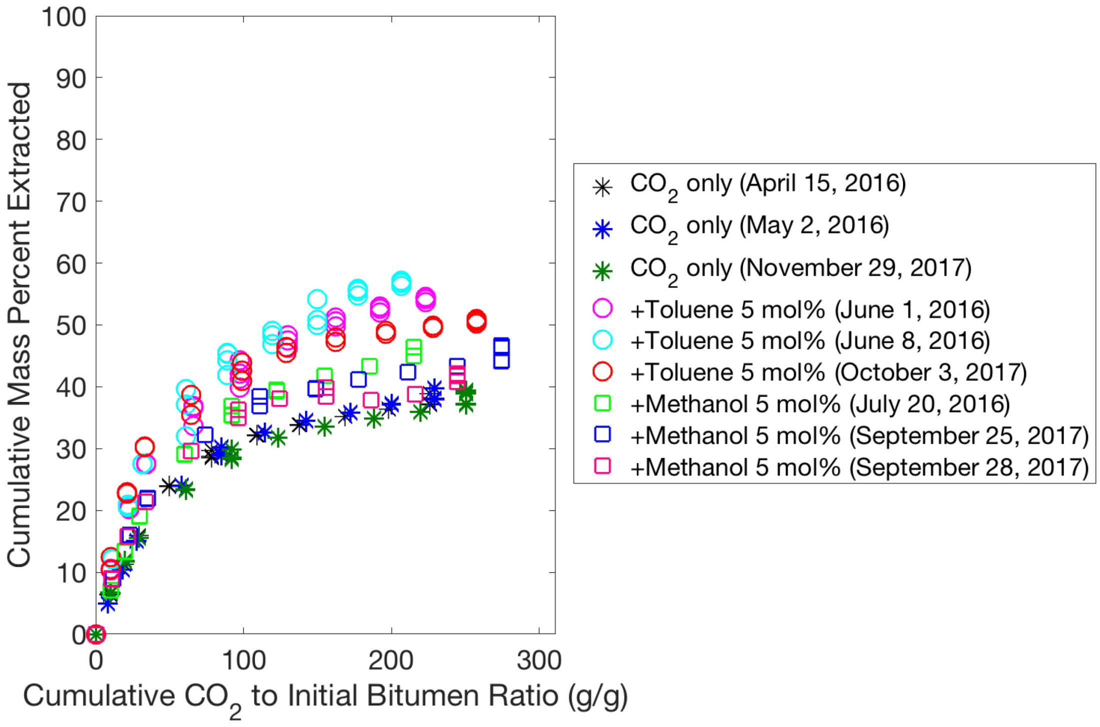


Figure 20. Effect of the addition of 5 mol% toluene or 5 mol% methanol to SC-CO_2 on the cumulative mass of hydrocarbons extracted from bitumen.

As discussed in Section 4.1.1.1, the extract curves in this thesis were developed by plotting the cumulative mass of hydrocarbons collected in each of vials *a* and *b*, as well as the carryover (*c/o*) and rinse vials. The different data points for vials *a*, *b* and *c/o* (for a given cumulative CO_2 to initial bitumen ratio) are more pronounced with toluene or methanol addition, as more extract is collected in each of these vials with the addition of a modifier. The extraction curve for the dynamic extraction with 5 mol% toluene conducted on June 8, 2016 has more data points than any of the other curves because every 15 minute period of this extraction had a different *c/o* vial.

The 'dip' in the cumulative mass percent of hydrocarbons extracted for the September 25, 2017 extraction with 5 mol% methanol at a cumulative CO_2 to initial bitumen ratio of approximately 190 g/g is due to the glass bead that was lost from vial 10*a*. This lost bead resulted in a negative difference between the original and final mass of vial 10*a*, and thus slightly lowered the cumulative mass percent of hydrocarbons extracted.

It should be noted that for the three dynamic extractions conducted in 2016 with a modifier (June 1, June 8 and July 20, 2016), Set 2 was only 60 minutes. It can be seen that the extraction curves for these three dynamic extractions are shorter and therefore the curve ends at a lower cumulative CO_2 to initial bitumen ratio of approximately 215 g/g. However, as previously discussed, the slopes of the extraction curves are low towards the end of the extraction. This means that the final mass of hydrocarbons extracted is less sensitive to the cumulative CO_2 to initial bitumen ratio near the end of the extraction. Thus the results of the dynamic extractions with modifier addition conducted in 2016 with a Set 2 duration of 60 minutes are still comparable to equivalent dynamic extractions conducted in 2017 with a Set 2 duration of 75 minutes.

As with previous 2016 dynamic extractions (April 5, 2016 and May 2, 2016), the three dynamic extractions conducted with a modifier in 2016 did not have an initial 60-minute static period. However, as seen in Figure 20, the extractions conducted in 2016 have initial slopes comparable to that of equivalent 2017 extractions. Again this likely indicates that the system is able to approach equilibrium with or without an initial static period, suggesting that mass transfer limitations are not substantial for dynamic extractions of bitumen.

As seen in Figure 20, the initial slopes of the 5 mol% toluene and 5 mol% methanol extraction curves are steeper than that of SC-CO_2 only curves. This is likely a result of increased solubility of hydrocarbons in modified SC-CO_2. The addition of either toluene or methanol increases the concentration of hydrocarbons in the SC-CO_2 mixture, thus increasing the mass of hydrocarbons extracted.

The addition of toluene or methanol to SC-CO_2 increases the percentage of hydrocarbons extracted for any given cumulative CO_2 to initial bitumen ratio.

However, toluene addition extracts a higher mass percentage of hydrocarbons than an equivalent molar concentration of methanol, despite being less polar than methanol. The initial slope of the toluene extraction curves are greater than that of the methanol extraction curves, suggesting that the solubility of hydrocarbons is greater in a mixture of SC-CO_2 and toluene than in a mixture of SC-CO_2 and methanol. At 5 mol%, toluene is capable of extracting 54.1 wt% of the original bitumen, a 38% increase from SC-CO_2 alone, whereas 5 mol% methanol extracts only 45.5 wt%, a 16% increase from SC-CO_2 alone. Thus, in terms of mass of hydrocarbons extracted, toluene is clearly the more effective modifier. This result is not surprising. Hwang and Ortiz (2000) examined the effects of modifiers in SC-CO_2 on the extraction of crude oil from dolomite rock and found that of methanol, isopropyl alcohol, hexane, toluene and light aromatic hydrocarbons, toluene produced the highest extraction yield and methanol produced the lowest.

Further, Magomedov et al. (2017) investigated the extraction of vacuum residue, a heavy petroleum feedstock, using SC-CO_2. The vacuum residue was made up of 10.3 wt% saturates, 40.3 wt% aromatics, and 49.4 wt% resins and asphaltenes. Magomedov et al. (2017) found that at equivalent concentrations of 20 wt%, toluene extracted 24.3 wt% of the original feedstock whereas methanol extracted only 6.3 wt%. The bitumen used in this thesis research was lighter, consisting of more saturates and fewer aromatics, resins and asphaltenes than the feedstock used by Magomedov et al. (2017), which explains the large differences in extraction efficiencies between this thesis research and the research conducted by Magomedov et al. (2017).

Even though toluene is less polar than methanol, the results in Table 13 suggest that toluene is a better modifier than methanol in terms of hydrocarbon extraction efficiencies. Al-Sabawi et al. (2011) suggested that because of its aromaticity, toluene enhances the compatibility of the solvent mixture with aromatic molecules of bitumen, promoting the stability (and solubility) of heavier aromatic compounds, decreasing the precipitation of asphaltenes and therefore increased extraction of hydrocarbons. Magomedov et al. (2017) found that the addition of aromatic hydrocarbons (such as toluene) to SC-CO_2 extracted higher mass percentages of hydrocarbons from vacuum residue, as compared to the addition of n-alkanes with the same carbon number (such as n-heptane). Magomedov et al. (2017) attributed this to the higher solvating power of toluene (and other aromatic hydrocarbons such as xylene) for aromatic hydrocarbons and polycyclic structures contained within the vacuum residue. Therefore, it is likely that the aromaticity of toluene is an important factor in its effectiveness over methanol in improving the extraction of hydrocarbons.

Hwang and Ortiz (2000) tested a mixture of toluene and methanol in SC-CO_2 on the extraction of crude oil from dolomite rock and found that it produced results intermediate between that of toluene and methanol alone. They also reported that increasing the toluene content of the toluene/methanol mixture produced greater results. Thus a mixture of toluene and methanol was not tested as part of this thesis research, as it was believed that a mixture would not likely have shown an improvement over the effects of toluene alone.

4.1.2.2 Type of Hydrocarbons Extracted

Figure 21 compares HTSD results from three bitumen extraction conditions: SC-CO_2 only (November 29, 2017), SC-CO_2 with 5 mol% toluene (June 1, 2016) and SC-CO_2 with 5 mol% methanol (July 20, 2016), at three different points during the extraction process. Though Figure 21 only displays HTSD results from three selected dynamic extractions, any one of the triplicate results for the given extraction conditions could have been graphed to produce similar curves. The CO_2 only curves and the virgin bitumen curve are provided for comparison purposes.

The curves representing a cumulative CO_2 to initial bitumen ratio of roughly 10 g/g are equivalent to vials 1*a* and reflect the hydrocarbons extracted at the beginning of each extraction. Cumulative CO_2 to initial bitumen ratios of approximately 90 to 100 g/g are equivalent to the middle of the dynamic extractions and thus these curves reflect the hydrocarbons extracted halfway through the extractions. HTSD curves for the vessel residues from each dynamic extraction are also displayed for comparison.

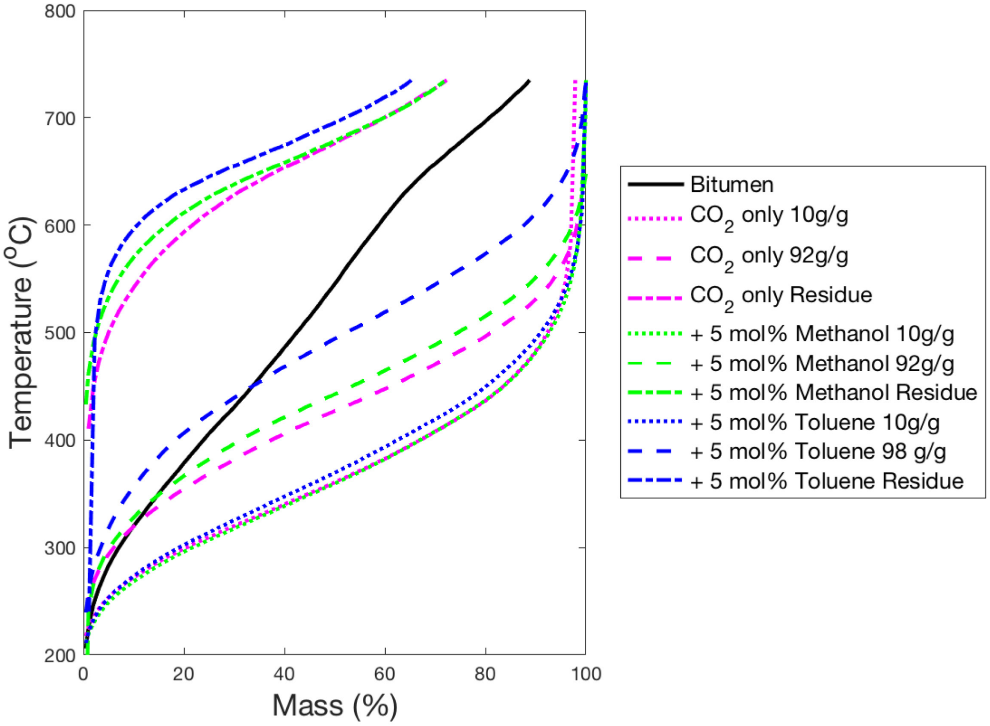


Figure 21. HTSD curves comparing hydrocarbon extracts and residue from three bitumen dynamic extractions: SC-CO_2 only, SC-CO_2 with 5 mol% toluene and SC-CO_2 with 5 mol% methanol.

For all three extraction conditions, as the dynamic extraction progresses, the distillation temperature of the extracts increases, thus indicating that slightly heavier hydrocarbons are being extracted. However, comparing samples with cumulative CO_2 to initial bitumen ratios of approximately 90 to 100 g/g, it is evident that the toluene and methanol curves are shifted upwards compared to that of the SC-CO_2 only curve. This indicates that the addition of a modifier not only extracts more hydrocarbons than SC-CO_2 alone, it also yields heavier hydrocarbons. This is to be expected, given that the addition of a modifier more polar than CO_2 is thought to enhance the solubility of polar hydrocarbons, which also tend to be heavier, in the CO_2/modifier mixture (La and Guigard 2015; Al-Marzouqi et al. 2009; Yoon et al. 2009; Speight 2006; Hwang and Ortiz 2000). These results agree with those of Al-Sabawi et al. (2011), who found that the API gravity of Athabasca bitumen extracts decreased (and thus the extract density increased) with the addition of modifiers to supercritical n-pentane.

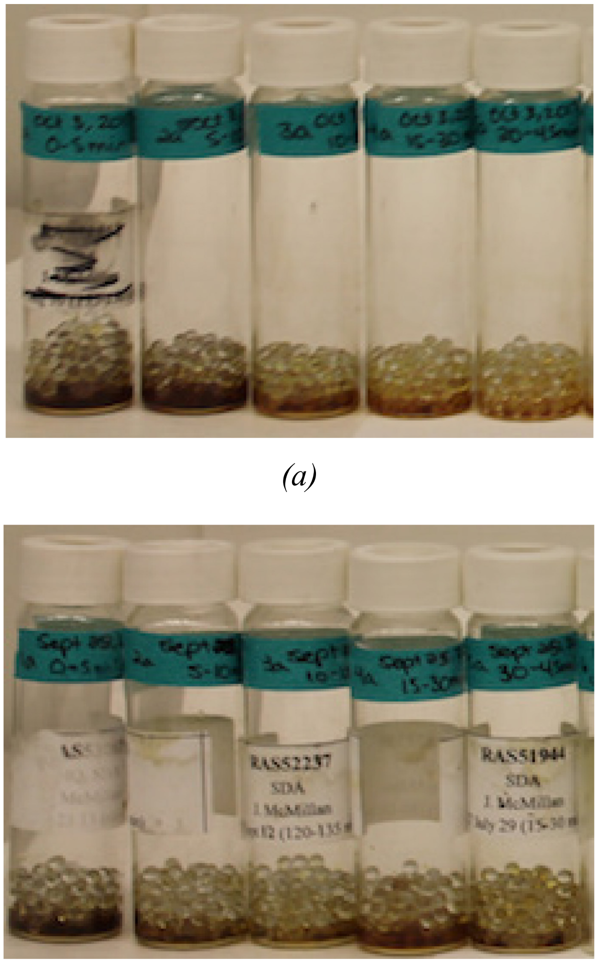
Because the November 29, 2017 SC-CO_2 only extraction was 15 minutes longer than the two dynamic extractions with 5 mol% modifier addition in Figure 21, the vessel residue collected during the SC-CO_2 only extraction is heavier than it would have been had the extraction been 15 minutes shorter. The overlap between the vessel residue HTSD curves for CO_2 only and 5 mol% methanol is likely a reflection of the different extraction times rather than the capability of SC-CO_2 to extract the same hydrocarbons as SC-CO_2 with 5 mol% methanol. Unfortunately because the vessel residue solutions for the dynamic extractions conducted in 2017 with 5 mol% toluene and 5 mol% methanol were not sent for HTSD analysis, it is not possible to compare 5 mol% modifier extractions of equivalent duration to the SC-CO_2 only extractions. Additionally, it appears that SC-CO_2 only and SC-CO_2 with 5 mol% methanol extract hydrocarbons of similar weight during the first 5 minutes of the extraction – again this is likely an error. As discussed previously, the SC-CO_2 only HTSD curve reflecting the extract collected in vial 1*a* appears to be composed of some heavy hydrocarbons that do not distil before 735 °C; however, because the extract collected midway through the extraction is completely distilled by 600 °C, this is likely an error. If sample 1*a* from the SC-CO_2 only dynamic extraction contained traces of heavier hydrocarbons, this would explain why the HTSD curves for the initial extracts from SC-CO_2 only and SC-CO_2 with 5 mol% methanol overlap.

Compared to an equivalent molar concentration of toluene, 5 mol% methanol is not as successful in extracting heavier hydrocarbons. SC-CO_2 with 5 mol% methanol overall extracts a lighter, lower mass percentage of hydrocarbons compared to SC-CO_2 with 5 mol% toluene. This is evident when comparing the toluene and methanol HTSD curves at a cumulative CO_2 to initial bitumen ratio of 90 to 100 g/g; toluene yields extracts that distil at higher temperatures, and thus are heavier than extracts obtained with methanol addition. This is also apparent when comparing the vessel residue curves; 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 hydrocarbons still remain in the vessel after the extraction and 20 wt% of the residue distils below 600 °C.

Toluene is known to be an excellent solvent for asphaltenes, which are polar, aromatic, high molecular weight compounds, and is thus capable of extracting heavier components of bitumen than methanol (Abu-Khader and Speight 2007; Zaki et al. 2003; Hwang and Oritz 2000; Hwang and Ortiz 1998). Toluene appears to have the most distinct effect on heavier hydrocarbons and as such, as the extraction progresses, consistently heavier hydrocarbons are extracted.

Figure 22 shows the extract collected in the Set 1 *a* vials from the dynamic extraction conducted on October 3, 2017 with 5 mol% toluene in SC-CO_2 and the dynamic extraction conducted on September 25, 2017 with 5 mol% methanol in SC-CO_2. Set 1 vials were collected during the first 45 minutes of the dynamic extraction, with vials 1, 2 and 3 (left to right) collecting extract for 5 minute intervals, and vials 4 and 5 collecting extract for 15 minute intervals.

Extracts collected using SC-CO_2 alone (seen in Figure 18) are bright yellow. However, the addition of a modifier, either toluene or methanol, yields darker extracts, especially at the beginning of the dynamic extraction (vials 1*a* and 2*a* as seen in Figure 22*a* and *b*). Further, comparing Figure 22*a* and *b*, it can be seen that 5 mol% toluene addition (Figure 22*a*) results in darker extracts, and a greater amount of extracts, compared to 5 mol% methanol addition (Figure 22*b*).



(a)

(b)

Figure 22. Extract collected in *a* vials during Set 1 of (a) October 3, 2017 dynamic extraction with 5 mol% toluene in SC-CO_2, and (b) September 25, 2017 dynamic extraction with 5 mol% methanol in SC-CO_2.

Hwang and Ortiz (2000) reported that, because the low polarity of SC-CO_2 causes the precipitation of asphaltenes in residual oil, SC-CO_2 alone produced a more upgraded oil compared to SC-CO_2-modifier mixtures. Hwang and Ortiz (2000) found that residual oil after an extraction with SC-CO_2 had the highest amount of asphaltics (nitrogen, sulfur, oxygen and asphaltenes), followed by SC-CO_2 with methanol, and that SC-CO_2 with toluene addition resulted in the lowest concentration of asphaltics in the residual oil. These results indicate that more heteroatoms and asphaltenes are being extracted with SC-CO_2 modified with toluene, than with SC-CO_2 only and SC-CO_2 modified with methanol. Further, Al-Sabawi et al. (2011) reported that extracts collected from extractions with supercritical n-pentane alone had the lowest nickel, vanadium and nitrogen concentrations, followed by n-pentane combined with methanol, and that extracts collected with supercritical n-pentane combined with toluene had the highest concentration of these elements. These results are consistent with toluene solubilizing and extracting heavier bitumen components, as the high molecular weight fractions of bitumen (resins and asphaltenes) are the most concentrated with heteroatoms and heavy metals (Al-Sabawi et al. 2011; Yoon et al. 2009; Speight 2006).

However, extracting heavier hydrocarbons with the addition of a modifier does not explain the dark color of the extracts collected at the beginning of the dynamic extractions with modifiers, since the lightest hydrocarbons are extracted first. Magomedov et al. (2017) showed that higher concentrations of metals (vanadium and nickel) are extracted with increasing extraction time (and increasing extract yield), thus indicating that these metals are generally extracted with the heavier components of the feed material. However, it is possible that, at the beginning of the extraction, small amounts of heavy metals and/or heteroatoms are being extracted and are forming these dark coloured compounds. An elemental analysis of these initial extracts would provide more information.

4.1.3 Effect of Modifier Concentration in SC-CO_2

4.1.3.1 Hydrocarbon Extraction Efficiencies

To determine the effects of modifier concentration on the extraction of hydrocarbons, two additional concentrations of toluene and methanol, 10 and 15 mol% in SC-CO_2, were tested in triplicate. After these dynamic extractions were conducted, it was hypothesized that toluene and methanol may be more comparable in terms of mass percent in SC-CO_2 rather than mole percent. Thus, the condition of 33.7 mol% methanol (or 26.98 wt%) was tested, which is equivalent to 15 mol% toluene in terms of mass percent in SC-CO_2. Given the low standard deviations of previous dynamic extractions, this additional condition was only tested in duplicate. The extraction efficiencies and mass balance results of all 14 dynamic extractions are presented in Table 14. The mass balance results are discussed in Section 4.1.4.

