University of Alberta

Extraction of Bitumen from Athabasca Oil Sand Slurry Using Supercritical Carbon Dioxide

by

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Abstract

Extraction of hydrocarbons from an Athabasca oil sand slurry were conducted using supercritical carbon dioxide (SC-CO_2). The oil sand was slurried to a 1:1 ratio with water and experiments were conducted using a laboratory-scale batch supercritical fluid extraction (SFE) system. Preliminary tests revealed the importance of mixing rate on hydrocarbon yields. A 2^3 factorial experiment was then conducted to test the effect of temperature, pressure, and modifier (toluene) addition on hydrocarbon extraction yield. When toluene was absent, hydrocarbon extraction yields were greater at the high temperature (60°C); however, when toluene was present, the combination of low temperature (31°C) and high pressure (24.1MPa) provided greater extraction yields. The experiment that produced the highest cumulative hydrocarbon extraction yield was analyzed by GC-FID for product-quality. Two composite samples and one time series sample revealed a carbon distribution range of the extract centering on C_{25}, corresponding to the light gas oil range as classified in petroleum fractions.

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List of Abbreviations

ANOVA	Analysis of variance
API	American Petroleum Institute
ARC	Alberta Research Council
CO_2	Carbon dioxide
CSS	Cyclic Steam Stimulation
EOR	Enhanced Oil Recovery
EOS	Equation of State
FID	Flame Ionization Detector
GC	Gas chromatography
ISC	*In-situ* Combustion
NSO	Nitrogen-Sulfur-Oxygen (also referred to as resins)
PSK	Phase Separation Kinetic
SAGD	Steam assisted gravity drainage
SARA	Saturate, Aromatic, Resin, Asphaltenes
SC-CO_2	Supercritical carbon dioxide
SCF	Supercritical fluid
SCO	Synthetic Crude Oil
SFE	Supercritical fluid extraction
SFE-PW	Supercritical Fluid Extraction-Processed-water
TAN	Total Acid Number
THAI	Toe-to-Heel Air Injection
VAPEX	Vapor Extraction

List of Symbols

2^3	2 levels and 3 factors analysis of variance test
A^+	Reactive asphaltenes
M^+	Reactive maltene
A^*	Asphaltene core
M^*	Nonreactive maltene
A^{1+}	Heavy asphaltenes fraction of A^+
A^{2+}	Light asphaltenes fraction of A^+
T_C	Critical temperature
P_C	Critical pressure
ρ_m	Liquid modifier density
ρ_{SC-CO_2}	SC-CO_2 density
ppm	Parts per million
bbl	Barrels

CHAPTER 1 Introduction

1.1 Problem Scenario

Diminishing supplies of global conventional light crude oil reserves, particularly from Middle Eastern regions, has shifted the energy focus to unconventional oil alternatives to satisfy the ever-growing global oil demand. Unconventional oil resources currently exceed conventional oil reserves by a factor of three (i.e. 6 trillion barrels) based on combined global oil reserves (Aguilera et al. 2009; Curtis et al. 2002). The world oil demand is expected to increase from the current 86 x 10^6 barrels per day ($bbl \cdot d^{-1}$) to 103.9 x $10^6 bbl \cdot d^{-1}$ by 2030, and increasing further to 111 x $10^6 bbl \cdot d^{-1}$ by the year 2035 (IEA 2010). Owing to the increases in oil prices, it has become economically appealing to extract and develop unconventional oils—such as the extra heavy oil from the Orinoco oil belt of Venezuela and natural bitumen from the Athabasca oil sands in Alberta, Canada. Unconventional oils are restricted to heavy (or extra-heavy) crude oil, bitumen from oil sands, and oil shale. Coal and natural gas are not considered unconventional as they are marketable in their natural state and will not likely be utilized in synthetic crude production (Mohr and Evans 2010). Extra-heavy oil and natural bitumen are the result of biodegradation of conventional oils resulting in an oil product of high viscosity, high density (e.g. low API gravity), and high levels of nitrogen, oxygen, sulfur and heavy metals (Head et al. 2003; Wenger et al. 2002).

The largest natural bitumen deposit can be found in Canada, followed by Russia and Kazakhstan (WEC 2007). In Alberta, Canada, natural bitumen is found in the oil sands from three different deposits—Athabasca, Peace River, and Cold Lake—situated at various depths from the surface. The two primary means of extracting bitumen from the oil sands deposits include surface mining of the shallow deposits (i.e. deposits less than 50m (Chow et al. 2008) to 75m (Chalaturnyk et al. 2002)) and *in-situ* methods for the deeper deposits. Production levels from the oil sands are currently at 1.3 x $10^6 bbl \cdot d^{-1}$ and are anticipated to increase to 3.5 x 10^6bbl·d^{-1} by the year 2023 to 2025 (CAPP 2010a; OSDG 2009a).

Approximately 2-3 barrels of freshwater, from the Athabasca River, is required for every barrel of bitumen production in surface mining applications and, as a result, poses a potential environmental stress to the Lower Athabasca River basin, especially under low-flow conditions in the winter season (AENV 2007; Allen 2008). Surface mining activities result in the disturbance and excavation of large areas of boreal forest and in the production of contaminated water and unconsolidated tailings stored on-site, awaiting future remediation solutions. The contaminated water and tailings are stored in large man-made dykes called tailings ponds (Chalaturnyk et al. 2002; GOA 2009). The tailings are chemically alkaline, consisting of sand, silt, clay, residual bitumen, and acute toxins (i.e. naphthenic acids) left over from the water-extraction process (Allen 2008). Currently, the tailings ponds cover 130km^2 in northern Alberta and continue to grow with further surface mining development (GOA 2010).

In-situ methods are required for oil sands reservoirs that are buried too deeply for recovery, which accounts for 80-90% of the deposits in Alberta (Chow et al. 2008; GOA 2010; Hyndman and Luhning 1991). The most commonly used method for *in-situ* operations in Alberta is SAGD (steam assisted gravity drainage), which relies on the injection of steam into the reservoir in order to reduce the viscosity of the bitumen so that it can be pumped to the surface for further processing (GOA 2009).

The extracted bitumen, from both surface mining and *in-situ* operations, requires a great degree of upgrading, consuming further energy and resources before it can be sold to the market as synthetic crude oil (SCO) (Chalaturnyk et al. 2002). Up to 50wt% of bitumen is a residuum (also known as pitch) that cannot be readily upgraded by conventional vacuum distillation (Chung et al. 1997; Zhao et al. 2001). Upgrading of bitumen serves several purposes including making the oil transportable by reducing the viscosity, density, and pour point of the oil; transforming the bitumen to resemble conventional crude oil; and most importantly, replacing conventional crude oil as a refinery feedstock (Hyndman and Luhning 1991).

1.2 Research Objectives

Currently, the oil sands industry is looking for innovative technologies to reduce the energy intensity and to minimize the environmental footprint of oil sands processing—especially for surface mining operations. Oil sands processing can potentially be streamlined, using supercritical fluid extraction, a non-aqueous extraction technology.

The purpose of this research is to investigate the extraction of bitumen from an oil sands slurry using supercritical CO_2 (SC-CO_2). A slurry is created by the addition of water at a 1:1 ratio as a slurrying agent and transportation medium of the oil sands for future applications in a continuous SFE process.

Specifically, the objectives of this research include the following:

1. Perform preliminary experiments at a SC-CO_2 density of $0.91 g\cdot mL^{-1}$ (specifically at 31°C and 24.1MPa) to identify important factors (e.g. mixing rate, static time, and premixing time) that should be used in further experiments to study the efficient recovery of hydrocarbons from 1:1, medium grade (~10wt%), Athabasca oil sand slurry.
2. Determine the role and effect of temperature and pressure, and hence the role of SC-CO_2 density, between the range of 31°C to 60°C and 13.8MPa to 24.1MPa respectively, on the extraction of bitumen from 1:1 Athabasca oil sand slurry.
3. Investigate the extraction efficiency using toluene as a modifier, on 1:1 Athabasca oil sand slurry, at 9.1 wt%.
4. Investigate the quality of the processed-water obtained from the 1:1 slurry after SFE treatment.
5. Qualitatively investigate the product quality of the extracted hydrocarbon under the best treatment condition (i.e. highest extraction yield).

This research will demonstrate the ability of SC-CO_2 to extract hydrocarbons from 1:1 Athabasca oil sand slurry. The findings from the results described herein will demonstrate the possibility of using a single stage extraction and upgrading process. Secondly, the results will help to increase the extraction efficiency of an oil sand slurry by adjusting the operating parameters (such as temperature, pressure, mixing rate, static extraction time, dynamic extraction time, etc.), and by using additives, such as a modifier. These results are expected to serve as a preliminary investigation into the future implementation of a continuous SFE application for oil sand slurries.

1.3 Thesis Organization

This thesis is divided into 5 sections. Chapter 1 provides an introduction to the challenges associated with oil sands extraction in Alberta; a brief overview of utilizing SC-CO_2 as the extraction fluid in SFE processes; and a list of specific objectives for the research conducted for this thesis. Chapter 2 is an in-depth literature review on the traditional bitumen recovery methods from the Alberta oil sands; the technical and environmental challenges that the oil sands industry currently faces; and emerging technologies including the application of using SC-CO_2 for the extraction of unconventional oil in a one-step extraction and upgrading process. Chapter 3 is an outline of the materials, equipment, and procedures used to conduct the research. Chapter 4 includes the results of the 2^3 factorial (single replicate) preliminary experiments; results of the 2^3 factorial (triplicate run) experiments investigating the effect of pressure, temperature, and toluene addition on the extraction yield; analytical results on the water chemistry and asphaltenes yield in the ARC bitumen; product quality analysis of the extracted hydrocarbon; and a discussion of potential sources of error throughout the experimentation process. Chapter 5 summarizes key conclusions and recommendations for future work in advancing the SFE technology to a continuous extraction process for oil sands.

CHAPTER 2 Literature Review

2.1 Unconventional Oil

Unconventional oils are restricted to heavy (or extra heavy) crude oil, bitumen from oil sands (also known as tar sands or natural bitumen), and shale oil from oil shale because they are not typically marketable in their natural state (Mohr and Evans 2010), and require vigorous extraction and upgrading to become SCO. In this section, first, the API (American Petroleum Institute) gravity—a method used by oil producers in the attempt to categorize different grades of crude oil will be defined. A brief description will be provided on how extra heavy oil and natural bitumen is formed followed by an illustration of the 4 chemical classes in bitumen. Lastly, a brief overview of oil shale will be given.

2.1.1 API Gravity

Because oil viscosity is sensitive to temperature, oil producers prefer using density in classifying a crude oil for market value. The density of an oil can be defined by the API gravity:

$$\mathrm{API} = \frac{141.5}{\rho_f} - 131.5 \qquad \textbf{Equation 1}$$

where ρ_f is the specific gravity of the oil at 0.1MPa and 15.6°C and API gravity is measured in degrees (°). The denser an oil, the lower the API gravity. Heavy oils have an API gravity ranging from 10 to 20°API, and extra-heavy oils (including bitumen from oil sands) range from 4 to 10°API (Ashar 2008; Curtis et al. 2002; Head et al. 2003; Singhal et al. 1997). The oil in the Canadian oil sands and the Venezuelan oil belt ranges from 6-12°API (Head et al. 2003). Non-biodegraded oils have an API gravity of 36-38 (Head et al. 2003). This lower gravity range includes hydrocarbons existing in a fluid or a semi-fluid state. Generally speaking, heavy oils have a specific gravity ranging from $0.934 \mathrm{g \cdot mL^{-1}}$ to $1.029 \mathrm{g \cdot mL^{-1}}$ (Schumacher et al. 1982).

2.1.2 *Extra-Heavy Oil and Natural Bitumen*

Extra-heavy oil and natural bitumen are believed to be the remnants of conventional oils that have been biodegraded under optimal reservoir temperatures (<80°C) allowing for microorganism proliferation and oil biodegradation activities to occur (Eschard and Huc 2008; Head et al. 2003; Wilhelms et al. 2001). Oil and gas generated by source rocks migrate upwards along permeable fractures, towards the surface, leading to a consequential decrease in temperature and optimal biodegradation conditions are approached. This upwards movement leads to a gradual biodegradation process, primarily by the action of anaerobic bacteria, and therefore, the oil becomes progressively heavier as it migrates towards shallower basins (Eschard and Huc 2008). With increasing biodegradation, crude oil becomes more viscous; distillate yields decrease; sulfur, metals (e.g. V, Ni, Fe), asphaltenes, and vacuum residua increase; total acid number (TAN: the mass of KOH required to neutralize 1 gram of crude oil) rises; and API gravity decreases (Head et al. 2003; Wenger et al. 2002; Wilhelms et al. 2001). Consequently, heavy oils and oil sands are commonly associated with foreland basins such as the forelands in the Canadian Rocky Mountains and eastern Venezuela (Eschard and Huc 2008).

Extra-heavy oil and natural bitumen deposits are predominantly located in Canada, Russia, Kazakhstan and Venezuela with smaller deposits found in the United States, Madagascar, Italy, Albania, Trinidad, and Romania (Rudzinski and Aminabhavi 2000; Schumacher et al. 1982; WEC 2007). In terms of heavy oil discoveries, the Orinoco Oil Belt of Venezuela is the only heavy oil deposit representing approximately 90% of the extra-heavy oil in place or 2.2 trillion barrels (WEC 2007). The three oil sands (Peace River, Cold Lake, and Athabasca) reserves in Alberta, Canada is the largest known natural bitumen deposit at an estimated 175 billion barrels of bitumen in place (ERCB 2010; WEC 2007). Together, the heavy oil and bitumen reserves in Venezuela and Canada represent more than 90% of the world's heavy oil and bitumen resources (Chow et al. 2008).

A number of stages are associated with the biodegradation of crude oil due to the preferential removal of light hydrocarbon components (Wenger et al. 2002; Zhou et al. 2008). In the early stages of biodegradation, the oil loses n-alkanes followed by the more resistant acyclic isoprenoids. The more highly branched polycyclic and aromatic hydrocarbons are more resilient to biodegradation (Jones et al. 2008). As a result, there is a relatively high proportion of high molecular weight polar hydrocarbon and asphaltene components in the degraded oil, which is responsible for the higher viscosity and concentration of contaminants such as sulfur, nitrogen and metals relative to conventional oil (Wenger et al. 2002). A further consequence of the oil degradation process is the formation of naphthenic acids, which leads to an increase in the acidity of the oil (or the TAN) (Eschard and Huc 2008).

The physical and chemical properties of heavy crude oils and bitumens prevent the use of standard recovery methods that are used for conventional crudes. Recovery of heavy crude and bitumen generally requires more energy to extract from the reservoir and to transport up the oil well to the surface. Processing unconventional oils for synthetic fuel is energy and resource intensive. For example, oil sands require an additional upgrading step to reduce the viscosity of the bitumen in order for it to be sent through the pipelines for further refining into useful petroleum products.

As seen in Figure 1, bitumen can be divided into 4 classes of compounds including saturates, aromatics, resins, and asphaltenes (SARA). The asphaltenes precipitation sequence in Figure 1 is a simple schematic of the removal sequence for n-pentane/n-heptane-soluble maltenes (SAR) components. Further steps to separate the maltene—into saturates, aromatics, and resins classes—are not discussed here because, as with asphaltenes determination, a standardized method does not exist. More common methods include, but are not limited to, ASTM D 4124 (ASTM 2009), ASTM D 2007 (ASTM 2003), IP-143 (IP 1997a) followed by IP-368 (IP 1997b), and Syncrude Methods (Starr et al. 1979). Comparing between different SARA methods should be done with precaution as each method can lead to different results (Fan and Buckley 2002; Kharrat et al. 2007).

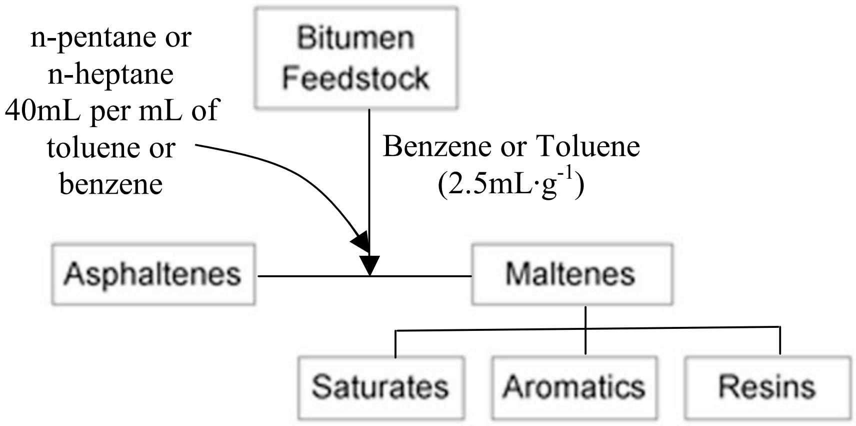


Figure 1. The break-down of bitumen feedstock into SARA, and the precipitation sequence of asphaltenes.

According to Koots and Speight (1975), the asphaltic content of a given crude is directly correlated to the sulfur content, and inversely related to the API gravity. Zhao et al. (2003) demonstrated that the resin and nitrogen content in bitumen pitch may be a direct predictor of coke production. Yoon et al. (2009) noted that, in infrared spectra, the resins demonstrated a strong absorption band ($3285cm^{-1}$) corresponding to the O-H and N-H polar functional groups. In Athabasca bitumen pitch, the dominant sulfur species are thiophenes (65-80wt%), although sulfides are also present (Zhao et al. 2000). Sulfides are predominantly associated with the aromatics class, while the nitrogen species tend to be concentrated in the resins. The saturates portion in Athabasca bitumen pitch is relatively free of sulfurous and nitrogen species (Zhao et al. 2003). Desulfurization by hydrocracking and hydrotreating of bitumen pitch has been found to be relatively ineffective for thiophenic sulfur and only moderately effective for sulphides (Zhao et al. 2002).

2.1.2.1 Definition of Asphaltenes

With the diminishing supply of conventional crude oil, petroleum producers have the added pressure to dig deeper into unconventional oil by cracking the heavier hydrocarbons into lighter fractions. Rejection and separation of asphaltenes prior to petroleum processing is a necessary step as they have a strong tendency to form coke, deactivate catalyst, create obstructions, and prevent proper flow through oil reservoirs and pipelines upon precipitation (Abu-Khader and Speight 2007). As a result, asphaltenes are of increasing concern to petroleum producers. Asphaltenes are dark brown to black solids, with no definitive molecular weight or melting point (Abu-Khader and Speight 2007; Andersen and Speight 2001; Speight 2004; Speight and Moschopedis 1981). The molecular weight of asphaltenes has been postulated to be in the range of 900 to 2 500 000 depending on the measurement method (Dickie and Yen 1967). Generally speaking, asphaltenes are high molecular weight hydrocarbons, aromatic in structure, and are polar due to the presence of nitrogen-sulfur-oxygen (NSO) constituents, and heavy metals (e.g. Ni and V) (Abu-Khader and Speight 2007). Asphaltenes are soluble in carbon disulfide, pyridine, carbon tetrachloride, benzene, and toluene, but precipitate in low molecular weight n-alkanes (Speight 1980). Under high temperatures, asphaltenes break down into black carbonaceous residue, or coke, and form volatiles. Their ability to remain suspended in solution is primarily a result of the peptization with the natural resins present in the original crude (Koots and Speight 1975). In fact, it is not possible to bring about asphaltenes peptization by using resins of other crudes that are lower in aromaticity and differ in heteroatoms (e.g. N, S, O) content (Speight and Moschopedis 1981). Asphaltenes separation in petroleum refining has become increasingly important with the increased frequency of utilizing heavy crude oil (such as bitumen) as a refinery feedstock for further upgrading.

Towfighi et al. (2002) postulated three methods by which coke formation occurs in heavy oil upgrading: radical initiation on the active site of the catalyst used in hydrotreating; asphaltenes combination; and reaction between activated asphaltenes and light molecular weight radicals. On similar lines, Wiehe (1993) postulated the phase separation kinetic model (PSK) according to the following reactions:

$$A^{+} \xrightarrow{k_A} aA^{*} + (1-a)(\text{volatile}) \qquad \textbf{Equation 2}$$

$$M^{+} \xrightarrow{k_B} a(A^{*} - \text{volatile}) + b(M^{*} - \text{volatile}) + \text{volatile} \qquad \textbf{Equation 3}$$

$$A^{*}_{ex} = A^{*} - A^{*}_{max} = A^{*} - S_L(M^{+} + M^{*}) \qquad \textbf{Equation 4}$$

$$A^{*}_{ex} \xrightarrow{k_C} C \qquad \textbf{Equation 5}$$

where A^{+} and M^{+}, represent the reactive asphaltenes and maltenes respectively, which form the asphaltenes core (A^{*}). The nonreactive maltene is represented by M^{*}. According to Equation 4, M^{+} and M^{*}, can solubilize up to an upper limit of asphaltenes, A^{*}_{max}, as defined by the solubility limit, S_L. Excess asphaltenes core, A^{*}_{ex}, is subsequently converted into coke according to Equation 5. As a result, according to this PSK model, it is best to retard the rate of coke production by lowering the rate of reaction, k_A and k_B, according to Equation 2 and 3, or enhance the solubility limit, S_L, in Equation 4.

Watanabe et al. (2010) supplemented to the PSK model by further defining reactive asphaltenes according to the following equation for A^{+}:

$$A^{+} = A^{1+} + A^{2+} \qquad \textbf{Equation 6}$$

In Equation 6, A^{+} is represented by both a heavy, A^{1+}, and a light fraction, A^{2+}, respectively. The A^{2+} fraction is soluble in the light maltene fraction, while the A^{1+} fraction represents the portion of asphaltenes that will readily combine to form coke (Watanabe et al. 2010). Evidence of a lighter asphaltenes fraction that may be pentane-soluble is also supported by Zhao et al. (2001) and was postulated by Mitchell and Speight back in 1973.

Asphaltenes quantification from bitumen is generally performed by dissolving it in an equal volume of benzene or toluene, followed by precipitation in a minimum of 40 volumes of n-pentane or n-heptane (Andersen and Speight 2001; IP 1997a; Mitchell and Speight 1973; Starr et al. 1979). Generally, lower carbon solvents will precipitate more asphaltenes and therefore the chemistry of the asphaltenes will depend on the choice of solvent (Figure 2).

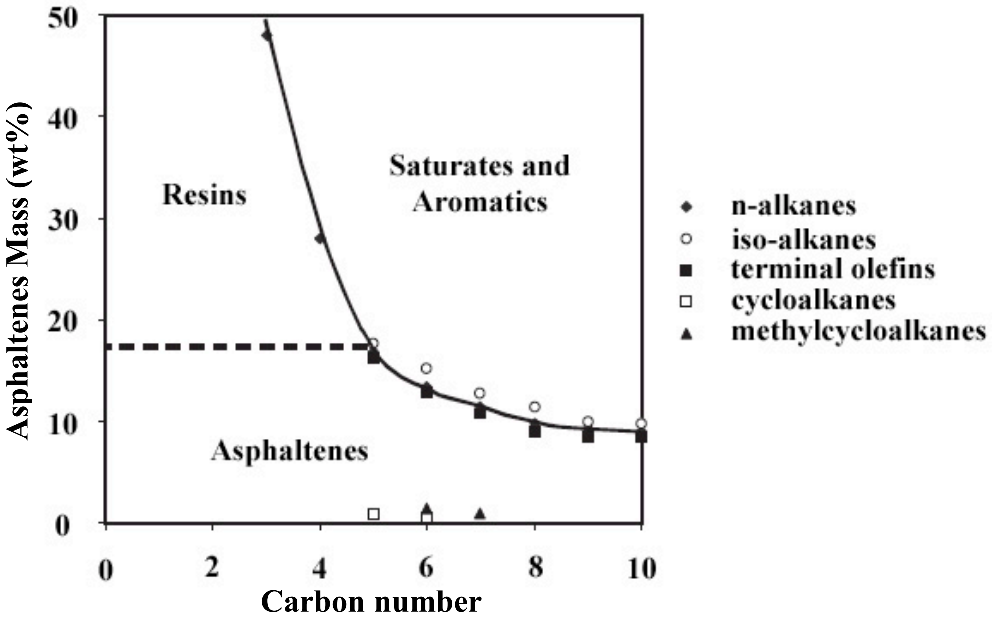


Figure 2. Solvent carbon number and asphaltenes recovery (modified from Andersen and Speight 2001).

The aromaticity and heteroelement content of asphaltenes precipitated by n-heptane tends to be higher as compared to n-pentane (Speight and Moschopedis 1981); therefore, asphaltenes precipitation is an arbitrary science. In fact, the amount the asphaltenes that will precipitate from a bitumen is dependent upon the type of solvent, the dilution ratio, contact time, and temperature (Yoon et al. 2009). Although the oil sands industry commonly uses n-pentane (Starr et al. 1979) in asphaltenes investigations, the Institute of Petroleum (IP 1997a) and ASTM (D-4124) (ASTM 2009) are two organizations pushing the use of n-heptane in order to thoroughly remove semi-solid materials adsorbed to the asphaltenes, that are best categorized under resins. Andersen and Speight (2001) have suggested a clean up step to remove adsorbed resins from the asphaltenes component by reprecipitating in more than 30mL of n-heptane per gram of feedstock and allowing 8-10 hours of contact time.

2.1.3 Oil Shale

Total global estimates (Hyndman and Luhning 1991) of shale oil is 2.8 trillion barrels (WEC 2007). Due to the added costs of mining and extracting oil from oil shale, the exploitation of oil shale deposits are limited to countries such as Brazil, China, Estonia, Germany, and Israel. Nevertheless, the largest known deposit is the Green River, of Wyoming, Utah, of the United States at an estimated 1.5 trillion barrels (Altun et al. 2006; Dyni 2003).

Oil shale is a fine-grained sedimentary rock consisting of organic matter, known as kerogen, within a mineral matrix (WEC 2007). Minor amounts of bitumen may also exist (Altun et al. 2006). Oil shales can be categorized into three basic groups defined by their depositional environments: terrestrial, lacustrine, and marine (Hutton 1987) which are derived from lipid-rich organic matter originating from terrestrial organisms, organisms that inhabited fresh and brackish water, and marine organisms, respectively. The origin of the organic matter in oil shale includes the remnants of algae, spores, pollen, plant cuticle, and corky components derived from herbaceous and woody plants, as well as cellular organisms from lacustrine, marine, and terrestrial plants (Hutton 1987).

Large amounts of shale oil and combustible gas can be extracted by retorting—a process of heating the crushed shale up to 500°C in the absence of oxygen (Sinag and Canel 2004). Low retorting temperatures provide an oil extract that is primarily paraffinic; intermediate temperatures provide an olefinic extract; and high temperatures provide an aromatic extract (Rudzinski and Aminabhavi 2000). The organic matter (OM) in oil shale is primarily comprised of carbon, hydrogen, oxygen, and minor amounts of sulfur and nitrogen. Additionally, oil shale is present in a varying mixture of mineral matter (MM). In commercial grades of oil shale, the ratio of OM:MM is 0.75:5 – 1.5:5. A small amount of bitumen may also be present in some oil shale. After retorting, some carbonaceous residues may remain but these can be utilized as an extra source of energy by burning. Oil shale is different from coal because it has a lower H:C atomic ratio, and the OM:MM ratio in coal is often larger than 4.75:5 (WEC 2007).

2.2 Alberta Oil Sands

The largest oil sand deposit is located in Alberta, Canada at an estimated 175 x 10^9bbl, and is further regarded as the second major petroleum reserve after Saudi Arabia (ERCB 2010). Currently, more than one third of the crude oil produced in Canada originates from the Alberta oil sands (WEC 2007).

Figure 3 is a diagram of the oil sands deposit. The combined area of the three deposits total 140 800km^2 (ERCB 2010). Of the three oil sand formations—including Cold Lake, Peace River, and Athabasca—the Athabasca formation contains the largest, most accessible reserve at an estimated area of 75 000km^2, and an in-place oil estimate of 144 x 10^9bbl, primarily situated in the McMurray Formation and the Lower Cretaceous Mannville Group (Chalaturnyk et al. 2002; Mossop 1980; Zhou et al. 2008). The range in depth of the reserve is between 0-500m, and approximately 10-20% of the deposit, primarily the Athabasca McMurray Formation, can be recovered by surface mining techniques (CAPP 2010a; Chalaturnyk et al. 2002; Zhou et al. 2008). The Cold Lake reserves are found in east-central Alberta at a depth of 985-1987m below the surface, and the Peace River reserves are located along the Peace River arch at the equivalent McMurray Formation depth of 550-700m below the surface. Both the Cold Lake and Peace River reserves cover an area of 22 000km^2 and 8 000km^2, respectively (Zhou et al. 2008). Currently, the industry produces 1.3 x 10^6bbl·d^{-1} representing up to 55% of western Canada's total crude oil production and this rate is expected to rise to 3.5 x 10^6bbl·d^{-1} by the year 2025 (CAPP 2010a).

Figure 3. Athabasca Oil Sands Formation in Alberta, Canada (modified from ERCB 2010).

2.2.1 Chemical and Physical Properties of Athabasca Bitumen

Bitumen is an oil form that is black in appearance and highly viscous (i.e. will not readily flow under ambient conditions). Figure 4 is a schematic of the untreated oil sand matrix. In this schematic, sand particles—hence the name oil sands—(and small amounts of silt and clay particles) are surrounded by a thin water-film layer. Void space between the sand particles are filled in by bitumen. Typically bitumen has a viscosity of 100 000 to 1 000 000 centipoise (cP) (Mossop 1980; Singhal et al. 1997; Upreti et al. 2007).

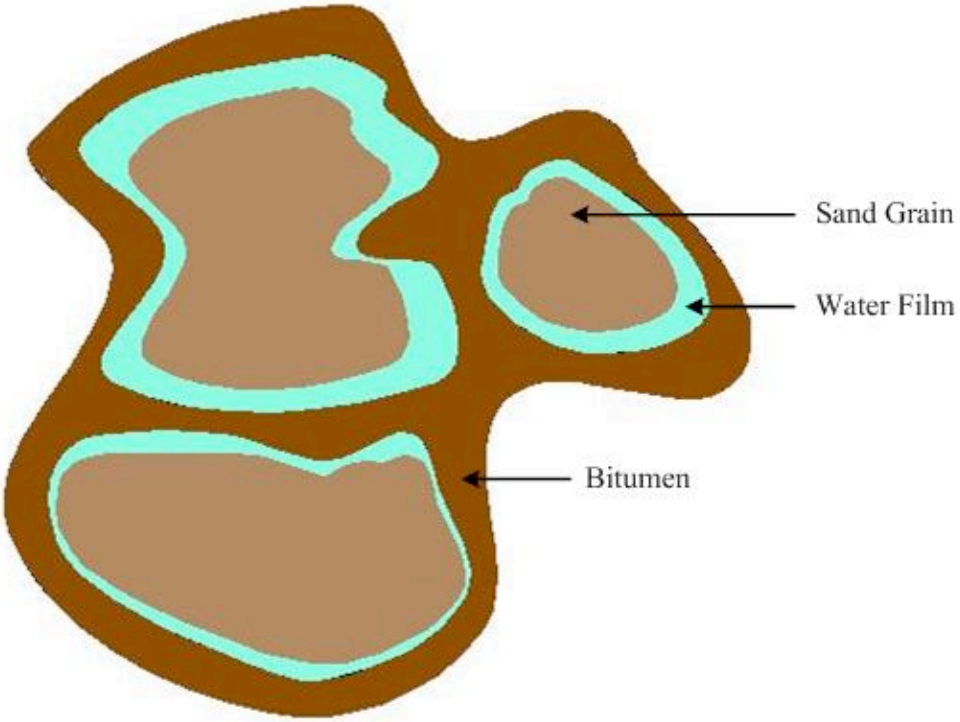


Figure 4. Bitumen embedded between sand and water film in a typical oil sand particle.

Representative chemical properties of bitumen from Alberta oil sand deposits, synthetic and conventional crude are presented in Table 1.

Table 1. Chemical properties of Alberta bitumen as compared to synthetic oil and conventional oil (adapted from Hyndman and Luhning 1991; Yoon et al. 2009).

Property (with unit of measurement)	Bitumen from Alberta Deposits	Synthetic Oil	Conventional Oil
°API	8	32	41
Viscosity (cSt* at 40°C)	3000	3	3.9
Pour Point (°C)	18	-4.5	-6
S (wt%)	4.78	0.08	0.2
N (wt%)	1.63	0.03	0.04
Ni (ppm)	68.5	<1	<1
V (ppm)	174	<1	<1
Asphaltenes (wt%)	15.59	n/a	n/a
Maltenes (wt%)	84.41	n/a	n/a
Saturate Aromatics (wt%)	67.97	n/a	n/a
Resin (wt%)	16.44	n/a	n/a
Distillate Yield (liquid volume, %)			
IBP-C_5	0	4	3
C_5-195°C	0	18	36
195°C-345°C	14	47	31
345°C-560°C	86	31	18
>560°C		0	12

* cSt = centistokes

The high percentage of asphaltenes (15.6wt%) is primarily responsible for the high viscosity of Athabasca bitumen (and heavy oil) (Abu-Khader and Speight 2007). In addition, the heteroatoms (N, O, S) and metals (V, Ni) content are relatively high in Athabasca bitumen, and is a cause for concern in the upgrading stage. These elements have a tendency to deactivate the catalysts that are used in hydrotreating (see Section 2.2.5.4). Further upgrading processes (e.g. such as vacuum distillation, pyrolysis, fluidized catalytic cracking, hydrocracking, hydro-desulfurization, coking, and gasification) are required at severe operational conditions. As a result, the higher energy consumption of heavy oil processing, relative to conventional oil, weakens the market return value of these heavy oils.

In Alberta, Canada, the two methods used to recover bitumen from oil sand include surface mining followed by extraction techniques, or *in-situ* methods (where the bitumen is extracted within the reservoir, and is then pumped to the surface). Once extracted from the oil sands, bitumen can be used in several ways: gasification as a fuel source for on-site operations; thinned down and put on the market; or upgraded to a SCO. The following sections will provide an in-depth description of the surface mining technique and *in-situ* methods for extracting bitumen from oil sands. Upgrading will also be discussed. Water use for extraction, as well as the issue of processed-affected water and water regulations relating to surface mining operations, will also be presented.

2.2.2 Surface Mining Recovery

Surface (or open pit) mining is an oil sands mining technique which is feasible for deposits situated at less than 50m (Chow et al. 2008) to 75m (Chalaturnyk et al. 2002; WEC 2007) from the surface. The current procedure of extracting bitumen from surface mined oil sands is a variant of the Clark's hot water extraction process (Clark and Pasternack 1932)—a flotation process to separate the bitumen from the sand, clay, and silt using hot water and caustic addition. Recovery rates of bitumen from this process are more than 90% from high-grade ore (i.e. ore with a bitumen content greater than 10%) (Chow et al. 2008). Surface mined oil sands are transported as a slurry from the mine to the plant to undergo the extraction process. Thereafter, the extracted bitumen is upgraded into a SCO. A simplified schematic of the surface mining extraction process is shown in Figure 5. Over the years, energy reductions to the extraction process have seen some progress. For example, Syncrude has been able to reduce the slurry extraction temperature from 80°C to 50°C (Hyndman and Luhning 1991).

A considerable amount of freshwater and natural gas (to heat-up the water and to provide a source of hydrogen in upgrading) is currently consumed in the surface mining extraction process and upgrading process. The by-product of the extracted bitumen is an extracted slurry of bitumen froth and rejected components, also known as tailings—comprised of sand, silt, clays, water, residual bitumen, and organic diluents (e.g. naphtha) used in the separation process. For every barrel of bitumen extracted, 2-3 barrels of fresh water from the Athabasca River is withdrawn and consumed. Due to a zero discharge policy, process-affected waters are stored on-site, with a current footprint of 130km^2 (GOA 2010). Currently, this water cannot be sufficiently reclaimed and returned to the river within a life cycle of a mine (Ohlson et al. 2010). Tailings are pumped into large man-made dikes for fine particle settlement and future treatment options. Currently, fluid fine tailings research is aimed at developing methods to allow fine particle settlement and eventual reclamation of the tailings ponds. In this section, the primary extraction process on surface-mined oil sands (including conditioning, separation, and froth treatment) is described in detail.

2.2.2.1 Conditioning

Bitumen is separated from the sand, silt, and clay matrix, using a mixture of mechanical energy, heat, and surfactants, in a process called conditioning (see Step 1 in Figure 5) (Mossop 1980). At present, the oil sands industry performs the conditioning steps in combination with the slurry transport. Mined oil sand is mixed with steam and water at 50-60wt% oil sand. To ensure sufficient release of the bitumen from the oil sand, a velocity, temperature, and residence time of 3.5m·s^{-1}, 41-53°C, and 7-12 minutes, respectively, are ensured throughout the slurry transport process (Chow et al. 2008). Caustic soda (NaOH) is added, during the conditioning step, to release water-soluble surfactants and to promote the dissolution of the oil sand ore structure (Chalaturnyk et al. 2002).

