University of Alberta

Extraction of Hydrocarbons from Oil Sand Using Supercritical Carbon Dioxide

by

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Abstract

This study investigates the extraction of hydrocarbons from oil sand using supercritical carbon dioxide (SC CO_2). Experiments were carried out on three different types of oil sands. After some preliminary experiments, the feasibility of extracting hydrocarbons from oil sands by SC CO_2 was confirmed and three experimental factors (pressure, temperature and mixing rate) were identified for further study. A 2^3 factorial experimental design was used to determine the significance of each factor and the significance of the interaction of the factors on the extraction efficiency. The extraction efficiency was calculated from Dean-Stark extraction analysis and was compared to the extraction efficiency based on gravimetric analysis. The results show that the extraction efficiency increased with pressure at a constant temperature. The effect of temperature on extraction efficiency is complex. The highest extraction efficiency was obtained at the high pressure (24.1MPa), high temperature (60°C) and a mixing rate of 250rpm.

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Glossary/Nomenclature

AR - Asphalt Ridge
AMW - Average molecular weights
bpd - Barrels per day
CCR - Conradson carbon residue
CO_2 - Carbon dioxide
COTBS - Crude oil tank bottom sludge
DAO - Deasphalted oil
GC - Gas chromatographic
GC-MS - Gas chromatography-mass spectrometry
GHG - Greenhouse gas
HHVs - Higher heating values
IEA - International Energy Agency
LAH - Light aromatic hydrocarbon mixture
PAHs - Polycyclic aromatic hydrocarbons
P_C - Critical pressure
PRS - PR Spring
$P_R = P/P_C$ - Reduced pressure
$\rho_R = \rho/\rho_C$ - Reduced density
SAGD - Steam assisted gravity drainage
SARA - Saturate, Aromatic, Resin and Asphaltene analysis
SC CO_2 - Supercritical carbon dioxide
SC ethane - Supercritical ethane
SCO - Synthetic crude oil
SC pentane - Supercritical pentane
SC propane - Supercritical propane
SC water - Supercritical water
SFE - Supercritical Fluid Extraction
S/O ratio - Mass ratio of solvent to oil feed
SS - Sunnyside
T_C - Critical temperature
$T_R = T/T_C$ - Reduced temperature
WR - Whiterocks

Chapter 1 Introduction

1.1 Why Oil Sand is So Important?

Since the world population is rapidly increasing, and since both modern industry and society strongly rely on fossil fuels, the global oil demand is growing at an incredible pace. The global oil demand in 2009 was 84.8 million barrels per day (bpd) (Flood 2009). From its monthly Oil Market Report, the International Energy Agency (IEA) said that the oil demand of 2010 would increase to an average of 86.3 million bpd (Sheppard 2010). The IEA also expects that the annual global oil demand growth rate will be 1.2 percent over the next five years, and the oil demand of 2014 will exceed 91 million bpd (Flood 2009). Although every year new conventional oil reserves are discovered, these oil reserves still may not meet the increase in oil demand. From 1970 to 2000, no major oil reserves (defined as more than one billion barrels) were discovered worldwide (Pasqualetti 2009). In 2006, the annual world oil consumption was 31 billion barrels but the newly discovered oil was only 9 billion barrels (Pasqualetti 2009).

The global oil demand has continually increased, and the market price of crude oil is high. From the posted crude oil prices, the highest crude oil price, which was $126.33 per barrel, occurred in June 2008. From that time until recently, because of the negative impacts of the economic downturn in 2009, the price of crude oil was as low as $69.43 per barrel in November 2009 (WTRG Economics 2009). In the long term, however, some have predicted that the crude oil price will reach $130 per barrel in 2030 (Energy Information Administration 2009).

For these reasons, some are now looking at unconventional oil resources, for example, oil sands. Canada’s oil sands, sometimes called “black gold” (Carlisle 2005), are considered an abundant, secure and affordable source of crude oil. Almost all of Canada’s oil sands resources, which account for more than 95% of Canada’s oil reserves, are located in the province of Alberta, and are distributed in three deposits: Peace River, Cold Lake and Athabasca (Government of Alberta 2009b). In 2008, the estimate of Alberta oil sands reserves was 170.4 billion barrels, and these reserves made Canada the second largest proven oil reserve in the world, behind Saudi Arabia (Government of Alberta 2009b). Canada's National Energy Board even called the bitumen in Alberta's oil sands "one of the world's largest known deposits of liquid hydrocarbons" (Fletcher 2005).