As seen in Table 14, for each extraction condition, the extraction efficiencies calculated based on hydrocarbon extracts or vessel residue are similar; this is especially true for the conditions of 10 and 15 mol% toluene to SC-CO_2 and 15 mol% methanol to SC-CO_2. However for all extraction conditions, there is less variability in the extraction efficiencies calculated based on hydrocarbon extracts, likely of a result of the increased handling and analysis required for vessel residue hydrocarbons. As previously mentioned, it is difficult to recover all of the hydrocarbons remaining in the vessel after the extraction, and as a result, extraction efficiencies calculated based on vessel residue hydrocarbons may experience more variability and may be biased high. As such, all further discussion of these results are based on extraction efficiencies calculated using hydrocarbon extracts.

SC-CO_2 with 10 mol% toluene is capable of extracting an average of 65.8 wt% of the original bitumen, with a standard deviation of 2.87 wt%. The addition of 15 mol% toluene further increases the average extraction efficiency to 75.8 wt%, with a standard deviation of 1.02 wt%. SC-CO_2 with 10 mol% methanol extracts on average 48.9 wt% of the original bitumen, with a small standard deviation of 0.690 wt%. The addition of 15 mol% methanol to SC-CO_2 increases the extraction efficiency to 50.9 wt%, on average, with a small standard deviation of 0.195 wt%.

Table 14. Extraction efficiencies and mass balance results for dynamic extractions of bitumen using 10 and 15 mol% toluene, and 10, 15 and 33.7 mol% methanol in SC-CO_2.

Date	**Modifier**	*Initial bitumen* (g)	*Mass of extracts* (g)	*Mass of hydrocarbons in residue* (g)	**Extraction Efficiency** (wt%)						**Mass Balance** [3] (wt%)
					Based on extracts [1]			*Based on residue* [2]			
					Replicate	*Average*	*SD* [4]	*Replicate*	*Average*	*SD* [4]	
11-03-17	10 mol% toluene	11.005	6.899	3.6895	62.7	65.8	2.87	66.5	65.1	3.06	96.4
11-06-17		10.649	7.277	3.4871	68.3			67.3			101.3
11-08-17		10.180	6.759	3.9079	66.4			61.6			104.9
10-16-17	15 mol% toluene	10.659	8.207	2.295	77.0	75.9	1.02	78.5	76.0	3.05	99.0
10-18-17		10.345	7.823	2.39	75.6			76.9			99.1
10-20-17		10.348	7.760	2.8381	75.0			72.6			102.6
11-10-17	10 mol% methanol	11.287	5.430	4.4129	48.1	48.9	0.690	60.9	55.9	4.44	87.6
11-15-17		10.674	5.260	4.8621	49.3			54.4			94.8
11-17-17		10.025	4.945	4.7729	49.3			52.4			97.5
11-20-17	15 mol% methanol	10.700	5.417	5.3999	50.6	50.9	0.195	49.5	49.6	3.19	101.5
11-22-17		10.006	5.103	5.3623	51.0			46.4			104.9
11-24-17		10.768	5.483	5.0837	50.9			52.8			98.6
03-05-18	33.7 mol% methanol	10.383	5.731	4.33	55.2	55.0	0.371 [5]	58.3	58.8	1.10 [5]	97.3
03-07-18		10.198	5.591	4.14	54.8			59.4			96.0

[1] Calculated using Equation 1

[2] Calculated using Equation 2

[3] Calculated using Equation 3

[4] SD - standard deviation (n=3)

[5] Range (n=2)

The reason for the higher standard deviation for the 10 mol% toluene extraction condition is that for the dynamic extractions with 10 mol% toluene in SC-CO_2 (which were conducted after the 15 mol% toluene extractions), jars from a different manufacturer were used. These jars did not have a good seal between the lid and the jar, and the silicone sealant did not stick well onto the jar lid. As such, during the dynamic extractions with 10 mol% toluene in SC-CO_2, toluene exiting the system was able to easily break the silicone seal, causing extract to exit the lid through the holes made for the outlet tubing, and through the poor seal between the jar and the lid. This leaking occurred only in jars *a* and *b* (as together they had a large enough volume to collect the extract exiting the system) and so the acetone/dry ice bath collected most of the leaked extract. After each of the three dynamic extractions with 10 mol% toluene in SC-CO_2, the contents of the acetone/dry ice bath were rinsed with toluene into a pre-weighed 250 mL jar. The jar was then left to dry in fumehood to evaporate the toluene and acetone, before measuring its final weight. The acetone/dry ice bath was rinsed before each dynamic extraction to ensure no residue was left over from a previous experiment. However, despite collecting much of this leaking extract in the acetone/dry ice bath, it still caused to some variability in these triplicate results.

Because methanol is not a solvent for silicone, substantially less extract escaped from the jars into the acetone/dry ice bath compared to that of dynamic extractions with toluene, and thus the results of the dynamic extractions with methanol have lower standard deviations.

Figure 23 and Figure 24 illustrate the effects of increasing concentrations (from 5 to 15 mol%) of toluene and methanol, respectively, on the cumulative mass percent of hydrocarbons extracted. The 5 mol% toluene and methanol extraction curves are provided for comparison purposes.

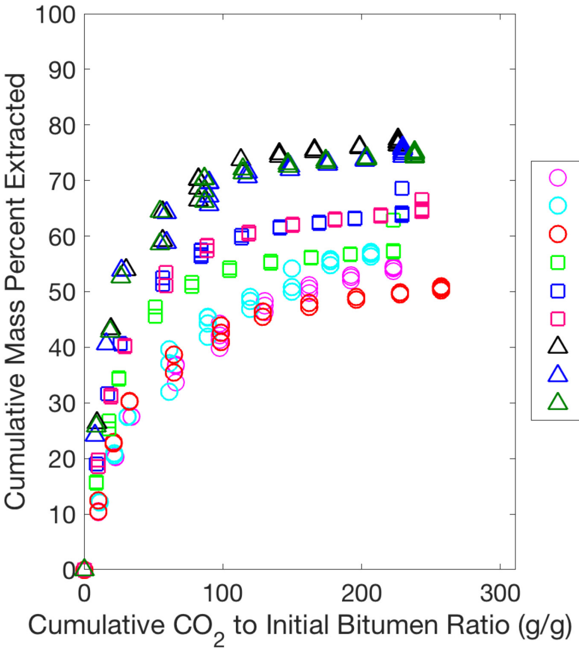


Figure 23. Effect of increasing concentrations of toluene in SC-CO_2 (5, 10 and 15 mol%) on the cumulative mass of hydrocarbons extracted from bitumen.

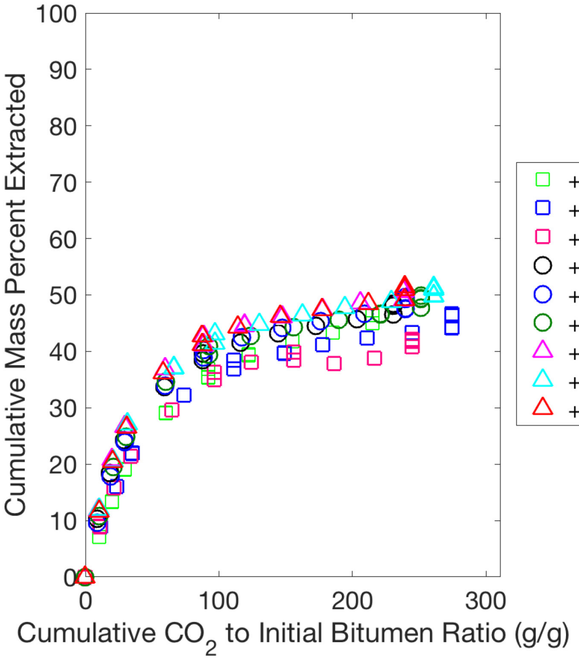


Figure 24. Effect of increasing concentrations of methanol in SC-CO_2 (5, 10 and 15 mol%) on the cumulative mass of hydrocarbons extracted from bitumen.

The ‘jump’ in mass percent of hydrocarbons extracted at the end of the three 10 mol% toluene extractions in Figure 23 is a reflection of the extract collected in the acetone/dry ice bath. Though this extract was collected throughout the duration of the dynamic extraction, it was not collected evenly – more extract leaked from the collection jars during the last 75 minutes of the extraction. Thus the extract collected in the acetone/dry ice was added to the end of the extraction curve, as it could not be distributed throughout the rest of the curve with accuracy.

As seen in Figure 23 and Figure 24, increasing the concentration of toluene or methanol in SC-CO_2 increases the percentage of hydrocarbons extracted for any given cumulative CO_2 to initial bitumen ratio. As the concentration of toluene or methanol increases, the initial slope of the extraction curves increases. This is likely a reflection of the enhanced hydrocarbon solubility (and therefore increased hydrocarbon concentration) in SC-CO_2 with increasing concentrations of the modifier.

However it can be seen that increasing the molar concentration of toluene is more effective, in terms of mass of hydrocarbons extracted, than increasing the concentration of methanol. The initial slopes of the extraction curves are much steeper with increasing toluene addition (Figure 23), compared to increasing methanol addition (Figure 24). Table 15 shows the percent increase in extraction efficiency (compared to SC-CO_2 alone) as a result of adding increasing amounts of toluene or methanol. Increasing the concentration of toluene to 15 mol% in SC-CO_2 improves extraction efficiency by 93% compared to SC-CO_2 alone. An equivalent molar concentration of methanol only improves extraction efficiency by 30% compared to SC-CO_2 alone. Again this illustrates the effectiveness of toluene over methanol. At a concentration of SC-CO_2 with 5 mol% toluene is capable of extracting more hydrocarbons than SC-CO_2 with 15 mol% methanol.

Table 15. Comparison of extraction efficiency for dynamic extractions of bitumen using SC-CO_2 only and SC-CO_2 with modifiers.

Extraction Condition	**Average Extraction Efficiency** (wt%)	**Increase in Extraction Efficiency compared to SC-CO_2 only** (%)
SC-CO_2 only	39.2	-
SC-CO_2 with 5 mol% toluene	54.1	38
SC-CO_2 with 10 mol% toluene	65.8	68
SC-CO_2 with 15 mol% toluene	75.9	93
SC-CO_2 with 5 mol% methanol	45.5	16
SC-CO_2 with 10 mol% methanol	48.9	25
SC-CO_2 with 15 mol% methanol	50.9	30

Increasing extraction efficiencies with increasing concentrations of toluene is consistent with the findings of Al-Sabawi et al. (2011) who found that increasing the concentration of toluene in n-pentane from 5 to 20 mol% resulted in increased DAO yields from Athabasca bitumen. Hwang and Ortiz (2000) used SC-CO_2 to extract hydrocarbons from dolomite rocks and also found that higher toluene concentrations led to increased extraction efficiencies. Magomedov et al. (2017) examined the effects of 15 to 35 wt% toluene on the SC-CO_2 extraction of vacuum residue and found that increasing the concentration of toluene resulted in a significant increase in extraction efficiency, from 10 to approximately 58 wt%. Additionally Magomedov et al. (2017) noted some slowdown in the rise of extract production rate with toluene concentrations greater than 30 wt%. A slight slowdown in the increase in extraction efficiency, relative to SC-CO_2 only, with increasing toluene concentrations is also seen in this thesis research. For example, when increasing the toluene concentration from 5 to 10 mol%, the extraction efficiency relative to SC-CO_2 only increases from 38 to 68%, but this increase is slightly less, from 68 to 93%, when increasing the toluene concentration from 10 to 15 mol%.

Though not as effective as toluene, increasing methanol concentrations in SC-CO_2 also results in higher extraction efficiencies. This result is inconsistent with the findings of Al-Sabawi et al. (2011) who studied the effects of increasing methanol concentrations in n-pentane on the extraction of DAO and found that hydrocarbon extraction decreased with methanol concentrations greater than 5 mol%. Al-Sabawi et al. (2011) noted that this decreasing trend associated with increasing the concentration of methanol was not inline with that of the other three modifiers studied (acetone, toluene and ethyl acetate) and that it required further investigation. This decreasing trend is not in agreement with the results of this thesis research and may be due to different interactions between methanol and n-pentane versus methanol and CO_2.

A slowdown in the increase in extraction efficiency, relative to SC-CO_2, with increasing methanol concentrations was also noted in this thesis research. Increasing the methanol concentration from 5 to 10 mol% increased the extraction efficiency, relative to SC-CO_2 only, from 16 to 25%, but the increase is less, from 25 to 30% when the methanol concentration is increased from 10 to 15 mol%. It is not known why there is a slight decline in extract production rate with increasing modifier concentrations, though it may be due to challenges in solubilizing and extracting the remaining, heavy hydrocarbons. This would be particularly true for higher methanol concentrations and would explain why methanol appears to experience this slowdown more so than toluene.

To determine if toluene and methanol would be more comparable in concentration units of mass instead of moles, a condition of 33.7 mol% methanol was tested in duplicate. At a concentration of 33.7 mol% (or 26.98 wt%), methanol is equivalent to 15 mol% toluene in terms of mass percent. The results of these two dynamic extractions are displayed in Table 14. Using the extraction efficiencies calculated based on hydrocarbon extracts, 33.7 mol%, methanol is capable of extracting an average of 55.0 wt% of the original bitumen with a range of 0.371 wt%.

Figure 25 compares the effects of equivalent mass concentrations of toluene and methanol on the mass of hydrocarbons extracted. Though 33.7 mol% methanol is an improvement over 15 mol% methanol (which extracts an average of 50.9 wt% of the original bitumen), 33.7 mol% (26.98 wt%) methanol still extracting over 20 wt% less than an equivalent mass percent of toluene, as seen in

Figure 25. Thus even in terms of mass percent, toluene is the more effective modifier for enhancing hydrocarbon extraction. However, this thesis research suggests that toluene and methanol are more comparable on a mass percent basis than on a mole percent basis. Comparing the effects of 15 mol% toluene and 15 mol% methanol in SC-CO_2, 15 mol% toluene extracts on average 25.0 wt% more hydrocarbons. However, comparing the effects of toluene and methanol at a concentration of 26.98 wt% in SC-CO_2, toluene extracts on average 20.9 wt% more hydrocarbons.

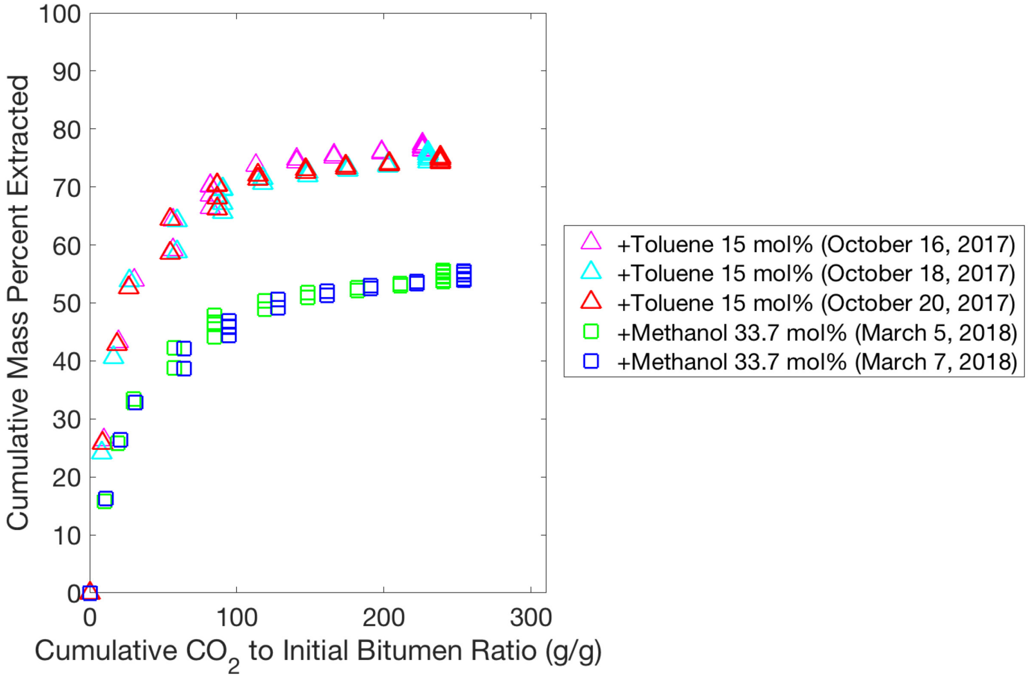


Figure 25. Effect of equivalent mass concentration of toluene or methanol in SC-CO_2 on the cumulative mass of hydrocarbons extracted from bitumen.

4.1.3.2 Type of Hydrocarbons Extracted

Figure 26 compares HTSD results from three bitumen extraction conditions with toluene: SC-CO_2 with 5 mol% toluene (June 1, 2016), SC-CO_2 with 10 mol% toluene (November 6, 2017) and SC-CO_2 with 15 mol% toluene (October 20, 2017). Figure 27 compares HTSD results from three bitumen extraction conditions with methanol: SC-CO_2 with 5 mol% methanol (July 20, 2016), SC-CO_2 with 10 mol% methanol (November 15, 2017), and SC-CO_2 with

15 mol% methanol (November 20, 2017). Unfortunately the HTSD results for the bitumen dynamic extractions with 33.7 mol% methanol were not available by the time this thesis is submitted. The 5 mol% toluene and methanol curves, as well as the virgin bitumen curve, are provided for comparison purposes.

Though these figures only display HTSD results from six selected dynamics extractions, any one of the triplicate results from the given extraction conditions could have been graphed to produce similar curves. In both Figure 26 and Figure 27, a cumulative CO_2 to initial bitumen ratio of roughly 10 g/g is equivalent to vial/jar 1*a* and reflects hydrocarbons extracted during the beginning of the extraction. HTSD curves from a cumulative CO_2 to initial bitumen ratios of approximately 80 to 120 g/g reflect hydrocarbons extracted roughly halfway through the dynamic extractions. Vessel residue curves are also displayed for comparison.

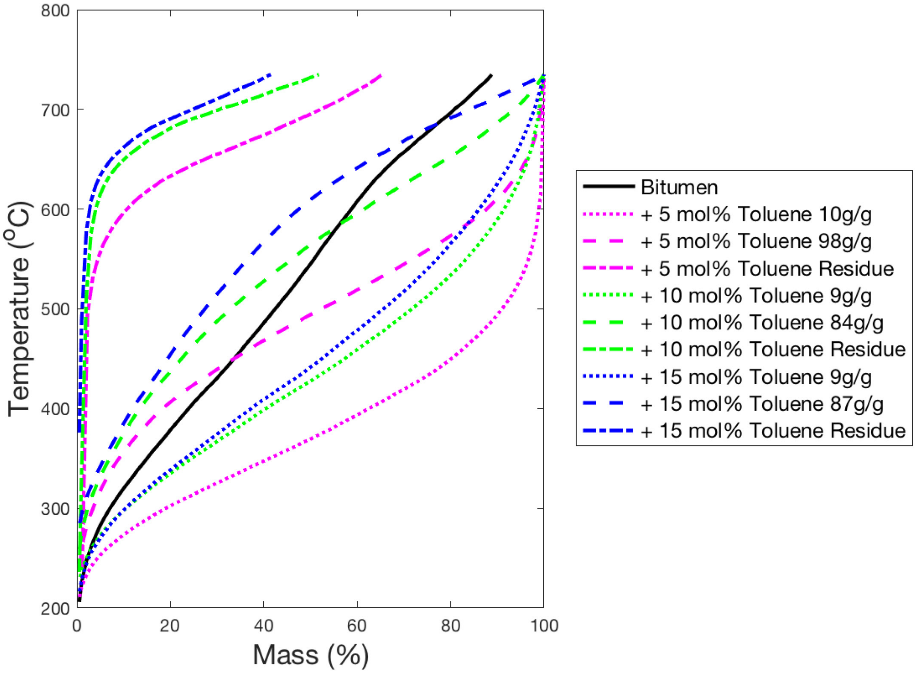


Figure 26. HTSD curves comparing hydrocarbon extracts and residue from three bitumen dynamic extractions: 5, 10 and 15 mol% toluene in SC-CO_2.