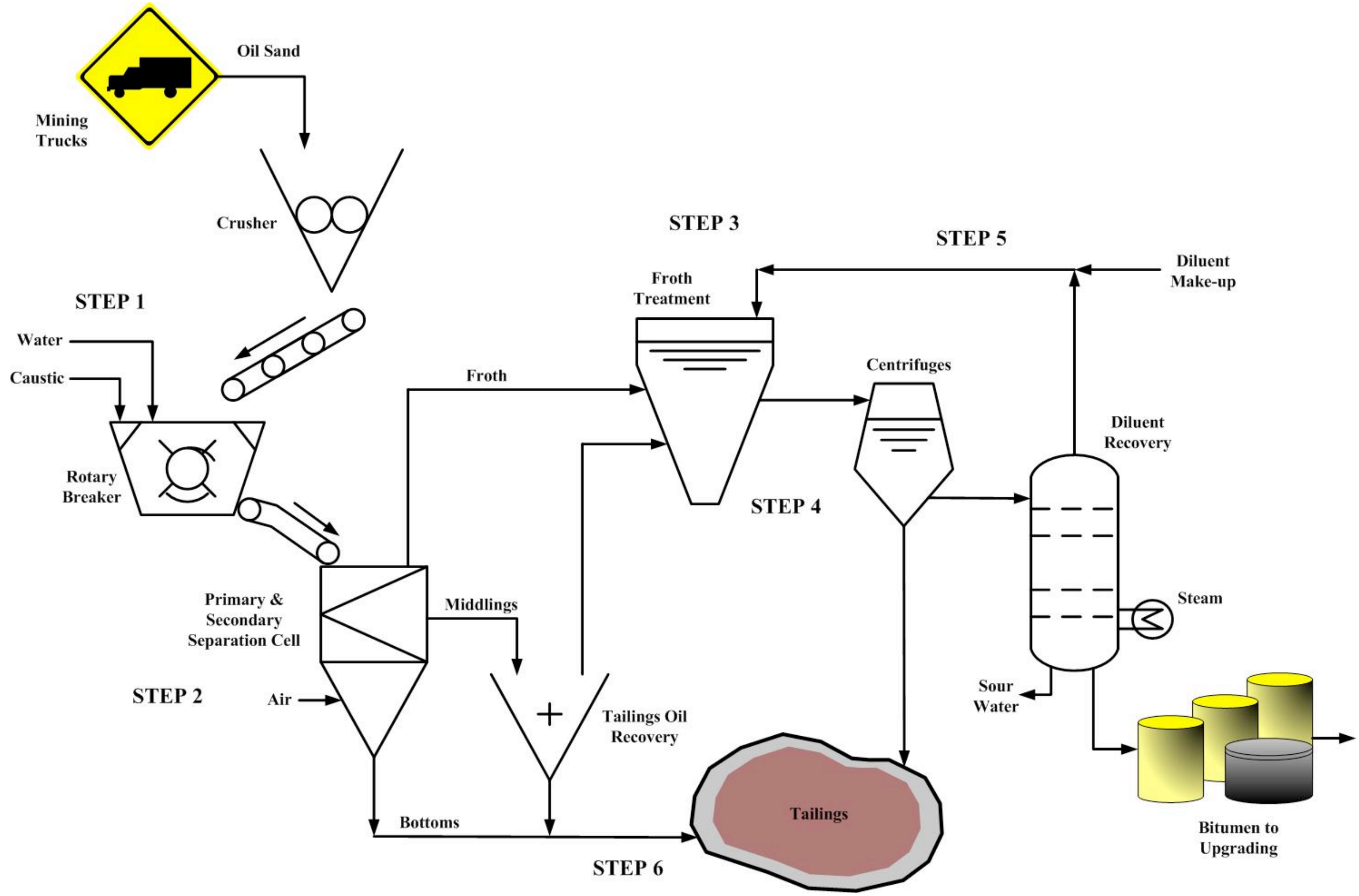


Figure 5. Conventional surface mining and water extraction process in the Athabasca oil sands in Alberta, Canada (modified from Chow et al. 2008 and Chalaturnyk et al. 2002).

2.2.2.2 Separation

The agitation results in an aerated slurry that is then piped to a primary separation vessel. In the primary separation vessel, the bitumen is separated from the solids by flotation, forming a froth that can be skimmed off of the surface and pumped to a froth treatment plant (Starr et al. 1979). As the density of bitumen is near $1g\cdot cm^{-1}$, or close to the density of water, at the process temperature conditions, air is added to increase the rate of flotation of the bitumen droplets. Air and water is added to the mixture and thereby creating a 1:4 oil sand to water ratio (Chow et al. 2008). The first stage of separation occurs in a large cone bottom vessel, or the primary separation vessel (see Step 2 in Figure 5). Aerated bitumen, or bitumen froth, is skimmed off the top of the vessel and conveyed to froth treatment (see Step 3 in Figure 5). Coarse solids from the bottom of the vessel are withdrawn for further process treatment in order to recover any residual bitumen. Residual bitumen left in the middlings of the primary separation vessel is also recovered for further processing and recovery of bitumen. Recent technologies by Suncor and Albian Sands have increased the efficiency of this stage by reducing the need for 2-3 stages of induced air flotation through the use of column flotation and hydrocyclones (Chow et al. 2008).

2.2.2.3 Froth Treatment

The suspended bitumen froth collected from the top of the primary separation vessel is comprised of 25wt% water and 10wt% solids. As the bitumen viscosity at the extraction temperature of 60°C is approximately equivalent to 5000cP, it is necessary to reduce the viscosity by the addition of heat and solvent (i.e. naphtha is a common diluent) to ensure efficient commercial separation rates (Starr et al. 1979). Combined froth from the primary and secondary separation are diluted with naphtha (Starr et al. 1979). Naphtha can also diminish the water-in-oil emulsions and assist in the recovery of bitumen (Chalaturnyk et al. 2002). Traditionally, the application of naphtha is used at the dilution ratio of 1:1 (Chow et al. 2008). This mixture proceeds to an inclined plate settler and centrifuges for the removal of solids and water (see Step 4 in Figure 5). At Shell (in partnership with CANMET's Energy Technology Center in Devon, Alberta), the froth treatment step is treated with an aliphatic diluent in replacement of the aromatic naphtha. The purpose of replacing naphtha with an aliphatic diluent is to lead to quicker settling of precipitated asphaltenes, water, and solids (Chow et al. 2008). Finally, the diluent is recovered for reuse (Step 5 in Figure 5), the bitumen is sent to upgrading, and the tailings are pumped to the tailings ponds.

2.2.2.4 Tailings

Every tonne of oil sands processed through the traditional water extraction process produces approximately $0.1m^3$ of fine tailings, of which 0.05-$0.06m^3$ eventually becomes mature fine tailings (MFT). Tailings are created at three stages in the extraction process (see Step 6 in Figure 5) including primary extraction (yielding coarse sand), froth treatment (yielding intermediate coarse tailings), and fluid tailings in the solvent recovery unit (GOA 2010). Although the sand settles out quickly, the clays only settle up to 30% concentration, and are the primary reason for the 120% volume increase of the original oil sands volume (Hyndman and Luhning 1991; Kasperski 1992). Approximately one third of the silt, clay, and residual bitumen from the slurry produced by the water extraction process forms a gel-like watery suspension in the center of the tailings ponds—these are the (fine) fluid tailings (Kotlyar et al. 1993). Fluid tailings are of primary concern to processed-affected water management as they have extremely poor settling and dewatering characteristics and gradually become MFT after 3-5 years of consolidation. Consolidation issues are directly related to the use of NaOH in the caustic addition during extraction and inadvertently promotes the dispersion of clay particles; therefore, neutral salt additions have been proposed as a replacement such as sodium silicate (Kotlyar et al. 1993). The resulting processed-affected water (i.e. the water released from the tailings) is slightly alkaline (pH of 8-8.4), slightly brackish (2000-$2500mg \cdot L^{-1}$ of total dissolved solids), moderately hard (15-$25mg \cdot L^{-1}$ of Ca^{2+} and 5-$10mg \cdot L^{-1}$ of Mg^{2+}), with an alkalinity of 800-$1000mg \cdot L^{-1}$ of HCO_3^-, and is an acute toxin to aquatic organisms due to the presence of organic acids such as naphthenic acids, which comprise ~80% of the dissolved organic matter (Allen 2008).

2.2.2.5 Fluid Fine Tailings Regulation

A draft directive issued in June 2008 to regulate the tailings systems as a result of surface mining operations was recently finalized in early 2009 by the Alberta Energy and Resources Conservation Board (ERCB): *Directive 074: Tailings Performance Criteria and Requirement for Oil Sands Mining Schemes* (ERCB 2009). The directive aims to hold oil sand operators accountable for tailings management and reclamation, requiring that steps be taken to reduce fluid fine tailings production and eventually transform them into trafficable deposits. A number of specific guidelines were issued including a sample of the following (ERCB 2009):

"......reduce fluid tailings through fines (<44μm) captured in dedicated disposal areas (DDAs), and

- *form and manage DDAs."*

and submit the latter three to ERCB:

"……DDA plans,

- *annual compliance reports for DDAs, and*
- *annual tailings plans and pond status reports."*

Between July 1, 2010 to June 30, 2011, fines captured in DDAs have a phase-in sequence period of attaining 20% total dry fines mass in the feed, 30% between July 1, 2011 to June 30, 2012, and 50% annually thereafter (ERCB 2009). DDAs are required to form trafficable deposits as determined by the following stipulations (ERCB 2009):

"……minimum undrained shear strength of 5 kilopascals (kPa) for the material deposited in the previous year;

- *removal or remediation of material deposited in the previous year that does not meet the 5 kPa requirement; and*
- *ready for reclamation within five years after active deposition has ceased. The deposit will have the strength, stability, and structure necessary to*

> *establish a trafficable surface. The trafficable surface layer must have a minimum undrained shear strength of 10 kPa."*

2.2.3 In-situ (in place) Recovery

Approximately 80-90% of the oil sand reserves in Alberta are buried too deep for surface mining and currently is recovered using *in-situ* techniques (Chow et al. 2008; GOA 2010). Bitumen has a consistency of tar (i.e. high viscosity) and is only conducive to flow by physically adjusting the reservoir conditions (Mossop 1980). There are three general methods of recovery for deep reserves: mechanical (also known as immiscible) displacement, thermal displacement, and chemical displacement (or miscible displacement). In immiscible displacement, water or nonmiscible gases are injected into the reservoir with the purpose of displacing and driving the oil out of the reservoir. This process is limited due to the high viscosity of the bitumen, and injected materials tend to pool at the bottom in a water saturation zone and will not be discussed further (Upreti et al. 2007). The following paragraphs will consider thermal and chemical displacement processes including SAGD, cyclic steam stimulation (CSS), *in-situ* combustion (ISC), toe-to-heel air injection (THAI) and Vapor Extraction (VAPEX) respectively. All of these processes are thermal recovery methods, with the exception of VAPEX, which is strictly a chemical recovery process.

2.2.3.1 Thermal Recovery Processes

SAGD is a common technique used in the recovery of bitumen from the oil sands in Canada. An illustration of the SAGD process is provided in Figure 6. The process involves injecting steam into the reservoir to reduce the viscosity of the bitumen and allow it to be pumped to the surface (Upreti et al. 2007). Two horizontal wells are superimposed 5m apart and situated near the bottom of the reservoir. The upper well (i.e. the injector well) injects steam that rises and develops a steam chamber, which continues to grow with increasing steam injection. As the rising steam hits and condenses on the outer boundary of the steam chamber, the oil becomes entrained and the oil and water are collected by the lower well (Chow et al. 2008). The water is disposed, treated, or recycled back to the steam generator by undergoing an oil/water separation.

A brief description of the oil/water separation is provided here (Ikebe et al. 2010): the resulting mixture of heated bitumen, condensed water, sand and clay proceeds to a separator where the sand and clay are separated by an internal weir plate (i.e. baffle). From there the bitumen and water mixture cools by flowing through a heat-exchanger before entering into a skim tank, where the bitumen is skimmed off the surface. Thereafter, the remaining processed-water can be treated for recycling. First, the processed-water is directed through an oil removal filter followed by a de-oiled tank to remove the remaining residual oil. Second, the processed-water is chemically softened (i.e. lime-softener) and neutralized by a weak acid cation softener. Finally, the processed-water can be recycled as boiler-feed water (Gwak and Bae 2010).

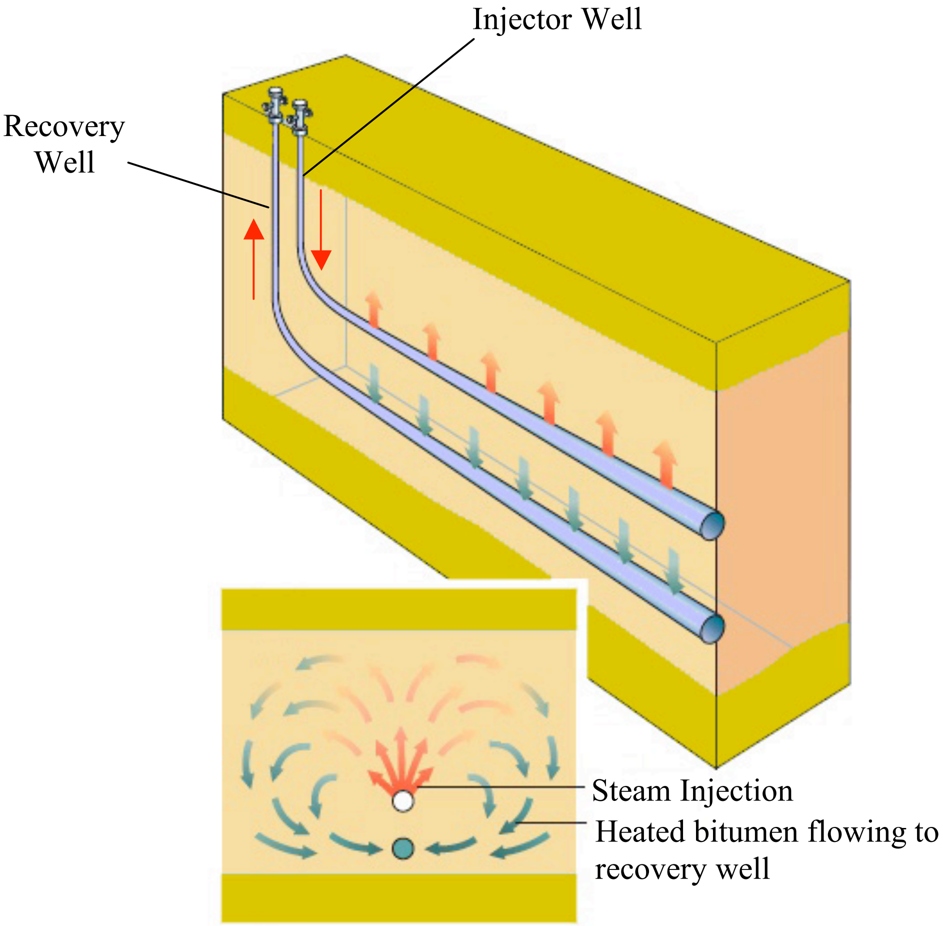


Figure 6. Stacked pair of horizontal wells used in SAGD operations (modified from Curtis et al. 2002).

A similar thermal recovery method to SAGD is CSS (Xia et al. 2002). In CSS, high-pressure steam is injected into the reservoir and a soak period of several weeks is required to reduce the viscosity of the bitumen, and to induce separation of the bitumen from the sand. Fractures are formed in the reservoir during the soak period and these fractures provide a route for the bitumen to flow back towards the injector wells. Subsequently, the recovered bitumen (and water) is pumped back to the surface through the injector wells. CSS is the method of choice at Imperial Oil's Cold Lake project and Canadian Natural Resources' Wolf Lake-Primrose project (OSDG 2009b).

Another common thermal technique is *in-situ* combustion (ISC) for enhanced oil recovery (EOR) processes in oil sands recovery (Xia et al. 2002).

ISC uses air injection to increase oil recovery. The strong exothermic reaction produced by the reaction between the oil and the air increases the temperature in the reservoir, thereby reducing the viscosity of the heavy oil. Unfortunately, a major pitfall of ISC is the large distance between the mobile oil zone and the producer well (i.e. long-distance displacement) leading to excessive gas injection losses and thereby preventing the maintenance of a high temperature oxidation operation (Xia et al. 2003).

Major disadvantages of using thermal recovery methods include the negative economic impact due to the large heat losses, high water-use requirements (with a water to oil ratio of 3:1) (Singhal et al. 1997), the need for large surface facilities (Luhning et al. 2003), and the challenge of recovery from thin reservoirs—since recoveries are dependent on the volume of the vapor chambers (Upreti et al. 2007).

A new technology called Toe-to-Heel Air Injection (THAI) by Petrobank Energy and Resources Ltd. has been developed to respond to these issues (PER 2009). In the THAI process, ISC is integrated with the horizontal well technology as seen in Figure 7 (Xia and Greaves 2006). A zone surrounding the horizontal and vertical wells is preconditioned by heating. Thereafter, air is injected to induce combustion in the reservoir. The combustion advances the burning front (propagating from 'toe' to 'heel'), which enables the heavy oil, combustion gases, and light hydrocarbons to mobilize towards the horizontal production well by gravity and by the pressure differential between the reservoir and horizontal producer well (Greaves et al. 2001; Xia et al. 2003). Due to the high viscosity of the cold heavy oil region, the mobile oil zone is automatically drawn into the horizontal production well immediately below. Therefore, THAI is a short distance displacement method and is important in maintaining and establishing control of oil production (Xia et al. 2003). An asphaltenic material, or coke, is left behind and acts as a fuel as long as the injection of air persists. The greater the airflow injection rate, the hotter the reservoir becomes and the faster the coke is burned. The production well collects and carries the heavy oil and gaseous water droplets to the surface where it is separated and treated.

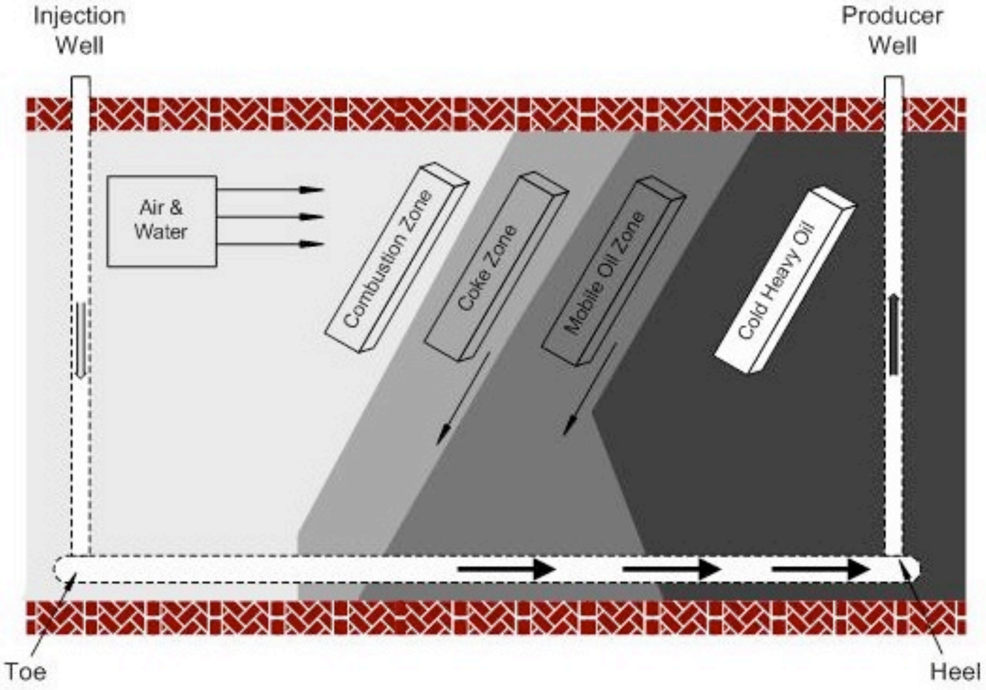


Figure 7. THAI process schematic (modified from Xia and Greaves 2006).

There are several benefits to the THAI process (Greaves et al. 2001; PER 2009; Xia and Greaves 2006; Xia et al. 2002; Xia et al. 2003):

- The surface footprint is greatly reduced relative to other *in-situ* methods,
- Recovery can be as high as 70-80% in difficult reservoirs relative to other *in-situ* methods,
- As in other thermal processes, natural gas and water are not required anywhere in the process,
- The prospect of capturing CO_2 in order to meet carbon emission targets—as targets are implemented,
- Partial upgrading (by thermal cracking, up to 10°API improvement) occurs during the process and,

- Produced gas can potentially be burned to provide electricity for all the necessary plant components (i.e. energy efficient plants that are self-sufficient)

2.2.3.2 Chemical Recovery Processes

As mentioned previously, a common *in-situ* chemical recovery process is the VAPEX process. Similar in design and concept to the SAGD process, the VAPEX process replaces steam with one or more light hydrocarbon solvents (Chow et al. 2008; Xia et al. 2002). In the conventional VAPEX process, a vaporized solvent (such as propane, butane, or a combination of propane and butane) and a non-condensable gas (including commercially available methane or natural gas) is injected into the reservoir (Talbi and Maini 2003). However, unlike SAGD, VAPEX is a miscible displacement process. The hydrocarbon solvent introduced through the injector well diffuses into the oil, reducing its viscosity and thereby allowing it to flow towards a lower collector well (Luhning et al. 2003; Upreti et al. 2007). The solvent is maintained near the vapor pressure as a reduction in injection pressure has been observed to dramatically decrease the rate of oil production (Haghighat and Maini 2010; Upreti et al. 2007). Thereafter, the solvent can be recycled for further extraction.

Following extraction, the live oil (i.e. with entrained butane or propane) undergoes a pressure drop prior to entering the flash tank where the oil and solvent is separated. The solvent vaporizes and travels to the top of the flash tank, where it can be captured and recycled for further extraction. As soon as the solvent is flashed off, the dead oil is ready for upgrading (El-Haj et al. 2009).

There are several advantages that the VAPEX process offers (Chow et al. 2008; Luhning et al. 2003; Singhal et al. 1997; Upreti et al. 2007). Since light hydrocarbons induce asphaltenes precipitation (as discussed in Section 2.1.2), the oil may be upgraded *in-situ*. Secondly, VAPEX is more economical than SAGD since the injection of solvents does not require extensive surface facilities for hot water or steam generation and subsequent wastewater treatment or recycling. Thirdly, VAPEX does not lead to the same energy losses experienced by thermal recovery processes. According to Singhal et al. (1997), VAPEX uses only 3% of the energy of the SAGD process and Luhning et al. (2003) claims that greater than 90% of the greenhouse gas emissions are reduced with this process. Fourthly, reservoirs that have been exploited using the VAPEX process can easily be used for CO_2 sequestration. After a well pair is depleted, the VAPEX solvent gas is reclaimed and recycled into a new well pair for further oil extraction—leaving an empty reservoir that must be maintained under pressure to prevent the VAPEX gas from seeping into the depleted well (Luhning et al. 2003). Consequently, CO_2 is an ideal candidate for maintaining reservoir pressure.

A major disadvantage with VAPEX is that the rate of oil production is much less than with SAGD due to increased asphaltenes precipitation and blockage of the formation. In a recent VAPEX study, Haghighat and Maini (2010) attempted to clean out asphaltenes blockages with toluene, but oil recovery rates did not improve.

2.2.4 Water Use

Water is used in the oil sands in both surface mining and *in-situ* recovery methods. In surface mining, approximately 16 barrels (Allen 2008) of water (of which 2-3 barrels is freshwater originating from the Athabasca River and the remainder is process-affected water) is used to produce one barrel of SCO; although 80-95% of this water is recycled up to 18 times through the extraction process (CAPP 2008). A typical water balance for a surface mining site is illustrated in Figure 8.

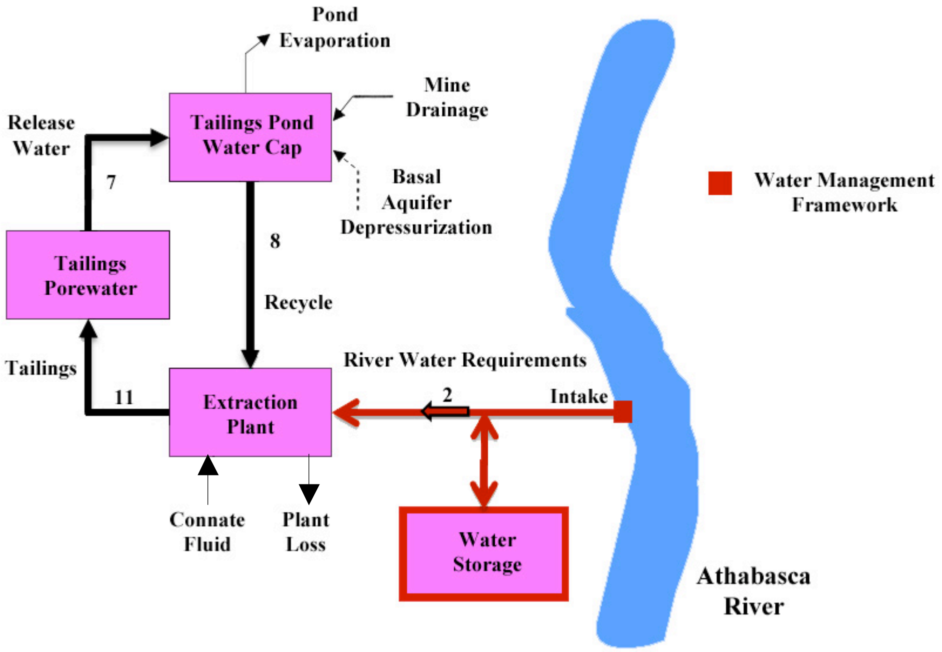


Figure 8. Water balance for surface mining oil sand operations, numbered flows are relative to the river water intake of 2 barrels (modified from OSDG 2009).

Where possible, *in-situ* processes utilize brackish waters from deep underground aquifers. Additionally, *in-situ* operations are much less water intensive as compared to surface mining, using 0.5 barrels of water to process every barrel of bitumen (CAPP 2008). In 2007, Devon Energy of the Jackfish *in-situ* project became the first oil sands operator to employ 100% saline water for steam generation in their SAGD operations (CAPP 2010b). The following section will discuss the water regulations on the lower Athabasca River basin as it pertains to surface mining operations.

2.2.4.1 Water Regulations on the Lower Athabasca River

The Athabasca River plays a critical role in the Alberta oil sands mining operations. Water from the Athabasca River is used in utilities, mining, bitumen extraction, and upgrading (Allen 2008). Water usage by the oil sands industry is regulated through the Department of Fisheries and Oceans at the federal level, and Alberta Environment (GOA 2010) under the Water Act at the provincial level (AENV 2007). Although a majority of the water that is taken from the river is recycled through the plant, there are costs incurred with pumping water from the river and managing processed-water on-site over the long-term. Whereas the industry's water requirement is nearly constant throughout the year, the potential negative implications of water withdrawals on the aquatic ecological assets in the Lower Athabasca River can be more important in the winter months when water levels are naturally lower than in the summer months. Additionally, river water requirements are higher for start-up mines and during initial periods, as the plant begins to perform at full capacity. Water requirements can drop substantially within two years of full operation once the recycling of the process-affected water has attained steady-state conditions, when tailings have settled sufficiently to provide recyclable water (OSDG 2009a).

2.2.4.2 Alberta Water Management Framework for the Lower Athabasca River Basin

Recognizing the ecological importance of the health and integrity of the Lower Athabasca River basin to northern Alberta, the Government of Alberta set up water withdrawal guidelines through *Alberta's Water Management Framework for the Lower Athabasca River* (AENV and DFO 2007) to limit the amount of water withdrawal from the river at different times of the year. In 2007, the framework established three flow conditions (green, yellow, and red) based on the aquatic habitat and the anthropogenic needs and to account for the different seasonal flow variations experienced by the Lower Athabasca River. A brief summary of the three flow conditions is provided here (AENV and DFO 2007):

(i) Green Management Zone – Up to 15% of the river flow is available for industrial withdrawal.

(ii) Yellow Management Zone – Up to 10% of the river flow is available to industrial allocation. Yellow conditions cap the maximum withdrawal at $15\text{m}^3{\cdot}\text{s}^{-1}$ in the winter and $34\text{m}^3{\cdot}\text{s}^{-1}$ in the summer.

(iii) Red Management Zone – Maximum withdrawals are allowed at 5.2% of the historical median flow rate for each week the red conditions are implemented.

Red conditions cap the maximum withdrawal rate at $15\text{m}^3\cdot\text{s}^{-1}$ in the winter and $34\text{m}^3\cdot\text{s}^{-1}$ in the summer.

As a result, some oil sand companies such as the Canadian Natural Resources Ltd. have begun to store water on-site for 30 days at their Horizon mine in preparation for low-flow winter conditions. Suncor Energy Inc. has also committed to a 40% reduction in water use in recent years (CAPP 2008).

A Phase 2 Framework Committee was formed in 2008 to stipulate new recommendations for a <u>*Phase 2 Water Management Framework*</u> based on ensuring aquatic ecosystem health and future sustainability (Ohlson et al. 2010). This framework establishes when and how much water can be withdrawn from the Lower Athabasca River, specifically for oil sands mining operations, based on future projections of up to 3.5 million barrels per day production by 2023-2025 (CAPP 2010a; OSDG 2009a). A base flow threshold was established at $87\text{m}^3 \cdot \text{s}^{-1}$—based on a 1 in 100 low winter flow statistics of average weekly flow records—and limits industry to withdraw up to $4.4\text{m}^3\cdot\text{s}^{-1}$ (Ohlson et al. 2010). Phase 2 recommendations are expected to be implemented in January 2011.

2.2.5 Bitumen Upgrading

The purpose of bitumen upgrading is to convert the bitumen into SCO, in place of conventional crude, that can be further refined into useful petroleum products. In other words, upgrading lowers the viscosity and increases the API gravity of the bitumen (Ashar 2008) by converting high molecular weight hydrocarbon residues into distillable fractions with a boiling point of less than 525°C. In order to accomplish the conversion, the H:C ratio is increased via one of two methods: increase hydrogenation or decrease the carbon content. Due to the high degree of polynuclear aromatic hydrocarbons present in the asphaltenes and resin constituents of bitumen, thermal cracking of bitumen results in a high production of coke (Abu-Khader and Speight 2007). In order to upgrade bitumen into synthetic crude, the bitumen is reduced in S and N contents; the boiling point range is modified by the removal of asphaltenes and related residuum; and the saturate content is enhanced, while ensuring no olefinic components are present (as natural crude oils are absent in olefins) (Hyndman and Luhning 1991).

Bitumen is atmospherically topped in a distillation tower to remove the distillable fraction (550°C of vacuum). Approximately 50% of bitumen is non-distillable, forming a residue called pitch, which requires further upgrading to obtain SCO (Brough et al. 2010; Chung et al. 1997; Zhao et al. 2003). Upgrading involves two stages: a primary stage (where the API gravity is increased and the viscosity decreased) and a secondary stage (where the product is hydroprocessed into a higher quality marketable product by removing S, N, and metals). Primary processes used to convert the bitumen to SCO can involve a combination of coking, cracking, and solvent deasphalting (Hyndman and Luhning 1991). Hydrotreating is the final upgrading step on the cracked product.

In the next sections, solvent deasphalting, thermal cracking, hydrocracking and hydrotreating processes will be presented. The thermal processes considered will include Delayed Coking and Fluid Coking. H-Oil and LC-Fining will be discussed as the hydrocracking processes. Finally, hydrotreating will be described.

2.2.5.1 Solvent Deasphalting

Solvent deasphalting typically involves the use of liquid propane and liquid butane, or a mixture of both, to separate the asphaltenes from the bitumen feedstock. As discussed in Section 2.1.2, the quality of the separated bitumen depends on the solvent choice. Although the disposal of the insoluble asphaltenes can be an issue, it can be directly used or blended with other residua to form asphalt (Abu-Khader and Speight 2007).

2.2.5.2 Thermal Cracking Processes: Coking

Thermal cracking processes produce a byproduct called coke—a carbon rich residue. Although thermal cracking was one of the earliest processes developed, it is not the method of choice in the industry due to the low conversion yields and high degree of S contents (25vol%) produced in pitch. Delayed coking was the first process employed and utilized by Suncor and is also preferred at

Total, Petro-Canada, and Conoco Phillips (Ashar 2008; Hyndman and Luhning 1991). The feedstock is heated up to 480-500°C in a furnace and then allowed to react in an insulated drum. In the drum, volatile components move into an overhead fractionator and coke accumulates in the drum. High boiling liquids in the fractionator are recycled into the coker furnace. The feedstock is allowed to react until the drum fills with coke and the feedstock is redirected into a second drum.

Fluid coking is a process used by Syncrude and combines coking and fluid solids processing (used in fluid catalytic cracking) (Ashar 2008). The unit typically treats bitumen pitch, but it can also be fed with the entire bitumen (Hyndman and Luhning 1991). The feedstock is sprayed onto the hot bed of fluidized coke. Incomplete vaporization of heavy hydrocarbon fractions in the thermal conversion process results in coke formation (Gauthier 2009). Volatile products are separated in an overhead fractionator and coke is withdrawn from the bottom of the reactor and partially burned for heat before returning back to the reactor. High boiling liquids are returned to the fractionator and scrubs the fine particulates within the vapor to improve the quality of the liquid product. Since fluid coking produces an excess amount of coke, some of it must be withdrawn. Yields are higher by fluid coking as compared to delayed coking; however, more energy is consumed and the product is more difficult to hydrotreat due to the greater aromatic character and higher boiling point (Hyndman and Luhning 1991).

The coke produced in delayed coking and fluid coking is comprised of ~50wt% asphaltenes and ~35wt% resins (Abu-Khader and Speight 2007). A flexicoker can be installed after the initial fluid coking process to gasify the coke into H_2, CO, N_2, and H_2S. Removal of the H_2S allows the gas to be burned as a fuel in one of the refinery processes.

2.2.5.3 Cracking Processes

Catalytic cracking produces better quality products from heavy oil and residua (i.e. higher gasoline and lower gas yields) than coking; however, higher quality feedstocks, than those used in coking, is required since the zeolite catalyst—which are expensive to replace—are negatively affected by the presence of Na, Ni, V, and N, as well as the amount of coke that can be burned in the regeneration step (Abu-Khader and Speight 2007). The feedstock is sprayed onto a zeolite catalyst in a short contact time riser reactor. Formed vapor products are progressed to a fractionator while the spent catalyst moves to a fluidized bed to be regenerated—where coke and hydrocarbons are burned off the catalyst (Gauthier 2009).

A similar process to catalytic cracking is hydrocracking. Hydrocracking processes are performed under a high pressure, hydrogen atmosphere—whereby the hydrocarbon components are cracked by hydrogen addition. This process can provide up to 90% conversion yields. It is believed that the addition of hydrogen will lengthen the coke induction period and thus preventing the amalgamation of polynuclear aromatic hydrocarbons into larger agglomerates—prone to coke formation—and consequently leading to higher yields (Abu-Khader and Speight 2007).

Both the H-Oil and LC-Fining are ebullating bed reactors with hydrogen addition and are the technology of choice for Albian Sands/Shell (Ashar 2008). Ebullated bed hydroconversion uses a combination of thermal cracking and high-pressure hydrogenation over metal-sulfide catalysts (Gauthier 2009). Although these methods require higher capital and operating costs than coking, they provide outstanding oil yields. It is believed that when H-Oil and LC-Fining are combined with gasification for the purpose of producing hydrogen, the cost of ebullating bed reactors and coking are almost the same. H-Oil utilizes an up-flow ebullated bed reactor—a bed of catalyst expanded through an upward flow of liquid—analogous to a gas fluidized bed. A grid distributor on the bottom of the reactor distributes hydrogen and liquid feed. The ebullating pump recycles and provides the upward velocity of liquid—thereby controlling the expansion of the catalyst bed. Catalyst can be added or withdrawn to maintain catalyst activity.

Likewise, the LC-Fining process is an ebullated bed reactor. There are two alternatives. One variant eliminates the recycle pump by making use of a powdered catalyst (i.e. fine catalyst operation). When no catalyst is added and the conversion is operating under mild settings, the process is termed hydrovisbreaking (Hyndman and Luhning 1991). A second variant of LC-Fining situates a cheap demetallization catalyst bed upstream of the conventional nickel-molybdenum, or cobalt-molybdenum, reactor in the attempt to reduce costs associated with catalyst replacement.

2.2.5.4 Hydrotreating

Following the above conversion processes, the oil must be further refined by hydrotreating methods. This process removes S, N, and unsaturated hydrocarbons from the products of the liquid conversion products in the primary conversion processes (e.g. coking). Presently, the most common method is to utilize Ni-Mo based alumina catalysts (Mann et al. 1987). Further conversion of the feedstock will take place as the heteroatoms are removed, allowing for further break down of the heavy hydrocarbons molecules into gasoline and middle distillate range.

2.2.5.5 Synthetic Crude Oil

Ultimately, the upgrading process, following hydrotreating, produces SCO which can then be further refined into useful petroleum products. Some of these include gasoline, diesel fuel, jet fuel, light fuel oil, heavy fuel oil, crude oil, and many other petroleum-derived products (CEP 2010). According to CEP (2010), approximately 70% of the crude oil produced in Canada are refined into transportation fuels.

2.3 Supercritical Fluid Extraction

This section will describe the development of utilizing supercritical fluids for the recovery of heavy oil. Included in this section are the advantages and disadvantages of using SFE in the recovery of hydrocarbons from unconventional oil (such as bitumen) from oil sands, extra heavy oil, and oil shale. To begin, the principles and premise of SFE will be provided. Second, a brief history of the early applications of SFE will follow. Third, an introduction of using SC-CO_2 for the recovery of unconventional oil will be given. Fourth, previous research utilizing SFE for the recovery of oil from unconventional sources will be discussed. Finally, batch and continuous SFE systems will be considered and the technical challenges of using this technology, on oil sands slurries, will be highlighted.

2.3.1 Theory and Properties of Supercritical Fluids

SFE is being considered as an alternative to hot water oil sands extraction. The current industrial and academic interest for supercritical fluids (SCFs) is highlighted by the tuning capabilities of SCFs for selective separation; materials processing under milder conditions; the possibility for some SCFs to replace toxic organic solvents as an extraction media; and the ease of concentrating target analytes (Cansell et al. 1998; McHugh and Krukonis 1994). Furthermore, the use of SCFs for the extraction of oil sands, and related heavy oil, may lead to a single stage extraction and upgrading—a further reduction in operating costs and material handling (Brough et al. 2010).

Upon reaching supercritical state, a solvent begins to behave intermediately between a liquid and a gas (Phelps et al. 1996). This behavior can be further observed in Table 2, where the density, diffusivity, and viscosity of an SCF falls in between those of a gas and a liquid; however, the solvation power of an SCF can approach that of a liquid upon increasing density (Abbas et al. 2008; Brunner 2005; Hawthorne 1990). SCFs therefore possess a density and solvation power similar to a liquid and mass transfer properties and compressibilities are similar to a gas. Additionally, SCFs experience near zero surface tension providing them the capability of easily entering into the porous matrix of a solid (Raynie 1997). In other words, SCFs have good mass transfer capabilities and extractions are achieved more easily than when using traditional liquid solvents (Hawthorne 1990).

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

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

A compound or solvent reaches the supercritical state when the system temperature and pressure is elevated beyond the critical temperature (T_C) and pressure (P_C) as shown in Figure 9. Once the critical point is exceeded, a single phase develops, and the observable differences between a liquid and a gas cease to exist. As the solvent enters the supercritical phase, abrupt changes in density and viscosity—commonly observed in the phase transition of a gas to a liquid—are not experienced (Brunner 2005).