Oil sand is a natural mixture of sand, clay or other minerals, water and bitumen. In fact, the bitumen in the oil sands is so heavy and so viscous that at room temperature, it behaves like cold molasses (Government of Alberta 2009c). After treatment, this heavy viscous oil can be upgraded to produce usable fuels such as gasoline and diesel (Government of Alberta 2009c). Depending on the depth of the oil sands reserves, there are two basic methods to recover the bitumen containing oil sands; surface mining-based operations and in-situ operations. Nearly 20% of the total 170.4 billion barrels established oil sand reserves can be recovered by surface mining methods and the remaining 80% must be recovered by in-situ methods (Government of Alberta 2009b).

1.2 Current Methods to Recover Bitumen from Oil Sands and Their Water Usage

Mineable bitumen deposits are located near the surface (i.e. up to 75 m deep) and are recovered by open-pit mining techniques (Humphries 2007). The relatively low cost and high efficiency of truck and shovel surface mining has led to this method becoming the most common oil sand surface mining method (ERCB 2009). Before the oil sands can be mined, the surface of the mining site must be cleared: wetlands are drained, rivers are diverted, and trees and vegetation are stripped from the surface, then the overburden (i.e. the material overlying the bitumen) can be stripped away (Johnson and Miyanishi 2008). Then, the oil sand is collected using giant hydraulic shovels and transported by massive trucks to the crushers. The oil sands from the trucks are dumped into crushers and mixed with water. After big chunks are broken up and well mixed with water, an oil sand slurry is generated. Then, this slurry is pumped to the facility’s extraction plant by pipeline. In the extraction facility, the bitumen is extracted from the oil sand and then subjected to upgrading. The remaining oil sand slurry forms tailings which are discharged to tailings ponds. In the end, the extraction process recovers more than 90% of the bitumen from the oil sand slurry (ERCB 2009).

In-situ recovery is used for oil sand deposits buried too deep (typically more than 75 meters below the ground surface) for mining to be practical. About 80% of the bitumen present in the oil sand reserves must be recovered by this method (Government of Alberta 2008). Unlike conventional crude oil, bitumen is very viscous and cannot flow at room temperature, so conventional oil recovery techniques cannot be adopted (Humphries 2007).

The most commonly used in-situ technology is called steam assisted gravity drainage (SAGD). In this process, high-pressure steam is injected into the oil sand formation to separate the bitumen from the sand. The process relies on the fact that, when the bitumen is heated by the injected steam, its viscosity is reduced so that it can flow into a well and be pumped to the ground surface (Humphries 2007). The process essentially involves placing two horizontal wells near the bottom of the oil formation, and these two wells are separated by a small vertical distance. High-pressure steam produced by a central facility at the ground surface is injected into the formation using the upper horizontal well. Then, a high-temperature steam chamber is formed above the upper horizontal well. Because of the high temperature, the bitumen inside the steam chamber is heated and becomes less viscous. Gravity will cause the heated bitumen and the water (from the condensed steam) to drain to the lower producer well. The mix of bitumen and water entering the lower producer well is pumped to the surface and returned to the central facility where water is separated from the bitumen and recycled to produce more steam (Alberta Chamber of Resources 2004). This in-situ technology can recover approximately 40 to 60% of bitumen in place (Fletcher 2005).

Both surface mining and in-situ recovery processes require large amounts of water to recover the bitumen. Based on the report of Mikula et al. (2008), during surface mining-based operations, in order to produce one barrel of bitumen, 12 barrels of water are needed. Although around 70% of this water is recycled, there is still a net use of about 4 barrels of water per barrel of bitumen produced (Mikula et al. 2008). For in-situ operations, every barrel of bitumen produced typically requires approximately 0.9 barrels of net water (IHS CERA Inc. 2009)[1].