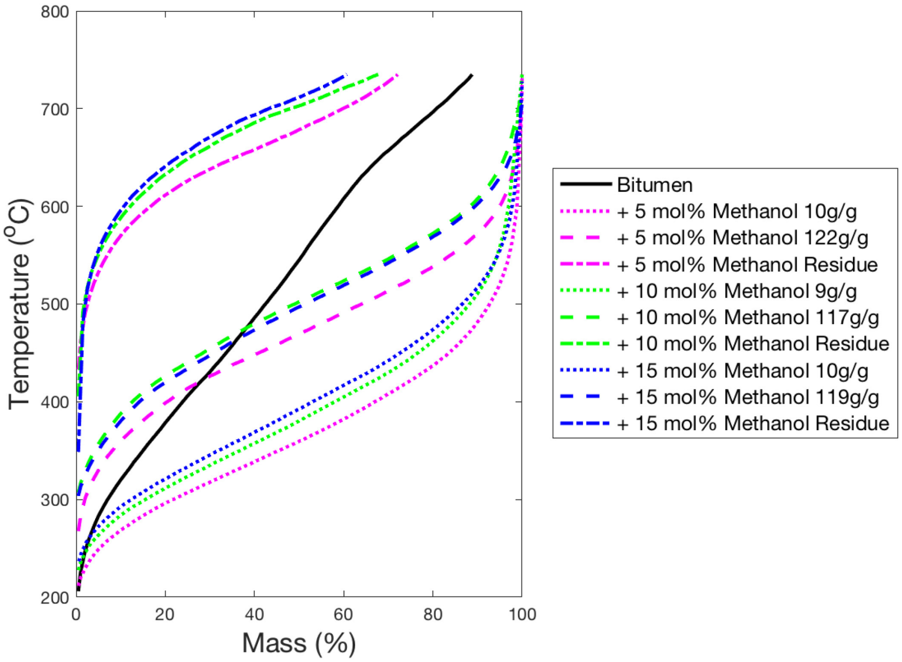


Figure 27. HTSD curves comparing hydrocarbon extracts and residue from three bitumen dynamic extractions: 5, 10 and 15 mol% methanol in SC-CO_2.

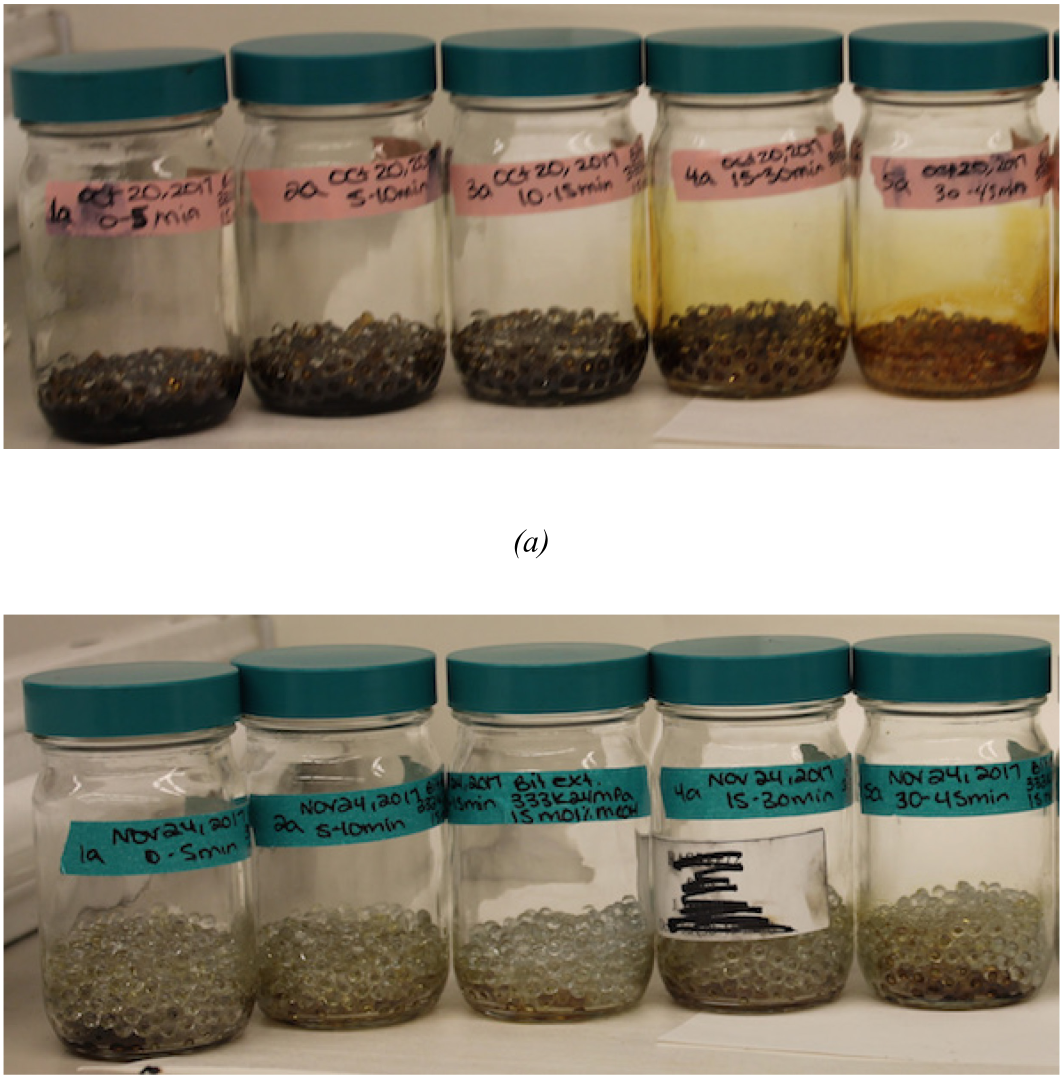
It should be noted that the extract collected in the acetone/dry ice bath for the three 10 mol% toluene extractions was not sent to Syncrude for HTSD analysis. This is because the acetone/dry ice bath extract was collected throughout the duration of the extraction instead of at 5 or 15 minute time intervals and is thus not representative of extract collected after a specific cumulative CO_2 to initial bitumen ratio. As such, the 10 mol% toluene HTSD curves may be affected, particularly the curve reflecting extract collected after a cumulative CO_2 to initial bitumen ratio of 84 g/g, as this is midway through the extraction. It is likely that lighter, more volatile hydrocarbons were more prone to this leakage and as such, the hydrocarbons collected in the extract jars and sent for HTSD analysis may be heavier than the hydrocarbons that leaked from the jars. Thus the HTSD curves for extractions with 10 mol% toluene may reflect the heavier portion of the extracted hydrocarbons.

It can be seen in both Figure 26 and Figure 27 that at higher modifier concentrations, the samples distil at higher temperatures and are thus heavier. For example, comparing equivalent extracts from dynamic extractions with 5 and 15 mol% toluene, after a cumulative CO_2 to initial bitumen ratio of 80 to 100 g/g, 60 wt% of the 5 mol% toluene extract is distilled by 500 °C whereas 60 wt% of the 15 mol% toluene extract distils at 640 °C. As the concentration of modifier increases, heavier hydrocarbons are extracted. It is anticipated that the HTSD results for dynamic extractions with 33.7 mol% methanol would also be inline with this trend.

In Figure 27, the HTSD curves illustrate that 10 and 15 mol% methanol are extracting similar hydrocarbons. There is only a 2 wt% difference between the mass of hydrocarbons extracted using 10 and 15 mol% methanol, thus the HTSD curves are similar, though 15 mol% methanol is extracting slightly heavier hydrocarbons as illustrated by the vessel residue HTSD curves – the vessel residue from the dynamic extraction with 15 mol% methanol distils at slightly higher temperatures than that of 10 mol% methanol.

Comparing the two figures, it is evident that in Figure 26 the HTSD curves are shifted upwards compared to the curves in Figure 27, as toluene extracts distil at higher temperatures than methanol extracts. This is particularly true midway through the extractions (represented by the 80 to 100 g/g cumulative CO_2 to initial bitumen ratio curves). As the extractions proceed, toluene extracts progressively heavier hydrocarbons than an equivalent molar concentration of methanol. Comparing the vessel residues from dynamic extractions with 15 mol% toluene and 15 mol% methanol, 2 wt% of the 15 mol% toluene vessel residue is distilled by 600 °C, whereas 15 wt% of the 15 mol% methanol vessel residue is distilled by 600 °C.

Figure 28 below shows the extract collected in the *a* jars from Set 1 for the October 20, 2017 dynamic extraction with 15 mol% toluene in SC-CO_2 and the November 24, 2017 dynamic extraction with 15 mol% methanol with SC-CO_2. Set 1 jars were collected during the first 45 minutes of the dynamic extraction, with jars 1, 2 and 3 (left to right) collecting extract for 5 minute intervals, and jars 4 and 5 collecting extract for 15 minute intervals.



(a)

(b)

Figure 28. Extract collected in *a* vials during Set 1 of (a) October 20, 2017 dynamic extraction with 15 mol% toluene in SC-CO_2, and (b) November 24, 2017 dynamic extraction with 15 mol% methanol in SC-CO_2.

Compared to the extracts collected using 5 mol% toluene and 5 mol% methanol (Figure 22*a* and *b*, respectively), the extracts collected with 15 mol% toluene and 15 mol% methanol (Figure 28*a* and *b*, respectively) are darker and there are a greater amount of them. Additionally, comparing Figure 28*a* and Figure 28*b* it can be seen that there are a larger amount of extracts collected using 15 mol% toluene and that these extracts are darker than that of 15 mol% methanol.

Al-Sabawi et al. (2011) used supercritical n-pentane to extract DAO from Athabasca bitumen and found that increasing molar concentrations of toluene in n-pentane from 5 to 20 mol% resulted in increased extraction of vanadium, nickel and nitrogen and less precipitation of asphaltenes. Magomedov et al. (2017) reported similar results using SC-CO_2 to extract hydrocarbons from vacuum residue. Magomedov et al. (2017) found that increasing the concentration of toluene in SC-CO_2 not only increased the extraction efficiency, there was also an accompanying increase in the concentrations of heavy metals (vanadium and nickel) in the extract. Thus increasing the hydrocarbon extraction efficiency with the addition of a modifier (and increasing concentrations of that modifier) produces an associated increase in extract impurities, thus reducing the quality of the extracted hydrocarbons.

Again the darker color of the extract during the first 45 minutes of the dynamic extraction may be due to the modifiers extracting small amounts of compounds containing heavy metals and/or heteroatoms along with the initial, lighter hydrocarbons. This would be consistent with the increased modifier concentrations producing darker extracts, as higher concentrations of toluene have been shown to increase impurities in the extract, and would also be consistent with toluene producing darker extracts than methanol, as extracts collected with the addition of toluene have been found to have higher concentrations of heavy metals and heteroatoms, compared to extracts collected with methanol (Al-Sabawi et al. 2011; Hwang and Ortiz 2000).

4.1.4 Hydrocarbon Mass Balances for Bitumen Dynamic Extractions

For each dynamic extraction of bitumen, a mass balance check was performed on the hydrocarbons by comparing the mass of hydrocarbons originally placed in the vessel, with the cumulative mass of hydrocarbons collected in the collection vials/jars and the mass of hydrocarbons remaining in the vessel residue. Mass balance results for bitumen dynamic extractions are displayed in Tables 12, 13 and 14. For the 23 bitumen dynamic extractions, the mass balances ranged from 86.5 to 119.9 wt% hydrocarbon recovery, though the majority of the mass balance results were within ± 5 wt% of 100 wt% hydrocarbon recovery. These mass balance results are good, and indicate that the hydrocarbons were quantitatively accounted for in the extracts and vessel residue.

For bitumen dynamic extractions, mass balances indicating less than 100 wt% hydrocarbon recovery may be due to loss of light end hydrocarbons during the dynamic extraction and/or the drying period. For dynamic extractions with modified SC-CO_2, extract may also have been lost during the dynamic extraction due to leakage from the silicone seals on the vial/jar lids. This is especially true when toluene is added as a modifier, as toluene is an excellent solvent for silicone. Mass balances showing greater than 100 wt% hydrocarbon recovery may be the result of residual toluene and/or methanol in the vials/jars after the two day drying period. Further, hydrocarbon residue in the SFE system from a previous experiment could also contribute to greater than 100 wt% hydrocarbon recovery. Collection, handling and analysis of vessel residue may also contribute to discrepancies in mass balance results.

4.2 Dynamic Extractions of FT Froth and Pond Froth

Dynamic extractions of FT Froth and Pond Froth were conducted in duplicate using SC-CO_2 only in order to determine the effects of water and solids on the extraction of hydrocarbons. In order to determine the effects of a modifier on the extraction of hydrocarbons from FT Froth and Pond Froth, the most successful modifier condition from the dynamic extractions of bitumen, 15 mol% toluene in SC-CO_2, was also tested in duplicate. An additional condition, 33.7 mol% methanol, was tested to determine the effects of toluene versus methanol on these two feed materials. However, given the success of 15 mol% toluene over 33.7 mol% methanol in the dynamic extractions of bitumen, this additional condition was only tested once on each of FT Froth and Pond Froth. All dynamic extractions were conducted at 24 MPa and 333 K, and at a CO_2 flow rate of 20 mL/min (measured at pump conditions of 24 MPa and 275 K).

HTSD data was not available for the dynamic extractions of FT Froth or Pond Froth by the time this thesis was submitted. Thus the type of hydrocarbons extracted from FT Froth and Pond Froth is not presented in this thesis.

4.2.1 Dynamic Extractions with SC-CO_2 only

4.2.1.1 Hydrocarbon Extraction Efficiencies

Table 16 displays the extraction efficiencies and mass balance results for dynamic extractions of FT Froth and Pond Froth using SC-CO_2. A discussion of the mass balance results is provided in Section 4.2.3.

The first two FT Froth dynamic extractions (one of which was SC-CO_2 only, one of which was 15 mol% toluene in SC-CO_2), were conducted using 50 g of FT Froth feed material, as had been done for bitumen-containing materials previously tested in the SFE research group. However, to avoid sample carryover into the outlet lines and to allow for comparison to bitumen dynamic extractions, 25 g of feed material was used for all remaining extractions of FT Froth and Pond Froth. The results of the dynamic extraction of 50 g FT Froth using SC-CO_2 are presented for completeness.

As seen in Table 16, for each extraction condition, the extraction efficiencies calculated based on hydrocarbon extracts are greater than the extraction efficiencies calculated based on vessel residue. This may indicate that the extraction efficiencies based on hydrocarbon extracts are biased high – potentially as a result of residual water and/or solids in the extracts. However, there is less variability in the ranges for extraction efficiencies calculated based on hydrocarbon extracts and as such, these results will be used for all further discussions.

Table 16. Extraction efficiencies and mass balance results for dynamic extractions of FT Froth and Pond Froth using SC-CO_2.

Feed Material	**Date**	*Initial bitumen* (g)	*Mass of extracts* (g)	*Mass in residue* (g)	**Extraction Efficiency** (wt%)						**Mass Balance** [3] (wt%)
					Based on extracts [1]			*Based on residue* [2]			
					Replicate	*Average*	*Range* [4]	*Replicate*	*Average*	*Range* [4]	
FT Froth	03-09-18 [5]	26.104	10.819	15.39	41.4	-	-	41.0	-	-	100.5
	05-28-18	15.560	7.168	8.79	46.1	45.9	0.289	43.5	44.0	1.06	102.6
	05-30-18	15.444	7.070	8.56	45.8			44.6			101.3
Pond Froth	06-20-18	12.894	4.913	7.93	38.1	38.3	0.425	38.5	37.2	2.52	99.7
	06-25-18	13.714	5.283	8.78	38.5			36.0			102.7

[1] Calculated using Equation 1

[2] Calculated using Equation 2

[3] Calculated using Equation 3

[4] n = 2

[5] 50 g of feed material used (as opposed to 25 g)

The results of the dynamic extractions of 25 g FT Froth indicate that SC-CO_2 alone is capable of extracting an average of 45.9 wt% of the hydrocarbons from FT Froth, with a range of 0.289 wt%. The dynamic extraction of 50 g FT Froth had an extraction efficiency of 41.44 wt%, which is less than the extraction efficiency from the dynamic extractions of 25 g of FT Froth. This may be because 50 g of FT Froth had a lower overall cumulative CO_2 to initial bitumen ratio (approximately 100 g/g) due to the higher initial mass of bitumen in the vessel. For dynamic extractions of 25 g of FT Froth, the overall cumulative CO_2 to initial bitumen ratio was approximately 165 g/g. The dynamic extractions of 25 g of FT Froth are more comparable to the dynamic extractions of bitumen in terms of both mass of bitumen in the vessel and cumulative CO_2 to initial bitumen ratio and as such, the results of the 25 g extractions will be used for all further discussions.

SC-CO_2 extracts a lower mass of hydrocarbons from Pond Froth than from FT Froth. SC-CO_2 alone extracts an average of 38.3 wt% of the hydrocarbons from Pond Froth, with a range of 0.425 wt%.

There are sources of error specific to the dynamic extractions of FT Froth and Pond Froth that may bias extraction efficiencies and/or produce variability in the results. Subsamples of FT Froth and Pond Froth (approximately 50 g) were provided by Syncrude in 120 mL jars. The dynamic extractions required only 25 g of feed material, and therefore only half of each subsample was used. Prior to placing 25 g of material in the vessel, the contents of the 120 mL jar were heated and mixed to achieve homogeneity. However it is possible the contents of the jar were not mixed well enough and therefore the composition of the 25 g sample transferred into the vessel was not the same as the composition detailed in Table 8. Additionally, for the extracts, it was assumed that all of the water was evaporated from the extracts and that no solids were collected. A visual inspection of the extracts was performed after the five day drying period to ensure no water or solids were collected. However it is possible that the final air-dried extracts contained small amounts of water and/or solids, which would overestimate extraction efficiencies calculated based on hydrocarbon extracts.

Mass closure of the solids was conducted using the mass of solids in the original sample and the mass of solids in the vessel residue (as determined by Dean-Stark extraction) to determine if solids may have been collected in the vials/jars along with the extracts. However, this mass closure is not entirely accurate as some solids were so fine that it was not possible to transfer them from the vessel into the vessel residue solution jar using toluene, as they would not remain suspended in the liquid. As such, some solids had to be wiped out of the vessel after the dynamic extractions of FT Froth and Pond Froth and so mass closure of the solids for these extractions will be less than 100 wt%. For the dynamic extractions of FT Froth, mass closure of the solids ranged between 87 and 89 wt% and for Pond Froth these values ranged from 80 to 82 wt% (detailed data not presented). Because the mass closures are not accounting for between 10 and 20 wt% of the solids, it is possible that a small amount of solids was contained within the extract collection vials/jars.

Figure 29 illustrates the cumulative mass percent of hydrocarbons extracted from FT Froth and Pond Froth using SC-CO_2. The CO_2 only bitumen dynamic extraction curves are provided for comparison purposes.

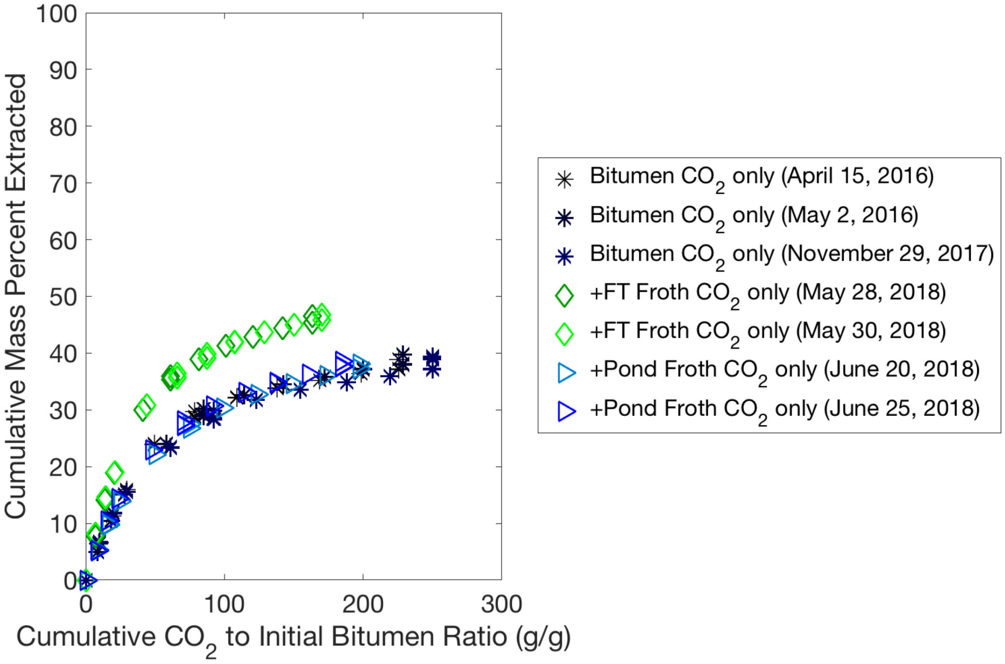


Figure 29. Effect of three different feed materials - bitumen, FT Froth and Pond Froth, on the cumulative mass percent of hydrocarbons extracted using SC-CO_2 at 333K, 24 MPa and a CO_2 flow rate of 20 mL/min.