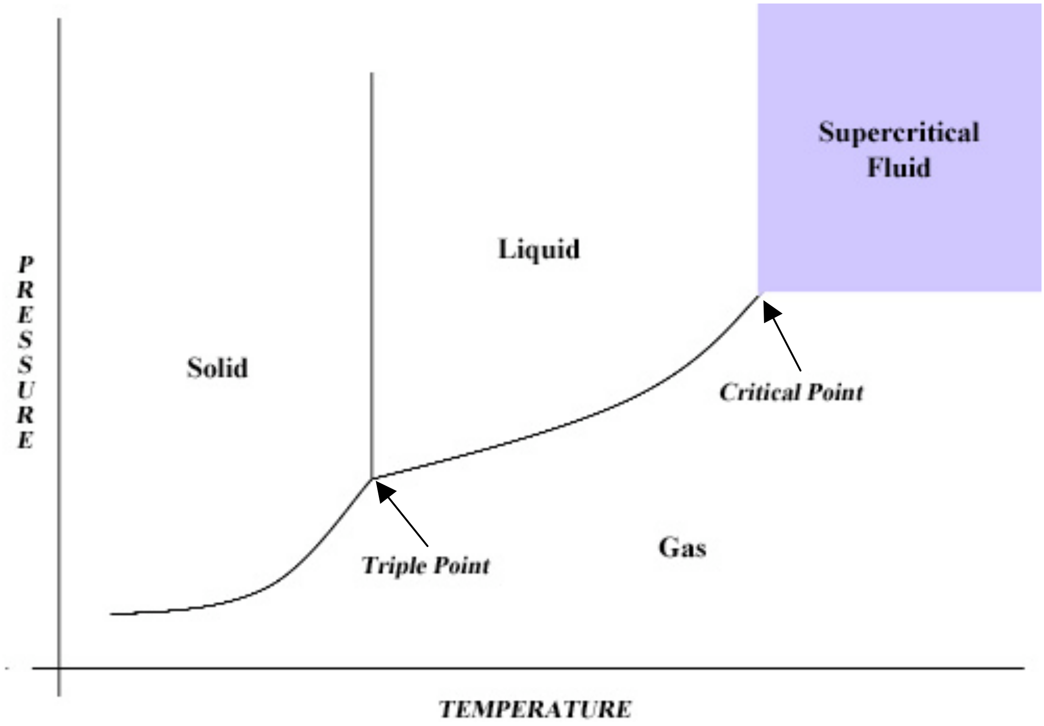


Figure 9. Pressure-temperature diagram of a pure fluid (modified from Knox 2005).

The greatest region of interest for an SCF is within the vicinity of its critical point: $0.9 \leq T_R \leq 1.2$ and $1.0 \leq P_R \leq 3.0$, where T_R (T/T_C) is the reduced temperature and P_R (P/P_C) is the reduced pressure (McHugh and Krukonis 1994). In this region, the SCF experiences liquid-like densities and gas-like diffusivities and enables superior extraction capabilities. The tunability of a SCF is an advantageous property to the operation of SFE systems. A small change in temperature and/or pressure near the critical point can result in a considerable change in the SCF density (Abbas et al. 2008; Akgerman 1993). For instance, by adjusting the temperature and pressure, the solvent property of SC-CO_2 can be varied between pentane to pyridine (Phelps et al. 1996); therefore, the extraction of a particular compound can be regulated by increasing the pressure since an increase in pressure results in an increase in the SCF density (i.e. shorter inter-molecular distances experienced). However, if both the temperature and pressure increase together, the solute concentration in the SCF-phase may increase as a direct result of solvent interaction and increased solute vapor pressure, which offsets the decrease in solvent density (Tai 1985). At constant temperature and low pressure, an SCF extracts mainly non-polar components. At a constant temperature and high pressure, an SCF will extract more polar components (Phelps et al. 1996). Upon depressurization of a SCF containing a dissolved compound, the density of the SCF decreases and results in a reduction in the solubility of most components. The dissolved compound will then precipitate out of solution. The sequence of pressurization and depressurization in the extraction and subsequent precipitation of the extract forms the backbone of the SFE operation.

2.3.1.1 Choice of Supercritical Fluids

The polarity of the substance to be extracted has a significant influence on the choice of solvent to be utilized as the SCF. For economical and practical reasons, the temperature and pressure requirements needed for the solvent to enter into the critical region must also be considered when choosing a SCF.

SC-CO_2 is often the solvent of choice for SFE studies because it has been deemed environmentally acceptable (Abbas et al. 2008; Phelps et al. 1996; Wai et al. 2003). However, due to its preference for non-polar substances, CO_2 may not be the solvent of choice for extracting polar analytes. Table 3 includes a list of commonly used SCFs for heavy oil applications. Note that most of these chemicals are non-polar organic solvents as the analytes of interest (i.e. hydrocarbons or oil) are primarily non-polar. Many of these fluids have a higher T_C than CO_2; therefore, with the exception of ethane, even though these fluids may exhibit greater solvating abilities, they usually require greater energy expenditures to reach supercritical conditions as compared to CO_2.

Table 3. Commonly used SCFs for heavy oil extractions and analysis (data obtained from NIST 2008).

Chemical	T_C (°C)	P_C (MPa)	ρ_C* ($g \cdot mL^{-1}$)
CO_2	31	7.4	0.47
H_2O	373.9	22.1	0.32
C_2H_6	31.2	4.8	0.21
C_3H_8	96.7	4.3	0.22
C_4H_{10}	152	3.8	0.23
C_5H_{12}	196.6	3.4	0.23
$C_6H_5CH_3$	318.6	4.1	0.27

*ρ_C = critical density

2.3.2 Applications of Supercritical Fluid Extraction

According to Knox (2005), the earliest documented application of SFE was based on an oil deasphalting method using supercritical propane in the 1930s by Wilson et al. (1936). In the 1940s, the Solexol process was developed by the Kellogg company, using propane in the sub-critical and supercritical region, primarily to obtain a clean separation of vegetable and fish oil extracts (Dickinson and Meyers 1952; Passino 1949). The best known process making use of sub-critical and supercritical regions was the ROSE™ (residuum oil supercritical extraction) process, developed by Kerr McGee in the 1970s, for deasphalting heavy oil (Gearhart and Garwin 1976). Using butane or propane, the ROSE™ process operates under sub-critical conditions to concentrate the contaminants in the residual stream while the solvent recovery step is performed under supercritical conditions (Schumacher et al. 1982).

In the 1970s, the commercialization of coffee decaffeination by SFE (Knox 2005; McHugh and Krukonis 1994) catapulted the use of SCFs as an attractive method for isolating or purifying specific compounds and substances (Yoon et al. 2000), enriching foods with nutrients such as vitamin E; removing unwanted constituents (such as cholesterol or alcohol); and processing thermally-sensitive components (Betz et al. 1999; Brunner 2005; McLachlan et al. 1992; Sun et al. 2010). The high diffusivities of SCFs has generated applications relating to compound impregnation in the manufacturing of drug patches (Kikic and Vecchione 2003), dyeing of textiles (Schmidt et al. 2003), adding aromas to food items (Bhattacharjee et al. 2003), and preserving wood through infusion (Muin and Tsunoda 2003). Additionally, cleaning operations, such as dry cleaning, have been developed based on the high diffusivity of SCF (Dewees et al. 1992). Other applications using SCFs include supercritical fluid fractionation (Chung et al. 1997), supercritical fluid chromatography (Roth 2004), and as a replacement solvent in green chemistry (Jessop et al. 2003).

Applications of SFE in petroleum-related processes include solvent recovery, upgrading in replacement of traditional upgrading processes (Scott et al. 2001), *in-situ* oil recovery (Hwang et al. 1996), and as an analytical tool for chemical characterization (Chung et al. 1997; Shi et al. 1997). SFE has been observed to combine extraction and upgrading of heavy oil in one step by selectively extracting light hydrocarbons while leaving behind the asphaltenes (Deo and Hanson 1994) that are known to readily form coke (as discussed in Section 2.1.2.1). In fact, a recent study by Brough et al. (2010) using a SC-CO_2/H_2/toluene mixture was able to extract and upgrade an Alberta oil sands into SCO at 100°C—a much milder temperature as compared to conventional upgrading—using several catalysts: $CoMo/Al_2O_3$, Rh/C, Pd/C, and Ru/C. Hydroconversion yields were highest with Ru/C, with only 10.3wt% residua remaining and up to 10°API increase.

2.3.3 Supercritical Carbon Dioxide

SC-CO_2 is a commonly used fluid for *in-situ* heavy oil recovery in enhanced oil recovery (EOR) processes (Hwang and Ortiz 1998; 2000; Parra-Ramirez et al. 2001; Xia et al. 2002) and in commercial applications such as in the decaffeination of coffee beans and hops extraction (McHugh and Krukonis 1994; Perrut 2000). The primary advantages of using SC-CO_2 are based on the following properties (Brunner 2005; McHugh and Krukonis 1994; Taylor 1996; Wai et al. 2003):

- Readily available in high purity

- Easily achievable critical properties at 31°C and 7.4MPa
- Does not leave behind a toxic residue
- Noncombustible
- Considered an environmentally acceptable fluid
- Relatively inexpensive
- Easily separated from the extracted components under ambient conditions

Another important fact is that CO_2 can be generated by industrial processes, captured, and recycled through a SFE process, to prevent contribution to the greenhouse gas effect (Hurren and Berger 1999; Wai et al. 2003).

As SC-CO_2 is a nonpolar solvent, it is capable of solubilizing moderately polar solutes as a result of its large quadruple moment (Rudzinski and Aminabhavi 2000). Laitinen and Kaunisto (2000) suggested that SC-CO_2 may be able to extract weakly basic hydrocarbons, such as pyridine in aqueous solutions, due to a weak acid-base reaction with SC-CO_2. Low molecular weight hydrocarbons experience the highest solubility in SC-CO_2, and solubilities of compounds in SC-CO_2 decreases with increasing molecular weight. Common species extracted by SC-CO_2 include alkanes, terpenes, aldehydes, esters, alcohols, and fats (Phelps et al. 1996). If more polar compounds are desired in the extraction using SC-CO_2, a polar modifier can be included to enhance its polarity (Eckert et al. 2000). Table 4 provides a summary of SC-CO_2 extraction studies on various petroleum feedstocks.

Table 4. Studies investigating the extraction of hydrocarbons from crude oil, oil shale, bitumen, vacuum residua, oil sand, and spiked environmental samples using SC-CO_2.

Feed	P (MPa)	T (°C)	Reference
High wax crude oil and source rock from Mahakam Delta; sedimentary rock from Handil, Fecocourt, Jouy aux Arches	12-50	6-80	Monin et al. 1988
Crushed Stuart Oil Shale	10.3-17.2	400-500	Kesavan et al. 1988
Crude Oil, Upgraded WR bitumen from Fluidized-bed pyrolysis, and White Rocks bitumen	5.5-30.9	24-93	Deo et al. 1992
Crushed New Albany Oil Shale	34.50	50-350	Furton et al. 1994
Crude Oil and Vacuum Residue	7.6-17.2	24-66	Hwang et al. 1996
Crude Oil	8.60	31	Hwang and Ortiz. 1998
Crude Oil	6.9-31	25-100	Zaki et al. 2003
Crude Oil (live and dead)	N/A	71	Parra-Ramirez et al. 2001
Crude Oil	2.52-16.1	55-75	Liu et al. 1999
Cold Lake Bitumen	4-16	50-250	Yu et al. 1989 Huang and Radosz. 1990;1991(a), (b), (c)
Utah Bitumen (Tar Sand Triangle and PR Spring Rainbow), and Athabasca Tar Sand	0.6-6.1	85-120	Deo et al. 1991
Posidonia and Kupfershiefer Oil Shale	34.50	50-350	Jaffe et al. 1997
Crushed New Albany Oil Shale	16-30	55-300	Jaffe et al. 1997
Peace River Bitumen	7.3-15	34-92	Rose et al. 2000
Posidonia and Kupfershiefer Oil Shale	34.50	50-350	Jaffe et al. 2000
Crushed middle Ordovician Oil Shale	40	45-150	Koel et al. 2000
Crushed Jordanian Oil Shale	14.3	375	Tucker et al. 2000
Sandy loam soil spiked with Bu Hasa crude oil	8-30	40-140	Al-Marzouqi et al. 2007

2.3.3.1 Role of Modifiers in SC-CO_2 Extractions

Both nonpolar and polar components can show increased solubility in a SCF upon the addition of a polar or nonpolar miscible fluid in small quantities (≤5%v/v) (Abbas et al. 2008; Phelps et al. 1996). These components are known interchangeably as a modifier, cosolvent, or entrainer (Taylor 1996). There are two basic methods of employing a modifier: mixing the modifier with the incoming CO_2 flow, or mixing the modifier into the feedstock in the extraction chamber. Of the two methods, the first is the most common approach (Abbas et al. 2008). The effect of adding a modifier is to either increase the solvent density of SC-CO_2, and hence the solvent power, in order to broaden the application of CO_2, reduce the operating costs of the extraction process, or tune specific chemical reactions by modifier-solute interactions (e.g. H-bonds) (Eckert et al. 2000). Increasing the solvent power of SC-CO_2 is of particular importance in reservoir injections where the density of the supercritical process is limited by the reservoir pressure. Utilizing a modifier—especially light aromatic compounds such as toluene—can lower the pressure threshold required to maintain miscible flood conditions in EOR (Hwang and Ortiz 2000).

Secondly, modifiers provide the benefit of decreasing the extraction time and increasing the extraction yield, especially for higher molecular weight paraffinic hydrocarbons (Bondar et al. 1998; Oschmann et al. 1998) including molecules with an increasing degree of branching and cyclic n-alkanes (Guiliano et al. 2000), leading to a reduction in operating pressure and temperature. Unfortunately, greater levels of asphaltenes and metals may also be extracted, and the separation of the modifier from the extracted oil may add to the cost of operation. A viable solution offered by Tai (1985) is to include an activated carbon bed, to capture the asphaltenic material, between the extraction vessel and the oil collection unit.

Adding small amounts of modifiers has the tendency to increase both the T_C and the P_C of the fluid mixture but this effect is more pronounced for polar and high carbon number modifiers (Gurdial et al. 1993). According to Taylor (1996), the new critical values of the mixed fluid solvent can simply be estimated by taking the arithmetic mean of the T_C and P_C between the two components as highlighted by Equations 7 and 8:

$$T_C = X_{CO_2} T_{C(CO_2)} + X_m T_{C(m)} \quad \textbf{Equation 7}$$

$$P_C = X_{CO_2} P_{C(CO_2)} + X_m P_{C(m)} \quad \textbf{Equation 8}$$

Here X_{CO_2} and X_m represent the mole fractions of CO_2 and the modifier, respectively. More involved methods of calculating the new critical values can also be used, such as the Peng-Robinson equation of state (EOS) (Taylor 1996).

2.3.4 Solubility of Compounds in SCFs

The solubility of a substance in an SCF is important in the design of an SFE system because it defines the upper limit at which the substance to be extracted can be present under a given set of pressure and temperature conditions (Cansell et al. 1998). Therefore, acquiring the solubility data of a substance provides the maximum extraction efficiency obtainable in an SFE process. A discussion of the solubility behavior of heavy oil in SC-CO_2 is provided below.

2.3.4.1 Solubility of Heavy Oil in SC-CO_2

Because heavy oils are complicated hydrocarbon mixtures of varying molecular weight and size, ranging from light gases to heavy asphaltenes, they exhibit complex phase behavior in SCF systems: single-liquid, vapor-liquid, vapor-liquid-liquid, and vapor-liquid-solid (Yu et al. 1989). Determining the solubility of bitumen in CO_2 is an important first step in understanding the bitumen-CO_2 system (Deo et al. 1991) particularly for *in-situ* bitumen recovery and EOR applications. Unfortunately, the literature has primarily focused on the solubility of CO_2 in bitumen, while bitumen in the vapor phase has been presumed to be negligible in most cases (Eastick et al. 1992), especially because it is much more difficult to measure (Han et al. 1998; Yu et al. 1989).

As noted earlier, the chemical structure of a hydrocarbon plays an important role in the degree of solubility in sub-critical and SC-CO_2. In 1954, Francis measured the solubilities of 261 substances in sub-critical CO_2 (6.2MPa and 25°C). In combination with the data obtained from Francis (1954), Dandge et al. (1985) attempted to determine the general structure of compounds that either limited or enhanced their solubility in both sub-critical and SC-CO_2. In particular, Dandge et al. (1985) observed that the solubility of iso-alkanes and alkenes were greater than n-alkanes in both sub-critical and SC-CO_2—possibly due to the enhanced intermolecular forces experienced by the iso-alkanes and alkenes. Moreover, the effect of branching, or methyl substitution, was generally observed to increase the solubility of various types of hydrocarbons such as aromatics, primary alcohols, and phenols among others. Generally speaking, utilizing an adequate extraction duration increases the thoroughness of extraction for saturates, and, followed by aromatics (Chung et al. 1997; Shi et al. 1997). For instance, SC-CO_2 has been demonstrated to extract higher carbon numbers, from pure crude oil, with successive extraction windows (Deo et al. 1992; Hwang et al. 1996), or in other words with increasing extraction time.

A primary disadvantage of using SC-CO_2 is that it does not possess the polarity necessary to extract complex analytes of broad molecular weight hydrocarbons found in most oils. In studying Cold Lake bitumen cuts, Huang and Radosz (1990) observed the solubility of bitumen in SC-CO_2 to decrease with increasing molecular weight. Similarly, Hwang and Ortiz (1998) observed that the hydrocarbon solubility in SC-CO_2 reduces with increasing carbon number especially beyond C_{25}. When sufficient SC-CO_2 is dissolved in heavy oil, the precipitation of high molecular weight polar compounds may be observed and is a direct result of SC-CO_2 exhibiting an anti-solvent effect (Zaki et al. 2003). The solvation power of SC-CO_2 has been likened to that of n-hexane (Koinecke et al. 1997; McHugh and Krukonis 1994) which is a solvent that may be used for the precipitation of asphaltenes. Hwang et al. (1996) provided further evidence of the solubility behavior experienced by SC-CO_2 as they were only able to extract 2wt% of vacuum residua from a crude oil at 93°C and 30.9MPa, conditions where SC-CO_2 experiences a moderately-high density of $0.7 g \cdot mL^{-1}$. The ability to leave behind heavy polar components from heavy oil is due to the components limited solubility in SC-CO_2, and is favorable prior to heavy oil upgrading as these components have a tendency to form coke (Wiehe 1993). In fact, this natural deasphalting property of SC-CO_2 has been used by Samedova et al. (2007) in replacement of low n-alkane solvents for the precipitation of asphaltenes.

The main advantages of using SC-CO_2 over traditional solvent precipitation is that it allows for a larger test sample mass (i.e. from 5-10g to 100g) which increases the precision of the test; dramatic reduction in solvent to feed ratio from 40:1 to 1-2:1; increased efficiency and increased thoroughness of asphaltenes recovery (Samedova et al. 2007).

On the other hand, Guiliano et al. (2000) was able to extract Bal 150 crude oil asphaltenes with SC-CO_2 and thereby demonstrating the unique mass transfer properties of SCFs as compared to liquid solvents. Some authors have suggested the destabilization of the aromatic-resin-asphaltenes colloidal structures as the primary reason for the agglomeration and precipitation of asphaltenic hydrocarbons (Deo and Hanson 1994; Koots and Speight 1975; Speight 2004).

The fraction of bitumen and crude oil that is unextractable by SCFs, has been coined the term end-cut by Chung et al. (1997), or raffinate by Shi et al. (1997), and is largely comprised of highly condensed aromatic-rings of cross-linked heteroatoms (e.g. S and N species) and metal species (e.g. Ni and V) arranged in porphyrin structures. This unextractable fraction is associated with high coke yields. In fact, Zhao et al. (2003) observed that the end-cut is approximately proportional to the asphaltenes portion in the original Athabasca bitumen (i.e. 20wt%). Zhao et al. (2001) discovered that using supercritical pentane on bitumen pitch leads to a residual that is similar in yield and in chemical property to that produced during n-pentane solvent precipitation. Deo and Hanson (1994) observed greater asphaltenes yields with the progression of extraction, or with the concurrent removal of light-end hydrocarbons. Some researchers are attempting to make use of the asphaltenes produced after extraction with SCFs by converting them into activated carbon for environmental purposes (Abourriche et al. 2008).

In enhanced oil recovery (EOR), the antisolvent effect of SC-CO_2 with respect to high molecular weight compounds is not desirable because it results in the deposition of asphaltic materials and leads to the clogging of the oil reservoir (Liu et al. 1999). Parra-Ramirez et al. (2001) observed two to three times more asphaltenes deposition on multiple contact for the same mol% of SC-CO_2 introduced, as compared to 1st-contact experiments thus indicating the propensity of asphaltenes precipitation upon increasingly thorough extractions of lighter-end hydrocarbon components. As Hu et al. (2004) observed, the amount of wax precipitation in EOR can be controlled by optimizing the level of CO_2 injections. As mentioned previously, asphaltenic materials are generally considered as a solubility class (i.e. molecules with an indefinite chemical composition and precipitates to varying degrees using various solvents) and the preferential extraction of light hydrocarbons by SC-CO_2 likely results in their subsequent precipitation (Hu et al. 2004; Hwang and Ortiz 1998; Parra-Ramirez et al. 2001).

2.3.5 Effect of Temperature, Pressure and Density on SC-CO_2 Extractions

Generally, the solvation power of SC-CO_2 is highly dependent upon the temperature and pressure of the system as it directly affects the density and viscosity of the SCF. Both the density and viscosity of the SC-CO_2 increase as the pressure is raised and the temperature is lowered. Increasing the density has the effect of allowing more substrate to be extracted by the SC-CO_2, unless the extraction is thermodynamically (solubility) controlled; however, decreasing the viscosity allows quicker penetration into the matrix. Generally, increasing the density of a system is typically deemed to be more important in increasing the solvation power of the SCF of pure components; however, for environmental samples, a high pressure and temperature may be more important. For instance, the best extraction condition of saturate and aromatic hydrocarbons from an oil shale was obtained at a high pressure and temperature 50MPa and 80°C (Monin et al. 1988). The micro-and macromolecular structure of environmental and geochemical matrices can sufficiently trap substrates from being thoroughly extracted; therefore, high temperature applications may induce thermal-matrix-rearrangement, releasing trapped components by physical relocation, and thereby potentially increasing extract yields (Furton et al. 1994; Jaffe et al. 2000).

Studies of crude oil extraction from spiked environmental samples have indicated that high pressures and temperatures are optimal for enhancing recoveries (Al-Marzouqi et al. 2007), which is advantageous for reservoir oil field injections that have high reservoir pressures and temperatures. For instance, upon increasing the pressure from 20 to 30MPa at a temperature of 120°C, Al-Marzouqi et al. (2007) was able to extract up to C_{31}—recovering the entire hydrocarbon range from the original crude oil. Increasing operating temperatures have also been observed to enhance the demulsification process of water-in-crude oil emulsions (Zaki et al. 2003). Emulsions in bitumen are believed to be a result of the organic rich solids, predominantly associated with ultra-fine clays, exhibiting a bi-wettable phenomenon similar to asphaltenic molecules (Fu et al. 2010; Kotlyar et al. 1998; Kotlyar et al. 1990). Therefore, matrix composition may directly influence extraction efficiencies by SC-CO_2 extraction. For instance, Koel et al. (1995) observed that oil shales with high clay mineral contents had a negative impact on extraction efficiency. A plausible explanation for this is due to the tendency for residual organic matter to associate with the clay minerals (Fu et al. 2010); as a result, petroleum-derived matrices of high clay contents can result in a greater proportion of residual organic matter adsorbing to the surface of the clays. The SC-CO_2 acts by either decreasing the viscosity of the crude oil—thereby destabilizing the emulsions—or by experiencing an enhanced solubility in the oil, resulting in a faster rate of asphaltenes precipitation. In spite of this, the role of the system temperature, pressure, and application of a modifier plays a large role in dictating the extraction efficiency of SC-CO_2 from heavy oil.

Unfortunately, the literature on the effect of temperature and pressure on the solubility of bitumen in SC-CO_2 systems are not in agreement with each other. Yu et al. (1989) observed an increase in the solubility of Cold Lake bitumen in SC-CO_2 under the following conditions: as the temperature increased from 50°C to 250°C at a constant pressure (at 4, 8, 12, and 16MPa); and as the operating pressure increased from 4 to 16MPa at a constant temperature (at 50°C, 100°C, 200°C, and 250°C)—although the increase was less dramatic at higher temperatures (e.g. 200 and 250°C) for the latter observation. Furthering the research by Yu et al. (1989), Huang and Radosz (1990) found that the solubility trends on the whole bitumen were in agreement with the first three bitumen cuts (i.e. the lighter hydrocarbon fractions). In contrast to these previous studies, three different bitumens were studied by Deo et al. (1992)—2 Utah deposits and another from the Athabasca oil sands—where an increase in temperature resulted in a decrease in bitumen solubility. Likewise, Rose et al. (2000) observed a decrease in Peace River bitumen extract yields upon increasing the temperature from 34°C to 55°C at a pressure of 12.2MPa. Han et al. (1992) observed a 38% enhancement in the solubility of Peace River bitumen by increasing the operating pressure from 7.2MPa to 13.9MPa, while increasing the temperature by 10°C slightly decreased the solubility.

The further away the temperature is from T_C, a parallel drop in solvent density and a decrease in the solubility of the bitumen in CO_2 will occur since the system is transitioning from a liquid-liquid system to a liquid-vapor system. Hwang et al (1996) observed that the extraction yield, from a crude oil, remained relatively constant between 24°C to 38°C at 10.3MPa despite a corresponding 20% decrease in solvent density (from 0.83 to $0.68 g \cdot mL^{-1}$, NIST (2008)), and the former temperature being in the sub-critical region. On the other hand, Liu et al. (1999) noted that the average molecular weight of the oil constituents extracted from crude oil using SC-CO_2 was not significantly affected by increasing both the temperature and the pressure (55°C at 8.95MPa, and 75°C and 16.1MPa), even though the density of the SC-CO_2 increased from 0.25 to $0.51 g \cdot mL^{-1}$ (density based on the data provided by NIST (2008)). Interestingly, the level of asphaltic deposition from the crude oil increased with operating pressure and decreased with temperature—coinciding with the solubility behavior of oil in SC-CO_2. Al-Marzouqui et al. (2007) suggests that when the system pressure is already high, the kinematic viscosity—the combined effects of density and viscosity—may become increasingly important: the lower the kinematic viscosity, the higher the mass transfer coefficient and the greater the extraction efficiency.

A number of studies have used SC-CO_2 for the extraction of hydrocarbons from oil shales. As compared to conventional retorting with either CO_2 or N_2, SC-CO_2 extraction provides an extract with a wider boiling point distribution (Kesavan et al. 1988) since the solvating properties of SC-CO_2 allow the extracts to maintain their hydrocarbon structure (Tucker et al. 2000). Even under high-temperature SFE on oil shale, products of pyrolysis (i.e. alkenes) are only present when the temperature is greater than 350°C (Furton et al. 1994; Jaffe et al. 2000; Jaffe et al. 1997a). Jaffe et al. (1997b) examined the role of temperature on the extraction of New Albany oil shale at three operating temperatures (55°C, 75°C, and 95°C) for the equivalent density of $0.7 g \cdot mL^{-1}$ at each condition. It was observed that the highest temperature (95°C) produced the highest maximum extraction efficiencies by enabling the release of desorption resistant hydrocarbons trapped in the micro- and macromolecular kerogen structure. Such occluded species, particularly the high molecular weight aromatic hydrocarbons, necessitate the application of high temperatures to induce thermal restructuring of the oil shale matrix for their release (Jaffe et al. 1997a). In fact, Jaffe et al. (2000) found that high temperature pretreatment of Posidonia shale subsequently resulted in higher extraction efficiencies by SC-CO_2, especially for aromatic hydrocarbons. That is, the high-temperature pretreatment led to the concomitant increase in matrix porosity, and decrease in the steric hinderance on polar functional groups.

Therefore, SFE of oil shale by SC-CO_2 is a strong function of extraction temperature and time, while less dependent on system pressure. However, the following must be kept in mind as two effects may influence the extraction efficiency: at increasing temperatures the oil is more volatile and leads to greater dissolution of its constituents; or with increasing temperature, the density of the SC-CO_2 decreases leading to the reduced solvation power of the solvent (Liu et al. 1999). As mentioned previously, hydrocarbon extractability by SC-CO_2 is dependent upon the mineral make-up of the substrate; oil shales containing high clay mineral contents affect yields negatively (Bondar and Koel 1998; Koel et al. 1995). Extraction efficiency therefore is a strong function of the chemical nature of the analytes and on the geochemical characteristic of the substrate (Jaffe et al. 1997a; Koel et al. 2000; Monin et al. 1988). In mass-transfer limited systems, decreasing SCF flow rate may increase extraction efficiency (Al-Marzouqi et al. 2007) by maximizing the extraction power per volume of CO_2 used, since this would provide an adequate contact time between the solvent and the environmental matrix. Adequate SCF contact time is less of a concern with pure hydrocarbon extractions (e.g. crude oil), where yields increase with time regardless of the flow rate; in other words, where thermodynamic equilibrium and not mass transfer resistance may be the controlling factor (Guiliano et al. 2000).

2.3.6 Effect of Modifier Addition on SC-CO_2 Extractions

Table 5 is a list of studies using one or more modifiers added to SC-CO_2, supercritical water (SCW), and other hydrocarbon-based SCFs for the extraction of hydrocarbons from a variety of heavy oil matrices. Unfortunately, this area is still in its infancy and more work focusing on the application of modifiers to heavy oil geological matrices is required. Adding a polar modifier can enhance the extraction of polar components and, hence, enhance overall extract yields; however, this is not always the case in petroleum extractions. For example, in the extraction of middle-eastern tar sand, the highest extract yields were observed with supercritical n-pentane/benzene mixtures (Demirbas 2000) whereas the lowest yields were observed with the more polar n-pentane/ethanol combination (Demirbas 2002). The effectiveness of a modifier is highly dependent on the petroleum matrix. Generally, the oil extracted using modified SC-CO_2 is greatly enhanced, saving time, energy and resources. For instance, Bondar and Koel (1998) observed that the effect of using methanol (MeOH) as a modifier in SC-CO_2 doubled extract yields of oil from kukersite (a chiefly carbonate matrix) relative to pure SC-CO_2 and yielded an increase of isoprenoids and polycyclic hydrocarbons. Lower pressures were required for a more enhanced extraction efficiency of an asphaltite (Erol et al. 1995) using hexane or methanol as a modifier in SC-CO_2. Hwang and Ortiz (2000) noted that both toluene and LAH (light aromatic hydrocarbon) added to SC-CO_2 produced the higher extraction efficiencies relative to SC-CO_2 with other modifiers while providing similar results to one another.

Shale oil, from an oil shale obtained by chemical treatment and isolation techniques, was used as a primary solvent in oil shale extraction, by Abourriche et al. (2008), to demonstrate the applicability of shale oil as a precursor to economical carbon fibers. Increasing the ratio of water to shale oil (2:1) in the extraction of a high organic matter oil shale pitch resulted in greater yields of maltenes (i.e. n-pentane solubles) with the concurrent decrease in asphaltenes due to hydrocracking reactions (Abourriche et al. 2008). A reduction in the percentage of asphaltenes and asphaltols were also seen in the extraction of a sub-bituminous coal when 5mol% ethanol was applied (daRocha et al. 1997). However, excessive modifier additions may be detrimental to yields as was observed by Yu et al. (1994) where decane solubility in SC-CO_2 increased at the cost of a concurrent decrease in bitumen solubility. Similarly, Erol et al. (1994) observed a decrease in the extraction power of toluene for lignites as the percentage of pentane increased in supercritical toluene.

In recent years, Scott et al. (2001) demonstrated the application of $H_{2(g)}$ in combination with activated carbon to upgrade an Athabasca bitumen coker feed using a saturated paraffinic or naphthenic hydrocarbon as the SCF. Where the $H_{2(g)}$ acts to hydrocrack the feed, and the activated carbon replaces traditional metallic catalysts for hydrotreatment. Although the reaction conditions used by Scott et al. (2001) are less than traditional upgrading processes, the temperatures were still quite high—ranging from 400-440°C—as a result of the high T_C requirements of the paraffinic SCFs used. More recently, Brough et al. (2010) used SC-CO_2 in combination with $H_{2(g)}$, toluene, and a series of metallic catalysts to demonstrate a single stage extraction and upgrading of bitumen from an Alberta oil sands. Much lower operational conditions were required due to the low T_C of CO_2.

Table 5. Extraction of bitumen, heavy oils and other hydrocarbons from various feed materials using SCFs.

Feed	SCF	Modifier	Reference
Cold Lake Bitumen	CO_2	Decane and Tetralin (25wt % of CO_2)	Yu et al. 1994
Tuncbilek and Elbistan Lignites and Goynuk Oil Shale	Toluene	Pentane (0-100%), hexane (5%), water (5%), and methanol (5%)	Erol et al. 1994
Avgamasya Asphaltite	Toluene	Methanol (5wt%) and Hexane (5wt %)	Erol et al. 1995
Crushed Sub-bituminous Coal from Brazil	Toluene	Ethanol (5mol%)	da Rocha et al. 1997
Crushed Oil Shale (0.02 mm): Lower Ordovician Dictyonema, Middle Ordovician Kukersite, Permian-Carbon Kenderlyk, Jurasic Kashpir, Lower Silurian Anabar, Boltysh, and Palaeogene Krasava	CO_2	Methanol (5wt% of oil shale)	Koel et al. 2000, Bondar and Koel 1998, Koel et al. 1995
Crushed Oil Shale from Boltysh Deposit	CO_2	Methanol (5wt%)	Bondar et al. 1998

Table 5. Extraction of bitumen, heavy oils and other hydrocarbons from various feed materials using SCFs (continued).

Feed	SCF	Modifier	Reference
Technical Paraffins: macrocrystalline (MIP), microcrystalline (MAP), a high molecular weight Fisher-Tropsch (FTP), and a well tube deposition (DL)	CO_2	Isooctane (5.2mol%)	Oschmann et al. 1998
Spiked dolomite rock	CO_2	Methanol, Toluene, Isopropyl alcohol, hexane, light aromatic hydrocarbons, and various mixtures of two modifiers (2.5-10% mixtures).	Hwang and Ortiz 2000
Asphaltenes from Arabian light crude	CO_2	Toluene (10.7%), Dichloromethane (8.6%)	Guiliano et al. 2000
Middle Eastern Tar Sand	Pentane, Benzene	Benzene (50%), Acetone (50%), Ethanol (50%)	Demirbas 2000

Table 5. Extraction of bitumen, heavy oils and other hydrocarbons from various feed materials using SCFs (continued).

Feed	SCF	Modifier	Reference
Powdered Coals and Oil Shale from Russia, Estonia, Bulgaria, and Uzbekistan	Water	Benzene, toluene, hexane, cylcohexane, methanol, ethanol, and 2-propanol (additives: alkali, sodium formate, ammonium carbonate, and urea)	Luik and Luik 2001
Middle Eastern Tar Sand	Pentane	Benzene (50%), Ethanol (50%)	Demirbas 2002
Crushed Goynuk Oil Shale	Toluene	Tetralin (5-40%)	Sinag and Canel 2004
Athabasca bitumen fluid coker feed	n-Dodecane Hexa-decane Decane Tetralin Decalin Varsol	$H_{2(g)}$, $N_{2(g)}$, and $CH_{4(g)}$ Various activated carbon material as catalyst	Scott et al. 2001
Chistina Lake, Bitumen Alberta Oil Sands	CO_2	Toluene (37.5mL) $H_{2(g)}$ Catalysts: Rh/C, Ru/C, $CoMo/Al_2O_3$, Pd/C	Brough et al. 2010

2.3.7 The Need for a Continuous Supercritical Fluid Extraction System for the Extraction of Bitumen from Oil Sands

SFE has, in recent years, been demonstrated to effectively extract, upgrade, and fractionate heavy oil; however, extractions from solid matrices have been limited to semi-batch scale operations and analysis. In a semi-batch extraction, the material to be treated is loaded into a pressure vessel. The vessel must undergo pressurization first before a continuous flow of SCF can be introduced and dissolve the compound of interest. As soon as the extraction process is complete, the vessel is depressurized in order to remove the treated material (or the residual).

A continuous SFE process would be desirable at a commercial scale. A possible solution method to develop a continuous process, as suggested by Akgerman and Yeo (1993), is to add water to the excavated material, creating a slurry that can be pumped through the SFE system in a continuous fashion. A continuous system would have a lower cost incurred on a per mass basis of production as compared to a batch or semi-batch system (Brunner 2005; Saldana et al. 2005). Additionally, the cost can be further reduced by treating large volumes of material (Perrut 2000). Employing a continuous mode of extraction could eliminate the high surface footprint and volume of pressurization equipment, required for a batch or semi-batch system, per mass of solids treated (Laitinen et al. 1994). In a continuous mode of operation, the material would be continuously fed and withdrawn from the high-pressure extraction chamber without having to completely depressurize the system. However, feeding a solid stream (oil sands for example) into a high-pressure extractor in a continuous mode poses a major challenge. Adding water to the oil sands and pumping it through a solid-liquid contactor—in a countercurrent mode—is an option being proposed (Ryan and Stiver 2007). Ryan and Stiver (2007) demonstrated the recovery of contaminated soil (spiked with naphthalene) previously slurried with water in a continuous countercurrent SFE operation. Although naphthalene recovery rates were observed to increase when the soil concentration rose from 0.28% to 2.7%, recovery rates dropped upon further increase to 7.2% due to a parallel drop in the mass transfer coefficient.

2.3.7.1 Effect of Water on SFE

The effect of water on the SFE of unconventional oil (i.e. bitumen, heavy oil, shale oil, etc.) using SC-CO_2 is not identified in the literature; however, many studies have been performed on the effect of water on the SFE of contaminated soil samples, either simulated by spiking the soil with a contaminant or by obtaining natural samples from a contaminated environment. These results may be similar to the effects on oil sands, which is primarily comprised of sand and, to a lesser degree, silts and clays, contaminated with a heavy hydrocarbon or bitumen.

A hydrocarbon analyte can exist in four phases within a wet solid matrix: as an independent free phase; adsorbed to the dry solid matrix; adsorbed to the solid matrix and nearby water molecules by forming H-bonds; and dissolved in the water-phase (Akgerman 1993). Studies have shown the presence of water can either increase or decrease SFE efficiencies. The water is either added or is naturally present in some environmental samples and can act as the modifier in SFE studies. A small amount of water dissolved in SC-CO_2 can help to increase the polarity, and thereby act as a polar modifier (Pratte et al. 1997). The pH of the water, when exposed to high pressure CO_2 is lowered to 3.5 (Laitinen and Kaunisto 2000). Under these acidic conditions, the excess hydrogen ions present can protonate highly basic components, or charge the hydrocarbon components leading to a reduced solubility in CO_2 (Toews et al. 1995); however, depending on the stability and charge of the analytes of interest, namely metals and ionizable hydrocarbons, at a pH of $\approx$3.5, their solubility may be enhanced by chelation reactions (Toews et al. 1995).