Water quantity is just one aspect of the water issues related to oil sands mining and extraction. Another issue is the water quality. During surface mining-based operations, large amounts of fresh water are used to extract the bitumen from oil sands. After contacting the oil sands, fresh water becomes waste water which is placed in tailings ponds (Simieritsch et al. 2009). The water in the tailings ponds contain toxic compounds, such as naphthenic acids, asphaltenes, polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, ammonia-ammonium, phthalates, toluene and heavy metals such as mercury and iron (Allen 2008). Naphthenic acids are a naturally occurring constituent of bitumen and are soluble in water. During the bitumen extraction process, naphthenic acids move into the water and accumulate in the tailings pond water. Moreover, naphthenic acids are considered as the most significant environmental contaminant and toxic component in oil sands deposits and tailings pond water (Allen 2008). Using the current technology, each barrel of bitumen produces 2-2.5m^3 of total tailings material (Nelson 2006). Over the last 40 years of commercial oil sands development, approximately 1 billion cubic meters (35 billion cubic feet) of tailings has been produced by the oil sands industries (IHS CERA Inc. 2009).

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Currently, the oil sands industries discharge tailings directly into tailings ponds. These tailings ponds occupy nearly 30 percent of the area currently affected by mining and they are growing at an incredible pace (IHS CERA Inc. 2009). Prior to 2005, the area covered by tailings ponds was less than 50 km^2, but in 2009, this number already exceeded 130km^2 (Government of Alberta 2009a). In a recent report, the National Energy Board claimed that the principal environmental threats from tailings ponds are the migration of pollutants through the groundwater system and the risk of leaks to the surrounding soil and surface water (National Energy Board 2006).

1.3 GHG Emissions of Surface-mining and In-situ Recovery of Bitumen from Oil Sands

Another significant environmental issue related to the oil sands industry is the intensity of greenhouse gas (GHG) emissions. Three gases are considered as principal GHGs and are discharged into the atmosphere through oil production: carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (NO_2) (Clearstone Engineering Ltd 1999). Charpentier et al. (2009) reviewed thirteen studies of GHG emissions associated with oil sands operations, including some studies which investigated the GHG emissions produced in the process of mining raw oil sands through to producing synthetic crude oil (SCO). The GHG emissions of surface mining-based operations and upgrading processes range from 62 to 164kg CO_2 eq per barrel of SCO. The GHG emissions of in-situ and upgrading processes range from 99 to 176kg CO_2 eq per barrel of SCO. Both ranges are higher than the GHG emissions for conventional oil production, which ranges from 27 to

58kg CO_2 eq per barrel of SCO (Charpentier et al. 2009). These numbers show that producing SCO from oil sands is more energy intensive than producing oil from conventional reserves.

Although the 2009 emissions of GHG from Alberta’s oil sands accounted for approximately 5% of Canada’s GHG emissions, oil sands GHG emissions are growing. As production increases and if all planned projects go ahead, emissions from the oil sands may reach 8% of Canada’s total GHG emissions by 2015 (Canada's Oil Sands 2009). A report from Environment Canada (2008) showed that, in 2006, the GHG emissions from oil sands operations occupied 4% of the Canada’s total GHG emissions, but also that emissions from oil sands will rapidly increase to 12% in 2020. Moreover, over this period (from 2006 to 2020), more than 44% of the total increase of Canada’s GHG emissions would be attributed to oil sands (Environment Canada 2008).

1.4 Alternative Technologies for the Recovery of Bitumen from Oil Sands

The oil sands industry is currently seeking alternative and new technologies to recover bitumen from oil sands. Industry is seeking technologies that would reduce water use, reduce GHG emissions and slow or eliminate the production of tailings ponds. Examples of some of these technologies include using ionic liquids and organic solvents to recover bitumen from oil sands (Painter et al. 2010), solvent extraction (using reformed gasoline as solvent) (Chen et al. 2009), extracting bitumen from oil sands ore-water slurries using lime and/or ozone (Babadagli et al. 2008).