It can be seen in Figure 29 that, at the end of the extraction, dynamic extractions of FT Froth and Pond Froth have lower overall cumulative CO_2 to initial bitumen ratios than bitumen extractions. While roughly the same mass of CO_2 is flowing through the vessel during each of the dynamic extractions, the FT Froth and Pond Froth extractions have greater masses of initial bitumen in the vessel and thus, lower cumulative CO_2 to initial bitumen ratios. The difference in cumulative CO_2 to initial bitumen ratio between FT Froth and Pond Froth is due to variations in the initial mass of bitumen in the vessel – even though 25 g of each feed material was added to the vessel, FT Froth contains approximately 61 wt% bitumen whereas Pond Froth is made up of 51 wt% bitumen. The FT Froth and Pond Froth extractions have overall cumulative CO_2 to initial bitumen ratios of approximately 165 and 200 g/g, respectively. For the three SC-CO_2 dynamic extractions of bitumen, after a cumulative CO_2 to initial bitumen ratio of 200 g/g approximately 36 wt% of the original bitumen has been extracted – this extraction efficiency value will be used for all further comparisons to equivalent dynamic extractions of FT Froth and Pond Froth. For dynamic extractions of bitumen, 200 g/g is equivalent to a total dynamic extraction time of 105 minutes (as opposed to 120 minutes).

The bitumen used in the dynamic extractions is lighter than the bitumen in both the FT Froth and Pond Froth feed materials (as seen in Figure 7). The virgin bitumen begins distilling at 200 °C and by 735 °C, 89 wt% of the original bitumen has distilled. The FT Froth bitumen begins distilling at 260 °C and 78 wt% of the FT Froth bitumen is distilled by 735 °C. Pond Froth bitumen is similar to that of FT Froth, though it begins distilling later, at 300 °C, and a higher portion of the Pond Froth bitumen, 84 wt%, is distilled by 735 °C. This research, as well as that of Hwang and Ortiz (2000), has shown that SC-CO_2 preferentially extracts lighter hydrocarbons. As such, it might be expected that dynamic extractions of bitumen would result in higher extraction efficiencies than dynamic extractions of FT Froth and Pond Froth, as these two feed materials contain bitumen with heavier hydrocarbons. However, this was not the case – more hydrocarbons were extracted from FT Froth and Pond Froth than from bitumen. Further, though FT Froth and Pond Froth contain hydrocarbons of similar weights, more hydrocarbons were extracted from FT Froth than from Pond Froth. Thus, the hydrocarbon extraction efficiency is influenced not only by the properties of the hydrocarbons, but by properties of the matrices as well.

It might be expected that mass transfer effects may be more important during FT Froth and Pond Froth extractions, as compared to bitumen extractions, because of the presence of both water and solids. However, there is no increase in the slopes of the extraction curves in Figure 29 following the second static period (which occurs at a cumulative CO_2 to initial bitumen ratio of 70 g/g for FT Froth and Pond Froth extractions, and 90 g/g for bitumen extractions), nor is there a substantial increase in the mass of hydrocarbons extracted following this static period. This is consistent with the system operating at or near equilibrium, and thus the extractions of all three feed materials are likely controlled by solubility at this point in the dynamic extraction.

Approximately 10 wt% more hydrocarbons were extracted from FT Froth than from bitumen, and 2 wt% more hydrocarbons were extracted from Pond Froth than from bitumen, despite FT Froth and Pond Froth containing heavier hydrocarbons than the bitumen feed material. FT Froth and Pond Froth consist of 27 and 44 wt% water, respectively, and 12 and 5 wt% solids, respectively. There are no reports of solids positively influencing such an extraction, and thus it is likely that the water content of these two feed materials is responsible for the higher hydrocarbon extraction efficiencies. Adding small amounts of water may have an effect similar to that of adding a chemical modifier – the addition of water or a chemical modifier that is more polar then CO_2 can enhance the solubility of polar hydrocarbons, thus increasing the hydrocarbon extraction efficiency (Al-Marzouqi et al. 2009). Macnaughton and Foster (1994) examined the solubility of two priority pollutants in SC-CO_2 and SC-CO_2 saturated with water. At a pressure of 20.8 bar and a temperature of 333 K, saturating the SC-CO_2 with water increased the solubility of the slightly polar pesticide 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT) by 10%. However at these same conditions, saturating SC-CO_2 with water increased the solubility of the highly polar herbicide (2,4-dichlorophenoxy)acetic acid (2,4-D) by 82%. Thus water addition can improve the solubility of polar compounds in SC-CO_2 and it appears that the higher the polarity of the compound, the greater the impact of water has on solubility.

As seen in Figure 29, the FT Froth extraction curves have a noticeably steeper initial slope than that of the bitumen curves. This is likely a reflection of the enhanced solubility of polar hydrocarbons in SC-CO_2 in the presence of water. Despite consisting of heavier hydrocarbons than the bitumen samples, 10 wt% more hydrocarbons were extracted from FT Froth than from bitumen, indicating the positive influence of water on the extraction of hydrocarbons. It is also possible that the addition of water has a stronger influence on the extraction of hydrocarbons from FT Froth than it would on the extraction of hydrocarbons from bitumen, as FT Froth consists of heavier hydrocarbons than the bitumen samples, and heavier hydrocarbons tend to also be more polar (Yoon et al. 2009; Speight 2006).

Approximately 8 wt% more hydrocarbons were extracted from FT Froth than from Pond Froth. It is not clear why more hydrocarbons were extracted from FT Froth than from Pond Froth, despite FT Froth containing roughly 7 wt% more solids, though it may be due to the lower water content in FT Froth. FT Froth consists of approximately 27 wt% water (equivalent to 7 mL of water for a 25 g sample) while Pond Froth consists of 44 wt% water (equivalent to 11 mL of water for a 25 g sample).

Authors have noted both positive and negative influences of water on the SFE of hydrocarbons from oil sands and soil matrices (La and Guigard 2015; Rudyk and Spirov 2014). For example, Al-Marzouqi et al. (2009) investigated the effects of 0-20 wt% water on the extraction of oil from soil using SC-CO_2. They reported that adding 5 and 10 wt% water increased the amount of oil extracted from 71.14 wt% (no water) to 77.24 and 81.57 wt%, respectively. However, adding 15 and 20 wt% water decreased the amount of oil extracted to 70.62 and 47.62 wt%, respectively. Studies of SFE of hydrocarbons from oil sands and soil matrices indicate that the addition of water can improve hydrocarbon extraction from these matrices, however too much water can have a negative effect on the extraction. In matrices with high solids content, excess water likely acts as a barrier to CO_2 penetration, shielding the hydrocarbons from CO_2, and thereby impeding the mass transfer of hydrocarbons into SC-CO_2 and/or out of their matrix (La and Guigard 2015; Al-Marzouqi et al. 2009; Camel et al. 1993). It is possible that the additional water in Pond Froth is creating a ‘shielding’ effect, limiting the mass transfer of hydrocarbons. However, mass transfer has more of an effect on the extraction of hydrocarbons from oil sands and soil matrices that have a relatively high solids content, compared to FT Froth and Pond Froth.

Because bitumen contains many non-polar compounds and water is highly polar, it is also possible that the additional water in Pond Froth, compared to FT Froth, reduced the capacity of CO_2 to extract non-polar compounds, resulting in a lower hydrocarbon extraction efficiency (Al-Marzouqi et al. 2009).

FT Froth contains roughly 12 wt% solids, while Pond Froth consists of 5 wt% solids. Both feed materials have solids with similar particle size distributions, though FT Froth solids are slightly larger. In FT Froth, 80% of the solids are ≤ 100 μm, compared to Pond Froth where 80% of the solids are ≤ 60 μm. Both feed materials consist of sands and fines, though the majority of the solids in both feed materials are fines. It is possible that the solids (particularly the fines) in these feed materials could affect mass transfer. One study found that SFE of organics from clays was less efficient because of the small particle size and high adsorption capacity of clays (Laitinen et al. 1994). Hawthorne et al. (1993) noted that pollutants in a soil sample may be inhibited by physical barriers such as being trapped between clay plates.

However, dynamic extractions of both FT Froth and Pond Froth extracted more hydrocarbons than dynamic extractions of bitumen, despite containing solids and consisting of heavier hydrocarbons. While the water content of these two feed materials likely explains the higher extraction efficiencies, it does not appear that the solids content of either feed material has had a substantial impact on the extractions. Further, both FT Froth and Pond Froth contain hydrocarbons of similar weights, and while FT Froth has a lower water content than Pond Froth, 8 wt% more hydrocarbons were extracted from FT Froth samples despite its 7 wt% higher solids content. Thus, it appears that the presence of solids at these low concentrations does not have a substantial impact on the extraction of hydrocarbons from FT Froth and Pond Froth.

4.2.2 Effects of Modifier Addition to SC-CO_2

4.1.2.1 Hydrocarbon Extraction Efficiencies

Dynamic extractions using SC-CO_2 with one of two modifiers, toluene or methanol, were conducted on both FT Froth and Pond Froth. Table 17 displays the extraction efficiencies and mass balance results for these dynamic extractions. Mass balance results are discussed in Section 4.2.3.

Table 17. Extraction efficiencies and mass balance results for dynamic extractions of FT Froth and Pond Froth using 15 mol% toluene and 33.7 mol% methanol in SC-CO_2.

Feed Material	**Date**	**Modifier**	*Initial bitumen* (g)	*Mass of extracts* (g)	*Mass in residue* (g)	**Extraction Efficiency** (wt%)						**Mass Balance**[3] (wt%)
						Based on extracts[1]			*Based on residue*[2]			
						Rep.	*Average*	*Range*[4]	*Rep.*	*Average*	*Range*[4]	
FT Froth	03-13-18[5]	15 mol% toluene	30.644	21.825	8.21	71.2	-	-	73.2	-	-	98.1
	03-19-18		14.919	10.760	3.71	72.1	72.6	0.910	75.1	74.8	0.656	97.0
	05-24-18		15.868	11.589	4.05	73.0			74.5			98.6
	07-09-18	33.7 mol% methanol	16.018	8.701	6.54	54.3	-	-	59.2	-	-	95.5
Pond Froth	06-27-18	15 mol% toluene	12.865	8.853	4.19	68.8	68.6	0.486	67.4	67.4	0.020	101.5
	06-29-18		13.225	9.037	4.31	68.3			67.4			100.9
	07-05-18	33.7 mol% methanol	12.975	6.500	6.17	50.1	-	-	52.4	-	-	97.9

[1] Calculated using Equation 1

[2] Calculated using Equation 2

[3] Calculated using Equation 3

[4] n = 2

[5] 50 g of feed material used (as opposed to 25 g)

As shown in Table 17, the extraction efficiencies calculated based on hydrocarbon extracts are lower than extraction efficiencies calculated based on vessel residue. There is also more variability in the extraction efficiencies calculated based on hydrocarbon extracts, which will be discussed later. However for consistency, extraction efficiencies calculated based on hydrocarbon extracts will be used for further analysis.

Dynamic extractions of 25 g of FT Froth indicate that SC-CO_2 with 15 mol% toluene is capable of extracting an average of 72.6 wt% of the hydrocarbons from FT Froth, with a range of 0.910 wt%. The dynamic extraction of 50 g of FT Froth with 15 mol% toluene extracted 71.2 wt% of the hydrocarbons from the feed material. This is fairly close to the values obtained using 25 g of FT Froth, despite having a much lower cumulative CO_2 to initial bitumen ratio of 82 g/g. The same dynamic extraction conducted with 25 g of FT Froth had a ratio of approximately 165 g/g. Thus it is likely that the dynamic extraction with 50 g of FT Froth had some carryover of the feed material into the outlet lines, resulting in a higher extraction efficiency than should have been achieved after a cumulative CO_2 to initial bitumen ratio of 82 g/g. The dynamic extractions with 25 g of FT Froth are more reliable and more comparable to the dynamic extractions of bitumen in terms of both mass of bitumen originally in the vessel and cumulative CO_2 to initial bitumen ratio. As such, the results of the 25 g FT Froth extractions with 15 mol% toluene will be used for all further discussion.

A single FT Froth extraction with 33.7 mol% methanol was performed. At this extraction condition, 54.3 wt% of the original bitumen in the FT Froth was extracted. As a duplicate extraction was not performed, there is no way to verify this result other than using the mass balance. Approximately 95 wt% of the original bitumen was recovered in the extract jars and the vessel residue. This good mass closure indicates that the extraction efficiencies calculated for this dynamic extraction are likely reasonable.

Dynamic extraction of 25 g of Pond Froth indicate that 15 mol% toluene in SC-CO_2 can extract on average 68.6 wt% of the hydrocarbons from Pond Froth with a range of 0.486 wt%.

At a concentration of 33.7 mol% methanol in SC-CO_2, 50.1 wt% of the original bitumen was extracted from 25 g of Pond Froth. This extraction was only conducted once, and thus the way to verify this result is with the mass balance. Approximately 98 wt% of the original bitumen in the Pond Froth was recovered from the extract collection jars and the vessel residue. This mass balance check indicates that the extraction efficiencies for this dynamic extraction are likely reasonable.

As with dynamic extractions of bitumen with 10 mol% toluene, dynamic extractions of FT Froth and Pond Froth with modifiers had a substantial amount extract leaking out of the jars such that the acetone/dry ice bath was used to collect the leaking extract. Leakage was particularly noticeable for later extractions (15 mol% toluene and 33.7 mol% methanol Pond Froth extractions, and 33.7 mol% methanol FT Froth extraction) as the seals on the jar lids got progressively worse as more modifier extractions were performed. As such, before each of the dynamic extractions of FT Froth and Pond Froth with modified SC-CO_2, the acetone/dry ice bath was rinsed with toluene and then following the dynamic extraction, the contents of the acetone/dry ice bath were poured and rinsed with toluene into a pre-weighed 250 mL jar and dried until the acetone and water were evaporated, at which point the final mass of the jar and extracts was measured. Despite trying to collect all of the leaking extract, some may have splashed out of the acetone/dry ice bath and/or may have evaporated. This may account for the increased variability seen in the extraction efficiencies calculated based on hydrocarbon extracts and for the lower extraction efficiencies based on hydrocarbon extracts (compared to extraction efficiencies based on vessel residue).

Extraction efficiencies calculated based on hydrocarbon extraction efficiencies may have been overestimated if a small amount of water and/or solids remained in the extracts after five days of drying. A mass closure of the solids was conducted using the mass of solids in the original sample and the mass of solids in the vessel residue to determine if solids may have been collected in the collections jars along with the extracts. However, as previously discussed, the mass closures are not entirely accurate due to difficulties in collecting all of the fine solids from the vessel after each extraction. As such, some solids had to be wiped out of the vessel after each extraction, and so the mass closure of the solids for FT Froth and Pond Froth extractions will be less than 100 wt%. For the dynamic extractions of FT Froth with a modifier, mass closures of the solids ranged between 85 and 95 wt%, and for Pond Froth these values ranged from 79 to 98 wt% (detailed data not presented). Thus, it is possible that a small amount of solids was contained within some of the extract collection jars.

Figure 30 and Figure 31 illustrate the effects of 15 mol% toluene and 33.7 mol% methanol, respectively, on the cumulative mass percent of hydrocarbons extracted from FT Froth and Pond Froth using SC-CO_2. The bitumen dynamic extraction curves for extractions with CO_2 only, 15 mol% toluene and 33.7 mol% methanol are shown for comparison purposes.

There is a 'jump' in the mass percent of hydrocarbons extracted at the end of the modifier extraction curves in Figure 30 and Figure 31, especially the 15 mol% toluene Pond Froth extraction curves, and the 33.7 mol% methanol FT Froth and Pond Froth extractions. This is a reflection of the extract collected in the acetone/dry ice bath. Though this extract was collected throughout the duration of the dynamic extraction, it was not collected evenly – more extract leaked out of collection jars during Set 2 of the extraction. Therefore, because the extract collected in the acetone/dry ice bath could not be accurately distributed throughout the rest of the curve, it was added to the end of each applicable extraction curve.

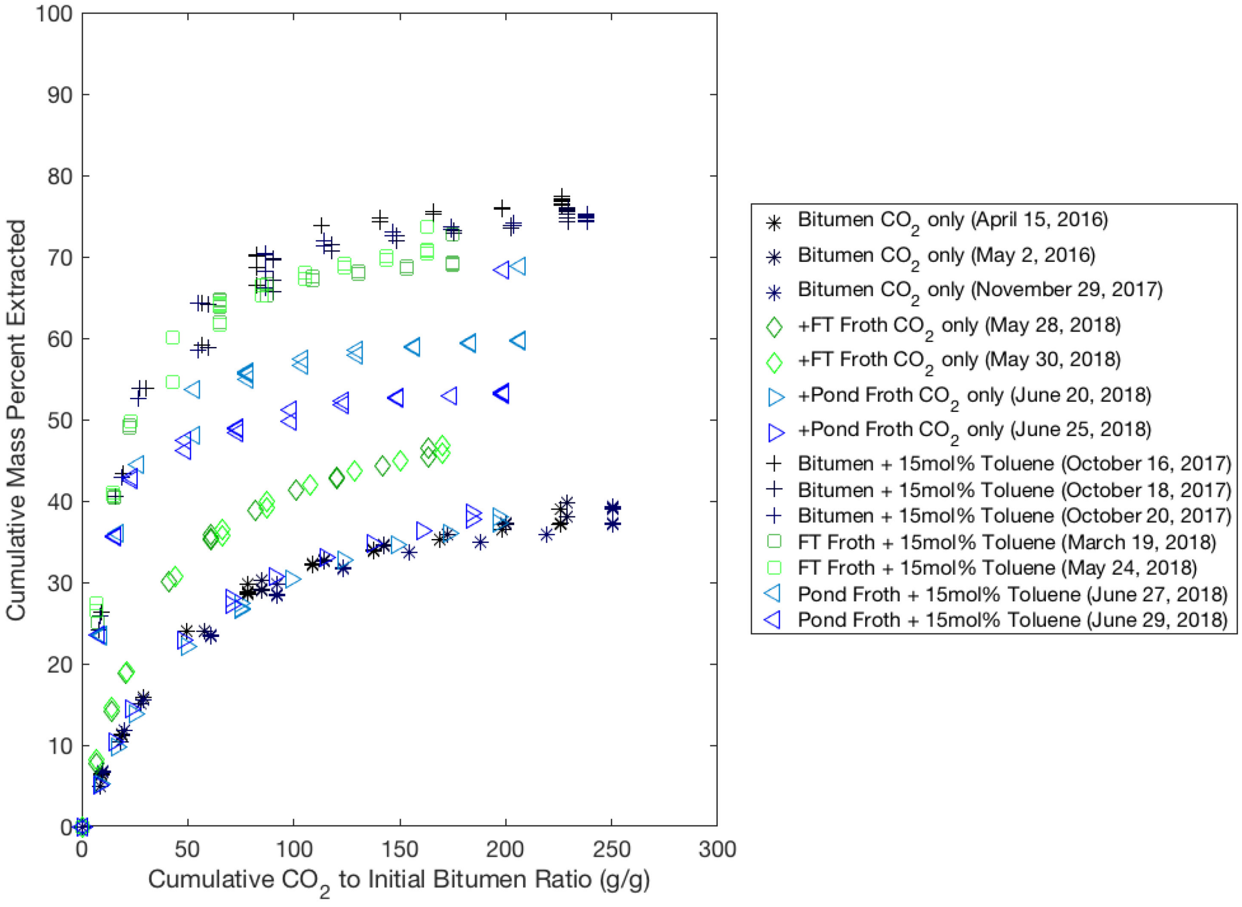


Figure 30. Effect of 15 mol% toluene in SC-CO$_2$ on the cumulative mass percent of hydrocarbons extracted from three different feed materials - bitumen, FT Froth and Pond Froth.