A small amount of water can beneficially increase extraction efficiencies by strongly interacting with the active sites on the soil matrix and thereby reduce bonding availability between the soil and the hydrocarbon analyte (Bowadt and Hawthorne 1995; Low and Duffy 1995). Furthermore, the effect of adding a small amount of water leads to an increase in vapor pressure of the hydrocarbons and ultimately an increase in the rate of desorption into the SC-CO_2 (Brady et al. 1987). An increased removal of spiked phenol on a soil sample was observed by Hess et al. (1991) when up to 10wt% water was added. In another study on spiked and aged soils, the addition of 3 to 10wt% water more than doubled the removal of PAHs (Schleussinger et al. 1996). Essentially, a small amount of water tends to participate in adsorption reactions with the analyte of interest—usually competing with the active sites on the surface of the matrix (Low and Duffy 1995). In some clay soil types, the water can swell the matrix and thereby further release trapped analytes for extraction (Becnel and Dooley 1998).

Increasing the water content can lead to entrapment of the analytes of interest due to the pore filling phenomenon and diffusion-resistance (i.e. shielding effect) experienced by the analyte as it travels through the water phase into the SCF. Water has a solubility of $2\times10^{-3}g\cdot g^{-1}$ in SC-CO_2 at 40°C and 14.5MPa (King et al. 1992; Sabirzyanov et al. 2002). Generally, the solubility of water is extremely low in SC-CO_2 ($<0.5\% w\cdot w^{-1}$) especially below temperatures of 100°C (Abbas et al. 2008; Brunner 2005). This low solubility in SC-CO_2 creates an effective barrier and can prevent the extraction of the analytes of interest by SC-CO_2. At the same time, the analytes are impeded by increased diffusional limitations through the water layer (Becnel and Dooley 1998).

A number of studies have shown a decrease in extraction efficiency with increasing water content. For instance, Hawthorne et al. (1992) recovered more extractable hydrocarbons when a waste sludge (originally 45wt% water) was dried to 2wt% water content. Brady et al. (1987) observed a decrease in the rate of removal of PCBs from a test soil of 20wt% water content as compared to a dry soil primarily due to decreased desorption and diffusion kinetics. Similarly, this trend was observed in the extraction of DDT (Dooley et al. 1990) and dioxin (Onuska and Terry 1989) from a 20wt% wet soil, requiring 1.5 to 2 times the amount of time, respectively, to attain the same level of removal from dry soil. Schleussinger et al. (1996) observed a reduction of extraction efficiency of perylene from a soil by a factor of 4 as the water content increased from ca.

10wt% to ca. 19wt%. At water contents ≥20wt%, the extraction of naphthalene on a spiked soil slurry was dominated by mass transfer limitations, dramatically reducing the extraction efficiency as estimated by a 10 to 50-fold decrease in the mass transfer coefficient (Pratte et al. 1997). The mass transfer coefficient for the removal of naphthalene from a soil was 200 times lower at 20wt% water content as compared to 10wt% (Smyth et al. 1999) due to the shielding effect, which lengthens the traveling path for the analyte of interest to the CO_2. However, applying sufficient mixing energy can ultimately break the shielding effect caused by the presence of water. In some instances, even small amounts of water may decrease extraction efficiencies. When only 8wt% of water was present, it was enough to cause a shielding effect of a diesel-spiked soil from the SC-CO_2, sufficiently trapping the analytes in the soil pores (Low and Duffy 1995).

Interestingly, a study on a 2:1 water to soil slurry, by Becnel and Dooley (1998) did not find a detrimental impact on the extraction efficiency for PAHs using SC-CO_2. Similarly, four phenol species, commonly found in hazardous waste sites, were successfully recovered from a 2:1 soil slurry between 35-45°C and 13-22MPa in a study conducted by Green and Akgerman (1996). In 1993, Akgerman and Yeo demonstrated that the extraction efficiency of a hydrocarbon solute may be understood by studying its chemical reaction in a three phase system. Akgerman and Yeo (1993) performed an extraction of phenol and naphthalene from a SC-CO_2, water, and solid system between 7.5MPa and up to 20MPa at 22 to 47°C. Phenol was more readily extractable from a soil-slurry system than an activated carbon slurry system owing to a stronger affinity to the surface of the activated carbon. On the contrary, due to the hydrophobic nature of naphthalene, the solubility in the water phase was much less, as compared to phenol, which forms a charged species upon dissociation in water, and this further impedes naphthalene solubility into CO_2. Interestingly, naphthalene solubility was highest at low pressures (~7.5MPa) than at high pressures (18MPa). Akgerman and Yeo (1993) contributed this observation to the increased adsorption of naphthalene (greater than water) to the solid surface with increasing pressure.

2.4 Summary

Oil sands, and other forms of heavy oil, are oils that are much more difficult to recover and process, as compared to conventional crude oil. Biodegradation processes have left heavy oils more viscous and contain a greater degree of problematic components such as heteroatoms (N, S, O), metals and asphaltenes, which in turns results in a greater amount of non-distillable pitch, an increase in TAN, and a lower API gravity. As a result, a greater amount of energy is required to recover and process these heavy oils, including oil sands.

SFE provides an economical and an energy-efficient alternative to the traditional water extraction process for bitumen recovery from oil sands. The literature presents a number of advantages that SFE has over the conventional water extraction process. First, SFE does not extract asphaltenes, which are known to (i) deteriorate the catalysts used in upgrading, (ii) form coke, and (iii) create obstructions in reservoirs and pipelines as they precipitate. Second, SFE with SC-CO_2, can potentially result in a process that combines extraction and upgrading in one step. Third, SFE does not require heated water for the extraction process therefore it is expected that SFE will be a less energy and water intensive process as compared to the water extraction process. SFE does not require caustic addition, which might resolve some of the current issues of tailings consolidation. Fourth, naphtha and other potential diluents are not required to induce asphaltenes precipitation or reduce the oil-in water emulsions since SFE, using SC-CO_2, has been demonstrated to do both of these activities without the need of these additives. Finally, if water is to used in a continuous SFE process, the water will be used strictly for the transport of the oil sands and not as the solvent in the extraction process; therefore, the extraction efficiency of hydrocarbon by SFE is not dictated by the quality of the water.

SC-CO_2 is considered the SCF of choice for many applications because it is environmentally-acceptable. On the other hand, SC-CO_2 can potentially limit the degree of extraction due to its preference for non-polar constituents. Although the extraction of some polar constituents may be desirable, other polar components, such as heteroatoms and heavy metals, can reduce the quality of the hydrocarbon extract.

Due to the chemical complexity of bitumen, information on the solubility of bitumen in SC-CO_2 systems is minimal and still requires extensive research. Most of the studies presented in this chapter agree that extraction efficiencies of hydrocarbons from bitumen tend to be dictated by thermodynamic equilibrium, or purely based on solubility effects. On the other hand, extraction of hydrocarbons from environmental matrices is controlled by mass-transfer limitations rather than solely on solubility. High temperature extractions and, or, pretreatment, may lead to thermal-matrix rearrangements and thereby release trapped components. Higher yields may be attainable by utilizing a modifier but the selection of the modifier is dependent on the petroleum matrix and on the desired extract quality. Lastly, the addition of water will be required for a continuous-scale SFE system; however, considerations need to be made to address the potential hindering effect of water on hydrocarbon extraction efficiencies.

CHAPTER 3 Materials and Methods

3.1 Summary of Experiments

A medium grade oil sand from the Athabasca formation in northern Alberta, Canada was purchased from the Alberta Research Council's (ARC) Oil Sands Sample Bank (ca. May 2009). Previous work was conducted on dry oil sands of low (~8%) and medium (~10%) grade to optimize the extraction efficiency using SC-CO_2 as the extraction fluid (Fang 2010). As a result of the work of Fang (2010), in this current thesis, a 1:1 oil sand slurry ratio was investigated for all conditions tested.

Preliminary experiments fixed the density of the SC-CO_2 at $0.91 g\cdot mL^{-1}$ (by fixing the temperature at 31°C and pressure at 24.1MPa) to investigate the significance of premixing time, static time, and mixing rate on the extraction yield of bitumen from the oil sand slurry by a 2^3 (3 factors at 2 levels per factor) factorial design. The purpose of the preliminary experiments was to rule out insignificant factors impacting the extraction efficiency of 1:1 oil sand slurry; therefore, only a single run was performed at each condition.

Following the preliminary experiments, a 2^3 factorial approach was used to study the effect of temperature (T), pressure (P)—and therefore the effect of the density of SC-CO_2—and the addition of a modifier on the extraction yields of bitumen from oil sand slurry. Experiments were performed in triplicate for each treatment combination. Toluene was selected as the primary modifier at 9.1wt% of the SC-CO_2. Three center-point replicates were conducted, at 18.9MPa and 45°C, to test for curvature between the high and low levels chosen for the three factors. Curvature was also tested in the preliminary analysis.

The principle result from the experiments was the hydrocarbon yield, which was determined by weighing the obtained extracts after every 2 weeks post-extraction for 6 weeks. Extracts were left for up to 6 weeks to evaporate any residual water or toluene. Dean-Stark extractions were conducted on the residual oil sand slurry remaining in the extraction vessel as a secondary verification of bitumen yields, and to perform a mass balance on the bitumen.

Additional results included water quality analysis on the slurry water after SC-CO_2 extraction. Asphaltenes precipitation in n-pentane was conducted in order to account for this non-extractable portion in extraction efficiency calculations. After each extraction by SC-CO_2, the water originally added to the slurry (i.e. the processed-water) was collected by centrifugation, and measured for pH, conductivity, and alkalinity.

3.2 Materials

This section will describe the chemicals, apparatus, and other materials used in this research.

3.2.1 Athabasca Oil Sands

The purchased ARC oil sand is a medium grade oil sand, containing approximately 10% bitumen. A 20L pail, containing the oil sand, was stored in a walk-in freezer (-5°C) in the Department of Civil and Environmental Engineering at the University of Alberta. For extractions, subsamples were transferred into 1L mason jars and stored in the freezer located in the Supercritical Fluid Extraction Laboratory. The untreated oil sands are dark-brown in color and consist of random aggregates of bitumen imbedded in sandy agglomerates ranging from 1mm in diameter or greater.

3.2.2 Chemical and Laboratory Consumables

Table 6 provides a list of the chemicals, their supplier, and their use in the experiments.

Table 6. List of chemicals, purpose of usage, and originating supplier.

Chemical	Use	Supplier/Manufacturer
Carbon Dioxide (liquid, grade 3 bone dry)	Supercritical solvent	Praxair (Mississauga, ON)
Toluene (HPLC grade)	Modifier and Dean-Stark solvent	Fisher Scientific (Fair Lawn, NJ)
Methanol (HPLC grade)	Modifier and cleaning solvent	Fisher Scientific (Fair Lawn, NJ)
n-Pentane (98%)	Asphaltenes precipitating agent	Fisher Scientific (Fair Lawn, NJ)
Ultrapure Water ($18.2 M\Omega \cdot cm^{-1}$)	For slurrying and water chemistry	Barnstead (Lake Balboa, CA)
997mW/cm Conductivity Standard	Conductivity meter calibration standard	Fisher Scientific (Fair Lawn, NJ)
pH Electrode Storage Solution	pH electrode storage solution	Oakton (Vernon Hills, IL)
4M KCl Saturated with AgCl	pH Electrode filling solution	Fisher Scientific (Fair Lawn, NJ)
pH 4, 7, and 10 Buffer Solutions	pH electrode calibration standard	Fisher Scientific (Fair Lawn, NJ)
Sodium Sulphate Anhydrous (10-60 Mesh)	Water removal prior to GC injection	Fisher Scientific (Fair Lawn, NJ)

3.3 Supercritical Fluid Extraction System (Batch Scale)

Each extraction on 1:1 oil sand slurry was performed one batch at a time using the laboratory-scale batch SFE apparatus. Figure 10 is a schematic of the extraction apparatus used throughout this research. A photo of the SFE apparatus is given in Figure 11. The suppliers and important specifications of the major components are provided in Table 7.

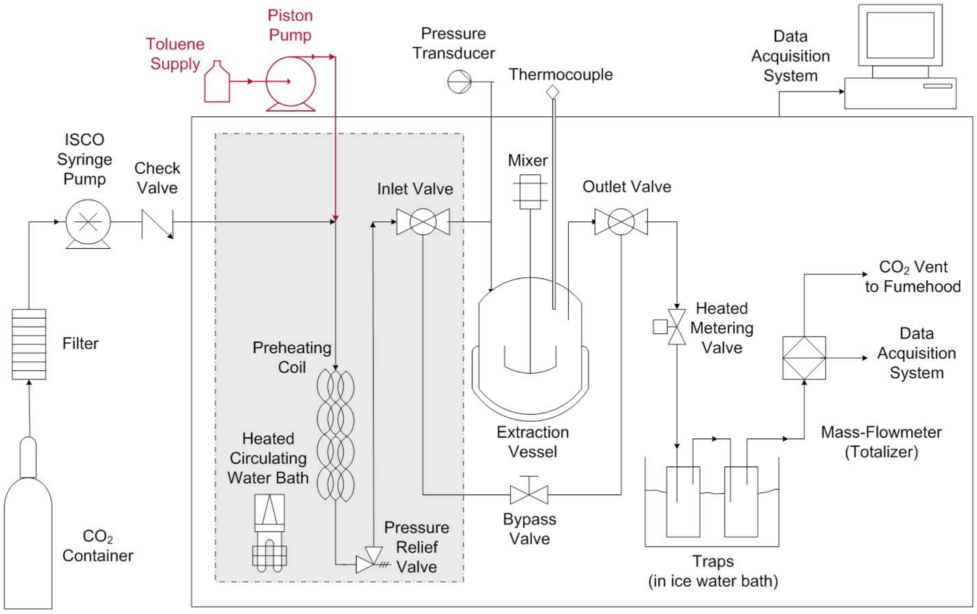


Figure 10. Process flow diagram of the laboratory-scale SFE system.

As indicated, the CO_2 cylinder supplies the liquid CO_2 for the laboratory-scale extraction process. First, the CO_2 enters through a filter to remove particulate matter before entering the ISCO syringe pumps. The syringe pumps operate in tandem in order to provide a continuous supply of compressed CO_2 for the extraction. A secondary pump substitutes the primary pump during refill (drawing from the CO_2 cylinder). As soon as the primary pump is filled, the CO_2 is compressed and the primary pump takes over again. The syringe pumps are each contained in a cooling jacket and fed with chilled water through a refrigerated water bath set to -2°C (not shown) ensuring the CO_2 is maintained in a liquid state for optimal pump performance. The compressed CO_2 passes through a check valve before entering the preheating coil. The check valve prevents reverse flow from the extraction vessel to the syringe pumps. The preheating coils are kept in a heated water-circulating bath and heats the compressed CO_2 to the desired experimental temperature prior to entering the extraction vessel. A pressure relief valve, rated at a pressure of 25.9MPa (which is also the upper pressure limit of the ISCO syringe pumps), is situated immediately following the preheating coils at a union tee.

During the vessel pressurization and extraction, the CO_2 is directed towards the vessel through the inlet ball valve and a second union tee, connecting it to the pressure transducer to record the pressure in the SFE system. The CO_2 then flows into the extraction vessel where the 1:1 oil sand slurry is placed. The extraction vessel is outfitted with an impeller operated by a MagneDrive® motor (not shown) and a mixing controller, and provides contact between the CO_2 and the oil sand slurry. A thermistor probe is placed in a stainless steel thermowell in the vessel to monitor the temperature throughout the extraction process. Heated water from the water-circulating bath circulates around the jacket of the extraction vessel to ensure the temperature remains constant.

The compound being extracted (i.e. bitumen) dissolves into the SC-CO_2 and exits through the outlet (plugged with glass wool to prevent solids carryover) at the top of the vessel, passing through the outlet valve towards the heated metering valve. The heated metering valve controls the CO_2 flow throughout the extraction process. Upon exiting the metering valve, rapid depressurization and cooling occurs and the CO_2 vaporizes, leaving the extracted compound behind. To prevent solute solidification and ice build-up from water extracted or entrained in the CO_2 during the extraction process, the metering valve is immersed in a hot water bath set at 70°C. Upon depressurization, the extracted components precipitate into two separate collection vials immersed in an ice-water trap to minimize the volatilization of hydrocarbon compounds. The first vial serves as the primary collection vial and the second vial, as the carryover vial to trap precipitated components potentially entrained in the CO_2 gas. The CO_2 is subsequently vented into the fumehood.

The SFE apparatus also contains a bypass line, which bypasses the extraction vessel, in order to clean the lines of any residual solutes. The pump controller, thermistor, and the pressure transducer are connected to the data acquisition computer, which records the temperature, pressure (from the pressure transducer and from the pump controller), and CO_2 flow rate. The stainless steel tubing used for all of the lines before the second union tee (connecting to the pressure transducer) has an OD of 1/16”, and all other lines thereafter are 1/8” OD.

For the modifier experiments, a piston pump (with a maximum back pressure rating of 28MPa) was used to feed the modifier into the CO_2 before the preheating coil. In experiments where the modifier was not employed, a stainless steel plug was secured in place of the modifier line on the union tee.

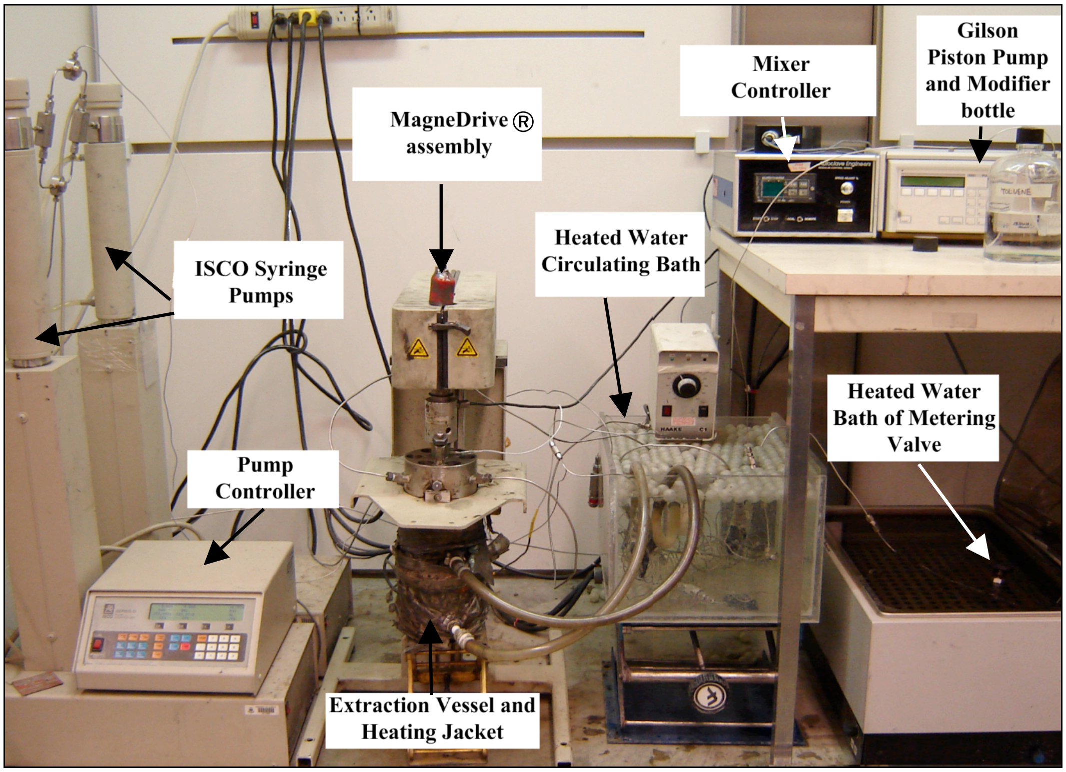


Figure 11. Laboratory-scale SFE apparatus.

Further details on some of these components are described in the following sections.

Table 7. SFE apparatus components with their suppliers and pressure ratings (where applicable).

SFE Parts	Manufacturer/Supplier	Pressure Rating (MPa)
CO_2 cylinder	Praxair (Edmonton, AB)	N/A
Filter	Swagelok (NUPRO)	N/A
ISCO syringe pumps (Model 500D) with controller	Canberra Packard	25.9
Check Valve (SS-CHS2-1/3)	Swagelok (NUPRO)	41.3 (at 37ºC)
Fluorocarbon FKM Seal Kit (SS-3K-CH4-VI)	Swagelok (Edmonton, AB)	41.3 (at 37ºC)
Heated Water Circulator (Model 002-4175)		N/A
Stainless Steel Tubing (i) 1/16" OD and 0.020” wall thickness (ii) 1/8" OD and 0.028” wall thickness	Swagelok (Edmonton, AB)	(i) 82.7 (ii) 58.6
Pressure Relief Valve (Model SS-4R3A with Spring R3A-F)	Swagelok (Edmonton, AB)	41.4 (assemble) 27.6 (spring)
Ball Valves (SS-83XKS4)	Swagelok (Edmonton, AB)	41.4
Pressure Transducer (Omega PX 502)	Omega (Laval, QC)	20.7
Stainless Steel Extraction Vessel: 300mL	Autoclave Engineers (Division of Snap-tite) (Union City, PA)	37.9
Helical Impeller	Custom-made	N/A
MagneDrive® (II, Series 0.75)	Autoclave Engineers (Division of Snap-tite) (Union City, PA)	37.9
Thermistor Probe (YSI 406)	Labcor Technical Sales Inc. (Anjou, QC)	N/A
Needle Metering Valve (Model SS-31RS4)	Swagelok (Edmonton, AB)	34.5
Hot Water Bath (Isotemp)	Fisher Scientific (Fair Lawn, NJ)	N/A
305 Piston Pump (25-SC pumphead)	Mandel Scientific Co. Inc. (Guelph, ON)	28
Teflon Tubing 1/6" (14-176-178)	Fisher Scientific (Fair Lawn, NJ)	N/A

3.3.1 Extraction Vessel, MagneDrive® Mixer, and Helical Impeller

The extraction vessel is made of stainless steel and has a maximum volume of 300mL. Figure 12 is a cross-sectional view of the extraction vessel. In this diagram, the heating jacket around the vessel is not shown. As mentioned earlier, the heating jacket is connected to the heated water-circulating bath to maintain the temperature in the extraction vessel.

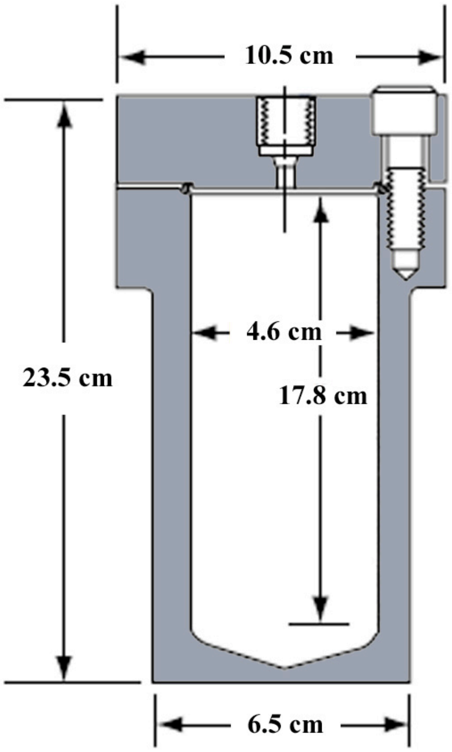


Figure 12. Cross-sectional view of the 300mL extraction vessel (modified from Autoclave Engineers 1998).

The lid of the vessel is shown in Figure 13, and is bolted to the top of the vessel with a Teflon o-ring (Zimco Gauge and Valves, Calgary, AB; part number 06-06250385) to ensure a pressure seal. The vessel lid includes ports for the thermowell (thermistor placement) and for the inlet and outlet lines. Other ports are also available but were sealed as they were not required. A stainless steel helical impeller, as shown in Figure 14, was used in all of the extractions of 1:1

oil sand slurry. The helical impeller provides minimal clearance from the vessel walls, thereby providing thorough mixing of the viscous oil sand matrix.

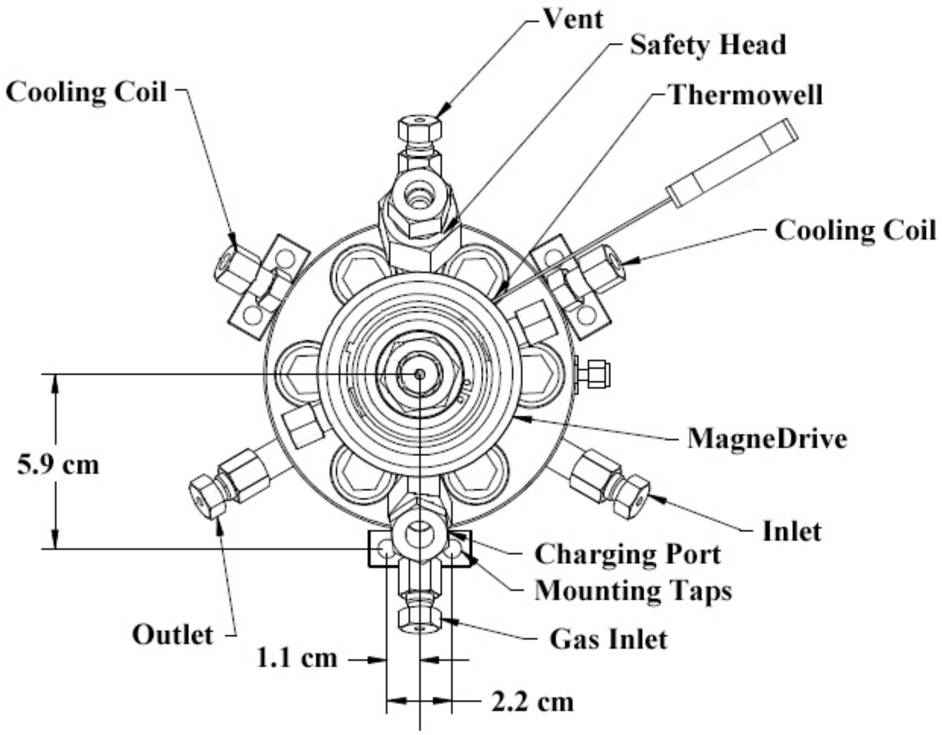


Figure 13. Top view of the vessel lid depicting various parts including the inlet and outlet ports (modified from Autoclave Engineers 1998).

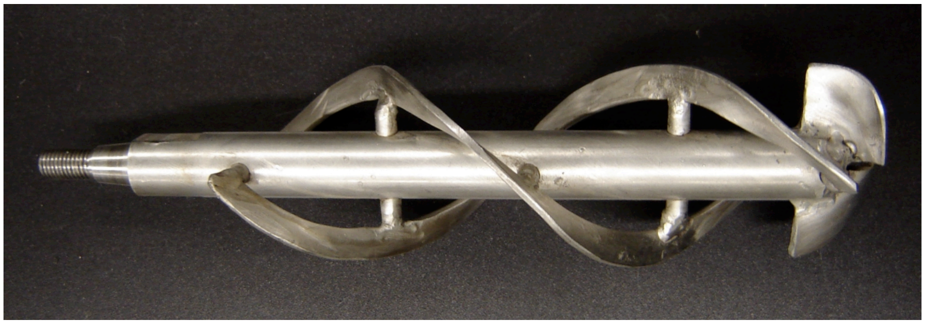


Figure 14. The helical impeller.

The helical impeller is driven by an external rotating magnet controlled by the MagneDrive® mixer, which is in turn driven by the MagneDrive® motor and a rubber chain. Maintaining the seal between the vessel and vessel lid is essential, and therefore necessitates the external positioning of the rotating magnet. Figure 15 is a photograph of the extraction vessel assembly when it is hooked up to the vessel lid.

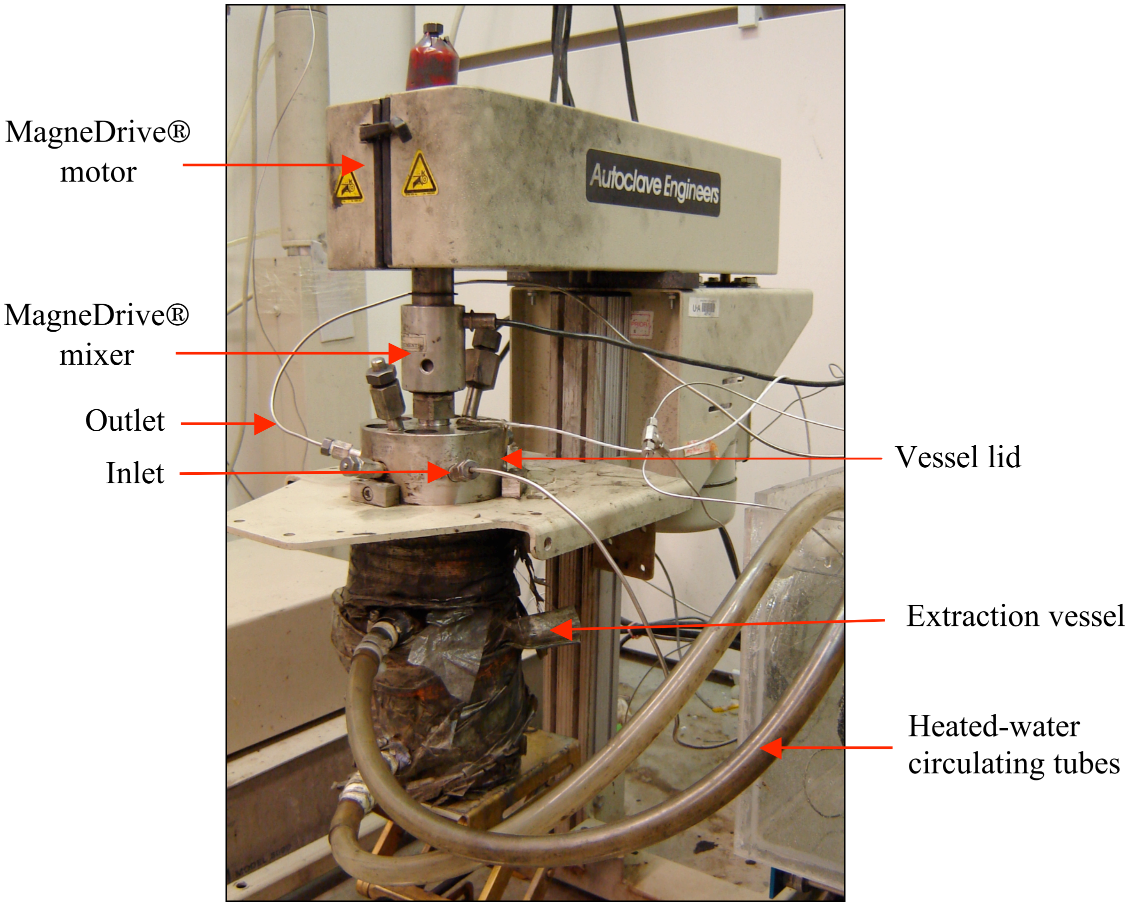


Figure 15. The extraction vessel assembly including the MagneDrive® motor and mixer.

3.3.2 Modifier Addition Apparatus

The modifier, contained in a glass bottle, is fed by a Teflon line into the 25SC pump head inlet on the 305 Gilson piston pump. An appropriate flow rate is set using the keypad located on the front panel. Underneath the display, a *Run* and *Stop* button controls the operation of the piston pump. When the pump head is operating, the modifier leaves the pump head outlet and enters the SFE system by 1/16” stainless steel tubing. To prevent back-pressure of CO_2 from flowing into the Gilson pump, a check valve is placed just before the union tee. In the case where the seals within the check valve becomes worn allowing CO_2 to enter the

Gilson pump, an outlet and inlet check valve, capable of handling a back pressure of up to 28MPa, are situated inside the 25SC pump head. The piston pump apparatus is shown in Figure 16.

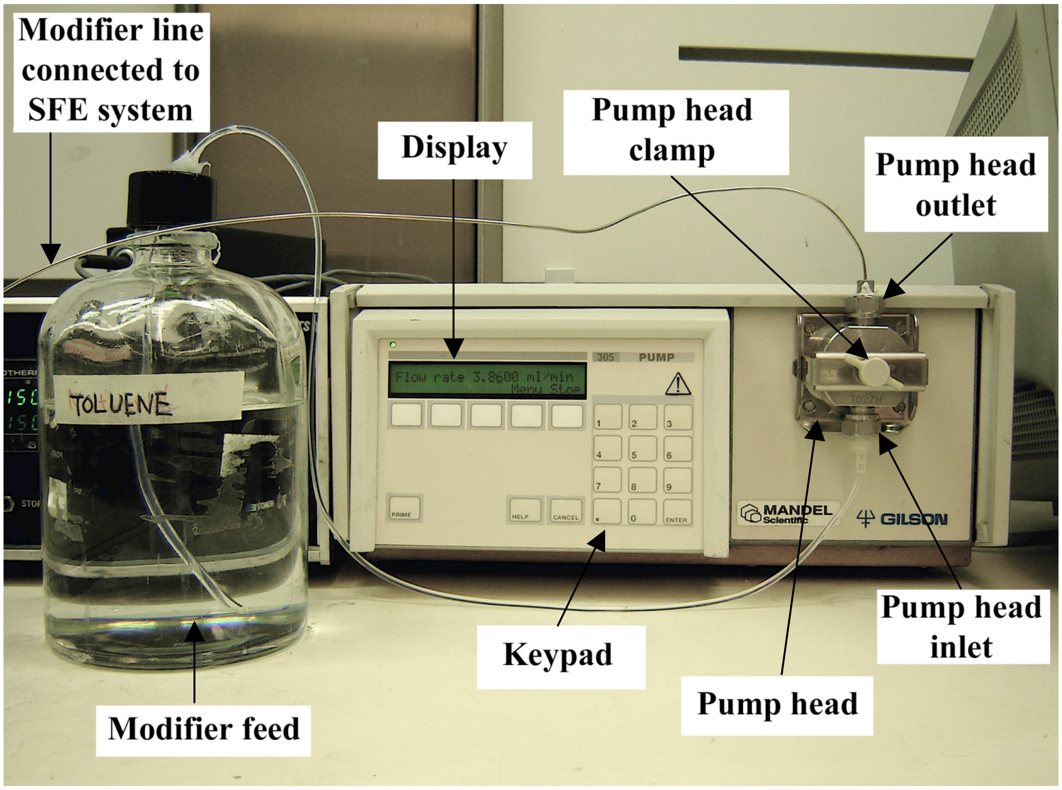
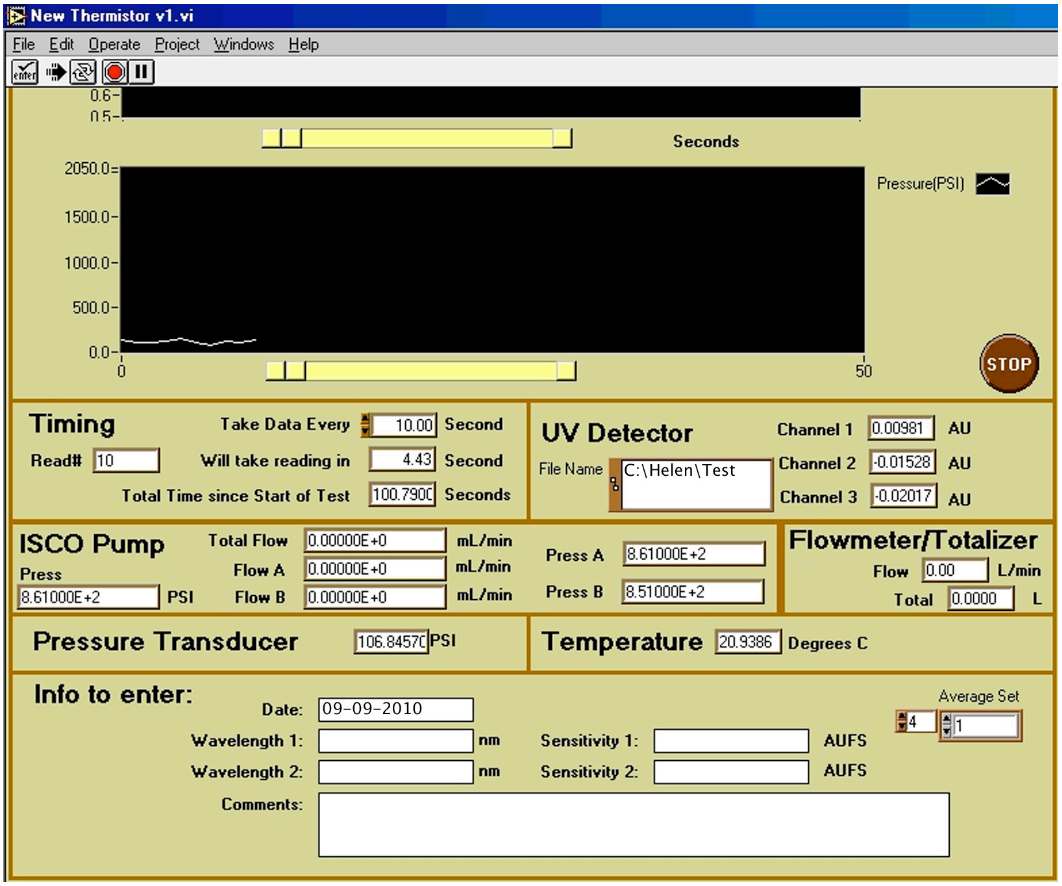


Figure 16. Front view of the 305 Gilson piston pump and the 25SC pump head.

3.3.3 LabVIEW™ Data Collection

The LabVIEW™ software records the temperature (as measured by the thermistor probe); pressure (as measured by the pressure transducer); and flow rate (as measured by the ISCO pump controllers) throughout the extraction process. Additionally, the LabVIEW™ software was able to capture the initiation and completion of each extraction as well as the pressure set-point as recorded by the pumps. Sample data collected by the LabVIEW™ software is listed in Appendix D. Figure 17 is a screen shot of the LabVIEW™ software. It should be noted that the UV detector and the flowmeter/totalizer were not used in the experiments and therefore no data was collected by LabVIEW™.



Take Data Every 10.00 Second
Read# 10
Will take reading in 4.43 Second
Total Time since Start of Test 100.790 Seconds

File Name C:\Helen\Test
Channel 1 0.00981 AU
Channel 2 -0.01528 AU
Channel 3 -0.02017 AU

Total Flow 0.00000E+0 mL/min
Flow A 0.00000E+0 mL/min
Flow B 0.00000E+0 mL/min
Press 8.61000E+2 PSI
Press A 8.61000E+2
Press B 8.51000E+2

Flow 0.00 L/min
Total 0.0000 L

Pressure Transducer 106.8457 PSI
Temperature 20.9386 Degrees C

Date: 09-09-2010
Wavelength 1: nm
Wavelength 2: nm
Sensitivity 1: AUFS
Sensitivity 2: AUFS
Comments:
Average Set 4 1

Figure 17. LabVIEW^{TM} window capturing temperature, pressure, and flow rate of extraction conditions throughout SFE.