Supercritical fluid extraction (SFE) is a technique that is currently being investigated at a laboratory scale to extract bitumen from oil sands. SFE is a solvent extraction technology that uses a supercritical fluid (SCF) as a solvent. Examples of SCFs that have been used in studies with bitumen and oil sands include ethane, propane, pentane, water and CO_2. Because of the properties of SFC, the extraction conditions can be modified by changing the experimental pressure and temperature, and the extracted hydrocarbons can be easily separated by decreasing the pressure of SFC. Not like traditional oil sands recovery process, SFE process is a non-aqueous process, so these is no water used in this process and there is no waste water produce. Most of the SFCs can be recycled and reused.

1.5 Objectives of This Study

The objective of this study is to investigate the use of SC CO_2 for the extraction of bitumen from Athabasca oil sands. In particular, the objectives of this work were to:

1. prove the feasibility of using supercritical CO_2 to extract hydrocarbons from raw oil sands
2. determine the extraction efficiency of the SFE process at extracting bitumen from oil sands at specific experimental conditions.
3. explore the effects of experimental conditions, such as pressure, temperature, mixing rate, soak period, dynamic period and premixing
4. determine the optimal experimental conditions of pressure, temperature and mixing rate that yields the highest extraction efficiency

1.6 Organization of Thesis

The body of this thesis includes five chapters. Chapter 1 provides some general background information on oil sands and the oil sands technology. Chapter 2 presents a review of the relevant literature, including literature related to oil sands and oil sands surface mining technology and relevant studies that use the SFE to extract hydrocarbons from crude oil, bitumen, heavy oil, and oil sands. Chapter 3 introduces the materials and methods used in this investigation, including characterization of the oil sands, description of the experimental apparatus and description of the methods for both SFE experiments and Dean-Stark extractions. The design of the 2^3 factorial SFE experiments will also described in detail in this chapter. Chapter 4 presents the experimental results of both preliminary experiments and formal experiments, and also discusses the results and the significance of these results. The final chapter, Chapter 5, will present the conclusions of this work and will give some recommendations for future studies.

Chapter 2 Literature Review

This chapter describes the current commercial oil sands surface mining technology, introduces the concept of SCFs and SFE, and reviews some previous research on the extraction of hydrocarbons (crude oil, heavy oil, and bitumen) using SFE technology. As discussed previously, there are currently two methods used to recover bitumen from oil sands: surface mining (followed by water extraction) and in-situ methods (such as SAGD).

Since the work of this thesis focuses on applying the SFE technology to surface-mined oil sands, the literature review will focus on surface mining followed by water extraction. The review will also focus on SFE as applied ex-situ (i.e. to mined oil sands or other mined materials).

2.1 Oil Sands and Bitumen Characteristics

Before discussing the surface mining method, the general characteristics of oil sands will be discussed. There are three oil sands deposits distributed in Alberta province: the Athabasca Wabiskaw-McMurray deposit, the Cold Lake Clearwater deposit and the Peace River deposit. The Athabasca Wabiskaw-McMurray deposit contains approximately 80% of the oil reserves, and the oil reserves of other two deposits are 12% and 8% respectively (Government of Alberta 2006). Figure 2.1 is a map of the oil sands deposits of Alberta. The mineable area is shown in black and this part of the Athabasca deposit has reserves shallow enough to make surface mining feasible. The core deposits in gray show the deeper deposits that are recovered by in situ processes.