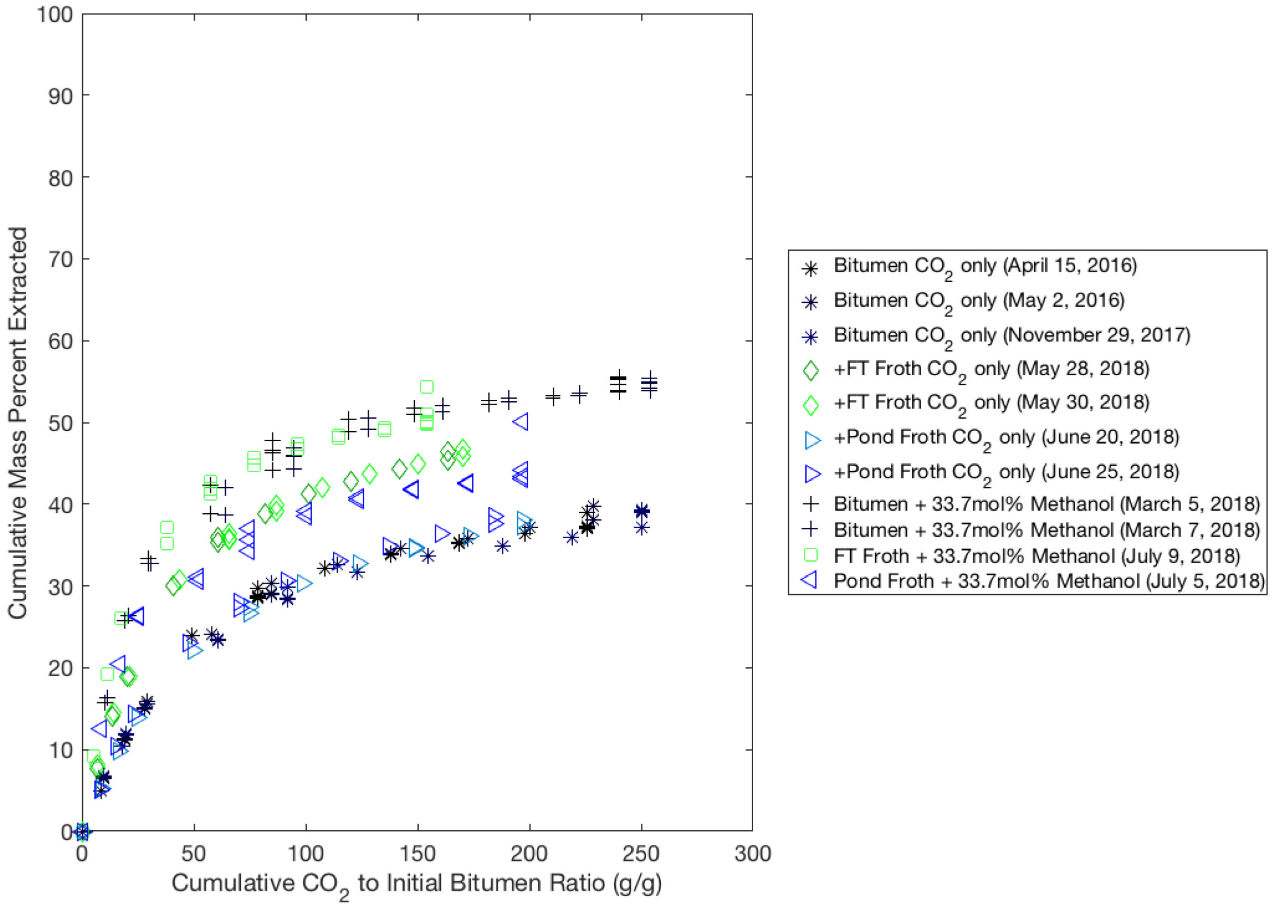


Figure 31. Effect of 33.7 mol% methanol in SC-CO_2 on the cumulative mass percent of hydrocarbons extracted from three different feed materials - bitumen, FT Froth and Pond Froth.

It can be seen in Figure 30 and Figure 31 that the FT Froth and Pond Froth extractions have lower overall cumulative CO_2 to initial bitumen ratios than bitumen alone. The dynamic extractions of FT Froth and Pond Froth have overall cumulative CO_2 to initial bitumen ratios of approximately 170 and 200 g/g, respectively. For the three dynamic extractions of bitumen with 15 mol% toluene, after a cumulative CO_2 to initial bitumen ratio of 200 g/g approximately 74 wt% of the hydrocarbons have been extracted. For dynamic extractions of bitumen with 33.7 mol% methanol in SC-CO_2, after a cumulative CO_2 to initial bitumen ratio of 200 g/g, 53 wt% of the hydrocarbons have been extracted. These extraction efficiency values will be used for all further comparison to equivalent dynamic extractions of FT Froth and Pond Froth.

Table 18 compares the average extraction efficiencies for dynamic extractions of bitumen, FT Froth and Pond Froth under three conditions: SC-CO_2 only, SC-CO_2 with 15 mol% toluene and SC-CO_2 with 33.7 mol% methanol. For all three feed materials, the addition of either toluene or methanol as a modifier increases the extraction efficiency by at least 17% compared to SC-CO_2 only. With toluene or methanol addition, the slopes of the extraction curves in Figure 30 and Figure 31 increase – likely a reflection of the increased solubility of heavier hydrocarbons in SC-CO_2, as previously discussed in section 4.1.2. Further, it can be seen that 15 mol% toluene is more effective than an equivalent mass percent of methanol (33.7 mol% methanol), in terms of extraction efficiency. The initial slopes of the extraction curves are considerably steeper with toluene addition (Figure 30) than with methanol addition (Figure 31). The reasons for this were discussed in sections 4.1.2 and 4.1.3.

Table 18. Comparison of extraction efficiency for dynamic extractions of three feed materials under conditions three conditions: SC-CO_2, SC-CO_2 with 15 mol% toluene and SC-CO_2 with 33.7 mol% methanol.

Feed Material	**Extraction Condition**	**Average Extraction Efficiency** [1] (wt%)	**Increase in Extraction Efficiency**[2] (%)
Bitumen	SC-CO_2 only	36	-
	15 mol% Toluene in SC-CO_2	74	106
	33.7 mol% Methanol in SC-CO_2	53	47
FT Froth	SC-CO_2 only	46	-
	15 mol% Toluene in SC-CO_2	73	59
	33.7 mol% Methanol in SC-CO_2	54	17
Pond Froth	SC-CO_2 only	38	-
	15 mol% Toluene in SC-CO_2	69	82
	33.7 mol% Methanol in SC-CO_2	50	32

[1] At a CO_2 to initial bitumen ratio of approximately 200 g/g

[2] Compared to SC-CO_2 only extraction condition

While the addition of toluene or methanol improves the extraction of hydrocarbons from FT Froth and Pond Froth, the presence of water in these two feed materials appears to influence the action of these modifiers. It can be seen in Table 18 that adding 15 mol% toluene to a dynamic extraction of bitumen improves extraction efficiency by 106% but adding 15 mol% toluene to dynamic extractions of FT Froth and Pond Froth improves the extraction efficiency by only 59 and 82%, respectively. Similarly, adding 33.7 mol% methanol to a bitumen extraction improves extraction efficiency by 47%, whereas adding 33.7 mol% methanol to FT Froth and Pond Froth extractions improves extraction efficiency by only 17 and 32% respectively. Using SC-CO_2 alone, FT Froth had the highest extraction efficiency and as previously discussed, this is likely due to its 27 wt% water content. The addition of a modifier to an FT Froth extraction improves the extraction of hydrocarbons, but not as substantially as the addition of a modifier to a bitumen extraction (which involves no water). After the addition of either 15 mol% toluene or 33.7 mol% methanol, the extraction efficiencies for dynamic extractions of bitumen and FT Froth are within 1 wt% of each other. This indicates that the presence of water in a feed material may lessen the effect of modifier addition on hydrocarbon extraction efficiency.

Fewer hydrocarbons were extracted from Pond Froth than from FT Froth, as before, but the addition of modifiers has a greater effect on Pond Froth than on FT Froth. It is not clear why modifiers appear to have a greater effect on the extraction of hydrocarbons from Pond Froth, despite it having a higher water content than FT Froth, though it may be due to challenges in solubilizing and extracting the remaining, heavy hydrocarbons in FT Froth. As seen previously, there was a slight decrease in extract production rate with increasing modifier concentrations and this may have been due to difficulties in extracting the remaining, heavy hydrocarbons. A similar situation may arise with the addition of high concentrations of a modifier to FT Froth extractions.

Methanol is water-soluble and as such, for dynamic extractions of FT Froth and Pond Froth, methanol may be dissolving into the water present in these feed materials, decreasing its effectiveness as a modifier to SC-CO_2. As cited in Roop et al. (1989), short-chain alcohols have been shown to favour the aqueous phase over the SC-CO_2 phase. This could explain why adding methanol to SC-CO_2 during a dynamic extraction of bitumen increases the extraction efficiency by a greater percentage than adding methanol to SC-CO_2 during a dynamic extraction of FT Froth or Pond Froth.

However, because toluene is insoluble in water, it would not favour the water-rich phase over the SC-CO_2-rich phase. Instead, it is possible that the presence of a high concentration of toluene in SC-CO_2 decreases the ability of water to act as a polar modifier. Toluene and SC-CO_2 enter the vessel presumably as a homogenous mixture, which may decrease the ability of water to mix with SC-CO_2, thus limiting water’s ability to enhance the solubility of hydrocarbons in SC-CO_2.

4.2.3 Hydrocarbon Mass Balances for FT Froth and Pond Froth Dynamic Extractions

For each dynamic extraction of FT Froth and Pond Froth, a mass balance check was performed on the hydrocarbons by comparing the mass of hydrocarbons originally placed in the vessel, with the cumulative mass of hydrocarbons collected in the collection vials/jars and the mass of hydrocarbons remaining in the vessel residue. Mass balance results for FT Froth and Pond Froth dynamic extractions are displayed in Tables 16 and 17. For the 12 dynamic extractions of FT Froth and Pond Froth, mass balances ranged from 95.5 to 102.7 wt% hydrocarbon recovery. These mass balance results are very good, and indicate that the hydrocarbons were quantitatively accounted for in the extracts and vessel residue.

In addition to the factors that may contribute to mass balance discrepancies that were discussed in Section 4.1.4 , there are sources of error specific to dynamic extractions of FT Froth and Pond Froth that could influence mass balance results. The composition of the FT Froth or Pond Froth feed material placed in the vessel may not have been the same as the composition detailed in Table 8, which would influence the initial mass of bitumen that was assumed to be in the vessel. Further, it was assumed that any water collected in the extracts was evaporated during the five day drying period and that no solids were collected along with the hydrocarbon extracts. However, it is possible that the air-dried extracts contained small amounts of water and/or solids, which would contribute to greater than 100 wt% hydrocarbon recovery. Additionally, because extract leakage out of the collection jars was particularly noticeable for dynamic extractions of FT Froth and Pond Froth with modified SC-CO_2, hydrocarbon recoveries less than 100 wt% may be the result of leaked extract that was not collected in the acetone/dry ice bath.

CHAPTER 5 Conclusions and Recommendations

5.1 Conclusions

This thesis research investigated the extraction of hydrocarbons from bitumen and bitumen-containing process and process waste streams using SC-CO_2. Initial dynamic extractions investigated the hydrocarbon extraction efficiencies and the type of hydrocarbons extracted from bitumen using SC-CO_2 at a density of 0.78 g/mL, and one of toluene or methanol as a modifier to SC-CO_2 at a concentration of 5, 10 or 15 mol%. The most successful modifier type and concentration was then tested for the extraction of bitumen from FT Froth and Pond Froth.

The research conducted in this thesis has answered the objectives presented in Chapter 1:

1. At a density of 0.78 g/mL, SC-CO_2 alone is capable of extracting 39.2 wt% of the original bitumen. The addition of either toluene or methanol at a concentration of 5, 10 and 15 mol% in SC-CO_2 increases the mass percent of hydrocarbons extracted for any given cumulative CO_2 to initial bitumen ratio. Toluene addition is more effective than methanol, in terms of increasing the hydrocarbon extraction efficiency, on both a molar and mass concentration basis. The most successful extraction condition was 15 mol% toluene addition to SC-CO_2, which resulted in an extraction efficiency of 75.9 wt%.

2. At a density of 0.78 g/mL, SC-CO_2 is capable of extracting 45.9 wt% of the original bitumen from FT Froth and 38.3 wt% of the original bitumen from Pond Froth. The presence of water in the feed materials had a slightly positive effect on the extraction of hydrocarbons, similar to the effects of adding a modifier. The presence of solids at low concentrations does not have a substantial impact on the extraction of hydrocarbons from FT Froth and Pond Froth. After a cumulative CO_2 to initial bitumen ratio of approximately 200 g/g, SC-CO_2 extracts 10 and 2 wt% more hydrocarbons from FT Froth and Pond Froth, respectively, than from bitumen which consists of lighter hydrocarbons than FT Froth and Pond Froth. At a concentration of 15 mol% in SC-CO_2, the addition of

toluene increases the extraction efficiency to 72.3 and 68.6 wt% for FT Froth and Pond Froth, respectively.

3. During dynamic extractions of bitumen, the lightest hydrocarbons are extracted initially. As the dynamic extraction proceeds, progressively heavier hydrocarbons are extracted. As the extraction efficiency increases, through the addition of increasing concentrations of either toluene or methanol, heavier hydrocarbons are extracted. The condition of 15 mol% toluene in SC-CO_2 produced the heaviest hydrocarbon extracts from bitumen.

Overall, this thesis has demonstrated the successful extraction of hydrocarbons from bitumen and bitumen-containing process and process waste streams using SC-CO_2 with and without modifiers.

5.2 Recommendations

Recommendations pertaining to the research conducted in this thesis are as follows:

1. Investigating the effects of a more readily available modifier, such as naphtha, in order to decrease the potential operating costs of this technology to the oil sands industry.
2. Testing the addition of varying concentrations of water on dynamic extractions of bitumen to enhance the understanding of the effects of water on the extraction of hydrocarbons.
3. Testing the addition of both water and a chemical modifier (toluene or methanol) on dynamic extractions of bitumen to provide additional insight into the combined effects of water and a chemical modifier. Modifier concentrations of 5 and 15 mol% are suggested in order to better understand these effects.
4. Conducting SARA analysis of extracted hydrocarbons and vessel residue hydrocarbons for further insight into the quality of the extracts and the upgrading potential of SFE. Heavy metals analysis of hydrocarbon extracts and residue would also provide insight into the upgrading potential of SC-CO_2. Elemental analysis would provide

insight into the elemental composition of C, H, S, N and O in the hydrocarbon extracts and residue, and, along with heavy metals analysis, may indicate why initial hydrocarbon extracts are darker when toluene or methanol is added as a modifier to SC-CO_2.

Recommendations for future work regarding the extraction of hydrocarbons from process and process waste streams generated from surface mined oil sands are as follows:

1. Conducting a cost-benefit analysis of modifier addition to determine the optimum modifier type and concentration. As chemical modifiers can be expensive, the financial cost of high concentrations of a modifier should be weighed against the economic and environmental benefits of the extracted hydrocarbons in order to determine an optimum concentration.
2. Given the current volume of tailings and the large amounts of process and process waste streams generated during ex-situ bitumen recovery, a continuous, commercial-scale SFE for hydrocarbon extraction from waste streams would be desirable, as opposed to a batch system.

References

Abu-Khader, M.M., and Speight, J.G. 2007. Influence of high asphaltene feedstocks on processing. Oil & Gas Science and Technology, **62**(5): 715-722.

Akgerman, A. 1997. Supercritical fluids in environmental remediation and pollution prevention. *In* Supercritical fluids: extraction and pollution prevention. *Edited by* M.A. Abraham and A.K. Sunol. American Chemical Society, Washington, DC. pp. 208-231.

Alberta Environment and Parks. 2018. Total area and volume of oil sands tailings ponds over time. Available from http://osip.alberta.ca/map/ [cited 6 July 2018].

Allawzi, M., Al-Otoom, A., Allaboun, H., Ajlouni, A., and Al Nseirat, F. 2011. CO_2 supercritical fluid extraction of Jordanian oil shale utilizing different co-solvents. Fuel Processing Technology, **92**: 2016-2023.

Allen, E.W. 2008. Process water treatment in Canada's oil sands industry: I. target pollutants and treatment objectives. Journal of Environmental Engineering and Science, **7**: 123-138.

Al-Marzouqi, A.H., Zekri, A.Y., Jobe, B., and Dowaidar, A. 2007. Supercritical fluid extraction for the determination of optimum oil recovery conditions. Journal of Petroleum Science and Engineering, **55**(1-2): 37-47.

Al-Marzouqi, A.H., Zekri, A.Y., Azzam, A.A., and Dowaidar, A. 2009. Hydrocarbon recovery from porous media using supercritical fluid extraction. Journal of Porous Media, **12**(6): 489-500.

Al-Sabawi, M., Seth, D., and de Bruijn, T. 2011. Effect of modifiers in n-pentane on the supercritical extraction of Athabasca bitumen. Fuel Processing Technology, **92**(10): 1929-1938.

American Society for Testing Materials (ASTM) International. 2011. Standard test methods for boiling point distribution of samples with residues such as crude oils and atmospheric and vacuum residues by high temperature gas chromatography (D7169). American Society for Testing Materials International, West Conshohocken, P.A.

American Society for Testing Materials (ASTM) International. 2017. Standard practice for classification of soils for engineering purposes (Unified Soil Classification System) (D2487). American Society for Testing Materials International, West Conshohocken, P.A.

Autoclave Engineers. 2002. Engineering data book for bolted closure assembly. Autoclave Engineers, Division of Snap-tite Inc., Erie, PA.

Avila-Chavez, M.A., Eustaquio-Rincon, R., Reza, J., and Trejo, A. 2007. Extraction of hydrocarbons from crude oil tank bottom sludges using supercritical ethane. Separation Science and Technology, **42**(10): 2327-2345.

Brady, B.O., Kao, C.P.C., Dooley, K.M., Knopf, F.C. and Gambrell, R.P. 1987. Supercritical extraction of toxic organics from soils. Industrial and Engineering Chemistry, **26**(2): 261-268.

Brunner, G. 2005. Supercritical fluids: technology and application to food processing. Journal of Food Engineering, **67**(1-2): 21-33.

Burk, R.C., Kruus, P., Lahmad, L., and Crawford, G. 1990. Supercritical fluid extraction of trace organics from solids. Journal of Environmental Science and Health, Part B, **25**(5): 553-567.

Butler, R. 1998. SAGD comes of age. The Journal of Canadian Petroleum Technology, **37**(7): 9-12.

Camel, V., Tambuté, A., and Caude, M. 1993. Analytical-scale supercritical fluid extraction: a promising technique for the determination of pollutants in environmental matrices. Journal of Chromatography, **642**: 263-281.

Canada's Oil Sands Innovation Alliance (COSIA). n.d.a. Tailings. Available from https://www.cosia.ca/initiatives/tailings [cited 20 July 2018].

Canada's Oil Sands Innovation Alliance (COSIA). n.d.b. Tailings reduction technology. Available from https://www.cosia.ca/initiatives/tailings/projects/tailings-reduction-technology [cited 20 July 2018].

Canada's Oil Sands Innovation Alliance (COSIA). n.d.c. Carbon dioxide amended tailings. Available from https://www.cosia.ca/initiatives/tailings/projects/carbon-dioxide-amended-tailings [cited 9 November 2018].

Canada's Oil Sands Innovation Alliance (COSIA). n.d.d. Tailings centrifugation. Available from http://www.cosia.ca/initiatives/tailings/tailings-centrifugation [cited 15 August 2017].

Canadian Association of Petroleum Producers (CAPP). 2018. Oil sands deposit map. Available from https://www.canadasoilsands.ca/en/what-are-the-oil-sands [cited 23 July 2018].

Cansell, F., and Rey, S. 1998. Thermodynamic aspects of supercritical fluids processing: applications to polymers and waste treatment. Revue de L'Institut Français du Pétrole, **53**(1): 71-98.

Chalaturnyk, R.J., Scott, J.D., and Özüm, B. 2002. Management of oil sands tailings. Petroleum Science and Technology, **20**(9-10): 1025-1046.

Chow, D.L., Nasr, T.N., Chow, R.S., and Sawatzky, R.P. 2008. Recovery techniques for Canada's heavy oil and bitumen resources. Journal of Canadian Petroleum Technology, **47**(5): 12-17.

Clemente, J.S., MacKinnon, M.D., and Fedorak, P.M. 2004. Aerobic biodegradation of two commercial naphthenic acids preparations. Environmental Science & Technology, **38**: 1009-1016.

Clark, K.A., and Pasternack, D.S. 1932. Hot water separation of bitumen from Alberta bituminous sand. Industrial and Engineering Chemistry, **24**(12): 1410-1416.

Deo, M.D., Hwang, J., and Hanson, F.V. 1992. Supercritical fluid extraction of crude oil, bitumen-derived liquid and bitumen by carbon dioxide and propane. Fuel, **71**(12): 1519-1526.

Deo, M.D., Hwang, J., and Hanson, F.V. 1993. The effect of cosolubilizing lighter components on the asphaltene content of heavy oils. Fuel Processing Technology, **34**(3): 217-228.

Devenny, D.W. 2009. Part B report: overview of oil sand tailings. Alberta Energy Research Institute, Edmonton, AB. Available from http://eipa.alberta.ca/media/40994/oil%20sands%20tailings%20treatment%20technologies%20-%20final%20report%20-%20part%20b.pdf [accessed 8 August 2017].

Eastick, R.R., Svrcek, W.Y., and Mehrotra, A.K. 1992. Phase behavior of CO_2-bitumen fractions. The Canadian Journal of Chemical Engineering, **70**(1): 159-164.

El-Haj, R., Lohi, A., and Upreti, S.R. 2009. Experimental determination of butane dispersion in vapor extraction of heavy oil and bitumen. Journal of Petroleum Science and Engineering, **67**(1-2): 41-47.

Elshani, S., Smart, N.G., Lin, Y., and Wai, C.M. 2001. Application of supercritical fluids to the reactive extraction and analysis of toxic heavy metals from environmental matrices-system optimisation. Separation Science and Technology, **36**(5-6): 1197-1210.