3.4 Supercritical Fluid Extraction Procedure

The extraction apparatus depicted in Figures 10 and 11 were used for all SFE experiments. A preliminary set of experiments using 2^3 factorial design was performed to test 8 different treatment combinations of premixing time, static time, and mixing speed at 24.1MPa and 31°C. The magnitude of the high and low level chosen for each factor in the preliminary experiments is displayed in Table 8.

Table 8. 2^3 factorial experimental design to identify the main variable(s) influencing the extraction yield at a SC-CO_2 density of 0.91g·mL^{-1} (at 31°C and 24.1MPa).

	Factor Levels	
	Low (-)	**High (+)**
Premixing time (min)	5	60
Mixing rate (rpm)	50	250
Static time (min)	30	90

The purpose of the preliminary experiments was to rule out insignificant factors in the extraction process; therefore, only a single run was performed. In subsequent tests on temperature, pressure, and toluene modifier addition, a 2^3 factorial design was applied and triplicate runs were performed for each extraction combination for a total of 24 extractions. The magnitude of the two levels chosen for each factor is displayed in Table 9.

Table 9. 2^3 factorial experimental design to examine the effect of pressure, temperature, and toluene on extraction yields of bitumen.

	Factor Levels	
	Low (-)	**High (+)**
Pressure (MPa)	13.8	24.1
Temperature (°C)	31	60
Toluene (wt%)	0	9.1

The amount of toluene used was 9.1wt% of the CO_2. In each factorial experiment, 3 center-point replicates were performed to test for curvature in the experimental data. Since temperature and pressure were varied in the experiment, the role of SC-CO_2 density was also studied in the process as seen in Table 10.

Table 10. Density of SC-CO_2 at the 4 conditions tested by varying pressure and temperature in the 2^3 factorial design.

	Density ($g \cdot mL^{-1}$)	
Temperature (°C) **Pressure (MPa)**	**31**	**60**
13.8	0.83	0.55
24.1	0.91	0.78

A detailed description of the extraction process is included in Appendix A. A brief description of the SFE methodology is included here.

A 50g oil sand sample was weighed on the analytical balance (Mettler Toledo AX205 DeltaRange®) and transferred to the extraction vessel that was previously rinsed and wiped with toluene, followed by rinsing three times with ultrapure water (18.2MΩ·cm, Barnstead NANOpure Diamond™). Using a 25mL glass graduated cylinder (Class A, 20°C, Sibata®), 50mL of ultrapure water was added to the extraction vessel. With the vessel loaded with 1:1 oil sand slurry, it was then bolted closed according to the manufacturer's suggested procedure and sealed with the Teflon o-ring. The hot water circulating bath was set between 4 to 10°C higher than the target temperature of 31°C and 60°C, respectively. The temperature was adjusted throughout the extraction experiment as needed thereafter. The refrigerated water bath was turned on and set to 2°C. The hot water bath for the metering valve was turned on and set to 70°C. The mixer was turned on and set to the target mixing-rate: the time was the beginning of the premixing. Collections vials were partially filled with glass beads and glass wool. The designated primary collection vial (e.g. static vial during the static time) and the carryover vial were secured and immersed in the ice water bath. As soon as the vessel temperature was approximately 4°C below the target temperature, the ISCO syringe pumps were refilled with CO_2 and compressed to the desired set point pressure. The inlet ball valve was opened to the extraction vessel and allowed to pressurize to the target pressure. As soon as the temperature stabilized in the vessel, timing for the static time commenced.

When the static time was completed, the flow of CO_2 was initiated: the outlet valve was opened to the outlet, and the metering valve was adjusted to approximately 40mL·min^{-1} as measured at the pumps. For the preliminary experiments (24.1 MPa and 2°C), an average flow of 41.1g·min^{-1} of CO_2 was achieved. In the 2^3 factorial experiments where pressure was varied between 13.8 to 24.1MPa, the flow varied between 40.0g·min^{-1} to 41.1g·min^{-1} of CO_2.

The primary collection vial was changed at 15-minute intervals. The mass of the collection vial was measured before and after the 15-minute interval to obtain the mass of hydrocarbon collected. The total flow period was 90 minutes.

At the end of the flow period, the flow of CO_2 from the syringe pump to the vessel was stopped and the vessel was allowed to depressurize. Upon depressurization, flow from the pumps were started again and directed through the bypass line in order to clean out any residual bitumen from the lines downstream of the extraction vessel. After this step, the collection vials in the ice water trap were detached from the outlet. Finally, the vessel was unbolted and the residual oil sand slurry was decanted into a pre-weighed glass jar. Clean toluene was poured into the vessel approximately ¾ full and raised to the helical mixer without bolting it down. The mixer controller was turned on again to 30rpm for 30 minutes to extract the residual bitumen left on the vessel wall and mixer. Following the final extraction of the residual bitumen left in the vessel, the toluene and bitumen solution was decanted into a separate clean glass jar and set aside, with the residual oil sand slurry, for Dean-Stark analysis.

3.5 Toluene Modified SC-CO_2

In the modifier experiments, SC-CO_2 was modified with 9.1wt% toluene during initial vessel pressurization and during the dynamic extraction. Since the total volume of the vessel is 300mL, it was assumed CO_2 was required to pressurize ≈200mL (300mL less ≈100mL occupied by 50g of oil sands and 50mL of slurry). During the pressurization stage, a predetermined toluene volume, as shown in Table 11, was pumped into the incoming liquid CO_2 flow for 1 minute. As soon as the static extraction period was complete, a predetermined flow rate of toluene was continuously added until the end of the dynamic period. The volume of toluene used during the dynamic period was based on a CO_2 flow rate of 40mL·min^{-1}. In between exchanging collection vials, the toluene flow was halted and the metering valve was put into the closed position in order to prevent toluene leakages at the outlet line.

Table 11. Volume of toluene added to liquid CO_2 per minute during vessel pressurization and dynamic extraction.

P (MPa)	T (°C)	Volume of Toluene Added (mL×min^{-1})		
		During Pressurization	During Extraction	Wt% of Toluene in CO_2
13.8	31°C	44.9	8.98	9.1
	60°C	29.8	5.95	9.1
24.1	31°C	49.2	9.85	9.1
	60°C	42.2	8.44	9.1
18.9*	45°C*	20.5	4.1	4.8

* Center-point conditions

A slight modification was made in the extraction process when a modifier was used in the SFE experiments and is described in this section. In the application of a modifier (e.g. toluene), 9.1wt% toluene was applied directly into the flow of the CO_2 before entering into the preheating coils. This method of modifier addition allows the toluene to mix into the SC-CO_2 flow prior to entering into the extraction vessel. The Gilson pump was set at a flow rate (in mL·min^{-1}) equivalent to 9.1wt% of the volume of CO_2 required to fill up the remaining volume of the vessel after accounting for the volume of slurry (i.e. 200mL of CO_2 + 100mL of 1:1 slurry). When the temperature of the vessel was 4°C less than the extraction temperature, the *Run* button was selected on the Gilson pump, and the inlet valve to the ISCO syringe pumps was directed towards the extraction vessel to pressurize the vessel to the extraction pressure. The flow rate calculated in Table 12 is based on 1 minute of pressurization, therefore the timer was used and the *Stop* button was pressed after 1 minute. During the static extraction time (i.e. 1 hour), the flow rate on the Gilson pump was adjusted to 9.1wt% of the CO_2 flow rate of the dynamic extraction. As soon as the static time was reached, the outlet ball valve was directed towards the metering valve, the *Run* button was selected on the Gilson pump and the metering valve was carefully opened to reach a SC-CO_2 flow rate of 40±5mL·min^{-1}. At higher densities of SC-CO_2, it was necessary to exchange the collection vials in smaller time intervals to compensate for the increased volume of toluene. For example, at a SC-CO_2 density of 0.91mL·min^{-1} (i.e. P = 24.1MPa and T = 31°C), the primary extraction vials had to be exchanged every 5 minutes. It was necessary to close the metering valve and temporarily halt the Gilson pump before exchanging the collection vials in order to prevent toluene spillage and overflow in the vessel.

3.6 Water Chemistry

The residual oil sand slurry was weighed on the analytical balance and subsequently transferred into two 50mL Teflon® centrifuge tubes. The aqueous layer (which will be referred to as the SFE-processed-water, or SFE-PW, for the purposes of this work) was obtained after centrifuging at 10 000 revolutions per minute (rpm) for 20 minutes, decanted, and filtered. In order to prevent contamination of the pH and conductivity electrodes with residual bitumen and solids, the remainder SFE-PW was filtered through a 0.45μm filter (25mm GD/X Whatman) prior to pH, conductivity, and alkalinity analysis.

3.6.1 pH, Alkalinity, and Conductivity

Alkalinity, conductivity, and pH measurements were made on the pH/conductivity meter (Accumet® Model XL20 Fisher Scientific). Calibrations were made on a daily basis. There are three calibration standards for pH: 4, 7, and 10. In between each calibration point, the slope was ensured at ≥95%, or at a minimum of 168.61mV (since a theoretical pH response is 59.16mV·pH^{-1} unit). Conductivity measurements were made on a 10mL SFE-PW, diluted by a factor of 4, in order to obtain a reading near the single point calibration of 997 μΩ·cm^{-1}. The SFE-PW was further diluted to ≈80mL in order to ensure the pH electrode junction is in contact with the sample, for alkalinity measurements. Alkalinity and pH measurements were made using a pH glass electrode (Ag/AgCl reference, Accumet® Fisher Scientific,). Detailed step-by-step instructions are listed in Appendix B. CO_2-free ultrapure water (used in the alkalinity measurements) and atmospheric-stabilized ultrapure water (used to create the 1:1 oil sand slurry) were also analyzed for pH, conductivity, and alkalinity as part of the quality control analysis.

3.7 Determination of Hydrocarbon Extraction Efficiency

The hydrocarbon extraction efficiency refers to the percentage of hydrocarbon that was extracted from the 1:1 oil sand slurry by SFE. The extraction efficiency, on a wt% basis, is determined by obtaining a cumulative mass of the air-dried hydrocarbons in the collection vials and comparing this mass to the total recoverable bitumen (i.e. SFE yields and residuals) in the untreated oil sands. The Dean-Stark analysis provides a measure of the amount of water, solids, and bitumen in the oil sand and oil sand slurry. As a result, it is possible to obtain a hydrocarbon extraction efficiency based on a dry mass basis. The following section is a description of the extracted hydrocarbon content (via SFE) determination by weighing to constant weight, the Dean Stark-extraction apparatus and methodology, asphaltenes determination by n-pentane addition, and finally the hydrocarbon range distribution—obtained under the SFE condition that provided the highest experimental yield—as determined by gas chromatography.

3.7.1 Constant Weight Determination

The hydrocarbons extracted by SFE were collected in the collection vials at 5 to 15 minute intervals, for 90 minutes, depending on the amount of toluene used in the modifier experiments. If no modifier was used, the vials were exchanged at 15-minute intervals. Residual water and toluene (used in the modifier experiments) were allowed to evaporate by air-drying the vials. Every two weeks for a total of 6 weeks, each vial was reweighed. The total hydrocarbon content was determined by obtaining the cumulative average at 2, 4, and 6 weeks of air-dry weights. Stabilization of the cumulative mass was observed after 2 weeks but in order to ascertain the possibility of residual toluene and water remaining in the vials, the mass of the collection vials were weighed again after 4 and 6 weeks.

3.7.2 Dean-Stark Method

The Dean-Stark method was used to determine the weight percent of solids, bitumen, and water content in the untreated oil sands and in the residual oil sand slurry after SFE. The method used in this work is a modified version described in Syncrude Analytical Method 2.7: "*Determination of Bitumen, Water, and Solids Content of Oil Sands, Reject and Slurry Samples (Classical)*" (Starr et al. 1979), as described below. A schematic of the Dean-Stark apparatus is illustrated in Figure 18.

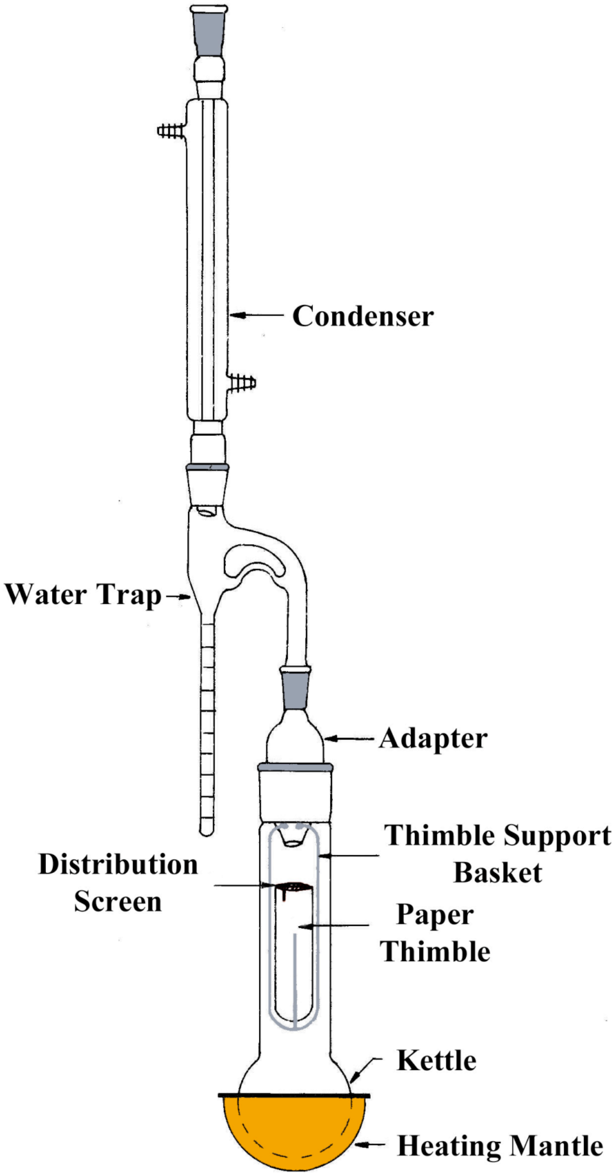


Figure 18. Dean Stark extraction apparatus including the paper thimble suspended by a thimble support basket connected to the adapter (modified from Starr et al. 1979).

Two Kimwipes™ (Kimberly-Clark) are inserted into each double thickness cellulose extraction thimble (43mm × 123mm, Whatman®) and dried in a 110°C oven for a minimum of 12 hours. Once dried, the extraction thimbles are then placed in a dessicator to cool for a minimum of 30 minutes.

For the analysis of untreated oil sands, approximately 50g of oil sand was added to a pre-weighed extraction thimble. HPLC grade toluene is transferred into the 500mL capacity heat-resistant glass kettle to the level of the heating mantle (≈125mL). The thimbles are placed onto the support wire baskets and attached to the adaptor. An illustration of the wire baskets is shown in Figure 19.

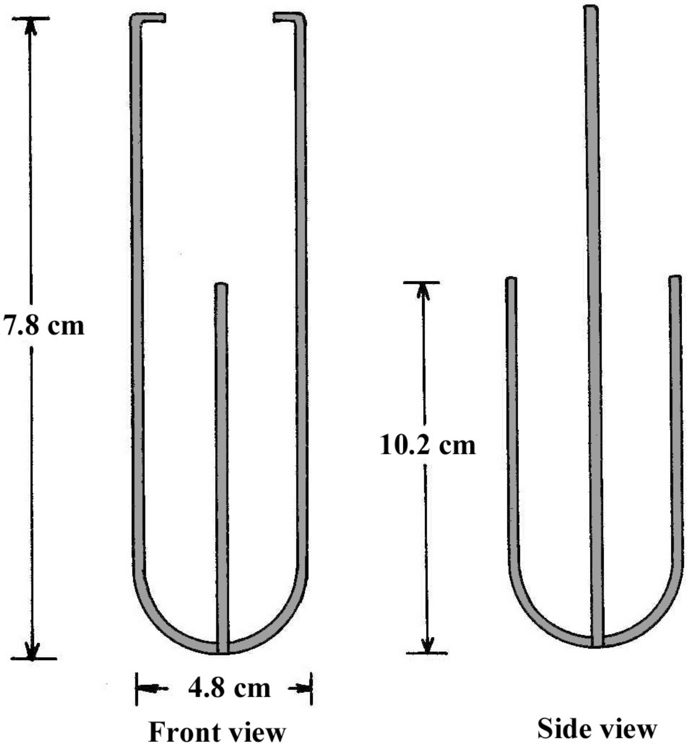


Figure 19. Front-view and side-view of the thimble support basket in used in the Dean Stark Extraction (modified from Starr et al. 1979).

A distribution screen is placed over the thimble opening for even distribution of toluene during the extraction process. The support basket and thimble are lowered into the kettle and suspended above the toluene. The water trap and condenser are placed on last before the heating mantle and cooling water are turned on. The reflux rate was maintained at 4-5 drops per second and allowed to continue until all the water and bitumen had been removed from the oil sand. Extraction was deemed completed when the water level in the traps remained unchanged and the toluene dripping through the thimble was colorless. Typically, the Dean-Stark extraction lasted approximately 4 hours.

For the analysis of the residual oil sands slurry after SFE, the same Dean-Stark methodology was followed. The slurry was placed in the thimble by carefully decanting the slurry from the glass jar using a metal spatula. The bitumen-toluene solution, obtained from rinsing the vessel and mixer, is carefully poured into the thimble while holding it above the kettle. Solids that may be present in the bitumen-toluene solution are captured by the thimble before entering into the kettle. As a result, the mass of residual oil sand slurry after SFE was determined through back-calculations, rather than weighing on the analytical balance, since the amount of toluene used to reclaim residual bitumen and slurry adhering to the vessel wall and mixer is several times larger than the volume of the thimble. For the steps taken in determining the amount of residuals extracted by the Dean Stark analysis, refer to Appendix B.

As soon as the Dean-Stark extraction was complete, the bitumen-toluene solution was allowed to cool to ambient temperature in the glass kettle. The water content was obtained by reading the graduation in the water trap and recorded. The bitumen content was determined from the bitumen-toluene solution. As soon as the kettle was cooled, the bitumen-toluene solution was transferred into a 250mL volumetric flask and diluted to the mark. In order to determine the bitumen content, two pieces of pre-dried (in drying oven at 110±5°C) 15cm glass microfiber filters (934-AH Whatman®, Fisher Scientific) were used. Specifically, 10mL of the bitumen-toluene solution was pipetted onto the double layered filters in a concentric pattern. The filters were air-dried in the fumehood for approximately 10 minutes. Finally, the difference between the before and after filter mass was multiplied by the dilution volume, or ×25. To determine the solids content, the solids remaining in the thimble after Dean-Stark extraction were placed in the oven (110±5°C) to obtain a dry weight by gravimetry.

3.7.3 Determination of Asphaltenes Content

The asphaltenes content of the oil sand was determined using a modified method of the asphaltenes precipitation method in the *"Syncrude Analytical Methods for Oil Sand and Bitumen Processing"* (Starr et al. 1979) using n-pentane as the precipitating agent. A Dean-Stark extraction was performed on approximately 25g of ARC oil sands. The resulting bitumen-toluene solution from the Dean-Stark extraction was transferred into a pre-weighed (to 0.0001g) acid-washed 250mL Pyrex round bottom flask and placed on a rotary evaporator. Following the method of Henry and Fuhr (1992), the toluene was removed at 60°C under vacuum using a water aspirator (controlled by the cold tap water flow rate). Once the toluene condensation had stopped, the rotary evaporator was stopped and the remaining bitumen (with residual toluene) in the round bottom flask was weighed to 0.0001g.

To the round bottom flask, 2.5mL of toluene was added to dissolve the bitumen. Slowly, 40mL of (98% purity) n-pentane per mL of toluene was added to the bitumen solution. For 2 hours, asphaltenes were allowed to precipitate in the dark (in order to avoid photo-degradation).

In preparation for this experiment, 40mL Gooch crucibles, and Whatman glass fiber filters (24mm diameter and 2μm nominal pore size) inserted into each crucible, were muffled at 550°C for 1 hour, cooled, and weighed to 0.0001g. Under vacuum, the asphaltenes were filtered through the Gooch crucibles and rinsed with n-pentane until the effluent ran clear. The Gooch crucibles with the asphaltenes precipitate were dried at 105°C overnight and reweighed to obtain a dry mass. The difference was the dry weight for asphaltenes content.

3.7.4 Hydrocarbon Distribution Analysis by Gas Chromatography

3.7.4.1 Standard Solution Preparation

The GC was calibrated according to the guidelines described in the Canadian Council of Ministers of the Environment (CCME) (CCME 2001) using n-alkane standard solutions. Although bitumen is comprised of a complex hydrocarbon mixture ranging from simple paraffins to large aromatic porphyrin (often polar) structures of large molecular weights, the purpose of this analysis was to provide a qualitative hydrocarbon range from the cumulative extracts obtained by the best conditions used in the 2^3 factorial design. The following is a general description for the preparation of the standard solution used to generate a calibration curve on the GC; however, for the purposes of this thesis, the hydrocarbons extracted from the 1:1 oil sand slurry was not analyzed for concentration.

Six n-alkane calibration standards were generated with equal volumes of decane ($C_{10}H_{22}$), hexadecane ($C_{16}H_{34}$), and tetratriacontane ($C_{34}H_{70}$) at the following concentrations: 5, 10, 25, 100, 250, and $500mg{\cdot}L^{-1}$. Lastly, a pentacontane ($C_{50}H_{102}$) standard was prepared at a concentration of $6.4mg{\cdot}L^{-1}$. To begin, the $500mg{\cdot}L^{-1}$ standard was prepared first by weighing approximately equal masses of $C_{10}H_{22}$, $C_{16}H_{34}$, and $C_{34}H_{70}$ into a 250mL volumetric flask on the analytical balance. The solutions were placed in an ultrasonic bath for 1 hour to ensure complete dissolution of the hydrocarbons in the toluene solution. A series of dilutions were used to prepare the lower concentration standards. Due to the limited solubility experienced by $C_{50}H_{102}$, only a $6.4mg{\cdot}L^{-1}$ standard was prepared. Calibration standards were stored in the fridge at 4°C to minimize decomposition.

3.7.4.2 Gas Chromatography Method

For the qualitative analysis of the cumulative hydrocarbon range extracted from 1:1 oil sand slurry under the best extraction conditions, the method used previously by Street (2008) and Jones (2010) was followed. A Varian CP-3800 (Varian Inc., Palo Alto, California, USA) GC equipped with a Flame Ionization Detector (FID) was used. Additionally, an autoinjector (CP-8410) with a capacity of holding 10×-2mL sample vials, and a split/splitless injection system (CP-1177) was employed. Results were analyzed using “Star Chromatography Workstation” (Version 5.5; Varian Inc.). A low bleed column, by Restek (Fisher Scientific, Edmonton, Alberta), composed of 100% poly(dimethylsiloxane) and dimensions at 30m in length and 0.32mm internal diameter was used. The column had a minimum and maximum bleed temperature or 330°C and 350°C respectively. Operational parameters used on the GC are included in Table 12.

Table 12. Operation descriptions for the GC in the qualitative analysis of hydrocarbon distribution from SC-CO_2 treatment.

Parameter	Description
Injection temperature	310°C
Oven temperature	Held at 40°C for 2 minutes Ramped to 320°C at 20°C·min^{-1} Held at 320°C for 14 minutes
FID temperature	340°C
Split/Splitless	Split initiated at a split ratio of 10 Split is turned off at 0.01 seconds Split is turned on at 0.75 seconds at a ratio of 50 Split ratio is reduced to 10 at 2 minutes
Hydrogen carrier gas	18mL·min^{-1} Grade: ultra high purity Supplier: Praxair (Edmonton, Alberta)
Nitrogen make-up flow	12mL·min^{-1} Grade: ultra high purity Supplier: Praxair (Edmonton, Alberta)
Detector hydrogen flow	11mL·min^{-1} Grade: ultra high purity Supplier: Praxair (Edmonton, Alberta)
Detector air flow	487mL·min^{-1} Grade: extra dry Supplier: Praxair (Edmonton, Alberta)
Injection volume	2mL

3.7.4.3 Quality Assurance and Control

A six-point calibration curve was generated according to the guidelines described in CCME. To ensure accuracy of the GC/FID, it was ensured that the FID response for each n-alkane standard was within 10% of each other. A maximum concentration of $C_{50}H_{102}$, at 15mg·L^{-1}, was injected and the response factor was ascertained to be within 30% of the average response from the lowest three n-alkane standard solutions. To assess the precision of the GC/FID, a

QA/QC check was made at the end of the run using the 5 and 100mg·L^{-1} standard calibration solutions. The lower and mid-point standard was ensured to be within 20% and 15% of the calibration response.

3.7.4.4 Sample Preparation for GC/FID Analysis

Following the 2^3 factorial experiment using a toluene modifier, the data was analyzed to determine the treatment combination that provided the best cumulative hydrocarbon yield. Two sets of replicates were prepared for cumulative hydrocarbon range analysis while the third replicate was analyzed for the hydrocarbon range at two different time series: initial 5 minutes and latter 7.5 minutes. For the cumulative hydrocarbon range analysis, each time series vial was rinsed in toluene, until the extract ran clear, and combined in a 1L beaker. It was ensured that the amount of toluene used would not reduce the total hydrocarbon concentration to <1g·L^{-1}. The contents in the 1L beaker were mixed thoroughly with a stirring rod. A portion of the solution was passed through 10-60 mesh size sodium silicate to remove water droplets from the liquid sample. Using a 5mL glass syringe, approximately 2mL of the hydrocarbon-toluene solution was withdrawn from the 1L beaker and filtered through a 0.45μm filter (PTFE-based) and into a 2mL sample holder. For the time series analysis, the same procedure was performed, with the exception that the added toluene was not decanted into a separate beaker, but left in the designated vial. The toluene was allowed to soak overnight to ensure the hydrocarbons were sufficiently purged from the glass wool and glass beads.

3.8 Analysis Procedure for 2^k factorial design

3.8.1 Factor Effect Estimate

A detailed description of the steps for analyzing the data from a 2^k factorial design are described in Montgomery (2005), and is briefly described here. The general design matrix is shown in Table 13, where A, B, and C represent the factors tested and the “plus” and “minus” signs indicate the two levels used for each factor: high (+) and low (-). In total there are 8 runs, with the addition of a ninth run to test for curvature. A general assumption of linearity between the (-) and (+) levels is assumed in the factorial experimental design. To test for curvature, three runs are made at the mid-point for each factor tested. If the linearity assumption holds, the average for the sum of the yields obtained at each treatment combination is approximately equal to the average of the extraction yields for the center-points. The labels *(1), a, b, ab, c, ac, bc,* and *abc* are the notations for each treatment combination and makes up a total of 8 observations in the 2^3 factorial design.

Table 13. 2^3 factorial design matrix.

Run	Treatment Combination	A	B	C
1	*(1)*	-	-	-
2	*a*	+	-	-
3	*b*	-	+	-
4	*ab*	+	+	-
5	*c*	-	-	+
6	*ac*	+	-	+
7	*bc*	-	+	+
8	*abc*	+	+	+

Once the data for each extraction condition has been collected, the effect of each factor and their respective interactions (**A**, **B**, **C**, **AB**, **BC**, **AC**, and **ABC**) are computed. The effect estimate for a factor is computed according to Equation 9.

$$\text{Effect} = \frac{\text{Contrast}}{2^{k-1}n} \qquad \textbf{Equation 9}$$

where *k* represents the number of factors tested and *n* represents the number of replicates used. The contrast for each effect can be determined by taking the signs for each corresponding column in Table 13 and multiplying it by the treatment combination. For example, the contrast for factor A is *a – (1) + ab – b + ac – c + abc – bc*.

In the next step, a regression model is formulated. In situations where the factorial experimental design is un-replicated, the regression model is generated by plotting the effects on a normality plot. If replicates ($n \geq 2$) are used, the data can be analyzed by the full ANOVA analysis.

3.8.2 Statistical Testing on the Replicated Design

The full analysis of variance regression model for predicting hydrocarbon yield according to the three factor factorial experiment can be described by Equation 10.

$$\hat{y} = \hat{\beta}_o + \hat{\beta}_1 x_1 + \hat{\beta}_2 x_2 + \hat{\beta}_3 x_3 + \hat{\beta}_{12} x_1 x_2 + \hat{\beta}_{13} x_1 x_3 + \hat{\beta}_{23} x_2 x_3 + \hat{\beta}_{123} x_1 x_2 x_3 \qquad \textbf{Equation 10}$$

Here $\hat{y}$ is the bitumen yield; x_1, x_2, and x_3 are variables that represent factor A, B, and C respectively; and the β's are ½ the effect value of the corresponding factor. On a coded scale, x_1, x_2, and x_3 take on values of -1 and +1. The most convenient method is to utilize a statistical software to compute the analysis of variance (in this thesis, SPSS version 17 was used); however, the sums of squares for each effect can be computed manually as per Equation 11.

$$\mathrm{SS} = \frac{[\mathrm{Contrast}]^2}{2^k \mathrm{n}} \qquad \textbf{Equation 11}$$

It is important to note that the sum of squares can only be computed when there is at least 1 replicate ($n \geq 2$) for an error estimate, to account for all of the possible interactions included in the model. The analysis of variance of a 3-factor model is shown in Table 14. A large divergence of F_o from 1 indicates a significant effect. In addition to the F_o, a statistical software would provide a p-value to test for the level of significance using a predetermined α value. In this thesis, the α-value was set at 0.05.

Table 14. Analysis of variance (ANOVA) for a 3 factor model, where *n* is the number of replicates.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F_o
A	SS_A	1	MS_A	MS_A/MS_E
B	SS_B	1	MS_B	MS_B/MS_E
C	SS_C	1	MS_C	MS_C/MS_E
AB	SS_{AB}	1	MS_{AB}	MS_{AB}/MS_E
AC	SS_{AC}	1	MS_{AC}	MS_{AC}/MS_E
BC	SS_{BC}	1	MS_{BC}	MS_{BC}/MS_E
ABC	SS_{ABC}	1	MS_{ABC}	MS_{ABC}/MS_E
Error	SS_E	$2^k(n\text{-}1)$	MS_E	
Total	SS_T	2^{k-1}		

3.8.3 Statistical Testing on the Unreplicated Model

The downside to an unreplicated factorial is the inability to obtain an internal estimate of error. In this case, the analysis of variance cannot be computed. To overcome this problem, the effects estimates for each factor or interaction is plotted on a normal probability plot. Negligible effects are normally distributed, and will fall on the straight line. Significant effects have a nonzero mean and will appear as outliers. Pooling all of the negligible effects will provide an estimate of error and the analysis of variance can then be computed.

3.8.4 Model Refinement and Diagnostic Checks

Once the analysis of variance has been computed either manually or by a computer software, the preliminary model is refined by eliminating non-significant effects. For example, if factor **A**, **B**, and **AB** are the only significant effects based on the analyses, then the regression model can be shortened to $\hat{y} = \hat{\beta}_o + \hat{\beta}_1 x_1 + \hat{\beta}_2 x_2 + \hat{\beta}_{12} x_1 x_2$.

The validity of the analysis of variance (ANOVA) approach needs to be confirmed by verifying three assumptions:

(i) the hydrocarbon yields can be described by the regression model and the errors (or residuals) are normally distributed.

(ii) the yields observed at each treatment combination are independently distributed (i.e. this can be ensured through randomization).

(iii) the yields observed at each treatment combination have the same variance (σ).

To check for the accurateness of the new regression model, a diagnostic check is performed by calculating the residuals, e, for each treatment combination (i.e. (1), a, b, ab, c, etc.) by taking the difference between the observed value, y (e.g. the experimental yield), and the predicted value $\hat{y}$ as shown in Equation 12.

$$e = y - \hat{y} \qquad \textbf{Equation 12}$$

The residuals are plotted on a normality curve. If the new model is accurate all of the residual points will lie near, or on, the line. For the second assumption, a plot of the residuals versus the run-order (or the time order of data collection) should provide a plot that is structureless, or where the residuals show no correlation trends. In the third assumption, a plot of the residuals versus the predicted yields, $\hat{y}$, should also provide a structureless plot to demonstrate that the residuals are unrelated to the predicted values.

CHAPTER 4 Results and Discussion

4.1 ARC Oil Sand Characterization

4.1.1 Bitumen, Solids, and Water content of ARC Oil Sand

A total of three Dean Stark extractions were carried out on untreated ARC oil sands in order to determine the bitumen, solids, and water content. An extraction was carried out for each of the three oil sand batches used for each replicate in this study. In this way, the average solid, bitumen, and water content are representative of all the oil sands used.

Table 15 shows the composition of the untreated oil sands used in this research. In this case, the ARC oil sand is confirmed as medium grade (as originally labeled by ARC) at 10.7% bitumen content. The water content is lower than when first purchased at 1.1wt% as compared to ca. 4.9wt% (Fang 2010) due to exposure to ambient laboratory conditions during division into experimental batches, weighing, and natural aging in storage. As a result, the solids and bitumen content are slightly higher than stated in Fang (2010), that is 88.2wt% solids content and 10.7wt% bitumen content.

Table 15. Average mass percentage of solid, bitumen, and water content in the ARC oil sand samples (number of samples = 3).

	Average Mass Composition (%)	Standard Deviation (%)
Solid	88.2	0.95
Bitumen	10.7	0.73
Water*	1.1	0.41

*Water is estimated through back calculation of the initial oil sands wet weight from the bitumen and solids dry weight obtained through the Dean Stark extraction since the collected water volume was less than the smallest graduation observed in the water trap.

4.1.2 Asphaltenes Content

The asphaltenes content of the ARC oil sand was determined for three samples of oil sand. Since 25.0000g of oil sand was used to obtain the bitumen for the determination of asphaltenes content by n-pentane precipitation, the bitumen content was assumed to be 10.7wt% based on Dean-Stark results (Table 16). The asphaltenes content of the ARC oil sand was found to be 0.411±0.039g, or 15.3% based on the average of triplicates presented in Table 16. This data is consistent with results obtained for Athabasca bitumen (Henry and Fuhr 1992; Hyndman and Luhning 1991; Yoon et al. 2009). Figure 20 is a photo of the asphaltenes precipitated from the ARC oil sands. The asphaltenes are physically free-flowing particulates and dark-brown in appearance.

Table 16. Asphaltenes content in ARC oil sands.

Mass of Oil Sand Used (g)	Expected Bitumen Content (g)	Asphaltenes Content (wt% of bitumen)	Asphaltenes Content (wt% of oil sand)
24.7912	2.6551	16.8%	1.80%
25.0843	2.6865	13.7%	1.47%
25.4051	2.7209	15.3%	1.64%
Average		15.3%	1.64%
Standard Deviation		1.55%	0.17%

Figure 20. ARC oil sands asphaltenes obtained by n-pentane precipitation.

4.2 Preliminary Experiments on the Effect of Premixing Time, Static Time, and Mixing Rate on 1:1 ARC Oil Sand Slurry

In order to study the significance of premixing time, static time (i.e. CO_2 soak time), and the mixing rate on SFE hydrocarbon yields from a 1:1 ARC oil sand slurry, a 2^3 factorial experimental design was implemented. The pressure, temperature, and flow-rate were maintained at 24.1MPa, 31°C, and 40±5mL·min^{-1}, respectively. A primary advantage of using the factorial design is to reduce the number of runs required to analyze the significance of each of these three factors on hydrocarbon yields as compared to analyzing each factor one at a time. In this case, each factor is varied at 2 levels each, thereby requiring only 8 runs in total. Furthermore, in a factorial design, interactions between any two or more factors can be deduced.

4.2.1 Evaporation of Water from Extracts Obtained by SFE

Because water is also soluble in SC-CO_2, the SFE extracts contain hydrocarbon along with water from the 1:1 ARC oil sand slurry through solubilization in SC-CO_2 and entrainment. Three masses were obtained from each preliminary experiment: right after extraction (M1), after 2 weeks or after 4 weeks (M2), and after 6 months (M3). The cumulative masses are presented in Table 17. The masses M2, and M3 are similar; therefore, it was assumed that the water is sufficiently evaporated within 2 to 4 weeks. Mass M1 is greater than M2 and M3 due to water solubilization and water entrainment during SFE. Additionally, as seen in Table 17, the cumulative mass of M1 is high when a high mixing speed is employed.

Table 17. Cumulative hydrocarbon yield right after SFE (M1), after 2-4 weeks (M2), and after 6 months (M3).

	Factor			**Hydrocarbon Yield (g)**		
	A	**B**	**C**			
Treatment Combination	**Mixing Rate (rpm)**	**Premixing Time (min)**	**Static Time (min)**	**M1**	**M2**	**M3**
(1)	50	5	30	0.8493	0.6544	0.6573
a	250	5	30	3.2494	1.4784	1.4651
b	50	60	30	0.7568	0.5383	0.5355
ab	250	60	30	2.7892	1.4085	1.4027
c	50	5	90	1.0036	0.8383	0.8391
ac	250	5	90	4.0512	1.5661	1.5403
bc	50	60	90	1.0317	0.8525	0.8471
abc	250	60	90	2.9026	1.5966	1.596
Center-point #1	150	32.5	60	1.9997	1.094	1.0963
Center-point #2	150	32.5	60	2.0661	1.0481	1.030
Center-point #3	150	32.5	60	1.1423	0.9011	0.9099

Treatment combinations *a*, *ab*, *ac*, and *abc* resulted in the highest hydrocarbon yield with a cumulative average of ≈1.5g. Whereas *(1)*, *b*, *c*, and *bc* resulted in a combined average of only ≈0.85g. The common factor contributing to the higher yields is factor **A** (or 250rpm). These preliminary observations are confirmed with a complete ANOVA statistical analysis of the main effects in the following sections.

4.2.2 Statistical Analysis of the Main Effects

4.2.2.1 Normality Plot of Main Effects and ANOVA analysis

In the preliminary experiments, each condition was tested in a single experiment. As mentioned in Section 3.8, a full ANOVA statistical analysis is not possible for single experiments as there is no error term. In order to rule out insignificant factors and interactions, the effects are plotted on a normality curve to observe for outliers as these are the potential main factor(s) in the experiments. This normality plot is presented in Figure 2, where **A** represents mixing rate, **B** is the premixing time, **C** represents the static time, and the remaining combinations (**AB**, **BC**, and **ABC**) represent the interactions between these factors.