Faisal, M., Atsuta, Y., Daimon, H., and Fujie, K. 2008. Recovery of precious metals from spent automobile catalytic converters using supercritical carbon dioxide. Asia-Pacific Journal of Chemical Engineering, **3**(4): 364-367.

Fang, Y. 2010. Extraction of hydrocarbons from oil sand using supercritical carbon dioxide. M.Sc. thesis, Department of Civil and Environmental Engineering, The University of Alberta, Edmonton, AB.

Fisher Scientific. n.d. Solvents. Available from https://www.fishersci.ca/ca/en/products/I9C8K3RF/solvents.html [accessed 26 July 2018].

Geranmayeh, A., Mowla, A., Rajaei, H., Esmaeilzadeh, F., and Kaljahi, J.F. 2012. Extraction of hydrocarbons from the contaminated soil of Pazanan II production unit by supercritical carbon dioxide. The Journal of Supercritical Fluids, **72**: 298-304.

Godin, M., Peachey, B., Jamieson, M., Lipsett, M., and Heidrick, T. 2009. Evaluation of oil sands research and innovation effectiveness. CanmetENERGY, Devon, AB.

Government of Alberta. 2016. Oil sands production profile: 2004-2014. Resource Development Policy Division, Energy Technical Services, Alberta Energy, Government of Alberta, Edmonton, AB.

Government of Alberta. 2017a. Oil sands: facts and stats. Available from https://open.alberta.ca/dataset/oil-sands-facts-and-stats/resource/063e27cc-b6d1-4dae-8356-44e27304ef78 [cited 30 June 2017].

Government of Alberta. 2017b. Recovery or extraction. Available from http://www.energy.alberta.ca/OilSands/1719.asp [cited 8 August 2017].

Government of Alberta. 2017c. Oil sands information portal. Available from http://osip.alberta.ca/map/ [cited 8 August 2017].

Government of Alberta. 2018. Oil production. Available from http://economicdashboard.alberta.ca/OilProduction#type [cited 2 February 2018].

Government of Canada. 2013. Oil sands: a strategic resource for Canada, North America and the global market. Available from http://www.nrcan.gc.ca/sites/www.nrcan.gc.ca/files/energy/pdf/eneene/pubpub/pdf/OS-brochure-eng.pdf [cited 4 July 2017].

Gray, M.R. 2015. Upgrading oilsands bitumen and heavy oil. University of Alberta, Edmonton, AB.

Greaves, M., Saghr, A.M., Xia, T.X., Turta, A.T., and Ayasse, C. 2001. THAI – new air injection technology for heavy oil recovery and in-situ upgrading. Journal of Canadian Petroleum Technology, **40**(3): 38-47.

Guigard, S., Underwood, E., Stiver, W., McMillan, J., and Bhattacharya, S. 2017. Dynamic extraction of bitumen using supercritical carbon dioxide. *In* Proceedings of the 16th European Meeting on Supercritical Fluids, Lisbon, Portugal, 25-28 April 2017.

Haghighat, P., and Maini, B.B. 2010. Role of asphaltene precipitation in VAPEX process. Journal of Canadian Petroleum Technology, **49**(3): 14-21.

Hawthorne, S.B. 1990. Analytical-scale supercritical fluid extraction. Analytical Chemistry, **62**(11): 633A-642A.

Hawthorne, S.B., Miller, D.J., Burford, M.D., Langenfeld, J.J., Eckert-Tilotta, S., and Louie, P.K. 1993. Factors controlling quantitative supercritical fluid extraction of environmental samples. Journal of Chromatography, **642**(1-2): 301-371.

Heins, W. and Peterson, D. 2006. Use of evaporation for heavy oil produced water treatment. Water & Process Technologies, General Electric Company, Trevose, PA.

Herrero, M., Mendiola, J.A., Cifuentes, A., and Ibáñez, E. 2010. Supercritical fluid extraction: recent advances and applications. Journal of Chromatography A, **1217**: 2495-2511.

Huang, S.H., and Radosz, M. 1990. Phase behavior of reservoir fluids II: supercritical carbon dioxide and bitumen fractions. Fluid Phase Equilibria, **60**: 81-98.

Husky Energy. 2011. Oil sands water de-oiling: challenges and innovation. Available from http://huskyenergy.com/downloads/InvestorRelations/Presentations/Oil-Sands-Water-De-Oiling-2011.pdf [cited 31 July 2017].

Hwang, R.J., and Ortiz, J. 1998. Effect of CO_2 flood on geochemistry of McElroy oil. Organic Geochemistry, **29**(1-3): 485-503.

Hwang, R.J., and Ortiz, J. 2000. Mitigation of asphaltics deposition during CO_2 flood by enhancing CO_2 solvency with chemical modifiers. Organic Geochemistry, **31**: 1451-1462.

Hyndman, A.W., and Luhning, R.W. 1991. Recovery and upgrading of bitumen and heavy oil in Canada. Journal of Canadian Petroleum Technology, **30**(2): 61-71.

Ikebe, H., Yokohata, H., Sakurai, M., and Morita, T. 2010. Method of produced water treatment, method of water reuse, and systems for these methods. US 2010/0264068 A1.

Jaffé, R., Diaz, D., Furton, K.G., and Lafargue, E. 1998. High temperature supercritical carbon dioxide extractions of geological samples: effects and contributions from the sample matrix. Applied Geochemistry, **15**: 79-89.

Jaremko, D. 2017. MEG seeks to expand eMVAPEX oilsands propane-injection plant. Available from http://www.jwnenergy.com/article/2017/3/meg-seeks-expand-emvapex-oilsands-propane-injection-pilot/ [cited 13 July 2017].

Kasperski, K.L., and Mikula, R.J. 2011. Waste streams of mined oil sands: characteristics and remediation. Elements, **7**(6): 387-392.

Keystone Energy Tools. 2017. Conventional oil vs. unconventional oil. Available from https://www.keystoneenergytools.com/conventional-oil-vs-unconventional-oil/ [cited 6 July 2018].

Knox, D.E. 2005. Solubilities in supercritical fluids. Pure and Applied Chemistry, **77**(3): 513-530.

Koots, J.A., and Speight, J.G. 1975. Relation of petroleum resins to asphaltenes. Fuel, **54**(3): 179-184.

La, H. 2011. Extraction of bitumen from Athabasca oil sand slurry using supercritical carbon dioxide. M.Sc. thesis, Department of Civil and Environmental Engineering, The University of Alberta, Edmonton, AB.

La, H., and Guigard, S.E. 2015. Extraction of hydrocarbons from Athabasca oil sand slurry using supercritical carbon dioxide. The Journal of Supercritical Fluids, **100**(1): 146-154.

Laitinen, A., Michaux, A., and Aaltonen, O. 1994. Soil cleaning by carbon dioxide extraction: a review. Environmental Technology, **15**(8): 715-727.

Lopez-Avila, V., Dodhiwala, N.S., and Beckert, W.F. 1990. Supercritical fluid extraction and its application to environmental analysis. Journal of Chromatographic Science, **28**: 468-476.

Louisiana State University (LSU). n.d. Polarity index. Available from http://macro.lsu.edu/howto/solvents/Polarity%20index.htm [cited 26 July 2018].

Low, G.K.C., and Duffy, G.J. 1995. Supercritical fluid extraction of petroleum hydrocarbons from contaminated soils. Trends in Analytical Chemistry, **14**: 218-225.

Luhning, R.W., Das, S.K., Fisher, L.J., Bakker, J., Grabowski, J., Engelman, J.R., Wong, S., Sullivan, L.A., and Boyle, H.A. 2003. Full scale VAPEX process – climate change advantage and economic consequences. Journal of Canadian Petroleum Technology, **42**(2): 29-34.

Magomedov, R.N., Pripakhaylo, A.V., and Maryutina, T.A. 2017. Solvent demetallization of heavy petroleum feedstock using supercritical carbon dioxide with modifiers. The Journal of Supercritical Fluids, **119**: 150-158.

Macnaughton, S.J., and Foster, N.R. 1994. Solubility of DDT and 2,4-D in supercritical carbon dioxide and supercritical carbon dioxide saturated with water. Industrial and Engineering Chemistry Research, **33**(11): 2757-2763.

McFarlane, R., Wiwchar, J., Frauenfeld, T., Coates, R., Budwill, K., Wang, X., Feng, Y., Golbeck, H., Huang, H., and Alvarez Martine, J. 2012. Artificial reservoir engineering study. Alberta Innovates – Technology Futures, Heavy Oil and Oil Sands, Edmonton, AB.

McHugh, M.A., and Krukonis, V.J. 1994. Supercritical fluid extraction: principles and practices, 2nd ed. Butterworth-Heinemann, Boston, MA.

Miyawaki, T., Kawashima, A., and Honda, K. 2008. Development of supercritical carbon dioxide extraction with a solid phase trap for dioxins in soils and sediments. Chemosphere, **70**(4): 648-655.

Mmualefe, L.C., Torto, N., Huntsman-Mapila, P., and Mbongwe, B. 2008. Supercritical fluid extraction of pesticides in sediment from the Okavango Delta, Botswana, and determination by gas chromatography with electron capture detection (GC-ECD) and mass spectrometry (GC-MS). Water SA, **34**(3): 405-410.

Mohamed, M.H., Wilson, L.D., Headley, J.V., and Peru, K.V. 2008. Novel materials for environmental remediation of tailing ponds water containing naphthenic acids. Process Safety and Environmental Protection, **86**(4): 237-243.

Mohr, S.H., and Evans, G.M. 2010. Long term prediction of unconventional oil production. Energy Policy, **38**: 265-276.

Mokrys, I.J., and Butler, R.M. 1993. In-situ upgrading of heavy oils and bitumen by propane deasphalting: the vapex process. *In* Proceedings of the SPE Production Operations Symposium, Oklahoma City, OK, 21-23 March 1993. Society of Petroleum Engineers, pp. 409-424.

Morgan, G. 2016. Changing the way crude is extracted from the oilsands is a daunting task but this entrepreneur believes his solution works. Available from http://business.financialpost.com/entrepreneur/fp-startups/change-the-way-crude-is-extracted-from-the-oilsands-is-daunting-task-but-this-entrepreneur-believes-his-solution-works/wcm/e4ad5a00-720a-48ff-9784-1d644ec87577 [accessed 12 July 2017].

Morselli, L., Setti, L., Iannuccilli, A., Maly, S., Dinelli, G., and Quattroni, G. 1999. Supercritical fluid extraction for the determination of petroleum hydrocarbons in soil. Journal of Chromatography A, **845**(1-2): 357-363.

Nagpal, V., and Guigard, S.E. 2005. Remediation of flare pit soils using supercritical fluid extraction. Journal of Environmental Engineering and Science, **4**(5): 307-318.

Nasr, T.N., and Ayodele, O.R. 2005. Thermal techniques for the recovery of heavy oil and bitumen. *In* Proceedings of the SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, Malaysia, 5-6 December 2005. Society of Petroleum Engineers, pp. 87-101.

National Institute of Standards and Technology (NIST). 2017. Thermophysical properties of fluid systems. Available from http://webbook.nist.gov/chemistry/fluid/ [cited 22 August 2017].

Natural Resources Canada. 2017. Oil resources. Available from https://www.nrcan.gc.ca/energy/oil-sands/18085 [cited 6 July 2018].

Oil Sands Magazine. 2017a. In-situ bitumen extraction. Available from http://www.oilsandsmagazine.com/technical/in-situ [cited 10 July 2017].

Oil Sands Magazine. 2017b. Surface mining techniques used in oil sands. Available from http://www.oilsandsmagazine.com/technical/mining/surface-mining [cited 2 August 2017].

Oil Sands Magazine. 2017c. Mining for bitumen. Available from http://www.oilsandsmagazine.com/technical/mining [cited 17 July 2018].

Oil Sands Magazine. 2017d. Products from the oil sands: dilbit, synbit & synthetic crude explained. Available from http://www.oilsandsmagazine.com/technical/product-streams [cited 26 July 2018].

Peng, H., Volchek, K., MacKinnon, M., Wong, W.P., and Brown, C.E. 2004. Application of nanofiltration to water management options for oil sands operations. Desalination, **170**: 137-150.

Pérez-Estrada, L.A., Han, X., Drzewicz, P., Gamal El-Din, M., Fedorak, P.M., and Martin, J.W. 2011. Structure-reactivity of naphthenic acids in ozonation process. Environmental Science & Technology, **45**(17): 7431-7437.

Perrut, M. 2000. Supercritical fluid applications: industrial developments and economic issues. Industrial & Engineering Chemistry Research, **39**(12): 4531-4535.

Phelps, C.L., Smart, N.G., and Wai, C.M. 1996. Past, present and possible future applications of supercritical fluid extraction technology. Journal of Chemical Education, **73**(12): 1163-1168.

Płotka-Wasylka, J., Rutkowska, M., Owczarek, K., Tobiszewski, M., and Namieśnik, J. 2017. Extraction with environmentally friendly solvents. Trends in Analytical Chemistry, **91**: 12-25.

Pourrezaei, P., Drzewicz, P., Wang, Y., Gamal El-Din, M., Pérez-Estrada, L.A., Martin, J.W., Anderson, J., Wiseman, S., Liber, K., and Giesy, J.P. 2011. The impact of metallic coagulants on the removal of organic compounds from oil sands process-affected water. Environmental Science & Technology, **45**: 8452-8459.

Powter, C.B., Biggar, K.W., Silva, M.J., McKenna, G.T., and Scordo, E.B. 2011. Review of oil sands tailings technology options. *In* Proceedings of the 14th International Conference on Tailings and Mine Waste 2010, Vail, CO, 17-20 October 2010. Taylor & Francis Group, London, pp. 381-391.

Quagraine, E.K., Headley, J.V., and Peterson, H.G. 2005. Is biodegradation of bitumen a source of recalcitrant naphthenic acid mixtures in oil sands tailing pond waters? Journal of Environmental Science and Health, **40**(3): 671-684.

Quinlan, P.J., and Tam, K.C. 2015. Water treatment technologies for the remediation of naphthenic acids in oil sands process-affected water. Chemical Engineering Journal, **279**: 696-714.

Rao, F., and Liu, Q. 2013. Froth treatment in Athabasca oil sands bitumen recovery process: a review. Energy & Fuels, **27**(12): 7199-7207.

Raynie, D.E. 1997. Meeting the natural products challenge with supercritical fluids. *In* Supercritical fluids: extraction and pollution prevention. *Edited by* M.A. Abraham and A.K. Sunol. American Chemical Society, Washington, DC. pp. 68-75.

Romaniuk, N., Mehranfar, M., Selani, H., Ozum, B., Tate, M.J., and Scott, J.D. 2015. Residual bitumen recovery from oil sand tailings with lime. Tailings and Mine Waste Conference, Vancouver, BC, 25-28 October 2015. doi:10.14288/1.0314304.

Roop, R.K., Hess, R.K., and Akgerman, A. 1989. Supercritical extraction of pollutants from water and soil. *In* Supercritical fluid science and technology, ACS symposium, Vol. 406. *Edited by* K.P. Johnston and J.M.L. Penninger. American Chemical Society, Washington, DC. pp. 468-476.

Rose, J.L., Svrcek, W.Y., Monnery, W.D, and Chong, K. 2000. Fractionation of Peace River bitumen using supercritical ethane and carbon dioxide. Industrial & Engineering Chemistry Research, **39**(10): 3875-3883.

Rose, J.L., Monnery, W.D., Chong, K., and Svrcek, W.Y. 2001. Experimental data for extraction of Peace River bitumen using supercritical ethane. Fuel, **80**: 1101-1110.

Rudyk, S., and Spirov, P. 2014. Upgrading and extraction of bitumen from Nigerian tar sand by supercritical carbon dioxide. Applied Energy, **113**: 1397-1404.

Rudyk, S., Hussain, S., and Spirov, P. 2013. Supercritical extraction of crude oil by methanol- and ethanol- modified carbon dioxide. The Journal of Supercritical Fluids, **78**: 63-69.

Rudyk, S., Spirov, P., and Hussain, S. 2014. Effect of co-solvents on SC-CO_2 extraction of crude oil by consistency test. The Journal of Supercritical Fluids, **91**: 15-23.

Rudyk, S., Spirov, P., Al-Hajri, R., and Vakili-Nezhaad, G. 2017. Supercritical carbon dioxide extraction of oil sand enhanced by water and alcohols as co-solvents. Journal of CO_2 Utilization, **17**: 90-98.

Scott, A.C., MacKinnon, M.D., and Fedorack, P.M. 2005. Naphthenic acids in Athabasca oil sands tailings waters are less biodegradable than commercial naphthenic acids. Environmental Science & Technology, **39**: 8388-8394.

Shu, Z., Li, C., Belosevic, M., Bolton, J.R., and Gamal El-Din, M. 2014. Application of a solar UV/chlorine advanced oxidation process to oil sands process-effected water remediation. Environmental Science & Technology, **48**: 9692-9701.

Singhal, A.K., Das, S.K., Leggitt, S.M., Kasraie, M., and Ito, Y. 1996. *In* Proceedings of the International Conference on Horizontal Wall Technology, Calgary, AB, 18-20 November 1996. Society of Petroleum Engineerings, pp. 867-876.

Speight, J.G. 2004. Petroleum asphaltenes – part 1: asphaltenes, resins and the structure of petroleum. Oil & Gas Science and Technology, **59**(5): 467-477.

Speight, J.G. 2006. The chemistry and technology of petroleum, 4th ed. CRC Press, Taylor & Francis Group, Boca Raton, FL.

Starr, J., and Bulmer, J.T. 1979. Syncrude analytical methods for oil sands and bitumen processing. Alberta Oil Sands Technology and Research Authority, Edmonton, AB.

Stubbs, J.M., and Siepmann, J.I. 2004. Binary phase behavior and aggregation of dilute methanol in supercritical carbon dioxide: a Monte Carlo simulation study. The Journal of Chemical Physics, **121**(3): 1525-1534.

Subramanian, M., and Hanson, F.V. 1998. Supercritical fluid extraction of bitumens from Utah oil sands. Fuel Processing Technology, **55**(1): 35-53.

Suncor Energy Inc. 2017. Tailings management. Available from https://sustainability.suncor.com/2017/en/environment/tailings-management.aspx?_ga=2.81362322.483750579.1531957355-848196585.1531957355 [cited 19 July 2018].

Suncor Energy Inc. 2018. Tailings management. Available from http://www.suncor.com/sustainability/environment/tailings-management [cited 19 July 2018].

Syncrude Canada Ltd. 2017a. Extraction. Available from http://www.syncrude.ca/our-process/understanding-our-process/extraction/ [cited 3 August 2017].

Syncrude Canada Ltd. 2017b. Tailings management. Available from http://www.syncrude.ca/environment/tailings-management/ [cited 11 August 2017].

Teja, A.S., and Eckert, C.A. 2000. Commentary on supercritical fluids: research and applications. Industrial & Engineering Chemistry Research, **39**(12): 4442-4444.

The Engineer. 2010. Shell begins atmospheric fines drying for oil sands project. Available from https://www.theengineer.co.uk/issues/august-2010-online/shell-begins-atmospheric-fines-drying-for-oil-sands-project/ [cited 20 July 2018].

Thomas, T.E. 2011. Hydrocarbon recovery from waste streams of oil sands processing. M.Sc. thesis, Department of Chemical and Materials Engineering, The University of Alberta, Edmonton, AB.

Upreti, S.R., Lohi, A., Kapadia, A., and El-Haj, R. 2007. Vapor extraction of heavy oil and bitumen: a review. Energy & Fuels, **21**(3): 1562-1574.

Vittoratos, E., Scott, G.R., and Beattie, C.I. 1990. Cold Lake cyclic steam stimulation: a multiwell process. SPE Reservoir Engineering, **5**(1): 19-24.

Wang, J.S., and Chiu, K. 2008. Extraction of chromated copper arsenate from wood wastes using green solvent supercritical carbon dioxide. Journal of Hazardous Materials, **158**(2-3): 385-391.

Wu, W., Ke, J., and Poliakoff, M. 2006. Phase boundaries of CO_2 + toluene, CO_2 + acetone, and CO_2 + ethanol at high temperatures and high pressures. Journal of Chemical & Engineering Data, **51**: 1398-1403.

Xia, T.X., and Greaves, M. 2006. In-situ upgrading of Athabasca tar sand bitumen using THAI. Chemical Engineering Research and Design, **84**(A9): 856-864.

Xia, T.X., Greaves, M., Turta, A.T., and Ayasse, C. 2003. THAI – a 'short-distance displacement' in-situ combustion process for the recovery and upgrading of heavy oil. Chemical Engineering Research and Design, **81**(3): 295-304.

Yeo, S., Park, S., Kim, J., and Kim, J. 2000. Critical properties of carbon dioxide + methanol, + ethanol, + 1-propanol, and + 1-butanol. Journal of Chemical & Engineering Data, **45**: 932-935.

Yoon S., Bhatt, S.D., Lee, W., Lee, H.Y., Jeong, S.Y., Baeg, J., and Lee, C.W. 2009. Separation and characterization of bitumen from Athabasca oil sand. Korean Journal of Chemical Engineering, **26**(1): 64-71.

Yu, J.M., Huang, S.H., and Radosz, M. 1989. Phase behavior of reservoir fluids: supercritical carbon dioxide and Cold Lake bitumen. Fluid Phase Equilibria, **53**: 429-438.

Zaki, N.N., Carbonell, R.G., and Kilpatrick, P.K. 2003. A novel process for demulsification of water-in-crude oil emulsions by dense carbon dioxide. Industrial & Engineering Chemistry Research, **42**(25): 6661-6672.

Zhou, S., Huang, H., and Liu, Y. 2008. Biodegradation and origin of oil sands in the Western Canada Sedimentary Basin. Petroleum Science, **5**(2): 87-94.

Zhu, R., Liu, Q., Xu, Z., Masliyah, J.H., and Khan, A. 2011. Role of dissolving carbon dioxide in densification of oil sands tailings. Energy & Fuels, **25**(5): 2049-2057.

Ziegler, J.W., Dorsey, J.G., Chester, T.L., and Innis, D.P. 1995. Estimation of liquid-vapor critical loci for CO_2-solvent mixtures using a peak-shape method. Analytical Chemistry, **67**: 456-461.

Zúñiga, M.C., Jover, E., Arancibia, V., and Bayona, J.M. 2009. Development of a methodology for the simultaneous determination of inorganic and organolead compounds using supercritical fluid extraction followed by gas chromatography-mass spectrometry and its application to environmental matrices. Talanta, **80**: 504-510.

Appendix A

Feed Material Properties

Appendix A1: Bitumen Properties

Table A1a displays the results of a SARA analysis conducted on the Syncrude bitumen. Table A1b displays additional select properties of Syncrude bitumen. The data in Tables A1a and A1b was provided by Syncrude.

Table A1a. SARA analysis results for Syncrude bitumen.

Components	(wt%)
Saturates	22.5
Aromatics	34.5
Resins	25.4
Asphaltenes	17.5

Table A1b. Select properties of Syncrude bitumen.

Property	**Value**
Density (g cm^{-3})	0.9875 (at 333 K)
Viscosity (cSt)	217.34 (at 372 K)
Sulphur (ppm)	4.79×10^4
Nitrogen (ppm)	4.93×10^3
Solids (wt %)	0.3

Appendix A2: FT Froth Properties

Figure A2 displays the particle size distribution for FT Froth solids. This data was provided by Syncrude and is based on Computerized Particle Analysis of applicable subsamples.

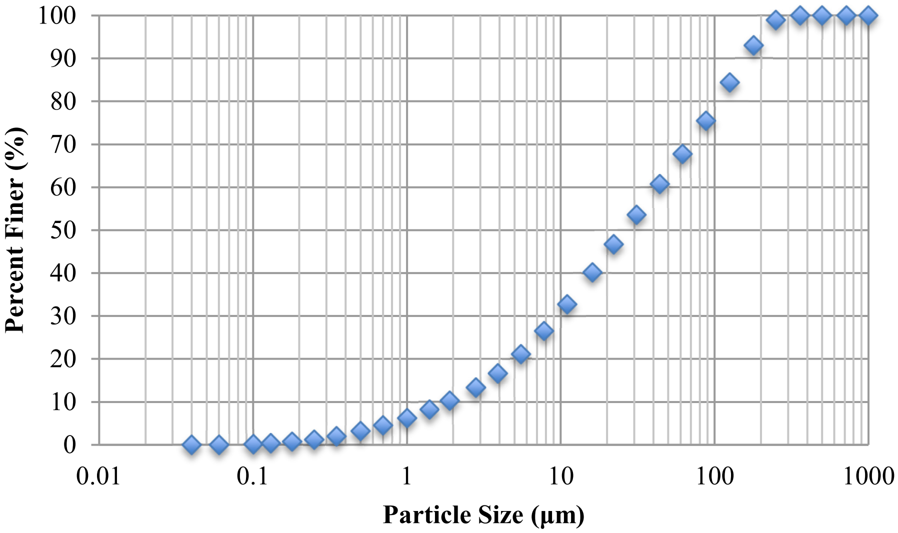


Figure A2. Particle size distribution for Syncrude FT Froth subsamples.

Appendix A3: Pond Froth Properties

Figure A3 displays the particle size distribution for Pond Froth solids. This data was provided by Syncrude and is based on Computerized Particle Analysis of applicable subsamples.

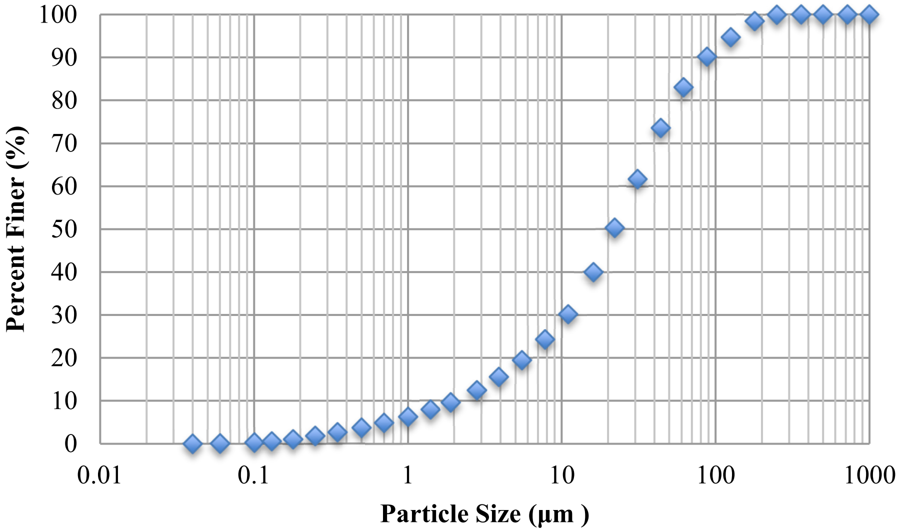


Figure A3. Particle size distribution for Syncrude Pond Froth subsamples.

Appendix B

LabVIEW™ Output Data

Appendix B: Sample of LabVIEW™ Output Data

Table B1 is a 4-minute sample of output data collected from LabVIEW™. In this particular data set, pump A is operating at the set-point pressure (3480 psi) with a flow rate of approximately 20 mL min^{-1} and pump B is on stand-by. The pressure transducer reading indicates that the pressure in the tubing just before the vessel is roughly 120 psi off the set-point. However given that the experimental conditions are well above the critical point of CO_2, this would not have a large impact on its supercritical properties, other than decreasing its density by approximately 0.01 g/mL (NIST 2017).

Table B1. Sample of output data collected from LabVIEW™

Scan #	**Time (s)**	**Pressure (psi)**	**Temperature (°C)**	**Pump Flow Rate (mL min^{-1})**		**Pump Pressure (psi)**	
				A	**B**	**A**	**B**
1079	10801	3360.769	60.466	19.658	0.263	3480	2981
1080	10811	3363.319	60.379	19.198	0.277	3481	2980
1081	10821	3365.069	60.466	18.28	0.684	3480	2979
1082	10831	3361.816	60.293	19.137	-0.041	3480	2980
1083	10841	3362.078	60.379	18.581	-0.395	3478	2977
1084	10851	3353.623	60.206	23.261	-0.224	3480	2981
1085	10861	3357.414	60.206	21.555	-0.056	3480	2980
1086	10871	3358.461	60.206	20.805	0.151	3480	2980
1087	10881	3359.164	60.206	20.644	0.062	3481	2980
1088	10891	3347.719	60.206	24.057	1.297	3478	2975
1089	10901	3343.826	60.206	24.673	-0.501	3477	2976
1090	10911	3355.815	60.034	21.888	-0.277	3480	2979
1091	10921	3357.109	60.206	21.632	0.124	3480	2980
1092	10931	3349.367	60.379	23.056	0.913	3477	2977
1093	10941	3345.581	61.166	25.162	0.184	3480	2979
1094	10951	3355.703	60.293	21.815	-0.18	3480	2980
1095	10961	3345.043	60.034	24.555	-0.303	3477	2977
1096	10971	3356.993	60.206	21.952	-1.031	3481	2980
1097	10981	3352.256	60.206	22.211	-0.92	3477	2978
1098	10991	3351.389	60.206	23.446	-0.039	3479	2980
1099	11001	3352.116	60.120	23.359	0.075	3480	2980
1100	11011	3353.609	60.206	23.268	0.179	3481	2980
1101	11021	3352.974	60.206	23.663	1.392	3481	2978
1102	11031	3359.576	60.206	21.617	0.639	3485	2980

Appendix C

SFE Procedure

Appendix C: SFE Procedure

Part 1: System Preparation

1. Turn on the refrigerated circulator (set to 2 °C) in order to cool the ISCO syringe pumps.
2. Drain the circulating water bath.
3. Turn on the computer and open the LabVIEW™ program. Start a new run, saving the file to the desired folder and under the appropriate name.
4. Turn on the pump controller and set the pumps to the desired pressure (3480 psi).
5. Turn on the hot water tap and let the water warm before filling up both the circulating water bath and the hot water bath. Filling the baths with hot water allows them to reach their desired temperature more quickly.
    a. Once the circulating water both is completely full, set the temperature to 66 °C (due to heat transfer losses, the vessel will only reach 60 °C if the circulating water bath is set to approximately 66 °C), turn it on and cover it with a Styrofoam lid to stop the water from evaporating.
    b. Once the hot water bath is filled such that the outlet tubing and the body of the outlet valve are completely submerged, set the bath to 60 °C and turn it on.
6. Ensure the inlet valve, outlet valve, metering valve, Gilson piston pump valve and Microlab® pump valve are closed.
7. Open the air and liquid CO_2 cylinders (the ISCO syringe pumps have air actuated valves and thus air is required in order to operate the pumps).
8. Label a total of 29 vials or jars for the dynamic extraction: six vials/jars are needed for three 5-minute extraction periods (1a, 1b, 2a, 2b, 3a and 3b); 14 vials/jars for seven 15-minute extraction periods (4a, 4b, 5a, 5b, 8a, 8b … 12b); two carryover vials/jars (6 c/o and 13 c/o); two rinse vials/jars (7 rinse and 14 rinse); two depressurization vials/jars; two high pressure clean vials/jars; and one time zero vial/jar. Jars were used for all dynamic extractions with ≥ 10 mol% modifier addition because of the

large volume of modifier exiting the system; vials were used for all other dynamic extractions. Add glass beads to all *a* vials/jars. Weigh the vials/jars and record the initial mass.

9. Sign out two scoops of dry ice for the acetone/dry ice bath.
10. Ensure the Teflon disc is in place underneath the extraction vessel lid to prevent carryover.
11. Ensure the helical impeller is clean and is securely attached. If it is not clean, rinse it with toluene and a Kimwipe®.
12. *For chemically modified SC-CO_2:* Ensure the correct modifier is hooked up to the Gilson piston pump (either toluene or methanol). Turn on the Gilson piston pump and enter the volume of modifier required during vessel pressurization (the vessel pressurizes for approximately 1 minute and the flow of the Gilson piston pump is in mL/min).
13. *For chemically modified SC-CO_2:* Prime the Gilson piston pump - open the Gilson piston pump valve and run the pump until the modifier runs out the vessel inlet tube, then stop the pump and close the Gilson piston pump valve.
14. Ensure the vessel is clean (if not, rinse it out with toluene and a Kimwipe®) and then place the stainless steel sleeve in the vessel.
15. Place a Teflon o-ring in the groove at the top of the vessel to ensure a pressure seal.
16. Ensure the hoses are connected between the circulating water bath and the vessel. This will allow the vessel to heat up while the sample is being prepared.
17. Wrap all six vessel bolts with nickel embedded Teflon tape to prevent the bolts from welding to the vessel during the extraction.

Part 2: Sample Preparation and Addition

1. *For dynamic extractions of bitumen:* Tare the analytical balance. Record the weight of an empty 120 mL glass jar and a spatula. Take a 1 L jar of bitumen out of the refrigerator and transfer approximately 13 g of bitumen

into the 120 mL jar (record the total weight of the jar, bitumen and spatula). Transfer the entire contents of the 120 mL jar into the extraction vessel using the spatula. Re-weigh and record the mass of the jar, bitumen residue and spatula. The mass of sample in the vessel (approximately 10 g) is determined by subtracting the weight of the jar, residue and spatula from the weight of the jar, bitumen and spatula.

2. *For dynamic extractions of process and process waste streams:* Take a 120 mL jar containing the process stream or process waste stream out of the refrigerator. Tare the analytical balance. Record the weight of the 120 mL glass jar (containing the feed material) with the lid and a spatula. Fill a beaker halfway with room temperature water and place the 120 mL jar containing the feed material (with the lid on) in the beaker. Place the beaker in the hot water bath for 20 minutes (for FT Froth) or 40 minutes (for Pond Froth) to warm the sample. Mix the sample well with the spatula and then transfer approximately 25 or 50 g (depending on the dynamic extraction) of the feed material into the vessel using the spatula. Re-weigh and record the mass of the jar, process stream or process waste stream residue, lid and spatula. The mass of sample in the vessel (approximately 25 or 50 g) is determined by subtracting the weight of the jar, residue, lid and spatula from the weight of the jar, feed material, lid and spatula.
3. Take a time zero sample of the bitumen, process stream or process waste stream for HTSD analysis.
4. With the sample in the vessel, lift the vessel, thread the vessel inlet into the groove in the stainless steel sleeve and then slide the lab jack under the vessel. Lift the vessel until it meets the vessel lid, and then raise the lab jack under the vessel so the vessel sits tight against the lid. Ensure the holes of the lid and vessel are properly aligned.
5. Seal the vessel by screwing in the six bolts in a star pattern to ensure even attachment to the lid. Tighten the bolts (also in a star pattern) using the torque wrench, first to 25 ft-lb, then 35 ft-lb, 42 ft-lb and 50 ft-lb.
6. Put the drive belt on the MagneDrive® mixer.

Part 3: Equilibration and Static Period

1. Check that the system temperatures have been reached. The refrigerated circulator should be reading 2 ºC and the vessel temperature (as shown in LabVIEW™) should be is approximately 45 ºC (this temperature will rise quickly to 60 ºC once the vessel is pressurized).
2. Refill the ISCO syringe pumps (if not already full from previous experiment) and run the pumps to pressurize them to 3480 psi.
3. Once pumps have equilibrated, open the inlet valve to pressurize the vessel. Once the vessel is pressurized (confirm by reading the pressure on LabVIEW™), ensure that the vessel is not leaking – this can be determined by ensuring that the pump flow rate reads ≤ 0 mL/min (since the vessel is pressurized but CO_2 is not exiting the system, the pumps should not be supplying a significant amount of CO_2 to the vessel, unless there is a leak). If there is a leak, the vessel must be depressurized and the system must be cleaned (see Parts 5 and 6). If the leak persists, the Teflon o-ring should be changed.
4. *For chemically modified SC-CO_2:* Immediately open the Gilson piston pump valve, start the Gilson piston pump and let it run for 1 minute so that the required initial volume of modifier is entering the vessel at the same time as it is pressurizing. The Gilson piston pump has a maximum flow rate of 25 mL/min. If an initial modifier volume of more than 25 mL is required, add in the amount that is greater than 25 mL prior to pressurizing the vessel, and then add the remaining 25 mL during vessel pressurization. Once 1 minute is complete, stop the Gilson piston pump and close the Gilson piston pump valve.
5. Turn on the MagneDrive® mixer and set the speed to 250 rpm.
6. Begin the stopwatch for a 60-minute static period. After 60 minutes stop the stopwatch and proceed to Part 4, Set 1.

Part 4: Dynamic Extraction

Set 1

1. Prepare the acetone/dry ice bath by adding acetone to a small container and then slowing adding dry ice as required.
2. Add approximately 20 mL of toluene to all *b* vials/jars for Set 1 (1b to 5b) as well as to 6 c/o.
3. Attach the first three collection vials/jars (1a, 1b and 6 c/o). Vials/jars *a* and *b* will be changed throughout Set 1 but 6 c/o will remain on the system as the third vial/jar for the entirety of Set 1. Put the first two vials/jars (1a and 1b) in the acetone/dry ice bath.
4. *For chemically modified SC-CO_2:* Set the Gilson piston pump to the flow rate of modifier that is required in order to maintain the desired concentration of modifier in SC-CO_2 during the extraction. Open the Gilson piston pump valve.
5. Record the start time from LabVIEW™, start the stopwatch, open the outlet valve and carefully open the metering valve to achieve a flow of 20 mL/min.
6. *For chemically modified SC-CO_2:* After opening the metering valve, immediately start the Gilson piston pump.
7. Allow the extraction to run for 5 minutes. During which time the flow should be maintained to within ± 3 mL/min of 20 mL/min.
8. At the end of 5 minutes, close the outlet valve and stop the stopwatch.
9. *For chemically modified SC-CO_2:* After closing the outlet valve, immediately stop the Gilson piston pump.
10. Disconnect the first two vials/jars (1a and 1b). Add a little more dry ice to the acetone/dry ice bath as necessary.
11. Connect the next two collection vials/jars (2a and 2b) and place them in the acetone/dry ice bath.
12. Repeat steps 5 to 11 for time periods of 5 – 10 min (2a and 2b), 10 – 15 min (3a and 3b), 15 – 30 min (4a and 4b) and 30 – 45 min (5a and 5b). Altogether the extraction period for Set 1 spans 45 minutes.

13. After the 30 – 45 min extraction period, disconnect all vials/jars (including the 6 c/o). The outlet valve should (already) be closed.
14. *For chemically modified SC-CO_2:* Close the Gilson piston pump valve.
15. Place the rinse jar/vial (7 rinse) in the first collection vial/jar position on the system.
16. Carefully depressurize the outlet line from the closed outlet valve onward by slowly opening the metering valve.
17. Once the line is depressurized, open the metering valve 4 – 5 full turns.
18. Open the Microlab® pump valve, turn on the Microlab® pump and rinse the outlet line with 25 mL of toluene (to clean the line of any residual extract).
19. Stop the Microlab® pump, close the Microlab® valve and the metering valve, and remove the rinse vial/jar.
20. Set 1 is complete. Start the stopwatch for a second 60 minute static period. After 60 minutes, stop the stopwatch and proceed to Part 4, Set 2.

Set 2

1. Prepare the acetone/dry ice bath.
2. Add approximately 20 mL of toluene to all *b* vials/jars for Set 2 (8b to 12b) as well as to 13 c/o.
3. Attach the first three collection vials/jars (8a, 8b and 13 c/o). Vial/jar 13 c/o will remain on the system as the third vial/jar for the entirety of Set 2. Put the first two vials/jars (8a and 8b) in the acetone/dry ice bath.
4. *For chemically modified SC-CO_2:* Open the Gilson piston pump valve.
5. Record the start time from LabVIEW™, start the stopwatch, open the outlet valve and carefully open the metering valve to achieve a flow of 20 mL/min.
6. *For chemically modified SC-CO_2:* After opening the metering valve, immediately start the Gilson piston pump.
7. Allow the extraction to run for 15 minutes. During which time the flow should be maintained to within ± 3 mL/min of 20 mL/min.

8. At the end of 15 minutes, close the outlet valve and stop the stopwatch.
9. *For chemically modified SC-CO_2:* After closing the outlet valve, immediately stop the Gilson piston pump.
10. Disconnect the first two vials/jars (8a and 8b). Add a little more dry ice to the acetone/dry ice bath as necessary.
11. Connect the next two collection vials/jars (9a and 9b) and place them in the acetone/dry ice bath.
12. Repeat steps 5 to 11 for time periods of 15 – 30 min (9a and 9b), 30 – 45 min (10a and 10b), 45 – 60 min (11a and 11b) and 60 – 75 min (12a and 12b). Altogether the extraction period for Set 2 spans 75 minutes. In cases where a high volume of modifier is being added to the system, the 13 c/o jar may get too full. In that case, 13 c/o may be disconnected from the system along with 10a and 10b and a second Set 2 c/o jar (19 c/o) may be connected in place of 13 c/o for the remaining 30 minutes of Set 2.
13. After the 60 – 75 min extraction period, disconnect all vials/jars (including 13 c/o (or 19 c/o)). The outlet valve should (already) be closed.
14. *For chemically modified SC-CO_2:* Close the Gilson piston pump valve. Turn off the Gilson piston pump.
15. Place the rinse jar/vial (14 rinse) in the first collection vial/jar position on the system.
16. Carefully depressurize the outlet line from the close outlet valve onward by slowly opening the metering valve.
17. Once the line is depressurized, open the metering valve 4 – 5 full turns.
18. Open the Microlab® pump valve and rinse the outlet line with 25 mL of toluene (to clean the line of any residual extract).
19. Stop the Microlab® pump and turn it off, close the Microlab® valve and the metering valve, and remove the rinse vial/jar.
20. Set 2 is complete.
21. Tare the analytical balance. Record the weight of each vial/jar from Set 1 and Set 2. After the mass immediately after run has been recorded, put lids on all vials/jars.