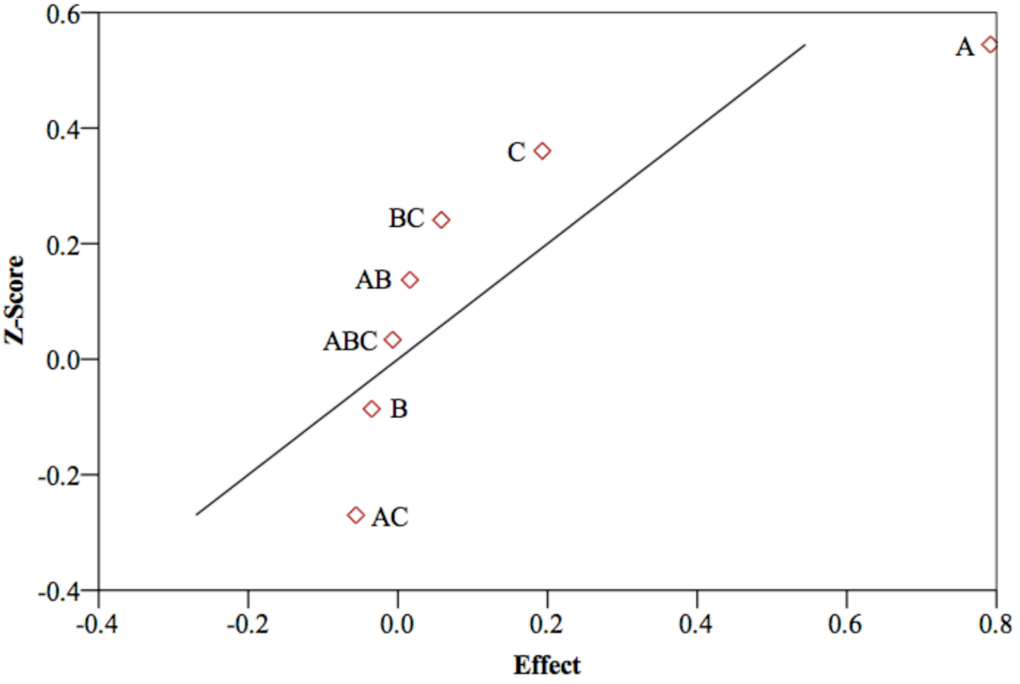


Figure 21. Normality plot of the effects of mixing rate (A), premixing time (B), static time (C), and their interactions.

According to the normality plot (Figure 21), the potential main effects include mixing rate and static time. In order to confirm these main effects, an ANOVA analysis on the three main factors (A, B, and C) alone (i.e. excluding the interaction terms in order to provide an estimate of the error term) is presented in Table 18. There is a main effect of mixing rate, with high mixing rates providing greater yields (*F*(1, 4) = 373.20, p<0.05). Additionally, there is a main effect of static time, with high mixing rates providing greater extractions yields (*F*(1, 4) = 22.29, p<0.05). The large F_o value for mixing rate indicates that this factor has a great influence on hydrocarbon yield obtained by SFE. The ANOVA analysis indicates premixing time has no significance on SFE hydrocarbon yields, and can be eliminated in future runs.

Table 18. ANOVA computation on the effect of mixing rate, premixing time, and static time based on single runs with the sum of all possible interaction terms included in the error term.

Source	df	Mean Square	F	Sig.
Corrected Model	3	0.44	132.081	.000
Intercept	1	9.98	2970.970	.000
Mixing	1	1.25	373.201	.000
Static	1	0.07	22.298	.009
Premixing	1	0	.743	.437
Error	4	0		
Total	8			
Corrected Total	7			

In Figure 21, the interaction AC may also be a potential outlier. In order to examine and affirm the existence of this interaction, AC is plotted in Figure 22. The plot confirms no interaction between static time and mixing rate as the lines are parallel; however, it is noted that static time has a positive linear effect on hydrocarbon yields at both a low and high mixing rate.

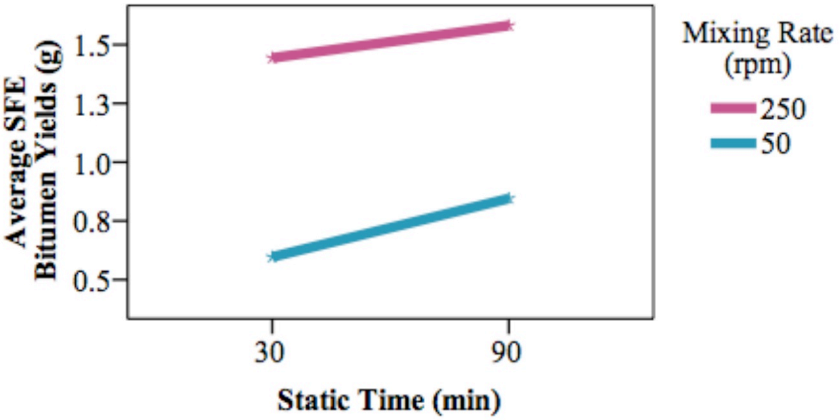


Figure 22. The effect of static time and mixing rate on hydrocarbon yield.

4.2.2.2 Model Adequacy Check

To confirm the adequacy of the refined regression model (i.e. $\hat{y} = 1.117 + 0.396x_1 + 0.097x_3$) the residuals are plotted in Figure 23.

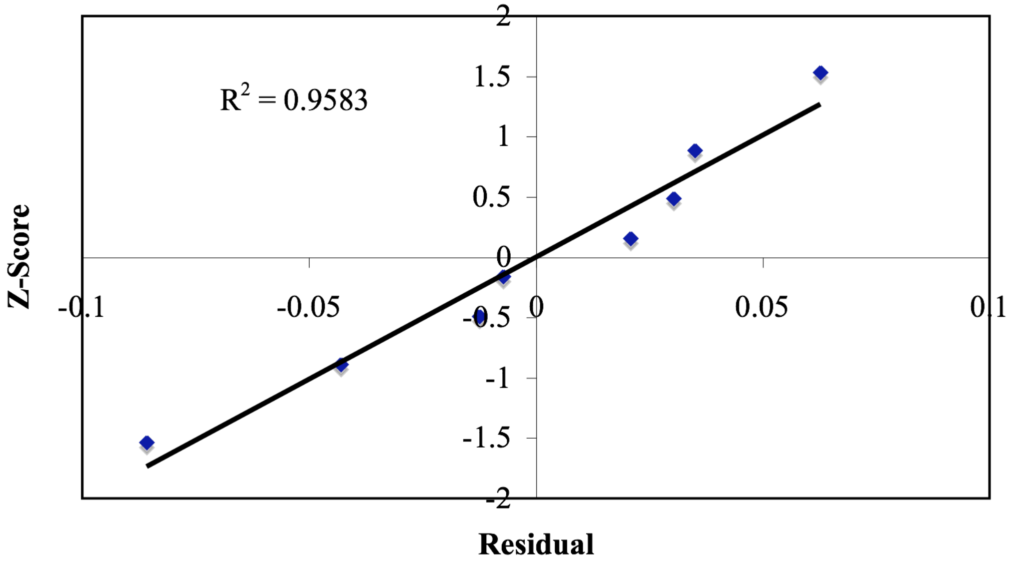
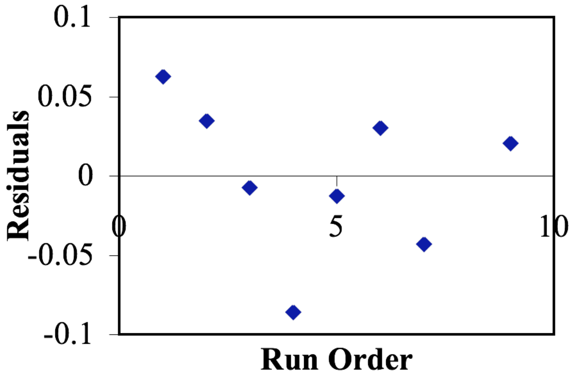
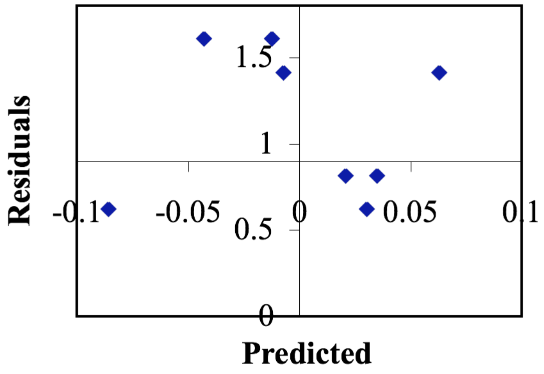


Figure 23. Normality plot of residuals based on data from the preliminary SFE experiments.

It can be seen that the error distribution is approximately normal. This normal distribution further supports the conclusion that the main effects are **A** and **C**, or mixing rate and static time. Finally, in order to verify that the independence and equality of variance assumptions are valid, a plot of (a) residuals versus run order and (b) residuals versus predicted values are shown in Figure 24.



(a)



(b)

Figure 24. Plot of residuals versus (a) run order and (b) predicted hydrocarbon yields.

Positive and negative residuals are evenly distributed in Figure 24(a), leading to the conclusion that there is no reason to suspect any violation of the independence or constant variance assumptions. Additionally, the residuals in Figure 24(b) display no obvious trends.

4.2.2.3 Test for curvature

The average for the sum of the treatment combinations used in the 2^3 preliminary factorial design is 1.1166g, whereas the average for the three center-point extractions is 1.0144g. In order to determine whether curvature is present between the (-) and (+) levels chosen for each factor tested (i.e. whether the means are statistically different), a t-test assuming unequal variances was performed. The results are displayed in Table 19.

Table 19. T-test assuming unequal variances between the average hydrocarbon yields obtained in the preliminary 2^3 factorial and center-point SFE experiments.

	Average hydrocarbon yields from 2^3 factorial	*Average hydrocarbon yields of center-point*
Mean	1.1166375	1.0144
Variance	0.191973503	0.01015437
Observations	8	3
Hypothesized Mean Difference	0	
df	9	
t Stat	0.617848191	
P(T<=t) two-tail	0.551986667	
t Critical two-tail	2.262157158	

As seen in Table 19, the p-value for a two-tailed t-test, assuming unequal variances, is 0.55. Therefore, at an α-level of 0.05, there is insufficient evidence to conclude that there is curvature between the (-) and (+) levels chosen for each factor tested.

4.2.3 Linear Regression of Mixing Rate and Static Time on Oil Yield

A linear correlation plot between mixing speed and hydrocarbon yield is shown in Figure 25. Since r^2 is 0.9035, this implies that mixing speed explains 90.4% of the variance in the observed SFE hydrocarbon yields. This imparts further evidence of the significance of mixing speed on hydrocarbon yields. On the other hand, only 5.4% of the variability on hydrocarbon yield can be explained by the static time as shown in Figure 26—indicating an increased soak time from 30 to 90 minutes does not enhance hydrocarbon yields to a great degree. Allowing sufficient mixing is much more important, than providing a prolonged static soak time, in overcoming the mass transfer resistance experienced by the 1:1 oil sand slurry at 24.1MPa and 31°C. High mixing speeds was used to break down the shielding effect caused by the presence of water, and thus increasing the exposure of the oil sand matrix to the SC-CO_2, especially for trapped hydrocarbon components.

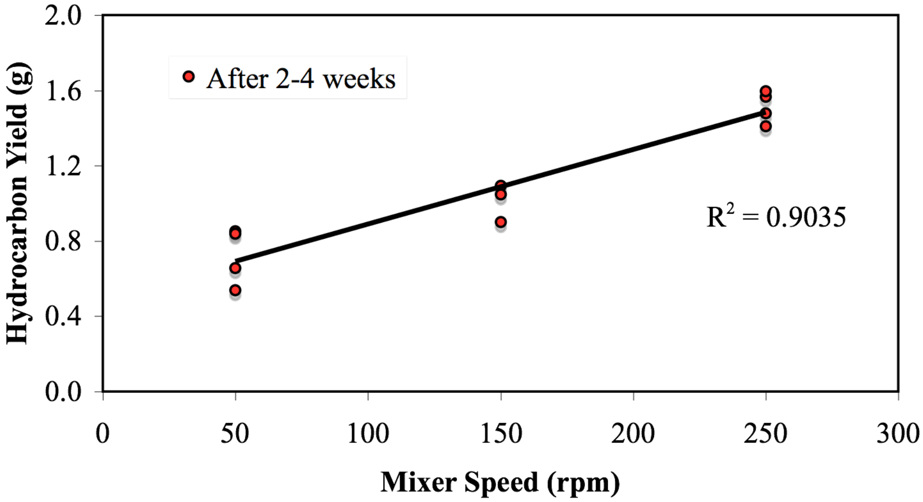


Figure 25. Linear correlation between mixing speed and hydrocarbon yield obtained by SFE.

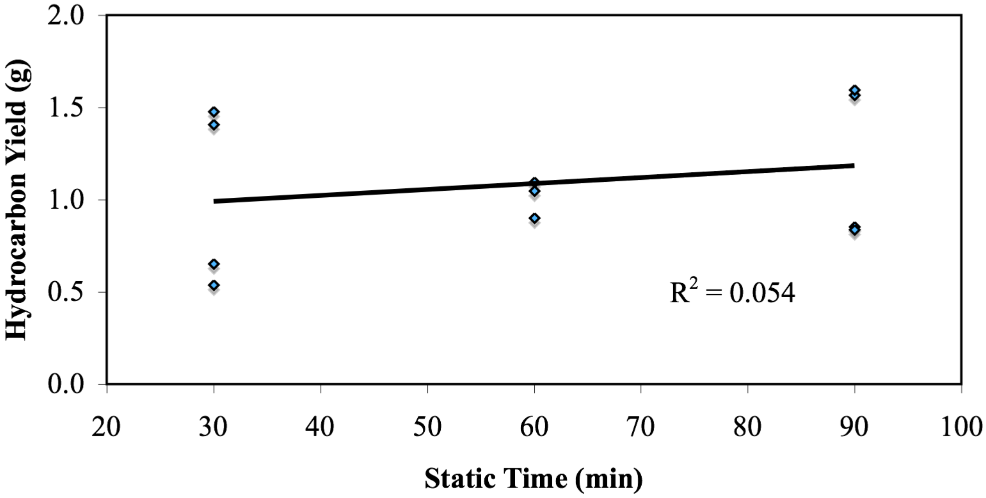


Figure 26. Linear correlation between static time and hydrocarbon yield.

These preliminary results suggest that mass transfer limitations and diffusion resistance dominates the extraction process due to the excessive water present creating an effective barrier between the trapped hydrocarbons and the SC-CO_2.

4.3 The effect of Temperature, Pressure, and Modifier Addition on the Extraction of Hydrocarbon

A 2^3 factorial experimental design was performed to directly compare the effect and influence of temperature, pressure, and the application of a modifier on SFE hydrocarbon yields. Static time and mixing rate was fixed at 1 hour and 150rpm. Flow rate was maintained at the same value used in the preliminary experiments at 40±5mL·min^{-1}. Although the highest mixing rate tested in the preliminary experiment (250rpm) provided the highest SFE hydrocarbon yield, the laboratory-scale SFE system experienced a greater tendency for clogging (slurry and bitumen entrainment) in the outlet lines during the extraction process and therefore an intermediate mixing rate, 150rpm, was selected.

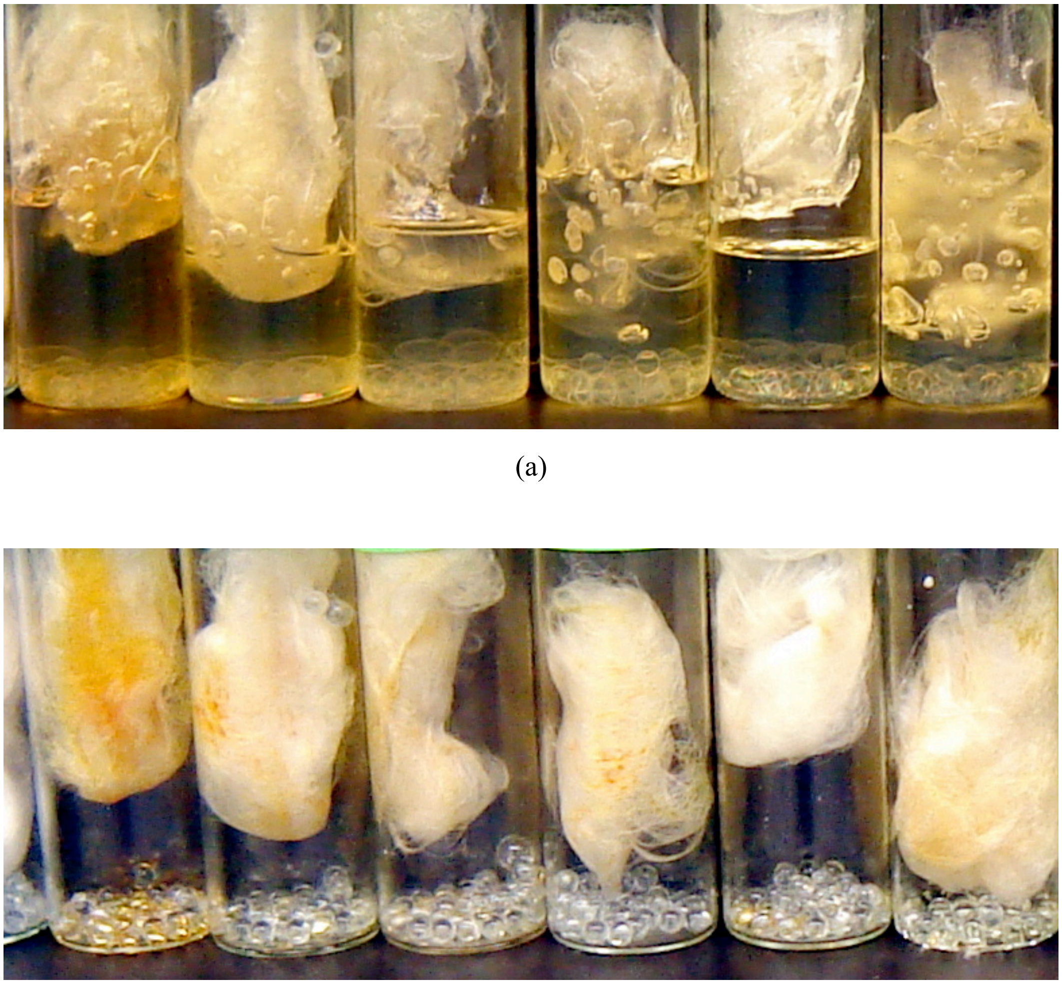
A summary of the experimental parameters tested (namely pressure, temperature, and modifier), the cumulative hydrocarbon yields obtained in triplicates, and the overall extraction efficiency for each treatment condition (excluding and including asphaltenes) are presented in Table 20.

4.3.1 SFE Hydrocarbon Yields

The next section includes a discussion of obtaining a cumulative hydrocarbon yield from each SFE experiment through air-drying in order to evaporate residual water and toluene that was also extracted via solubilization in SC-CO_2 and entrainment in the lines. Statistical analysis by ANOVA, hydrocarbon characterization of the cumulative extracts, and discussions related to the extraction efficiency are based on the air-dried hydrocarbon contents extracted by SFE.

4.3.1.1 Evaporation of Water and Toluene from Hydrocarbons Obtained by SFE

In the experiments conducted using toluene as a modifier, depending on the pressure and temperature employed in the SFE process, toluene was also extracted along with water and hydrocarbons. For consistency, all collection vials were weighed every two weeks (for a total of 6 weeks) until a constant mass was achieved. Two weeks was sufficient in evaporating the residual toluene and water (as observed in the preliminary experiments and discussed in Section 4.2.1) leaving behind the extracted hydrocarbon as seen in Figure 27.



(a)

(b)

Figure 27. SFE collection vials (a) immediately after extraction and containing toluene, water, and hydrocarbon; and (b) two weeks after extraction.

In fact, the standard deviation between the weights after two weeks (M1), after four weeks (M2), and after six weeks (M3) were observed to be <0.005g; therefore, in order to minimize potential hydrocarbon losses during the evaporation process, a final weight can be obtained between 2-4 weeks. This level of standard deviation between the masses was similarly experienced in the preliminary experiments with water only.

Table 20 shows the results from the 2^3 factorial experiments to investigate the effect of pressure, temperature, and modifier application on the extraction of hydrocarbons from a 1:1 oil sand slurry.

Table 20. Hydrocarbon yields obtained under the test conditions used in the 2^3 factorial experimental design and the extraction efficiency (including and excluding asphaltenes).

	Factor			*Hydrocarbon Yield*						*Average Extraction Efficiency*	
	A	**B**	**C**								
Treatment Condition	**P (MPa)**	**T (°C)**	**Modifier (wt%)**	**Replicate #1 (g)**	**Replicate #2 (g)**	**Replicate #3 (g)**	**Average (g)**	**Standard Deviation (g)**	**Relative Standard Deviation (%)**	**Including Asphaltenes (%)**	**Excluding asphaltenes (%)**
-1	13.8	31	0	1.2388	0.6769	0.7397	0.8851	0.3079	35%	16.5%	19.3%
a	24.1	31	0	1.1453	1.3019	1.2532	1.2335	0.0801	6%	22.5%	27.5%
b	13.8	60	0	0.4480	0.3199	0.6820	0.4833	0.1836	38%	9.6%	10.6%
ab	24.1	60	0	1.4373	1.7032	1.3778	1.5061	0.1733	12%	27.9%	33.2%
c	13.8	31	9.1	0.8269	1.2851	1.6943	1.2688	0.4339	34%	26.2%	27.9%
ac	24.1	31	9.1	2.1327	1.7082	1.9667	1.9359	0.2139	11%	37.2%	42.3%
bc	13.8	60	9.1	0.5830	0.4081	0.8327	0.6079	0.2134	35%	13.4%	13.2%
abc	24.1	60	9.1	1.9909	1.3603	1.6849	1.6787	0.3153	19%	33.7%	36.6%
Center-point	18.9	45	4.8	1.3850	1.1739	1.6107	1.3899	0.2184	16%	29.4%	30.4%

The highest yields occurred at a $\rho_{\text{SC-CO}_2}$ of 0.91g·mL^{-1} in the presence of toluene (run *ac*). If the extraction of hydrocarbon from 1:1 oil sand slurry is a direct function of the SC-CO$_2$ density alone, the order of greatest to least hydrocarbon yields in the absence of toluene is expected to be run *a* > run *(1)* > run *ab* > run *b*. Similarly, the order of greatest to least hydrocarbon yields in the presence of toluene is expected to be run *ac* > run *c* > run *abc* > run *bc*. Since run *abc* and *ab* are the second and third largest hydrocarbon yields, the results suggest that temperature may play a role in enhancing hydrocarbon yields from the 1:1 oil sand slurry. Extractions benefiting from high temperature applications have been observed in other unconventional oil extractions using SC-CO$_2$ (Al-Marzouqi et al. 2007; Yu et al. 1989; Zaki et al. 2003). Although an increase in temperature leads to a decrease in density, and hence a decrease in the solvation power of SC-CO$_2$, Tai (1985) noted that when temperature and pressure are increased together the solute vapor pressure may increase sufficiently to offset the negative effects of a decrease in density and allow greater dissolution of the hydrocarbons into the SCF-phase.

Additionally, the oil sand matrix may sufficiently trap some of the hydrocarbons through micro and macromolecular interactions and that, under higher temperature applications, the matrix undergoes thermal rearrangement and releases the trapped hydrocarbons in the SC-CO$_2$ phase. As mentioned earlier, the mixing energy applied to the oil sand slurry is intended to break any opportunities for shielding effect caused by the excess addition of water; however, the same mixing may enhance emulsification of the hydrocarbons in water, and vice versa. In this case, the application of high temperatures may be beneficial. For example, Zaki et al. (2003) found that an increase in temperature led to a parallel increase in demulsification effects.

Figure 28 is the cumulative hydrocarbon yield over the dynamic period for the highest extraction yield (*ac*) under the experimental conditions of 24.1MPa, 31°C, and 9.1wt% toluene addition.

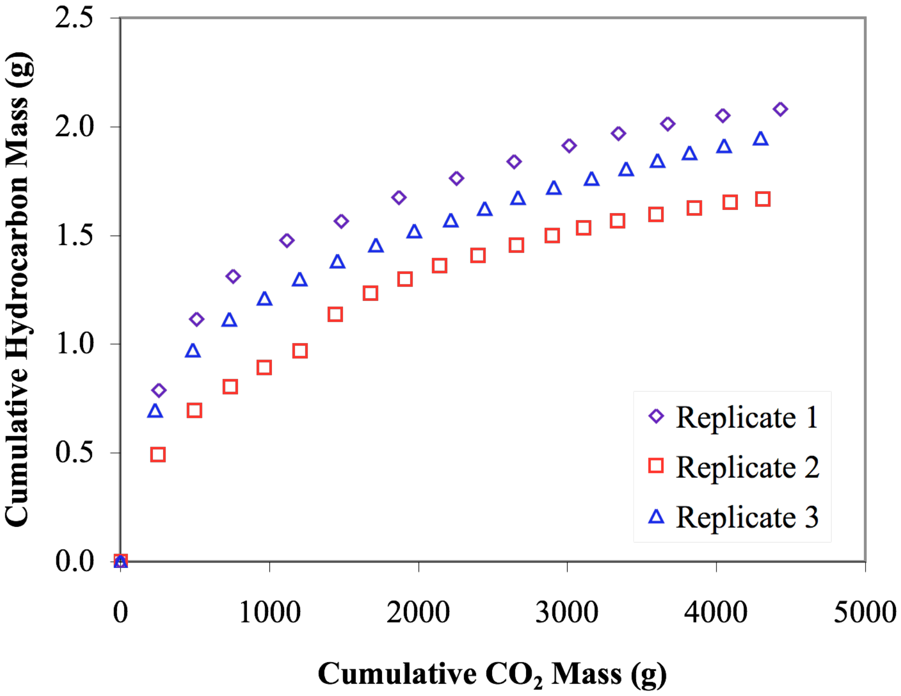


Figure 28. Cumulative mass of extracted hydrocarbons and cumulative mass of CO_2 for the experimental condition of 24.1MPa, 31°C, and 9.1wt% toluene addition.

A large degree of the hydrocarbon yield is obtained within the first 30 minutes (≈1200g cumulative CO_2) of the dynamic phase as seen by the steep slope of the curve. Saturated hydrocarbons are likely extracted during this initial phase as they are typically preferentially extracted in SFE treatments (Chung et al. 1997; Deo et al. 1993). Furthermore, samples that have been stripped of light-end hydrocarbons (as a result of photodegradation, volatilization, etc.) and are predominantly comprised of heavier organics such as olefins and aromatics are not likely to exhibit preferential extraction (Deo et al. 1992). After this point, the extraction occurs at a gentler pace and the curve begins to reach a plateau towards the end of the extraction. From this curve, it appears that exhaustive extraction may not have been reached; however, due to the small increments in cumulative mass contributions made in the latter stages of the extraction, the extraction was stopped at 1.5 hours, or approximately 3700g of CO_2.

As mentioned in Section 2.3, CO_2 preferentially extracts light end, hydrocarbons (e.g. saturates). Although a SARA analysis was not performed (aside from the sole determination of asphaltenes only), it is not likely that resin fractions were extracted in this short time frame. For instance, Chung et al. (1997) used up to 8 hours to fractionate an Athabasca oil sand vacuum residua (e.g. coker feed)—into SARA—using supercritical n-pentane. Due to the complexity and polar nature of resin hydrocarbons (NSO), SC-CO_2 may not have the solvation power to extract these compounds in an efficient time-scale. Although a modifier was used, toluene is a non-polar organic compound and its purpose is to enhance the extraction efficiency of SC-CO_2 for similarly non-polar components. A more polar modifier such as methanol could be employed in the attempt to extract the resin fraction more thoroughly; however, polar functional groups may also be extracted, including NSO, and the product would be less desirable. Another alternative is to tune the operating conditions, namely temperature and pressure, to increase the reduced density of SC-CO_2 and thereby increasing the solvation power. Unfortunately, the experimental apparatus used in this work is limited to a pressure of 25.9 MPa, as dictated by the pressure limits of the pumps. A higher density could therefore not be achieved using the current experimental apparatus.

Since SC-CO_2 leaves the polar asphaltenes behind in the extraction process, it was necessary to deduct the asphaltenes portion based on n-pentane precipitation to determine the overall extraction efficiency for each set of experimental conditions. In Table 20, the average extraction efficiency, for each experimental condition, is based on the mass of hydrocarbons recovered by SFE divided by the bitumen content (excluding and including asphaltenes). The average total bitumen (not shown in Table 20) was determined by the sum of the SFE recovered hydrocarbons and the residual hydrocarbons validated by Dean-Stark analysis. As seen in Table 20, the relative standard deviation of the bitumen yields range from 6% (for run *a*) to 38% (for run *b*). The errors contributing to these observed variations are discussed in Section 4.4.

4.3.2 Mass Recovery

A mass recovery was determined for each experimental run (Table 21) for the 2^3 factorial experimental design on pressure, temperature, and toluene-modifier application. Included in Table 21 is the hydrocarbon yield obtained by SFE and bitumen in the remaining residual slurry after SFE treatment—the sum of which is represented as the total bitumen recovered. The mass recovery is the percentage of total bitumen that can be accounted for in each experiment based on the theoretical bitumen content of 10.7wt% in the ARC oil sand.

As seen in Table 21, all experimental runs had a mass recovery greater than 74%. Low mass recoveries may be due to incomplete recovery in the collection vials, incomplete recovery of the bitumen from the slurry remaining in the vessel and incomplete recovery of any hydrocarbons remaining in the outlet lines. Further losses of hydrocarbons may have occurred during the evaporation of toluene to obtain constant weight.

Low and high mass recoveries (i.e. mass recoveries greater than 100%) may be the result of assuming that the initial oil sands samples were homogenous in bitumen content, that is all initial oil sands samples contained 10.7wt% bitumen. If the bitumen content of the original sample was less than 10.7wt%, the method of calculation of mass recovery provided in Table 21 would yield low mass recoveries. If the bitumen content of the original sample was greater than 10.7wt%, mass recoveries greater than 100% would be calculated.

Table 21. Mass recovery for 2^3 factorial experiments based on the expected bitumen content of 10.7wt%.

Treatment Condition	Replicate	SFE Yield (g)	Residuals (g)	Total Bitumen Recovered (g)	Expected Bitumen Content (g)	Mass Recovery (%)
-1	1	1.2388	4.8400	6.0788	5.4072	112%
	2	0.6769	4.5125	5.1894	5.4055	96%
	3	0.7397	4.1175	4.8572	5.3366	91%
a	1	1.1453	4.1025	5.2478	5.2899	99%
	2	1.3019	4.4925	5.7944	5.3939	107%
	3	1.2532	4.1900	5.4432	5.3825	101%
b	1	0.4480	5.0125	5.4605	5.3969	101%
	2	0.3199	4.6450	4.9649	5.3862	92%
	3	0.6820	4.0100	4.6920	5.4313	86%
ab	1	1.4373	3.8400	5.2773	5.3485	99%
	2	1.7032	3.8175	5.5207	5.5254	100%
	3	1.3778	4.0225	5.4003	5.3810	100%
c	1	0.8269	3.7775	4.6044	5.3732	86%
	2	1.2851	3.5500	4.8351	5.4016	90%
	3	1.6943	3.4050	5.0993	5.4118	94%
ac	1	2.1327	3.1550	5.2877	5.3991	98%
	2	1.7082	3.0350	4.7432	5.3926	88%
	3	1.9667	3.6100	5.5767	5.4110	103%
bc	1	0.5830	4.4725	5.0555	5.4330	93%
	2	0.4081	3.6150	4.0231	5.4203	74%
	3	0.8327	3.6775	4.5102	5.3594	84%
abc	1	1.9909	3.4975	5.4884	5.4132	101%
	2	1.3603	2.8950	4.2553	5.4179	79%
	3	1.6849	3.5025	5.1874	5.3882	96%
Center-point	1	1.3850	2.7075	4.0925	5.3958	76%
	2	1.1739	3.2525	4.4264	5.3980	82%
	3	1.6107	3.4350	5.0457	5.3755	94%

4.3.3 Statistical Analysis

4.3.3.1 ANOVA Analysis

The data was analyzed using a 2^3 ANOVA as seen in Table 22. There was a main effect of pressure, with high pressures providing greater yields than at conditions under low pressures, $F(1, 16) = 53.17$, $p<0.05$. There was also a main effect of temperature, with low temperatures providing greater yields than at high temperatures, $F(1,16) = 6.04$, $p<0.05$. Additionally, there was a main effect of toluene as a modifier, with 9.1wt% toluene providing greater hydrocarbon yields by SFE than when no toluene was added $F(1,16) = 10.54$, $p<0.05$. Finally, there was an interaction between pressure and temperature, where both a low and high temperature under high pressures provided similarly yields under the conditions tested in these experiments $F(1,16) = 6.40$, $p<0.05$.

Table 22. Analysis of variance for the 2^3 factorial experiment on SFE hydrocarbon yields.

Source	df	Mean Square	F	Sig.
Corrected Model	7	.786	11.534	.000
Intercept	1	34.561	507.258	.000
Pressure	1	3.623	53.172	.000
Toluene	1	.718	10.544	.005
Temperature	1	.412	6.045	.026
Pressure * Toluene	1	.050	.737	.403
Pressure * Temperature	1	.437	6.408	.022
Toluene * Temperature	1	.234	3.432	.082
Pressure * Toluene * Temperature	1	.027	.401	.535
Error	16	.068		
Total	24			
Corrected Total	23			

As seen in Figure 29, the main effects of **A**, **B**, and **C** are plotted against the average hydrocarbon yields. Both **A** and **C** are positive, and **B** is negative. If only these effects are considered, to maximize the hydrocarbon yields the pressure, and toluene would be run at the high level while maintaining the temperature at the low level. However, it is also necessary to examine the interaction between temperature and pressure based on their level of significance in the ANOVA results since individual effects do not have direct implications if they are involved in significant interactions.

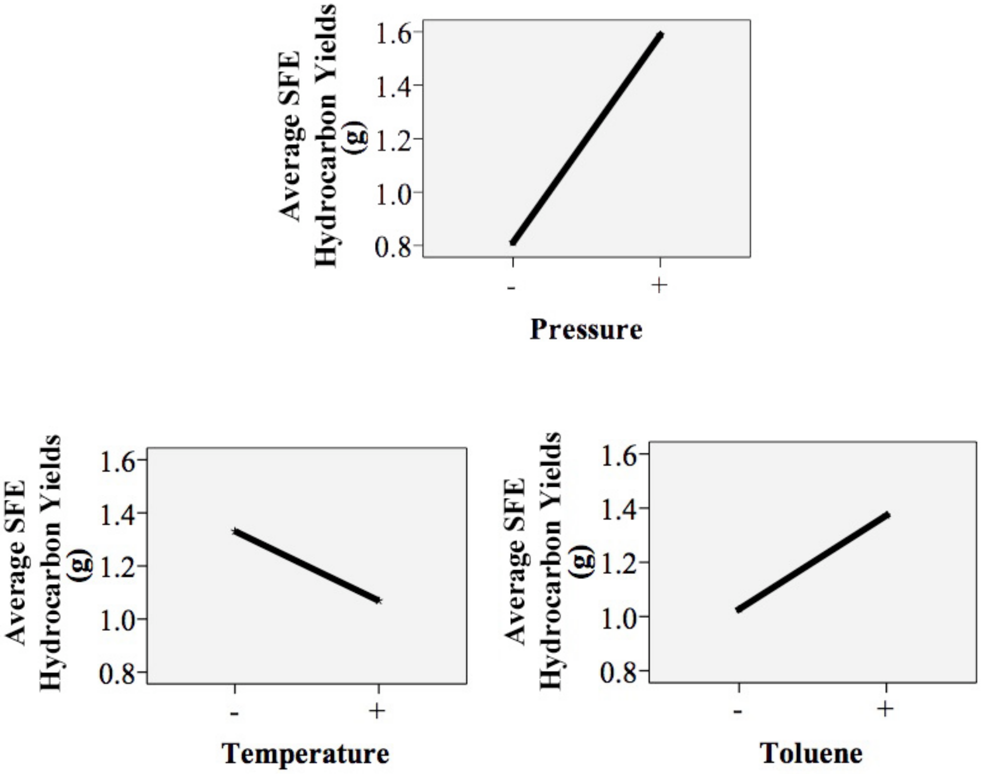


Figure 29. Main effect plots of pressure, temperature, and toluene addition on SFE hydrocarbon yields.

The interaction between pressure and temperature is displayed in Figure 30.

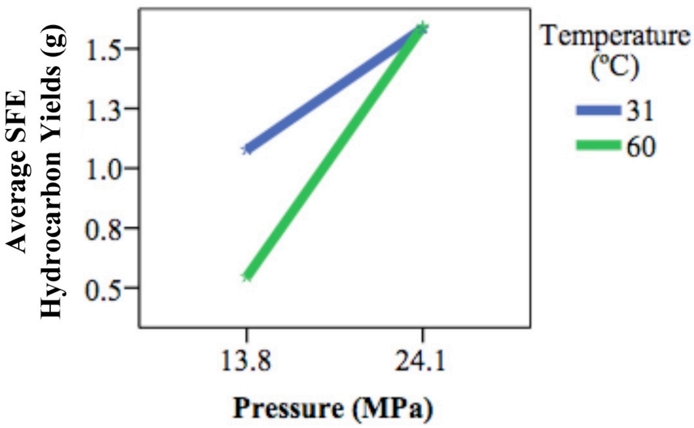


Figure 30. Interaction plot between pressure and temperature.

The **AB** interaction indicates that the temperature effect is smallest when the pressure is at the low level. The best results appear to occur at a high pressure and at either a low or high temperature level. Density effects are more important at the low pressure levels as a high temperature level results in 50% less hydrocarbon yields than at the low temperature level. Since the slope is steeper at 60°C than at 31°C, with increasing pressure, yields may be even higher by increasing temperature beyond 60°C in the presence of toluene-modifier. The dependence on a high temperature may indicate one of the following effects: an increase in the matrix porosity; a decrease in steric hindrance and physical relocation of the hydrocarbon analytes; an increase in the vapor pressure of the hydrocarbon; or a combination of the above.

4.3.3.2 Model Adequacy Check

To confirm the adequacy of the refined regression model, $\hat{y} = 1.2 + 0.3885x_1 - 0.1310x_2 + 0.1730x_3 + 0.1349x_1x_2$, a normality plot of the residuals (in Figure 31) shows that the underlying model holds up as there are no obvious outliers.

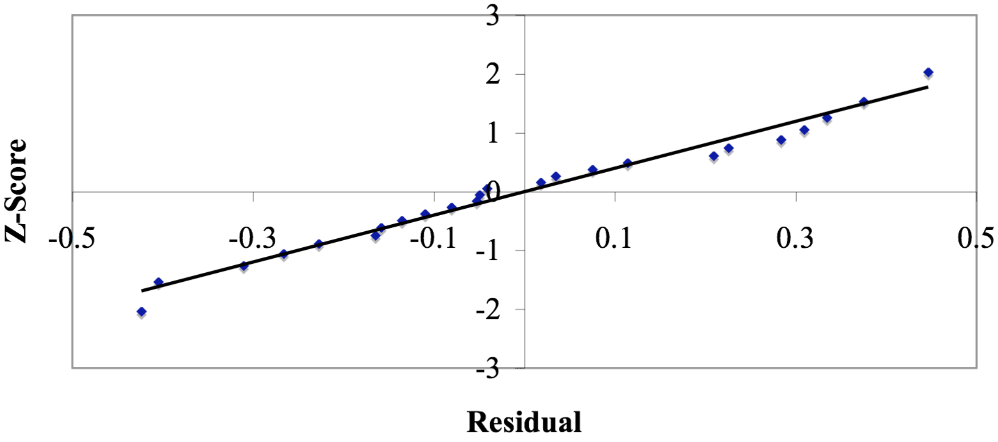
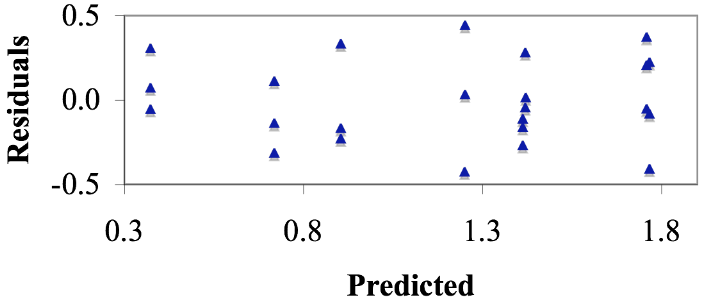


Figure 31. Normality plot of residuals based on data from the 2^3 factorial SFE experiments on T, P, and toluene addition.

Two other underlying assumptions in using ANOVA include independency of the runs and equality of variance; these are confirmed by the structureless plots of the residuals versus run order (a) and the residuals versus the predicted, $\hat{y}$, values (b), respectively, as shown in Figure 32. It is noted that the $\hat{y}$ plot, in Figure 32 (b), indicates that there is a slight tendency for the variance of the residuals to increase as the hydrocarbon yields increase; however, the model also predicts more runs to end up in the higher yield region than in the lower end and therefore a higher variance as $\hat{y}$ increases is not unreasonable.

(a)



(b)

Figure 32. Plot of residuals versus (a) run order and (b) predicted hydrocarbon yields.

4.3.3.3 Test for Curvature

The average for the 2^3 factorial design in triplicate runs for each treatment condition resulted in an overall average of 1.1999g. For the three center-point replicates, the average was 1.3899g. A t-test assuming unequal variances was performed between the hydrocarbon yields of the 2^3 factorial experiment (on P, T, and modifier application) and the three center-point experiments. The results of the t-test are displayed in Table 23.

Table 23. T-test assuming unequal variances on the 2^3 factorial hydrocarbon yields on P, T, and modifier application and the center-point experiments.

	2^3 factorial	*Center-point*
Mean	1.199908333	1.389866667
Variance	0.286461461	0.047716323
Observations	24	3
Hypothesized Mean Difference	0	
df	6	
t Stat	1.138448319	
P(T<=t) two-tail	0.29833942	
t Critical two-tail	2.446911846	

Since the p-value for the two-tailed analysis is 0.298, there is insignificant evidence of curvature between the high and low levels tested for the three factors tested (temperature, pressure, and toluene-modifier addition) at an α-level set at 0.05.

4.3.4 Hydrocarbon distribution by GC/FID

The hydrocarbon range collected in Run *ac* (24.1MPa, 31°C, 9.1wt% toluene) in the toluene-modifier SFE experiment was determined using the GC/FID. A composite sample solution was made by combining all of the extraction vials from each of two *ac* runs. The results are presented in Figure 33.

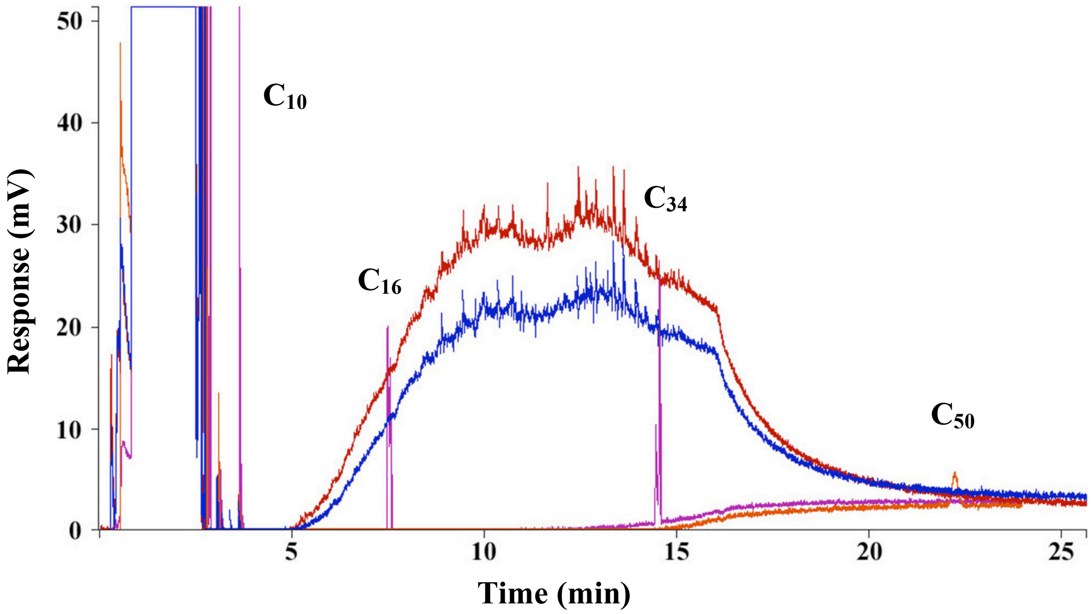


Figure 33. Hydrocarbon distribution of two composite samples obtained from the SFE experiment at 24.1MPa, 31°C and 9.1wt% toluene addition.

The red and a blue peak represent two different composite samples analyzed on the GC/FID. This analysis was strictly a qualitative analysis of the product quality as the composites were obtained by diluting the contents with an excess quantity of toluene in order to combine the samples into a composite representation. As a result, the peaks do not have the same response because they were diluted to different extents, but they both show a similar distribution. It should be noted that the average retention times for the three n-alkane standards presented in Figure 33 and Table 24 are based on results by Jones (2010).

Table 24. Average GC/FID retention times for 3 n-alkane standard solutions (adapted from (Jones 2010)).

n-Alkane	Average Retention Time (min)
n-decane	3.77
n-hexadecane	7.63
n-tetratriacontane	14.59

Both composite samples have a mid hydrocarbon range between C_{16} and C_{34}, or approximately C_{25}. This corresponds to the light gas oil (LGO) range (C_{15}-

C_{30}; 270-450°C) in petroleum fractions from which diesel and jet fuels are derived from. In fact, this fraction is also more broadly known as the wide cut gas oil, or the vacuum gas oil found in distillate fractions (C_{20}-C_{44}; 345-540°C) (Altgelt and Boduszynski 1994; Rudzinski and Aminabhavi 2000; Yoon et al. 2009). Treatment combination *ac* was further analyzed for the hydrocarbon distribution at two different time series including the initial 0-5 minutes and from 82.5-90 minutes of the dynamic extraction period (Figure 34). As seen in Figure 34, the 0-5 minutes (green curve) and the 82.5-90 minutes (red curve) curves are nearly similar in distribution and shape. One apparent difference is that the 0-5 minute sample elutes a few minutes before the 82.5-90 minute sample; thus indicating lighter hydrocarbons are present in the 0-5 minute sample and are therefore extracted at the beginning of the experiment. The complete hydrocarbon range (up to C_{50}) appears to be extracted within the first 5 minutes of extraction. These qualitative results suggest that SC-CO_2 in the presence of 9.1wt% toluene will extract up to C_{50}, centering on C_{25} with some light hydrocarbons being extracted at the beginning of the experiment.

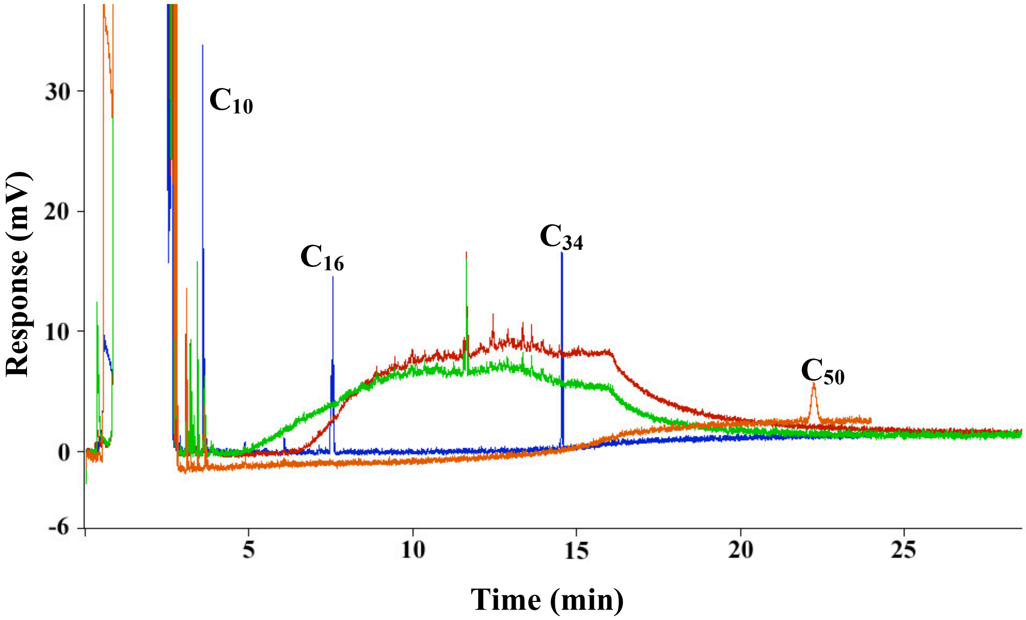


Figure 34. Hydrocarbon distribution of two time series samples from an extraction at 24.1MPa, 31°C and 9.1wt% toluene addition: 0-5minute (green line) and 82.5 to 90 minutes (red line).

4.3.5 Process-Water Chemistry

The oil sands process-water was obtained from each 1:1 slurry after SFE with SC-CO_2. As a result, it is possible to statistically analyze the water chemistry—pH, conductivity, and alkalinity—by the same 2^3 factorial design as described earlier and specifically determine whether pressure, temperature, and the absence or presence of 9.1wt% toluene-modifier affects these water chemistry parameters.

4.3.5.1 pH

The pH of the processed-water after SFE treatment is shown in Table 25. A similar pH was observed throughout all the treatment combinations, at an average pH of approximately 7. Oil sands tailings waters generally have a pH value of 7.9-8.7 (Allen 2008; Nix and Martin 1992). During the SFE experiments, the water within the vessel drops to a pH of approximately 3.5 due to the reaction of CO_2 in the carbonic acid system. As soon as the extraction is over, and the vessel is slowly depressurized, the pH of the water slowly increases as the excess dissolved CO_2 leaves the sample. On average, the amount of time required to obtain and prepare the processed-water sample for water chemistry analysis was 3-4 hours after each extraction, which was sufficient time for the pH to rise to approximately 7. The pH of the processed-water samples would likely increase further if they were allowed to sit out longer.

Table 25. Processed-water pH values from the 1:1 oil sands slurry after SFE treatment.

Treatment Combination	Run #1	Run #2	Run #3	Average	Standard Deviation
(1)	7.14	7.29	6.87	7.10	0.21
a	7.40	7.51	6.84	7.25	0.36
b	7.16	7.14	6.79	7.03	0.21
ab	6.78	7.63	7.48	7.30	0.45
c	6.86	7.33	6.74	6.98	0.31
ac	6.87	6.61	6.30	6.59	0.29
bc	7.34	7.12	6.70	7.05	0.33
abc	7.24	6.44	7.15	6.94	0.44

As seen in Table 26, the pH value of the processed-water was independent of pressure, temperature, and 9.1wt% toluene modifier as the p-value is >0.05 for these factors and their respective interactions.

Table 26. ANOVA results for pH of the oil sand processed-water in the 2^3 factorial experimental design of pressure, temperature, and toluene.

Source	df	Mean Square	F	Sig.
Corrected Model	7	.140	1.242	.338
Intercept	1	1186.242	10544.766	.000
Pressure	1	.002	.020	.890
Temperature	1	.061	.542	.472
Toluene	1	.462	4.107	.060
Pressure * Temperature	1	.057	.507	.487
Pressure * Toluene	1	.311	2.760	.116
Temperature * Toluene	1	.076	.675	.423
Pressure * Temperature * Toluene	1	.009	.082	.779
Error	16	.112		
Total	24			
Corrected Total	23			

4.3.5.2 Conductivity

Conductivity values of the processed-water samples ranged from 3.87 to 6.12mS·cm^{-1} after the SFE treatment as seen in Table 27. This is similar to the MFTs from Syncrude's Mildred Lake Settling Basin at 4.2mS·cm^{-1} (Siddique et al. 2006). Typical Athabasca oil sands processed-water possesses a conductivity value between 0.8mS·cm^{-1} to 3.6mS·cm^{-1} (Allen 2008; Gao et al. 2003; Nix and Martin 1992).

Table 27. Conductivity values for the processed-water from 1:1 oil sand slurry after SFE treatment (units are in mS·cm^{-1}).

Treatment Combination	Run #1	Run #2	Run #3	Average	Standard Deviation
(1)	3.82	5.52	5.84	5.06	1.09
a	4.64	3.69	4.17	4.17	0.48
b	3.82	4.58	4.95	4.45	0.58
ab	4.98	3.87	3.99	4.28	0.61
c	6.30	5.67	6.40	6.12	0.39
ac	3.65	4.17	3.79	3.87	0.27
bc	3.73	3.45	5.04	4.07	0.85
abc	4.24	5.14	4.20	4.53	0.53

ANOVA results for the 8 treatment combinations on conductivity are displayed in Table 28. There is a main effect between the interaction of pressure and temperature on processed-water conductivity, *F*(1, 16) = 5.81, $p<0.05$. To examine this interaction, the average conductivity response at low and high pressure (i.e. 13.8MPa and 24.1MPa) and at the two temperatures (31°C and 60°C) tested are plotted against the processed-water conductivity results (Figure 35). At the high temperature condition, an increasing pressure coincides with an increase in conductivity, while at the low temperature condition, an increasing pressure results in a decrease in conductivity, but the decrease is much more dramatic (>1mS·cm^{-1}). Conductivity is lowest and approximately at the same value, of 4.31mS·cm^{-1}, when the temperature and pressure combination is 60°C and 13.8MPa, and 31°C and 24.1MPa.

Table 28. ANOVA results for conductivity of the oil sand processed-water in the 2^3 factorial experimental design of pressure, temperature, and toluene.

Source	df	Mean Square	F	Sig.
Corrected Model	7	1.363	2.439	.066
Intercept	1	514.237	920.404	.000
Pressure	1	2.136	3.823	.068
Temperature	1	2.107	3.772	.070
Toluene	1	.463	.829	.376
Pressure * Temperature	1	3.249	5.816	.028
Pressure * Toluene	1	.025	.044	.836
Temperature * Toluene	1	.709	1.270	.276
Pressure * Temperature * Toluene	1	.850	1.522	.235
Error	16	.559		
Total	24			
Corrected Total	23			

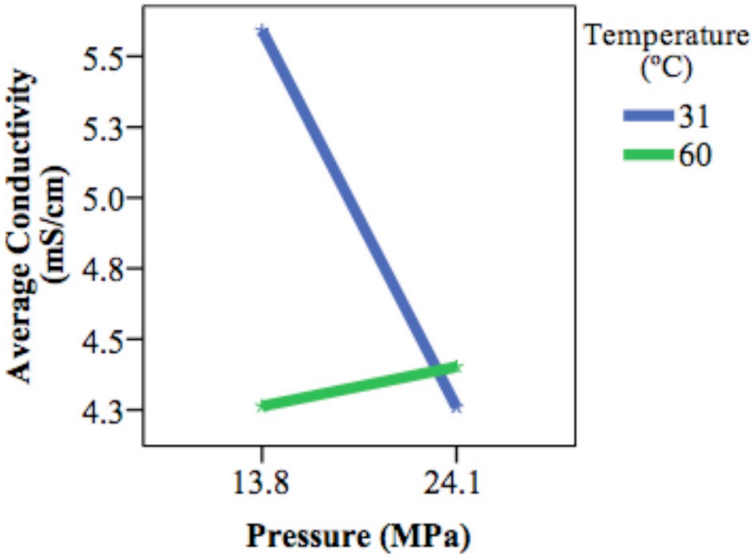


Figure 35. Interaction plot of pressure and temperature on the average conductivity of oil sands processed-water.

4.3.5.3 Alkalinity

Average alkalinity results ranged from 1481.31mg·L^{-1} to 2178.05mg·L^{-1} of $CaCO_3$ as seen in Table 29. According to Allen (2008), typically Athabasca oil sand processed-water has an alkalinity value of 635-779mg·L^{-1} of $CaCO_3$. Even lower results were found by Burchfield and Hepler (1979) for both Suncor (called the Great Canadian Oil Sands Ltd. at the time) and Syncrude at 540mg·L^{-1} of $CaCO_3$ and 230mg·L^{-1} of $CaCO_3$, respectively. A higher alkalinity has been reported in MFTs from the Mildred Lake Settling Basin of Syncrude at 1570mg·L^{-1} of $CaCO_3$ (Siddique et al. 2006). Alkalinity ANOVA results are presented in Table 30. Temperature and the interaction between pressure and temperature are statistically significant at $F(1, 16) = 11.94$, $p<0.05$ and $F(1, 16) = 8.20$, $p<0.05$. Since the temperature effect is present in the interaction, only the interaction term is to be considered. Figure 36 presents the interaction between temperature and pressure on alkalinity results. Alkalinity of the process-water decreases with increasing temperature at both low and high pressure (13.8MPa and 24.1MPa); however, the reduction appears to be steeper at the lower pressure, and lower alkalinity is achieved under low pressure and high temperature (13.8MPa and 60°C) conditions. These results are promising as they coincide with the best extraction conditions.

Table 29. Alkalinity results for the processed-water obtained from the 1:1 oil sand slurry after SFE treatment.

Treatment Combination	Run #1	Run #2	Run #3	Average	Standard Deviation
(1)	1648	2482	2402	2178	459
a	1984	1467	1719	1723	258
b	1431	1793	1714	1646	190
ab	1868	1834	1368	1690	279
c	2618	2558	2618	2598	34
ac	1458	995	1517	1323	285
bc	1499	1286	1657	1481	186
abc	1503	1979	1603	1695	250

Table 30. ANOVA results for alkalinity of the oil sand processed-water in the 2^3 factorial experimental design of pressure, temperature, and toluene.

Source	df	Mean Square	F	Sig.
Corrected Model	7	390481.855	3.827	.012
Intercept	1	8.249E7	808.522	.000
Pressure	1	358669.031	3.516	.079
Temperature	1	1.218E6	11.942	.003
Toluene	1	46690.347	.458	.508
Pressure * Temperature	1	837338.103	8.208	.011
Pressure * Toluene	1	9235.487	.091	.767
Temperature * Toluene	1	170028.282	1.667	.215
Pressure * Temperature * Toluene	1	93115.951	.913	.354
Error	16	102020.149		
Total	24			
Corrected Total	23			

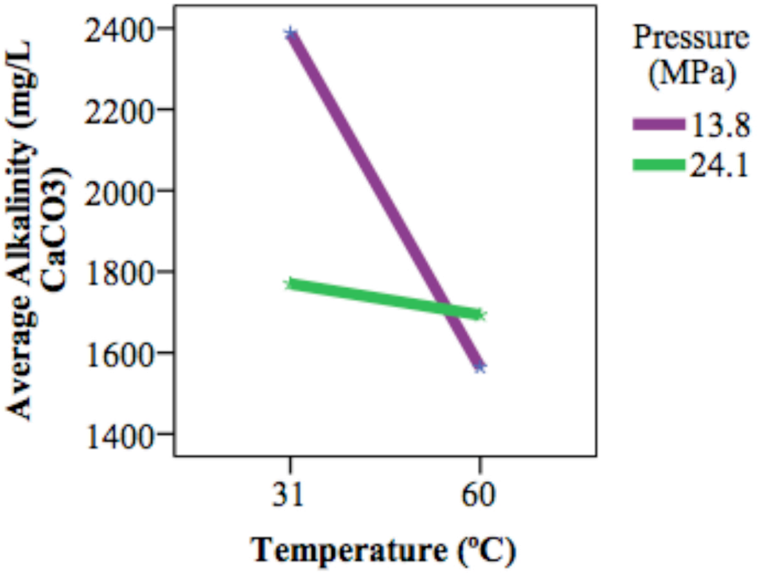


Figure 36. Interaction plot of pressure and temperature on the average alkalinity of oil sands processed-water by SFE.

4.3.5.4 Potential Changes of pH, Conductivity, and Alkalinity with Time

The pH of the processed-water sample from SFE-treatment may continue to increase as a result of CO_2(g) degassing from the solution until equilibrium conditions have been achieved. The total alkalinity should remain constant unless $CaCO_3$(s) precipitation is induced. $CaCO_3$ precipitation can potentially occur since tailings pond water is usually moderately hard at 15-25mg·L^{-1} of Ca^{2+} (Allen 2008). Initial concentrations of free Ca^{2+} are likely much higher right after extraction. Future SC-CO_2 studies on oil sand slurry should consider determining alkalinity, conductivity and pH at different time intervals after extraction to make note of the differences in these parameters as CO_2 is vented from the sample. Since there is only enough slurry sample to conduct these measurements once per extraction using a 1:1 (50g) slurry, there would need to be at least two replicates to have enough processed-water sample to obtain a measure of the water chemistry changes with time. $CaCO_3$(s) precipitation may also be occurring in surface-mining water extraction processes in the Athabasca region. Consequently, the pH, alkalinity and conductivity of a thoroughly vented SFE processed-water sample may be very similar to tailings ponds water in the Athabasca region.

4.3.5.5 Implications of Water Chemistry to Industrial Processes

The results of the above water chemistry serve as a good starting point for further studies of the processed-water chemistry. The water chemistry of the resultant slurry is important to industrial operation processes. When considering the design of a commercial-scale SFE system, important considerations include materials selection, corrosion control, and economics (Farraro and Stellina 1996). Of great concern if using SFE with SC-CO_2 in the extraction of oil sands slurry is the formation of carbonic acid due to the excess CO_2 present, which may lead to significant corrosion to the vessels and piping materials, especially if carbon steel is used (Thodla et al. 2009). Hence, stainless steels are the preferred material as a result of its corrosion-resistant properties. The disadvantage to using stainless steel is the increased cost of this material (Farraro and Stellina 1996) as compared to carbon steel.

Typically, the preferred industrial material is carbon steel for economical reasons; however, carbon steel is very susceptible to corrosion by the reactions of CO_2 (Olsen 2003). Using thicker carbon steel material to augment the corrosion allowance is a possibility. Industrial practices commonly increase the material thickness, if the rate of corrosion and the expected plant life is known (Farraro and Stellina 1996). On the downside, using thicker material adds not only to the complexity of the design (in order to ensure proper supports are in place), but incurs an additional cost for the extra material (Farraro and Stellina 1996).

Not measured in this study was the naphthenic acid content of the SFE process-water. Naphthenic acids are important in the extraction and transport of the slurry through the plant due to the vulnerability of naphthenic acids corrosion on the vessels and pipes during oil refining. Additionally, naphthenic acids have been shown to be acutely toxic to a diverse range of organisms, and therefore the processed-water cannot be released back into the environment; instead it is recycled, to a large extent, for further extraction (Yen et al. 2004).

According to Babaian-Kibala and Nugent (1999), higher alloys (i.e. increasing the content of chromium, molybdenum, titanium, nickel, etc.) can increase the resistance to naphthenic acid corrosion. Selecting the appropriate alloys requires thorough accounting of potential corrosion issues related to a selected material (Farraro and Stellina 1996). For instance, although some steel alloys are corrosion-resistant to sulfides but may be susceptible to corrosion by naphthenic acids (Kane and Cayard 1999). A high throughput rate and high temperatures of 220°C to 400°C has been determined to favor corrosion (Kane and Cayard 1999), especially at the bends, elbows, and various impingement points (Babaian-Kibala and Nugent 1999).

Another parameter not measured in this study is dissolved inorganic ions present in the processed-water, which, with increasing concentrations, will diminish the quality of the recycle water and reduce the extraction of bitumen in traditional oil sands water extraction processes (Allen 2008; Kasperski 1992). Typical dissolved ions that have been measured in tailings and recycle water include Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, $Fe^{2+/3+}$, NH_4^+, HCO_3^-/CO_3^{2-}, Cl^-, SO_4^{2-} HPO_4^{2-},

$H_2PO_4^-$, and SiO_2-derived ions (Kasperski 1992). The most abundant cation and anion is Na^+ and HCO_3^-, respectively (MacKinnon 1989). Studies of Syncrude and Suncor's tailings ponds water and recycle water has indicated the increasing concentrations of dissolved ions over time (Kasperski 1992). According to Allen (2008), this increasing concentration of dissolved ions in the tailings pond water and thus in the recycle water will ultimately lead to a decline in the extraction of bitumen from oil sand by the conventional water extraction process.

It would be desirable for future SFE studies using SC-CO_2 to monitor the quality of the processed-water and recycle water (if applicable) after achieving equilibrium conditions (i.e. once the excess CO_2 has vented out of the solution) for dissolved ions and naphthenic acid concentrations.

4.3.5.6 Quality Assurance and Control

The CO_2-free (e.g. dilution medium used in alkalinity measurements) and ultrapure water were analyzed as blanks for pH, conductivity, and alkalinity measurements of the processed-water samples. Computed average and standard deviation measurements for the 24 runs (from the 2^3 factorial experiment) are presented in Table 31.

Table 31. Average pH, conductivity, and alkalinity results for ultrapure water and CO_2-free water blanks.

	pH		**Conductivity ($\mu S\cdot cm^{-1}$)**		**Alkalinity ($mg\cdot L\ CaCO_3^{-1}$)**	
	Ultrapure	**CO_2-free**	**Ultrapure**	**CO_2-free**	**Ultrapure**	**CO_2-free**
Average	6.06	6.65	1.61	1.78	1.72	2.10
Standard Deviation	0.38	0.32	0.26	0.26	0.37	0.32

As expected, a higher pH was experienced with the CO_2-free water at 6.65±0.32. Pure water that is virtually free of CO_2 has a pH of 7. The method of CO_2 removal was by boiling, and the small amount of time required to cool the water before transferring it into a storage bottle likely resulted in the dissolution of CO_2 from the atmosphere. A second atmospheric exposure opportunity occurred while transferring from the bottle into a beaker to conduct the measurements, and exposure was unavoidable while making the readings. Ultrapur**e** water had a slightly lower pH at 6.06±0.38. Natural waters have a pH of ≈5.6 due to being in equilibrium with the CO_2 in the atmosphere.

Conductivity and alkalinity values are slightly higher in the CO_2-free water than for the ultrapure water. This is likely due to cross contamination from coming into contact with more glassware in order to boil off the CO_2. Alkalinity measurements are expected to be higher in the ultrapure water due to greater exposure to the atmosphere; however, these values for the two waters are very similar to each other and minimal such that they are not a cause for concern.

4.4 Sources of Error

4.4.1 Controlled Variables

Controlled variables in the SFE study included the amount of ARC oil sand and water placed in the extraction vessel, the mixing rate, premixing time, both the static and dynamic extraction time, the temperature and pressure used in each experiment, the CO_2 flow rate, and the modifier input rate.

The CO_2 flow rate is controlled by manual adjustments to the metering valve. A typical flow rate versus time experienced in an SFE experiment is shown in Figure 37. The first 60 minutes is a static period and the latter 90 minutes is the dynamic flow period. On average the flow rate was maintained at approximately $40mL\cdot min^{-1}$ during the dynamic phase. Where the curve dips is the time at which one of the pumps is refilled, and the other pump is flowing to maintain the CO_2 flow rate in the system. The curve rises when the pump is compressed to the desired experimental pressure.

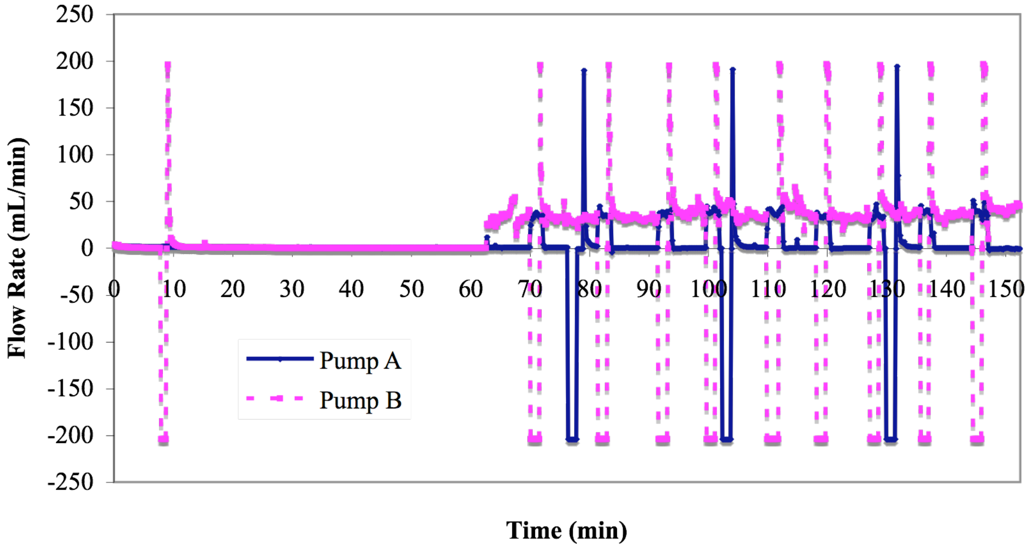


Figure 37. Flow rate data for a general SFE experiment at a flow rate of approximately 40mL·min^{-1}.

Temperature was also an experimental parameter that was manually controlled by the heated water-circulating bath, which circulated heated water around the jacket of the extraction vessel to maintain the desired extraction temperature. A typical temperature versus time plot during an SFE experiment is shown in Figure 38.

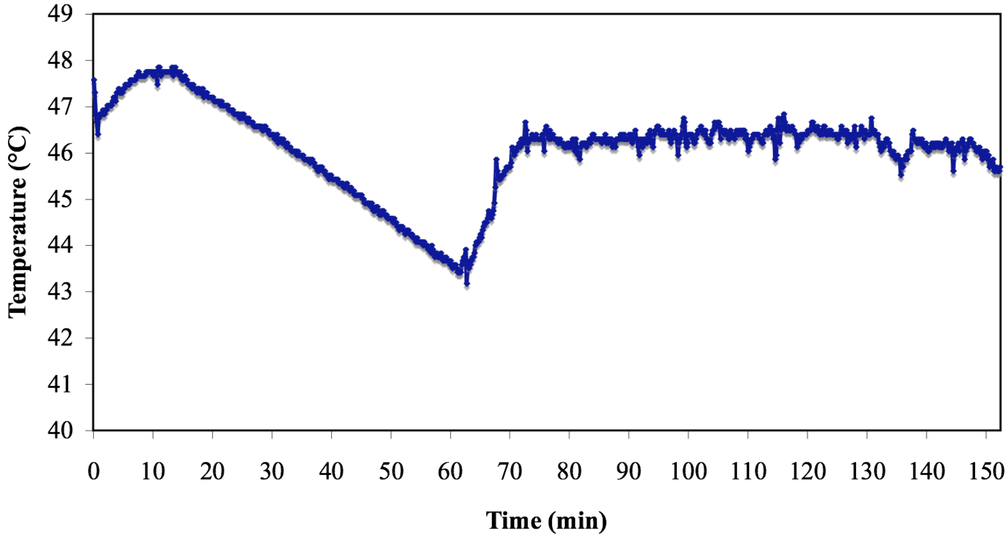


Figure 38. A general temperature profile during an SFE experiment at 18.7MPa and 45°C.

In this particular experiment, the aim was to maintain a 45°C temperature throughout the extraction. As seen, the temperature is more variable during the first 60 minutes of the static phase. Initially, when the vessel is being pressurized, a parallel increase in temperature is also observed, coinciding with the rules of the ideal gas law. However, as the system stabilizes, the temperature begins to drop to equilibrium conditions. It is therefore important to monitor the temperature of the water bath and adjust accordingly. Usually, the water bath should register ≈2°C above the desired temperature. As soon as the dynamic phase began, the temperature was maintained at approximately 46°C, which is only 1°C higher than the desired test temperature. The 1°C difference has a small effect on the density of the SC-CO_2. In this particular instance, the density of the SC-CO_2 at 18.9MPa and 44°C to 46°C contributes a relative percent difference of 1.46% towards the SC-CO_2 density (i.e. from $0.80622 g \cdot mL^{-1}$ to $0.79443 g \cdot mL^{-1}$, respectively (NIST 2008)). Therefore, the small density change due to a ± 1°C adjustment from the target temperature is not expected to impact the extraction efficiency.

In some cases, the temperature was difficult to control due to initial overheating; either too much or too little hot tap water addition at the start of the experiment; poor water circulation in the circulating bath; and malfunctioning of the water heater.

A third parameter that was physically monitored throughout the experiment was pressure. The two ISCO syringe pumps controlled the pressure in the extraction vessel. As seen in Figure 39, the pressure was maintained at the experimental test conditions very close to the target pressure of 18.9MPa throughout the experiment. During the dynamic extraction period, there was a consistent drop in the pressure relative to the static phase (from 19.07 ± 0.08MPa to 18.45 ± 0.22MPa) as the pumps attempted to maintain pressure at the $40 mL \cdot min^{-1}$ flow rate. Therefore, the density of the SC-CO_2 ranged from $0.78884 g \cdot mL^{-1}$ (at 18.45MPa and 46°C) to $0.80816 g \cdot mL^{-1}$ (at 19.07MPa and

44°C) (NIST 2008). This change in density during the extraction correlates to a relative percent difference of only 2.39%. As a result, the effect of the density changes is likely minor on the hydrocarbon extraction efficiency.

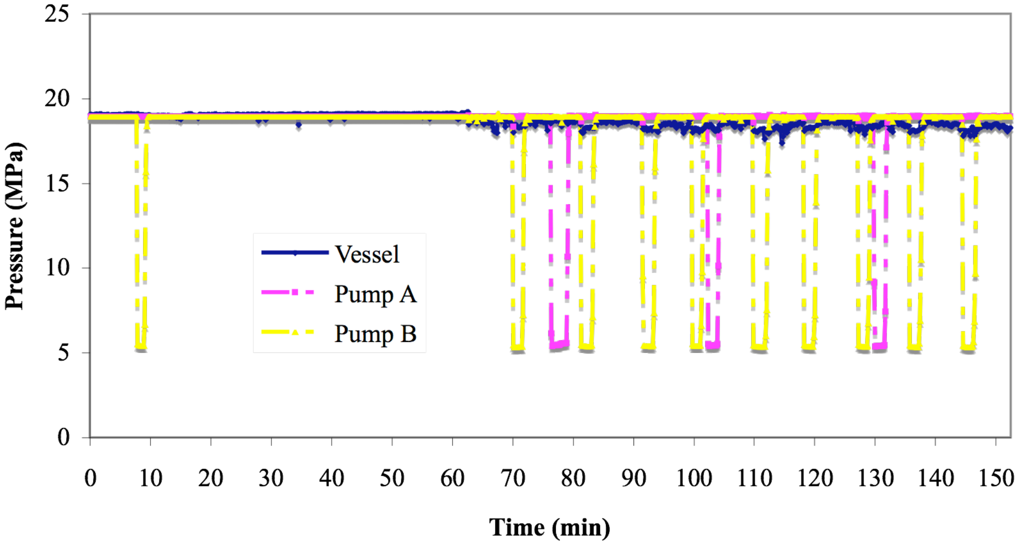


Figure 39. Pressure data of a general SFE experiment at 18.7MPa and 45° C.

The mixing rate was steady throughout the premixing interval (e.g. preliminary experiments), and during the static and dynamic extraction times. Generally, the mixing rate fluctuated approximately ± 1-2rpms from the target mixing rate of 50-250rpm. This small deviation was not considered a concern during the oil sand slurry experiments.

Timing for the premixing time, static and dynamic time, and modifier addition (especially during pressurization) was done manually using a stopwatch. In the pre-mixing experiments, the time was initiated as soon as the target mixing rate was achieved—usually taking approximately 5-10 seconds. Static time commenced as soon as the target temperature was stable in the vessel. In general, the target temperature in the vessel was reached relatively quickly at the low temperature conditions. In the higher temperature experiments, depending on how high the temperature of the water-circulating bath was at the time of pressurization, it took up to 2-5 minutes to reach the stable target temperature. Since the static time was 1 hour in total, an extra 2-5 minutes likely had no significant impact to the hydrocarbon extraction yield especially since static time only correlates to 5.4% of the variability observed on the hydrocarbon yield (as mentioned in section 4.2.3).

The dynamic extraction time varied between the modifier addition versus no modifier addition experiments. Experiments conducted with toluene application required an extra 15 seconds, where the metering valve was manually closed, each time the collection vial had to be exchanged. A higher number of exchanges, up to 17 times, were made for experiments requiring a higher rate of toluene addition. Hence, up to an additional 4.5 minutes of static time (since no flow rate occurred in the system) was added on to experiments conducted at the highest SC-CO_2 density tested (31°C and 24.1MPa). As mentioned previously, since static time only explains 5.4% of the hydrocarbon yield, an extra 4.5 minutes is likely not significant.

The Gilson pump was calibrated manually every couple of weeks using a graduated cylinder and a stopwatch. The pump rate became less accurate as the internal check valve became worn and at which point it was replaced. In general, the Gilson pump was precise and reliable during the course of the experiments.

4.4.2 Variability in the Starting Material (oil sand ore)

The ARC oil sand is a non-homogeneous mixture of sand, silt, clay, bitumen, and minor amounts of water. Each 50g of starting material used in an experiment may have had various degrees of bitumen content. For instance, if one sample contained a higher proportion of sand particles than another sample that contained a higher degree of silts and clays, it may be possible that there would be more bitumen associated with the latter sample due to the larger surface areas associated with smaller particles. Ultimately, the varying degrees of bitumen content would have affected the extraction efficiency calculations for the experiments.