22. Photograph all *a* and *b* vials/jars from sets 1 and 2 after the extraction is complete.

Part 5: Depressurization

1. Close the inlet valve and stop the ISCO syringe pumps. Refill the pumps before turning off the pump controller.
2. Once the pumps have been refilled, turn off the refrigerated circulator and close the air and liquid CO_2 cylinders.
3. Turn off the circulating water bath and the hot water bath.
4. Turn off the MagneDrive® mixer.
5. Attach the two depressurization collection vials (labelled 15 Dep and 16 Dep).
6. Open the vessel outlet valve. Open the metering valve only slightly, to allow the vessel to slowly depressurize over night. If it depressurizes too fast, the residue left in the vessel will carryover into the outlet lines.

Part 6: Vessel Residue and High Pressure Clean

1. Ensure the vessel has depressurized. If it is still pressurized, open the metering valve slightly until the vessel is approximately 16 to 19 psi.
2. Open the depressurized vessel by removing the drive belt on the MagneDrive® mixer, loosening the six bolts on the vessel lid with a torque wrench and removing the lab jack.
3. Photograph the helical mixer and the underside of the vessel lid.
4. Unhook the hoses between the vessel and circulating water bath.
5. Take the vessel to the fumehood for cleaning. If there is any dry vessel residue in the vessel collect it in a pre-weighed vial.
6. Remove the helical mixer and take it to the fumehood for cleaning.
7. Rinse the underside of the vessel lid with toluene until it is clean, collecting the rinse in a 250 mL jar (labelled vessel residue solution).

8. In the fumehood, rinse the helical mixer, Teflon o-ring, stainless steel sleeve, and the contents of the vessel with toluene into the same 250 mL vessel residue solution jar until clean.
9. Pour approximately 80 mL of toluene into the vessel.
10. Put the Teflon o-ring back in the groove and place the stainless steel sleeve back in the vessel. Reattach the helical mixer and reconnect the hoses between the vessel and circulating water bath.
11. Seal the vessel: with the toluene in the vessel, lift the vessel, thread the vessel inlet into the groove in the stainless steel sleeve and then slide the lab jack under the vessel. Lift the vessel until it meets the vessel lid, and then raise the lab jack under the vessel so the vessel sits tight against the lid. Ensure the holes of the lid and vessel are properly aligned. Seal the vessel by screwing in the six bolts in a star pattern to ensure even attachment to the lid. Tighten the bolts (also in a star pattern) using the torque wrench, first to 25 ft-lb, then 35 ft-lb, 42 ft-lb and 50 ft-lb.
12. Put the drive belt on the MagneDrive® mixer.
13. Drain the circulating water bath before filling both the circulating water bath and hot water bath with warm water. The hot water bath should only be filled until the outlet tubing and body of the outlet valve are completely submerged. Turn both baths on and set to 66 and 60 °C, respectively. Cover the circulating water bath with the Styrofoam lid.
14. Turn on the refrigerated circulator (set to 2 °C).
15. Turn on the computer and open the LabVIEW™ program. Start a new run, saving the file to the desired folder name ‘Test’.
16. Turn on the pump controller and set the pumps to the desired pressure (3480 psi).
17. Ensure the inlet valve, outlet valve and metering valve are closed.
18. Open the air and liquid CO_2 cylinders.
19. Check that the system temperatures have been reached. The refrigerated circulator should be reading 2 ºC and the vessel temperature should be is approximately 45 ºC.

20. Attach the two high pressure clean vials/jars (labelled 17 Hi-P and 18 Hi-P).
21. Refill the ISCO syringe pumps (if not already full from previous experiment) and run the pumps to pressurize them to 3480 psi.
22. Once pumps have equilibrated, open the inlet valve to pressurize the vessel.
23. Turn on the MagneDrive® mixer and set the speed to 250 rpm.
24. Allow the system to mix for approximately 30 minutes to maximize cleaning before opening the outlet valve.
25. Open the outlet valve and carefully open the metering valve to achieve a flow of approximately 20 mL/min. The flow rate of CO_2 during the high pressure clean is less critical than that of a dynamic extraction.
26. Allow the system to run for approximately 10 minutes, or until at least 50 mL of the toluene has flowed into the high pressure clean collection vials/jars.
27. Close the inlet valve and stop the ISCO syringe pumps. Refill the pumps before turning off the pump controller.
28. Once the pumps have been refilled, turn off the refrigerated circulator and close the air and liquid CO_2 cylinders.
29. Turn off the circulating water bath and the hot water bath.
30. Turn off the MagneDrive® mixer.
31. Leave the outlet valve and metering valve open to allow the vessel to depressurize. Since there is only toluene left in the vessel, carryover is not a concern and so the system can be depressurized quickly.

Part 7: Sample Drying

1. Place all 28 collection vials/jars in the fume hood under drying apparatus (the time zero sample is not dried).
2. *For dynamic extractions of bitumen:* Leave vials/jars under drying apparatus for 2 days (this is enough time to vaporize the toluene and any other modifier added during the extraction). Weigh and record the mass

after 2 days – this is the final mass.

3. *For dynamic extractions of process and process waste streams:* Leave vials/jars under the drying apparatus for 5 days (due to the water content of both the process stream and process waste stream, these samples need more time to dry than samples from dynamic extractions of bitumen). Weigh and record the mass after 5 days – this is the final mass.
4. Take pictures of the dried vials/jars before sending them to Syncrude for HTSD analysis. The vessel residue solution jar also gets sent to Syncrude for Dean-Stark extraction and HTSD analysis. The time zero sample is also sent for HTSD analysis.

Appendix D

Dynamic Extraction Data

Appendix D1: Example Bitumen Dynamic Extraction Spreadsheet

Tables D1a and D1b display the results of a bitumen dynamic extraction with 5 mol% toluene in SC-CO_2 conducted on October 3, 2017.

Table D1a. Summary of dynamic extraction conditions and initial data collected.

Description:	**Syncrude Bitumen Extraction - 20 mL/min - 5 mol% Toluene**						
Run pressure (psi/MPa)	3480	24	**Mass of sample in vessel (g)**	10.2228	**Static time (mins)**	Set 1	60
Run temperature (^{o}C/K)	60.1061	333.26	**Co-solvent**	Toluene		Set 2	60
Pump Temperature (^{o}C/K)	2	275.15	**Volume co-solvent added during pressurization (mL)**	19.278	**Sample Jar ID (#)**	7/19 (January 7, 2015)	-
Density of CO_2 at run conditions (g/mL)	0.77553	-	**Rate of co-solvent feed (mL/min)**	2.6125	**Mass jar + spatula (g)**	136.7665	-
Density of CO_2 at pump conditions (g/mL)	1.0277	-	**-**	-	**Mass jar + spatula + bitumen (g)**	150.3163	-
Mixing speed (rpm)	250	-	**-**	-	**Mass jar + spatula + residue (g)**	140.0935	-

Table D1b. Experimental data collected from a bitumen dynamic extraction.

Vial ID	Sampling time (min)	Initial mass (g)	Final mass (g)	Mass of sample collected (g)	Volume of CO_2 from pumps (mL)
1a (0-5 min)	5	36.3950	37.4554	1.0604	100.1847
1b (0-5 min)		24.7887	25.0062	0.2175	
2a (5-10 min)	5	35.3467	36.3948	1.0481	110.0366667
2b (5-10 min)		21.5952	21.6108	0.0156	
3a (10-15 min)	5	34.8916	35.6366	0.7450	117.5423333
3b (10-15 min)		24.8529	24.8667	0.0138	
4a (15-30 min)	15	35.0539	35.5800	0.5261	314.647
4b (15-30 min)		21.7221	22.0552	0.3331	
5a (30-45 min)	15	34.9742	35.1956	0.2214	339.5620
5b (30-45 min)		25.0276	25.1969	0.1693	
6 (c/o)		25.0022	25.1390	0.1368	
7 (rinse)		24.8447	24.8525	0.0078	
8a (0-15 min)	15	35.0897	35.2411	0.1514	299.0108333
8b (0-15 min)		21.8971	21.9987	0.1016	
9a (15-30 min)	15	37.1724	37.2514	0.0790	332.7082
9b (15-30 min)		22.0995	22.1739	0.0744	
10a (30-45 min)	15	35.5566	35.6190	0.0624	338.7433
10b (30-45 min)		24.7728	24.8178	0.0450	
11a (45-60 min)	15	34.9528	35.0076	0.0548	314.2437
11b (45-60 min)		24.8629	24.8943	0.0314	
12a (60-75 min)	15	36.1586	36.2046	0.0460	292.8313
12b (60-75 min)		24.8181	24.8466	0.0285	
13 (c/o)		24.9549	24.9761	0.0212	
14 (rinse)		25.2017	25.205	0.0033	
15 (dep)*		24.5847	24.5851	0.0004	
16 (dep)*		24.9454	24.9448	-0.0006	
17 (clean)		22.1988	22.2068	0.0080	
18 (clean)		24.6215	24.6294	0.0079	
Time 0 Sample		25.255			

*dep - depressurization

Appendix D2: Example FT Froth Dynamic Extraction Spreadsheet

Tables D2a and D2b display the results of an FT Froth dynamic extraction with SC-CO_2 conducted on May 28, 2018.

Table D2a. Summary of dynamic extraction conditions and initial data collected.

Description:	**Syncrude FT Froth 25 g Extraction - 20 mL/min**						
Run pressure (psi/MPa)	3480	24	**Mass sample in vessel (g)**	25.6943	**Static time (mins)**	Set 1	60
Run temperature (^{o}C/K)	60.4231	333.57	**Co-solvent**	-		Set 2	60
Pump Temperature (^{o}C/K)	2	275.15	**Volume co-solvent added during pressurization (mL)**	N/A	**Sample Jar ID (#)**	FT Froth 5	-
Density of CO_2 at run conditions (g/mL)	0.77392	-	**Rate of co-solvent feed (mL/min)**	N/A	**Mass jar + spatula + froth sample + jar lid (g)**	164.2072	-
Density of CO_2 at pump conditions (g/mL)	1.0277	-	**Mass of solids in vessel (g)**	3.09873258	**Mass jar + spatula + residue + jar lid (g)**	138.5129	-
Mixing speed (rpm)	250	-	**Mass of water in vessel (g)**	7.03509934	**Mass of bitumen in vessel (g)**	15.56046808	-

Table D2b. Experimental data collected from an FT Froth dynamic extraction.

Vial ID	Sampling time (min)	Initial mass (g)	Final mass (g)	Mass of sample collected (g)	Volume of CO_2 from pumps (mL)
1a (0-5 min)	5	37.6643	38.8522	1.1879	102.5623
1b (0-5 min)		25.5114	25.5128	0.0014	
2a (5-10 min)	5	37.4419	38.4263	0.9844	105.1341667
2b (5-10 min)		25.4134	25.4144	0.0010	
3a (10-15 min)	5	37.6796	38.4133	0.7337	100.0766667
3b (10-15 min)		25.1906	25.1899	-0.0007	
4a (15-30 min)	15	38.5618	40.2801	1.7183	308.7818333
4b (15-30 min)		25.5571	25.5562	-0.0009	
5a (30-45 min)	15	38.7823	39.5985	0.8162	297.0765
5b (30-45 min)		25.2460	25.2451	-0.0009	
6 (c/o)		25.3374	25.3417	0.0043	
7 (rinse)		25.2398	25.3299	0.0901	
8a (0-15 min)	15	37.0821	37.5440	0.4619	312.9811667
8b (0-15 min)		25.5287	25.5295	0.0008	
9a (15-30 min)	15	37.1929	37.5560	0.3631	291.0202
9b (15-30 min)		25.3950	25.3951	0.0001	
10a (30-45 min)	15	36.8634	37.1030	0.2396	290.0712
10b (30-45 min)		25.2523	25.2515	-0.0008	
11a (45-60 min)	15	37.5605	37.7993	0.2388	321.4582
11b (45-60 min)		25.3865	25.3856	-0.0009	
12a (60-75 min)	15	38.8057	38.9652	0.1595	325.4933
12b (60-75 min)		25.4477	25.4472	-0.0005	
13 (c/o)	45	25.3995	25.3997	0.0002	
14 (rinse)		25.5918	25.7636	0.1718	
15 (dep)		25.5827	25.5847	0.0020	
16 (dep)		25.4103	25.4106	0.0003	
17 (clean)		25.3267	25.3298	0.0031	
18 (clean)		25.3393	25.3411	0.0018	
Time 0 Sample		25.6147			

*dep - depressurization

Appendix E

Dean-Stark Extraction

Appendix E: Dean-Stark Extraction

Note: Syncrude staff conducted all Dean-Stark extractions.

1. Insert three rolled Kimwipes® into a Whatman® cellulose thimble. Place the thimble (with the Kimwipes®) into a weighing bottle and dry, uncapped for one hour at 120 °C. Cap the weighing bottle and store in a desiccator until needed.
2. Weigh the weighing bottle (plus thimble and Kimwipes®) to the nearest 0.001 g. Remove the Kimwipes® and place the thimble in its wire support basket. Mount the thimble and basket in the neck of the kettle.
3. Clean the outside of the vessel residue solution jar and weigh to the nearest 0.01 g. Transfer the solution into the thimble, wash the jar clean with toluene and wipe the jar dry with Kimwipes®. Place the Kimwipes® in the thimble and then weigh the empty vessel residue solution jar.
4. Fill the kettle with toluene to a final volume of approximately 200 mL and then cover the thimble with the solvent distribution screen.
5. Assemble the adapter, water trap and condenser.
6. Apply heat and adjust the reflux rate such that liquid does not overflow the thimble. Continue refluxing for 30 minutes after no water is visible in any part of the apparatus except the water trap and the toluene dripping from the thimble is colorless.
7. *Water content:* Allow the water trap and its contents to cool to room temperature. Estimate the volume of water in the trap to the nearest 0.05 mL.
8. *Solids content:* Disassemble the apparatus, remove the thimble from its wire support basket and return it to its original weighing bottle. Dry the uncapped weighing bottle and its contents for three hours at 120 °C. Cool the capped weighing bottle in a desiccator and weigh the final mass to the nearest 0.001g. The difference between this final mass and the original mass of the weighing bottle, thimble and Kimwipes® is the solids content of the vessel residue.

9. *Bitumen content:* The bitumen/toluene solution in the kettle is separated using a Rotary Evaporator (Rotavap). Weigh the empty evaporation flask and then place the bitumen/toluene solution into the flask. Lower the flask into the water bath and allow the solution to evaporate. The toluene will evaporate into the receiving flask. Once complete, weigh the final mass of the evaporation flask and its contents. The difference between this final mass and the original mass of the empty flask is the bitumen content of the vessel residue.

Appendix F

High Temperature Simulated Distillation

Appendix F: High Temperature Simulated Distillation

Note: Syncrude staff conducted all HTSD analyses.

1. *Retention Time Calibration Standard*: To prepare the retention time calibration standard, place approximately 20 mL of CS_2 into a flask, along with 25 g of a mixture of Polywax and 10 mg of a mixture of paraffins. Transfer a 2 mL aliquot of the final mixture into a 2 mL auto sampler vial.
2. *Verifying System Performance:*
   a. *Column Resolution*: Inject 0.1 to 0.2 μL of the retention time calibration mixture and calculate the column resolution by comparing the retention time and peak width at half height for $n\text{-}C_{50}$ and $n\text{-}C_{52}$. The resolution, R, should be between 1.8 and 4.0.
   b. *Detector Relative Response Test Mixture*: Since this test method assumes all hydrocarbons have the same relative response (regardless of retention time), this mixture is prepared in order to determine relative response factors. Prepare a solution of paraffins by adding 100 mg of each of eight paraffins (one of which is eicosane) to a 50 mL volumetric flask and filling the remainder of the 50 mL with CS_2. Ensure the paraffins dissolve completely. Transfer an aliquot of the mixture to a 2 mL injection vial and inject 0.1 to 0.2 μL. Calculate the relative response factor, F_i, of each paraffin relative to eicosane using the masses, peak area and % purity of the paraffin and eicosane. F_i should be between 0.95 to 1.05 – values outside this range may indicated inlet problems, lack of constant flow, and/or partial blockage of the flame tip orifice.
3. Set the initial oven temperature – chosen based on the sample type. For samples with an initial boiling point greater than 100 °C, such as vessel residues, the initial oven temperature can be set at 35 to 40 °C. If the sample type is not known start with an initial temperature of -20 °C. The oven temperature increases at a rate of 15 °C/min.
4. *Blank (Baseline) Run:* At the beginning of each sequence, a blank run is performed by injecting a volume of CS_2 equivalent to the sample injection

volume. An acceptable blank run should show a stable plateau at the highest temperature of the oven and should not show any residual sample elution.

5. *Retention Time Calibration Standard*: Insert the retention time calibration vial into the auto sampler for injection. On the chromatogram of the retention time calibration mixture, identify all carbons up to C_{110}. This chromatogram is in turn used to develop a Boiling Point versus Retention Time curve. Using the mixture of Polywax and paraffins, the system is calibrated for C_5 to C_{110} and can therefore analyze samples with a boiling point range from 40 to 735 °C. Insert the vial again at the end of the analysis in order to ascertain the stability of the column.
6. *Response Factor Standard*: The detector response factor is necessary in order to determine sample recovery. Reference Oil 5010 is used for this purpose because it fully elutes from the column under the conditions of the test method – it is an external standard available from various chromatography suppliers. To prepare the Response Factor Standard, weigh 0.2 to 0.25 g of Reference Oil 5010, then add 10 mL of CS_2 and record this new weight. Transfer a 2 mL aliquot of this solution into an auto sampler vial. Insert this vial in the auto sampler for injection. Inject this standard in duplicate. The response factor, *RF*, is calculated using the mass of Reference Oil 5010 in solution, the mass of the solvent used in the solution and the net area of the Reference Oil 5010 chromatograph (calculated after the zeroing procedure in step 8). The response factor should not vary by more than 2%.
7. *Sample Analysis:* Ensure the extract, time zero or vessel residue samples are at room temperature prior to weighing. Weigh 0.2 to 0.25 g of a sample, add 10 mL of CS_2 and record this new weight. Transfer a 2 mL aliquot of the solution into an auto sampler vial. Inject the sample. Repeat this process for all samples to be analyzed. Additional blank runs are conducted throughout the analysis to confirm the absence of carryover from previous samples.

8. *Zeroing of the Reference Oil 5010 and Sample Chromatographs:* Set up an array for the Reference Oil 5010 chromatograph. By visual inspection of the chromatograph, ensure that the first 5 slices (each slice is a time interval of 0.1 s) do not contain sample or solvent elution. Calculate the average of the first five area slices and subtract this average from each slice in the chromatograph (set any negative numbers to zero). Zero the blank (baseline) chromatograph and the sample chromatographs in the same manner. Subtract each zeroed blank baseline slice from each corresponding zeroed Reference Oil 5010 slice (set any negative numbers to zero). Subtract each zeroed blank baseline slice from each corresponding zeroed sample slice (set any negative numbers to zero).
9. *Calculating Boiling Point Distribution for Reference Oil 5010:* The corrected slices for Reference Oil 5010 are subjected to a Test Method D6352 calculation to determine boiling point distribution. These boiling points are then compared to consensus values reported in Test Method D6352 to ensure they fall within the specified window. If this requirement is not met, correct any chromatographic problems before proceeding. Problems may include: contaminated solvent, sample preparation errors, sample residue in the inlet or column, quality of the baseline used, and/or a partially blocked detector jet.
10. *Quenching Correction*: A quenching factor is applied to the time segment corresponding to the elution of CS_2 – this factor corrects for the diminished FID response when CS_2 co-elutes with sample components. Select the time that corresponds to the beginning of the elution of CS_2 and the time corresponding to the end of the elution of CS_2. For each slice in this time interval, multiply the diminished response by the quenching factor, 1.930. Apply the quenching factor to all applicable sample chromatographs.
11. *Calculating Percent Recovery of Sample*: The percent recovery of the sample is calculated using the mass of sample in the solution, the mass of solvent used in the solution, and the mass of sample eluted (determined by

multiplying the net area of the sample chromatograph by the response factor, RF). Calculate percent recovery for each sample that was analyzed.

12. *Determining Boiling Point Distribution*: Multiply each slice of the sample chromatograph by the percent recovery of the sample, and then divide each slice by the total area of the sample. Repeat this process for each sample that was analyzed. For each sample, determine the time required to yield exactly 0.5, 1, 2, 3 … % recovery. Convert the retention times to boiling points using the Boiling Point versus Retention Time curve developed in step 5. Graphing the cumulative percent recovery of each sample versus the corresponding boiling points produces HTSD curves.