4.4.3 Variability within SFE

The relative standard deviation experienced in the toluene-modifier factorial experiment ranged from a 6% to 38% (Table 20). It was observed that the carryover vial(s) within a set of replicates provided sufficient differences in mass to contribute to overall variability in the total cumulative mass. For example, treatment combination **BC** experienced 1% to 20% of the total mass extracted in the carryover vial among the different replicates. This contribution to variability from the carryover vial(s) is likely due to the strength of the seals made between the collection vials and outlet line. The seals were made using silicon and had to be resealed frequently. The silicon seals were often compromised by the toluene in experimental runs that included the application of toluene as a modifier. Typically, the seals would tear near the middle or end of the dynamic extraction period, and inevitably result in some losses of extracted hydrocarbons through leakage. Also, it is possible that, some of the hydrocarbons were also transferred past the carryover vial and vented into the fumehood; although, measures were taken to prevent this as much as possible (by exchanging the carryover vial halfway through the dynamic extraction period to prevent over-filling, for example). An abrupt flow of CO_2 may have also contributed to some loss or inadvertent carryover of hydrocarbons into the carryover vial or vented into the fumehood. Occasionally, the system would register a negative flow on the pump controllers for a few seconds before suddenly ramping up in pressure, possibly indicating a clog and the system responding to the back-pressure and thus removing the clog.

As shown in Table 21, the mass closure on the total recoverable bitumen through SFE and Dean-Stark analysis on the residuals ranged from 74 to 112%. Much of the variability was a direct result of working with oil sand slurry. The slurry was a difficult matrix to work with and hydrocarbon losses occurred during the SFE treatment by several routes and contributed to errors that were both systematic and random in nature. A common problem was the loss of bitumen slurry if the system was depressurized too quickly, resulting in the entrainment of slurry through the vessel outlet line and consequential clogging. Generally, a 2 hour period was allowed for depressurization to occur; however, the rate at which depressurization occurred was solely controlled by manually adjusting the metering valve which sometimes led to inadvertent rapid depressurization. Second, the amount adhered to the vessel wall and helical mixer was likely similar from one experiment to another, but this contributed to the overall loss of bitumen from the residual slurry mass. Other factors include deposition within the lines and volatilization as CO_2 is depressurized. Mass recoveries that were observed to be greater than 100% may be the result of the initial oil sands sample containing more bitumen than 10.7wt% due to the non-homogeneous nature of the oil sands ore. Mass recoveries greater than 100% may also be the result of solids entrainment during the Dean-Stark analysis that would result in an artificially elevated bitumen content in the residuals.

4.4.4 Variability within Dean-Stark on Raw and SFE Treated Oil Sands Slurry

Dean-Stark was performed on the raw and SFE treated ARC oil sands to determine the mass composition of solids, bitumen, and water content. There are several potential sources of error in this analysis. First, in the untreated oil sands, much of the water initially present at the time of purchase had evaporated, so less than 1mL of water was collected which could not be measured on the Dean-Stark apparatus (graduations of the water trap begin at 1mL). As a result, the volume of water was estimated by back calculation after subtracting the initial wet weight from the mass of dry solids and bitumen. Second, some of the fines (<45μm) passed through the thimbles during the Dean-Stark extraction process, into the kettle holding the bitumen and toluene solution. In determining the bitumen content, there is a likelihood that some of these fines contributed to the final estimate of the bitumen mass. Third, the high heat application may have led to the loss of light end hydrocarbons from the bitumen solution, as was experienced by Henry and Fuhr (1992).

There are also a few errors associated with the Dean-Stark validation tests on the SFE treated slurry. First, it was inevitable to have remaining residual slurry left on the inner vessel walls and helical impeller. After decanting most of the slurry after each SFE experiment, clean toluene solution was placed into the vessel and the mixer was turned on to clean off some of the remaining slurry and bitumen; however, toluene (non-polar organic solvent) cannot reduce the adherence of the hydrophilic fines and water from the vessel walls, which may contain adsorbed bitumen. Second, it was impossible to obtain an initial wet weight, as the paper thimbles (used in the Dean-Stark extraction) are not capable of holding the excess water from the slurry and the toluene rinse solution. As a result, the Dean-Stark validation tests will invariably underestimate the remaining bitumen content in the residual slurry.

Another important source of error is in the bitumen determination by gravimetry. The filter papers, used in collecting the 10mL of bitumen and toluene solution were hygroscopic and maintaining a stable reading on the analytical balance was not possible. The initial and final weight measurements were read after timing from 10-15 seconds in an attempt to maintain consistency in the weighing process in the analysis. A similar procedure was used in obtaining weight measurements for the paper thimbles used in the solids content determination.

4.4.5 Asphaltenes Precipitation

There are several systematic and random errors associated with the precipitation of asphaltenes. In order to obtain pure bitumen for this step, a Dean-Stark and a rotary evaporator step had to be employed with the potential consequence of the loss of light end hydrocarbon due to the application of heat in both cases. A random error made throughout the experiment was the exposure of the bitumen solution to light (i.e. photodegradation) (Starr et al. 1979). Due to the series of steps taken to obtain the bitumen, it was not possible to avoid exposure of the bitumen solution to light. As a result, there may have been further reduction in hydrocarbon contents in addition to the vaporization by heat (e.g. Dean-Stark extraction). It should be noted that asphaltenes obtained by the Dean-Stark method may lead to the removal of 1-3% low boiling point materials from the

Athabasca bitumen as this was experienced by Henry and Fuhr (1992). Since asphaltenes are a solubility class (as discussed in Section 2.1.2.1) and depend on the light-end hydrocarbon fractions in keeping them in solution, there may have been more asphaltenes that were inadvertently precipitated in this set of experiments.

A second error occurred in the precipitation sequence, where it was not possible to decant all of the precipitated asphaltenes. Due to the non-polar nature of n-pentane and the polar nature of the asphaltenes, the asphaltenes precipitate was prone to adhering to the glass wall of the round bottom flask, as seen in Figure 40.

Figure 40. Residual asphaltene particles remaining on the glass wall after decanting with n-pentane.

Furthermore, in the decanting process, a small amount of precipitate was observed to pass through the 2μm (pore size) glass fiber filter and into the vacuum flask. In the future, if this experiment is to be performed again, it is recommended that filters with <2μm nominal pore size be used. Finally, as mentioned in previous sections, lower carbon number solvents, such as n-pentane, tends to precipitate adsorbed resins in addition to asphaltenes (Andersen and Speight 2001). Resins would have therefore contributed to the precipitate and thereby artificially elevating the mass of asphaltenes collected.

4.4.6 Variability within Processed-Water Chemistry

Determining the amount of processed-water reclaimed by centrifugation was based on the decanted mass, which also included a small fraction of bitumen and toluene. Toluene was inevitably present in the modifier experiments, and this resulted in the presence of toluene and bitumen in the reclaimed processed-water samples, as seen in Figure 41, where bitumen and toluene droplets are dispersed throughout the water sample. Some of this was skimmed off the top by siphoning with a glass pipette, but it was impossible to eliminate this fraction in its entirety. In order to prevent the transfer of bitumen and toluene for the pH, conductivity, and alkalinity measurements, the sample was filtered through a 0.45μm filter.

Figure 41. Processed-water samples, from a toluene-modifier experiment, collected after centrifugation. Bitumen droplets and toluene is dispersed throughout the sample.

Preferably, samples are run without dilution for conductivity measurements; however, in this work samples were diluted by a factor of 4 in order to be within the calibration range of the single-point calibration standard. The samples were further diluted (by ≈8x in total) in the alkalinity measurements in order to ensure that the pH electrode was completely submerged. A potential source of error in calculating alkalinity is that the formula for alkalinity determination ignores the impact of dilution on pH, which controls the end-point in the titration. The impact to the dilution on pH is important, since the end-point (pH 4.5) is based on the total acidity of the system, and not solely due to the contribution of carbonate species. But since the total dilution of the sample is only 8x, consequently, the alkalinity measurements in this thesis are based on the assumption that the dilution effect is insignificant to the final results.

4.4.7 Variability of the hydrocarbon distribution by GC/FID Analysis

The primary source of error of the hydrocarbon distribution for the time series and the cumulative extracts is length of time the samples were sitting at ambient conditions before they were processed for analysis. As a result, hydrocarbons may have been lost due to vaporization. The time series hydrocarbon distribution was determined after 6 months of extraction, and the cumulative range was analyzed after 4-5 months of extraction.

Furthermore, n-alkane standards cannot accurately measure the molecular weight distribution of more complex hydrocarbons. For a given boiling point, n-paraffins have the highest carbon number and molecular weight (Altgelt and Boduszynski 1994). As an example, naphthenes, polynuclear aromatics, thiophenes, and pyridinones, have progressively higher boiling temperatures for a given carbon number. The true molecular weight distribution of natural bitumen is not easily measured due to the immense number of compounds of varying complexities typically present. Therefore, it is highly possible the GC/FID results have overestimated the carbon number distribution of the extracted hydrocarbons from the 1:1 oil sand slurry.

CHAPTER 5 Conclusions and Recommendations

5.1 Conclusions

This thesis investigated the use of SFE for the extraction of hydrocarbons from a 1:1 oil sand water slurry. Preliminary experiments, using the 2^3 factorial approach investigated the significance of premixing time, static time, and mixing rate on the extraction yield of hydrocarbons from a 1:1 oil sand slurry. Subsequently, 2^3 factorial experiments on temperature, pressure, and the addition of a modifier in the form of toluene, at 9.1wt%, was used to determine their effects on extraction yields from 1:1 oil sand slurry. A water chemistry analysis was performed on the slurry water thereafter, namely, for pH, alkalinity, and conductivity.

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

1. Premixing time does not have a significant effect on the extraction yield. On the other hand, a high mixing rate (250rpm) and a long static time (up to 90 minutes) has a positive effect on extraction yields. It is postulated that in the oil sand slurry, the water acts as an effective barrier between the trapped hydrocarbons and the SC-CO_2. A long static time alone is insufficient in overcoming the diffusion-resistance limitations experienced by the oil sand slurry. A high mixing rate appears to be effective at breaking the shielding effect caused by the presence of water and decreasing the mass transfer limitations in the oil sand slurry-SC-CO_2 system.
2. The density of the SC-CO_2 is important in influencing extraction yields only when the toluene-modifier is present. At a SC-CO_2 density of $0.91 g \cdot mL^{-1}$, the highest extract yield, excluding asphaltenes, was obtained (extraction efficiency of 42.3% for a 1 hour static and 1.5 hour dynamic extraction). When the toluene-modifier was not employed, the highest yield, 33.2wt% (excluding asphaltenes), was obtained under the high temperature conditions (60°C). High temperatures can lead to thermal matrix rearrangement, such as physical relocation of trapped components,

or a decrease in steric hindrance of hydrocarbon components due to an increase in matrix porosity, and an increase in volatility of the hydrocarbons.

3. Toluene-modifier application at 9.1wt% was statistically significant in increasing the extraction efficiency of hydrocarbons from the 1:1 oil sand slurry. Despite a drop in the mixing rate, to 150rpm, cumulative yields were highest when toluene-modifier was present. Therefore, the employment of the modifier helped to increase the extraction efficiency without employing high mixing rates.
4. The pH, conductivity and alkalinity of the SFE-processed-water were 7, 3.87 to $6.12 mS \cdot cm^{-1}$, and 1481.31 to $2178.05 mg \cdot L^{-1}$, respectively. With the exception of pH, conductivity and alkalinity of the processed-water is generally greater than typical oil sands processed-water by at least one order of magnitude. However, these values may change with increasing exposure to the atmosphere, allowing excess CO_2 that may be dissolved in the sample to vent from the solution and achieve equilibrium with the ambient air.
5. GC-FID results on two composite hydrocarbon extracts and a time series sample (at 0-5 minutes and 82.5-90 minutes of dynamic extraction), under the treatment combination *ac* in the toluene-modifier study, centered on C_{25}, the light gas oil range in petroleum fractions.

5.2 Recommendations

The following are recommendations pertaining to the research conducted in this thesis:

1. Higher water contents should be tested on the laboratory-scale SFE system in order to determine if increased water contents may help to decrease clogging issues during extraction and depressurization but not negatively impact the extraction efficiency results.
2. Higher temperatures, greater than 60°C, should be tested in an effort to determine if increased temperature leads to decreased mass transfer limitations.
3. A polar modifier, such as methanol, should be tested in future studies on oil sand slurries. A polar modifier may lead to increased extraction efficiencies. On the other hand, a polar modifier may also lead to the extraction of more polar hydrocarbon components (such as NSO), which would decrease the product quality.
4. If possible, it would be best to also measure the pH, alkalinity, and conductivity of the water sample after 24 hours to allow the sample to come to equilibrium with the atmosphere. Performing the measurement upon equilibrium would allow better confirmation of whether the values of these three parameters are similar to the values for typical tailings ponds water.
5. For Dean Stark extractions, it is recommended that a thimble of smaller nominal pore size be used and that toluene is not able to rise above the thimble at any given time. These two precautions would minimize the amount of entrained fines during the Dean Stark extractions, thus providing more accurate results.
6. For future product quality analysis, GC-simulated distillations to measure beyond 500°C should be employed. Elemental analysis on an elemental analyzer can deduce the elements of C, H, S, N, and O. Also, a SARA analysis should be carried out on the hydrocarbon extracted by SFE.

7. It is recommended that extractions using recycled SFE process affected water be performed. These extractions would determine the effects of any slurry water chemical properties on the extraction of hydrocarbons from oil sand slurries.
8. A more detailed water chemistry analysis should be performed on the SFE process affected-water (and/or recycled water), focusing on dissolved inorganic ions and naphthenic acids. These analyses will provide further insight on the quality of the slurry water in order to identify the applicable construction material(s) (in terms of corrosion allowance) for the reactor(s) and piping to be used on the industrial scale SFE system. The chemistry of the recycled water will provide a measurement of the dissolved ion concentration with repeated water processing, which may have an impact to the hydrocarbon extraction efficiency from oil sand.

CHAPTER 6 References

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Appendix A: SFE Procedure

Part 1. ARC Oil Sand Slurry Preparation

1. Rinse the stainless extraction vessel with ≈10mL of toluene. Using a clean paper towel and a metal spatula, wipe the inner vessel wall until the paper towel appears to be free of residual bitumen (i.e. translucent in color). Thereafter, rinse the vessel with DI water three times, if trace chemical analysis on the aqueous sample is planned, to ensure that no contaminants are carried over from previous runs into the next extraction for trace metals/inorganic ions analysis at the parts per million or parts per billion level.
2. Take note of the mass of the designated oil sand beaker (M_{beaker}). Add approximately 50g of ARC oil sand to this beaker and record this weight ($M_{beaker+oilsand}$). Decant the oil sand, in its entirety, into the vessel. Weigh the empty beaker to capture the residual oil sand left over ($M_{beaker+residual}$). Using a 50mL glass pipette (Class A), pipette 50mL of DI water into the vessel to make a 1:1 oil sand slurry. Thes mass of oil sand slurry placed into the vessel is calculated as follows:

$$M_{oilsandslurry} = M_{beaker+oilsand} - M_{beaker+residual} + 50\text{mL (DI)} \qquad \text{Equation A1}$$

3. The helical mixer will provide sufficient mixing of the oil sand slurry, once the vessel is bolted in place, prior to the introduction of CO_2.

Part 2. SFE Extraction Procedure

1. Turn on the refrigerated water-cooling system and set the temperature to 2°C in order to cool the ISCO syringe pumps to this temperature.
2. Turn on the hot water tap in order to sufficiently heat up the water prior to filling the hot-water circulating bath and hot-water bath for the metering valve. Fill the hot-water circulating bath halfway with the hot tap water if the desired temperature is 31°C, or fill it completely full if the desired temperature is 60°C. Turn on and set the hot-water bath of the metering valve to 70°C. This temperature is necessary to prevent the precipitation and solidification of water and bitumen from plugging the outlet.

3. The outlet port must be plugged with silane-treated glass wool in order to prevent the entrainment of solids. Additionally, a Teflon piece acts as a secondary barrier to solids. Ensure that the helical mixer blade is securely attached.
4. Fasten the extraction vessel to the stand and bolt the vessel to the lid. The bolts are tightened in a star pattern to ensure even attachment to the lid of the vessel. This is followed by tightening the bolts with a torque wrench in a succession of three torque values: 25, 35, and 42 ft·lbs.
5. The mixer belt is attached to the mixer motor and the MagneDrive®, and the mixer controller is set to a desired mixing speed.
6. Connect the hoses between the hot-water circulating bath and the vessel. Turn the dial on the water circulator to approximately 34°C for 31°C and 70°C for a 60°C extraction temperature. The higher value for the 60°C extraction T is to enhance the heating rate in the vessel. Once the temperature is approximately 60°C, the dial can then be readjusted to between 60 and 62°C.
7. Open the LabVIEW^{TM} software to record the temperature, pressure, and syringe pump flow rate. Save the file.
8. During the heating period, the trap vials are labeled, partially filled with glass beads and glass wool, and weighed on the analytical balance. For the dry experiments (i.e. without the use of modifiers), 9 vials are prepared: carryover, static, 6 x 15 minute time intervals, and one remaining vial for the depressurization phase.
9. Connect two vials partially filled with glass wool to the outlet lines. The CO_2 cylinder is opened and the ISCO syringe pump is refilled for pressurization. Set the pumps to the desired extraction pressure and compress to the set-point by running the pumps. As soon as the temperature in the vessel is 4°C short of the desired temperature, switch the inlet and outlet ball valves towards the bypass line and allow CO_2 to flow through the lines to flush out residual hydrocarbon from the previous run. Allow 30 seconds of flushing. *(Note: The bypass can be reserved to after the end of the extraction period; however,*

there is a possibility of partially re-pressurizing the vessel through a leaking ball valve.)

10. Connect the static and carryover vial to the outlet of the SFE system. Bring an ice water bath to the vials to inhibit the volatilization of precipitated hydrocarbon.

11. The CO_2 can now be introduced into the vessel. Switch the inlet ball valves to the vessel and direct it towards the vessel. In the application of a modifier, turn the Gilson pump on by pressing *Run* before introducing the CO_2 to the system.

12. During pressurization of the vessel, monitor the pressure on the LabVIEW™ software. The pressure in the vessel should rise to the set point (although the old pressure transducer used in this research read ≈100psi above the actual pressure in the vessel). At pressurization, the temperature in the vessel will require a little bit of time to stabilize. Static time (or the soak period) commences as soon as the temperature stabilizes to the desired target level—use a stopwatch to time this period. In this research, the static time varied between 30 and 90 minutes. During this time, the flow rate as read by the pumps should be at most < $2\text{mL}\cdot\text{min}^{-1}$. Ensure that no leaks are occurring at any of the connection points (i.e. visible bubbling in the water baths).

13. If a leak occurs, which will be notable by an audible sound, the pumps have to be stopped and the vessel is depressurized by opening the outlet ball valve. Upon depressurization, unbolt the vessel and reattach it as described in step 4. The Teflon o-ring may have to be replaced if the leak persists.

14. As soon as the static period is complete, the outlet ball valve is opened towards the metering valve. If a modifier is being used turn on the Gilson pump by selecting the *Run* button. The metering valve is carefully opened to obtain a flow rate of $40 \pm 5\text{mL}\cdot\text{min}^{-1}$ as read by the pump controllers. The stopwatch is initiated for dynamic extraction.

15. The flow rate is monitored throughout the extraction period. Adjust the metering valve as necessary to ensure a flow rate of $40 \pm 5\text{mL}\cdot\text{min}^{-1}$. Refill the pumps and run them as necessary throughout the extraction process. This is to ensure a constant supply of CO_2 passing through the vessel.

16. At every 15 minute interval, the primary trap vial is exchanged for the next trap vial. For the modifier addition extraction experiments, the vials are changed at every 5-7.5 minutes depending on the target SC-CO_2 density—to prevent overfilling of the 40 mL trap vials. In addition, the Gilson pump needs to be temporarily halted (to prevent overflow in the vessel) by pressing the *Stop* button and the metering valve needs to be closed before exchanging the primary collection vial to prevent toluene spillage. Upon removal, the trap vials are degassed of residual CO_2 for 15 minutes before recording the weight of the vial and collected hydrocarbon (and modifier when it is used). The mass of hydrocarbon extracted is then determined by taking the difference between the weight of the empty vial and the vial with the collected hydrocarbons.

17. When the 90 minute extraction time is up, stop the pumps and terminate the flow from the pumps by shutting the inlet ball valve. Allow the vessel to depressurize through the outlet ball valve. Shut down the mixer, the hot water circulator, the refrigerating water bath, and close the CO_2 cylinder.

18. Unbolt the vessel from the lid and stand. Drain both hot water baths using a siphon.

Appendix B: Dean Stark and PW Analysis

Part 1. Processed-water and Dean Stark Residual Solids Preparation

1. Decant as much slurry as possible from the vessel wall and the mixer, using a spatula, into a pre-weighed 150mL jar. Fill the vessel ¾ full with clean toluene and bring it up to the vessel lid using the mechanical hand jack. The vessel does not need to be bolted down. Attach the mixer belt onto the mixer motor. Turn on the mixer motor and the set the mixing speed to 30rpm. Allow the toluene to extract the residual toluene left on the vessel wall and on the helical mixer for 30-45 minutes.
2. Transfer the toluene and residual bitumen solution into a 500mL glass jar. Rinse the vessel and the helical mixer to collect any residual bitumen left over and add this to the 500mL glass jar.
3. Split the residual slurry into two pre-weighed Teflon centrifuge tubes (M_{cent}). Record the weight of the slurry and the centrifuge tube ($M_{cent+slurry}$). Balance each of the centrifuge tubes containing the slurry with another centrifuge tube filled with sand and water before placing them in the centrifugation machine. The mass of the oil sand slurry (M_{slurry}) is as follows:

   $$M_{slurry} = M_{cent+slurry} - M_{cent} \qquad \text{(Equation A2)}$$
4. Centrifuge at 10 000 rpm for 20 minutes. Decant the water from the oil sand solids into a pre-weighed trace-cleaned 40mL glass vial (M_{vial}) and obtain the mass of the processed-water and glass vial ($M_{vial+PW}$). If significant amount of toluene and bitumen remains, siphon it off and add it to the 500mL glass jar.
5. The mass of processed-water (M_{PW}) reclaimed from the SFE treatment can then be determined as follows:

   $$M_{PW} = M_{vial+PW} - M_{vial} \qquad \text{(Equation A3)}$$
6. Preserve a small portion of the PW for IC analysis by filtering ≈4mL of the PW using 0.2μm filters into trace cleaned IC vials, and place them into the refrigerator until ready for analysis. For IC analysis, traditional preservation by dilute acid solutions is not applicable as they may interfere with measurements of certain anions and cations (e.g. SO_4^{2-}, Cl^-, NO_3^-, NO_2^-). The

remaining PW aqueous solution is filtered through a 0.45μm filter into a 40mL vial for pH, conductivity and alkalinity measurements.

7. Obtain the weight of the oil sands solid in each centrifuge tube ($M_{cent+solids}$). Transfer the remaining solids into the original glass jar until ready for Dean Stark analysis. Rinse the centrifuge tubes with a little bit of toluene as necessary to remove as much solids and residual bitumen as possible. Record the weight of the residual solids left in the centrifuge tubes after the toluene has dried ($M_{cent+residual}$). The total amount of SFE treated solids transferred to the jar (M_{solids}) can be determined as follows:

$$M_{solids} = M_{cent+solids} - M_{cent+residual} \qquad \text{(Equation A3)}$$

Part 2. pH Measurement

1. Turn on the Accumet® pH/conductivity meter and wait for the main screen to come on. Select *Ch1*, *pH*, and finally *Single Channel* to access the main screen for making pH measurements.
2. Calibrate the Accumet® pH/conductivity meter using certified calibration standards: pH 4, pH 7, and pH 10. Take the pH glass electrode out of the electrode storage solution bottle by unscrewing the cap and carefully withdraw the glass electrode (pulling the bottle without releasing the cap may damage the junction).
3. Rinse the electrode with DI water; aiming at the junction for a few seconds. Wipe the exterior gently with a KimWipe before inserting the electrode into the pH 4 buffer solution. Select the *Standardize* icon and wait for the pH reading to stabilize. Select *Confirm* to accept the reading.
4. Ensure that the slope is >95% between each calibration point (a theoretical pH response of 59.16 $mV \cdot pH^{-1}$ unit); therefore, the millivolt difference between a pH 4 and pH 7 certified calibration standard is 177.48mV at 100%, and 168.61mV at 95%.
5. Repeat step 3 for the pH 7, and pH 10 buffer solutions.
6. If the electrode is experiencing lagged response, there may be at least one possibility: (i) the bulb may be contaminated: wash the bulb with mild soap

and warm water, followed by restabilizing the electrode in the storage solution; (ii) there may be a temperature difference between the sample and the electrode: allow the electrode to achieve the sample temperature; (iii) the sample may be nonaqueous: make 30 second reading in the sample and transfer the electrode into the pH 4 buffer for one minute in between measurements; (iv) excessive crystallization inside the electrode probe: remove the supersaturated electrolyte solution from the fill hole, dissolve precipitated crystals with 60-80°C water and refill probe with electrolyte solution (ensure refill hole is closed when the electrode is not in use to prevent this from occurring). Refer to the Fisher Scientific Accumet® pH/Temperature, Combination, Refillable Electrodes instructions manual for proper maintenance.

7. Pipette 10mL of the filtered PW into a 25mL glass vial. Insert the pH probe into the sample, make sure the junction is immersed in the sample, and record the pH.
8. Obtain a pH measurement of the CO_2-free water (i.e. dilution water for alkalinity measurements) and atmospheric-stabilized water (DI water used in the SFE treatment of 1:1 oil sand slurry). Rinse the electrode with DI water in between each readings and wipe the surface with the KimWipes.
9. Replace the pH electrode back into the electrolyte storage solution. To get back to the main screen, select *Mode*.

Part 3. Conductivity Measurement

1. On the main screen, deselect *Ch 1* before selecting *Ch 5*, *Conductivity* and *Single Channel*.
2. Remove the conductivity electrode probe from the DI storage solution. Thoroughly rinse the probe with DI water and wipe the exterior with a KimWipe.
3. Standardize the conductivity probe with a single point certified standard solution of $997\mu S\cdot cm^{-1}$. Insert the thermistor probe and the conductivity probe into the standard. Ensure the surface of the probe is completely in contact with

the solution by dipping the probe several times and the side holes are completely immersed in the sample. Select *Standardize* and a keypad will be displayed for the standard concentration to be entered. Ensure that the entered concentration value is in the correct units (i.e. $\mu S \cdot cm^{-1}$ or $mS \cdot cm^{-1}$). Allow 5× the amount of time for the thermistor probe to stabilize before reading the conductivity as measured by the conductivity electrode. Select *Confirm* to accept the single-point calibration value.

4. Take a preliminary reading of the PW conductivity and dilute the sample using CO_2-free water (i.e. the same sample is also used in the alkalinity measurements) as necessary in order for the conductivity to fall within the vicinity of the single point standard. In this research, the sample was consistently diluted 4×.
5. Use the CO_2-free water dispenser bottle to rinse the conductivity and temperature probe. Allow any residual samples adhering to the conductivity probe to fall into a glass beaker designated for alkalinity measurements.
6. Pour the diluted PW, in its entirety, into the glass beaker. Rinse the 25mL glass vial with CO_2-free and transfer the solution into the glass beaker.
7. Replace the conductivity electrode probe back into the DI water. Refill the DI water level as necessary to ensure the electrode is completely immersed. Refer to the Accumet® Conductivity Cells Instruction Manual for troubleshooting of the conductivity electrode probe.

Part 4. Alkalinity Measurement

1. Boil DI water to prepare 1L of CO_2-free water. This should be done 1-day in advance to allow the water to come to equilibrium with the room temperature.
2. Prepare 0.05N sodium carbonate solution (Na_2CO_3). Dry 3-5 g of Na_2CO_3 at 250°C for a minimum of 4 hours and allow it to cool in a dessicator. Weigh 2.5 ± 0.2g ($M_{Na_2CO_3}$) and transfer to a 1L volumetric flask. Fill to mark with distilled water (DW). Mix well.

3. Prepare a 1N sulfuric acid (H_2SO_4) acid standard. To a 1L volumetric flask, add ≈50mL of DW. Transfer 28mL of concentrated H_2SO_4 using a graduated cylinder. Dilute to the mark with DW.
4. Prepare a 0.02N H_2SO_4 standard solution. Dilute 20mL of the 1N H_2SO_4 to a 1L volumetric flask using DW or DI water. Standardize the solution by potentiometric titration using 15.00mL of 0.05N Na_2CO_3 ($V_{Na_2CO_3}$) to a 4.5 pH endpoint. Repeat this two more times. Determine the average volume of acid ($V_{H_2SO_4}$) to reach the endpoint, and calculate the corrected H_2SO_4 normality (N):

$$N = \frac{M_{Na_2CO_3} \times V_{Na_2CO_3}}{53.00 \times V_{H_2SO_4}} \qquad \text{(Equation B1)}$$

5. Return to the main screen by selecting *Mode*. Deselect *Ch5*, and select *Ch1*, *pH*, and *Single Channel*. Insert the glass pH electrode, thermistor probe, and a magnetic stirring bar into the glass beaker containing the PW sample. Ensure the junction of the pH electrode is completely immersed in the PW sample.
6. Carefully turn the dial on the magnetic stirring plate while adjusting the position of the pH glass electrode away from the magnetic stirring bar.
7. Titrate to the end point 4.5 (and 8.3 if the PW is highly alkaline) without recording intermediate pH values and without undue delay. Upon approaching the respective end points, make smaller additions and ensure that the solution comes to equilibrium before further additions. Compute the alkalinity in $mg \cdot L^{-1}$ of $CaCO_3$:

$$\textit{Alkalinity},\ mg \cdot L^{-1}\ CaCO_3 = \frac{M_{Na_2CO_3} \times N \times 50000}{\textit{mL}\ \text{sample}} \qquad \text{(Equation B2)}$$

Part 5. Dean Stark

1. Place each of 2 double thickness Whatman® paper thimbles into a pre-labeled beaker, and put 2 pieces of KimWipes into each thimble. Dry the thimbles and 2×-15cm Whatman® glass microfibre filters overnight in the oven (110°C). Cool the filters and the thimble + beaker in a dessicator.

2. Weigh the thimble + beaker on the analytical balance and record the weight ($M_{thimble+beaker}$).
3. For raw oil sands, place approximately 50g into the corresponding thimble and obtain a mass of the thimble and raw oil sands ($M_{o.s+thimble}$). For post-extracted oil sands, empty the entire jar into the corresponding thimble; wipe as much slurry as possible using the KimWipes into the thimbles. Because an excess amount of toluene is present in this jar, it is not possible to obtain a mass of the slurry. Since the amount of slurry that was placed in the jar is known, M_{solids} from Equation A3, the mass of slurry in the thimbles ($M_{residual}$) can be determined by subtracting from the residuals left in the jar ($M_{jar+residual}$):

   $$M_{residual} = M_{solids} - M_{jar+residual} \qquad \text{(Equation B3)}$$
4. Plug in the mantle and ensure that the apparatus is in the off position.
5. Support the kettle by clamping it to the stand and transfer toluene until it is level with the surface of the mantle (or ≈125mL).
6. Place the thimble into the support wire basket and attach the basket to the adapter. Cap the thimble with the distribution screen and lower the thimble into the kettle.
7. Assemble the trap and condenser and turn on the cooling water. Ensure the water is cool to the touch. Turn the dial on the heating mantle to the maximum setting (i.e. 10), or ensure that the toluene does not rise into the condenser. Ensure that the reflux rate is approximately 4-5 drops per second. Lower the heating mantle by turning down the dial if necessary.
8. Reflux the sample until all the water and bitumen have been removed from the thimble contents. This will be evident when the level of water in the trap remains constant and toluene dripping through the thimble is colorless. This step will require ≈4 hours.
9. When the extraction of raw oil sands is complete, turn the heating mantle off and turn off the water to the condensers. Continue to Step 11.
10. Keep the mantle on to collect the excess toluene from the kettle through the toluene reflux. Drain the water layer into a 25mL class A, graduated cylinder and record the volume to the first decimal place (this is the water content of

the residual slurry that was not extracted by centrifugation and minor contributions from the original oil sand). Drain the toluene from the water trap into a designated container (the toluene will contain residual water droplets and can be used for cleaning bitumen off of labware) until ≈125mL remains in the kettle. Continue to Step 12.

11. Transfer the water from the water trap into a class A graduated cylinder. Record the volume to the first decimal place. If necessary, use a stirring rod to loosen any water droplets present on the sides of the water trap.
12. Allow the apparatus to cool for a few minutes before dismantling the parts. To enhance the cooling of the bitumen collected in the kettle, raise the kettle a few inches above the mantle while securing it in place on the stand with the clamps.
13. Remove the thimble from the kettle and place it in the beaker it was originally weighed in. Dry the thimble overnight at 110°C. Cool in a dessicator.
14. Quantitatively transfer the toluene-bitumen solution from the kettle into a 250mL volumetric flask. Rinse the kettle until the toluene is clear and add the toluene to the kettle. Cool the flask to room temperature and bring up to volume with toluene and mix well.
15. Weigh two pieces of filter and record this weight (M_{filter}). Using a 10mL glass pipette, quantitatively transfer the toluene-bitumen solution onto the double-layered filters in a circular motion starting from the center. Pin the filters up on a string line in the fumehood and time for 10 minutes to allow the toluene to evaporate. Obtain a final weight of the bitumen-laden filters ($M_{filter+bitumen}$). The amount of bitumen in the sample ($M_{bitumen}$) is calculated as follows:

    $$M_{bitumen} = (M_{filter+bitumen} - M_{filter}) \times 25 \qquad \text{(Equation B4)}$$

16. Obtain the weight the dried solids ($M_{thimble+solids}$) remaining in the thimble tand calculate the weight of the dried solids ($M_{drysolids}$) by difference:

    $$M_{drysolids} = M_{thimble+solids} - M_{thimble+beaker} \qquad \text{(Equation B5)}$$

Appendix C: Asphaltenes Precipitation

Part 1. Concentrating Bitumen from Oil Sands Using Rotary Evaporation

1. For each bitumen solution to be prepared, rinse a 250mL Pyrex round bottom flask in toluene to dissolve any residual organics. An acid bath (e.g. aqua regia) can also be prepared to digest hydrocarbons in the round bottom flasks. Air dry the flask and obtain an empty weight.
2. Follow the method for Dean-Stark extraction as described in Appendix B, on 25g of bitumen.
3. Transfer the bitumen-toluene solution from the glass kettle to the 250mL round bottom flask. Fill the water bath on the rotary evaporator with demineralized water (to minimize scaling on the equipment). Heat the water bath to 55±5°C. Fasten the round bottom flask to the rotary evaporator and secure the connection with a pinch clamp.
4. Ensure that the waste container is empty and that the pinch clamp is securely attached to the condenser. Turn on the cold-water tap all the way (or set the vacuum rate with the digital control if available) and test to see if the water aspirator is functioning with sufficient suction. Seal any loose connection with Teflon™ tape as necessary.

Part 2. Asphaltenes Precipitation

1. Place a glass fiber filter of a pore size of 2μm into each 40mL Gooch crucible and muffle at 550±5°C for 1 hour, and cool in a dessicator. Weigh the crucibles to 0.0001g.
2. Obtain a weight of the round bottom flask with the concentrated bitumen (usually residual toluene was present at a theoretical volume of ≈1mL or 0.9g). To the bitumen solution, transfer 2.5mL of toluene into the round bottom flask and heat to dissolve the bitumen if necessary. Slowly add 40mL of n-pentane/n-heptane per milliliter of toluene added. Allow the asphaltenes to precipitate in the absence of light for a minimum of 2 hours.

3. While the asphaltenes are precipitating out of solution, set-up the vacuum apparatus. If a glass vacuum apparatus is used, ensure the primary filtering flask is connected to a secondary flask as a precautionary measure to ensure that fluids are not carried-over into the vacuum line. In case asphaltenes precipitate passes through the crucibles, obtain an empty weight of the primary vacuum flask.
4. Attach the Gooch crucibles to the vacuum apparatus and turn on the vacuum. Carefully decant the asphaltenes precipitate into the crucibles. Rinse out particles stuck to the round bottom flask with n-pentane as much as possible. Wash the precipitate in the crucibles with n-pentane until the effluent runs clear.
5. Dry the Gooch crucibles and the primary vacuum flask at 105±5°C for a minimum of three hours (vent off any residual n-pentane and toluene fumes prior to placing the crucibles in the oven). Reweigh and obtain the difference for the mass of asphaltenes. Convert to a mass percent based on the original bitumen (e.g. 10.7wt%) used:

$$\text{Asphaltenes (wt\%)} = \frac{\text{Mass of precipitate (g)}}{\text{Mass of oil sands (wet weight, g)} \times \text{Expected bitumen content (wt\%)}} \times 100\%$$

Appendix D: Sample Output Data from LabVIEW™

Table D1 is a small sample of the output data produced by the LabVIEW™ software. Here only 4.5 minutes of the data scan is shown. The pressure transducer, situated just before the inlet, often registered a background pressure of approximately 60±40psi higher than the set pump pressure of A and B.

Table D1. Sample output data collected on LabVIEW™.

Scan#	Time (s)	Pump (psi)	Temperature (°C)	Pressure Transducer (psi)	Pump A (psi)	Pump B (psi)
750	7511	2750	44	2814	2750	2748
751	7521	2750	44	2825	2750	2752
752	7531	2742	44	2794	2746	2709
753	7540	2750	44	2839	2750	2751
754	7550	2750	44	2820	2750	2744
755	7560	2750	44	2824	2750	2743
756	7570	2750	44	2807	2750	2751
757	7580	2750	44	2819	2750	2751
758	7590	2750	44	2818	2750	2749
759	7600	2753	44	2785	2745	2731
760	7611	2750	44	2816	2750	2750
761	7621	2750	44	2809	2750	2750
762	7631	2750	44	2803	2750	2750
763	7641	2750	44	2796	2750	2751
764	7651	2750	44	2797	2750	2751
765	7661	2750	45	2802	2750	2748
766	7671	2750	45	2791	2750	2748
767	7681	2750	45	2791	2750	2748
768	7690	2747	45	2759	2746	2742
769	7700	2750	45	2725	2750	2748
770	7710	2750	45	2723	2750	2750
771	7720	2748	45	2715	2750	2748
772	7730	2750	45	2712	2750	2747
773	7740	2750	45	2863	2750	2780
774	7751	2750	46	2858	2750	2748
775	7761	2750	46	2822	2750	2726
776	7771	2750	45	2809	2750	2750
777	7781	2750	45	2825	2750	2751