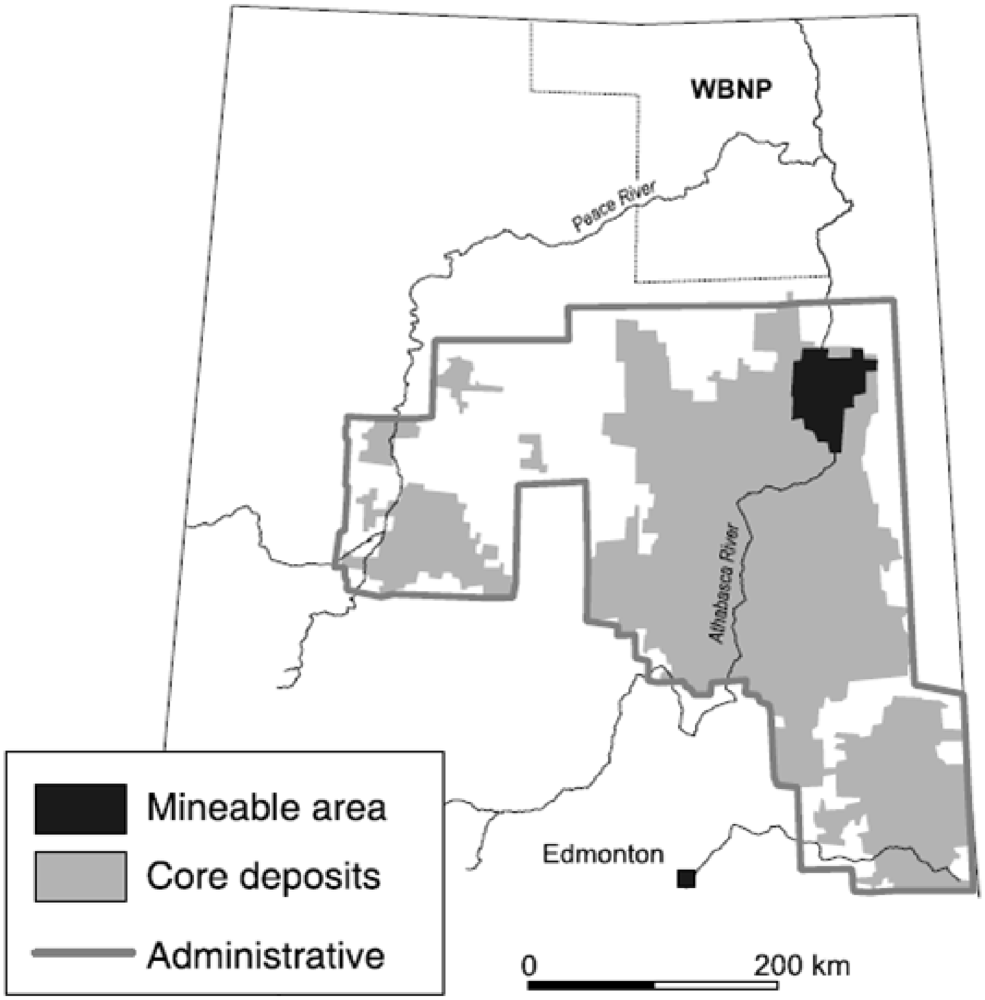


Figure 2.1: Map of Alberta's oil sands deposits (taken from Schneider 2002)

All the oil sands deposits are covered by a layer of overburden, which consists of muskeg, glacial tills, sandstone and shale. Because the characteristics and geological conditions of the different areas and deposits are different from each other, the techniques used to recovery bitumen from oil sands are different (Oil Sands Discovery Centre 2009). In the Athabasca area around Fort McMurray, the oil sands are located close the surface, so this deposit is the only area where surface-mining technology is adopted. The oil sands of other two deposits have to be recovered by underground, or using in-situ methods (Oil Sands Discovery Centre 2009). Generally, the oil sands mined from the Athabasca area are called Athabasca oil sands.

Typically, oil sand is a mixture of bitumen, water and mineral matter, and for different oil sands, the proportions of these three components vary. Take Athabasca oil sand (Ft. McMurray formation, Alberta, Canada) for example: it contains 0 wt% to 19 wt% bitumen with an average of 12 wt%. Water content ranges from 3 wt% to 6 wt%, and increases as the bitumen fraction decreases. The mineral content, which is predominantly quartz, silts and clay, is relatively constant and varies from 84 wt% to 86 wt% (Chalaturnyk et al. 2002).

The oil sand particle arrangement is very simple. In the middle of the oil sands particles are mineral sand particles, which are coated with a water envelope. Outside the water envelope is a layer of bitumen, and the bitumen layer of one particle connects to that of another particle, and causing the particles to stick together (Camp 1977). Figure 2.2 presents an arrangement of typical oil sand particles.

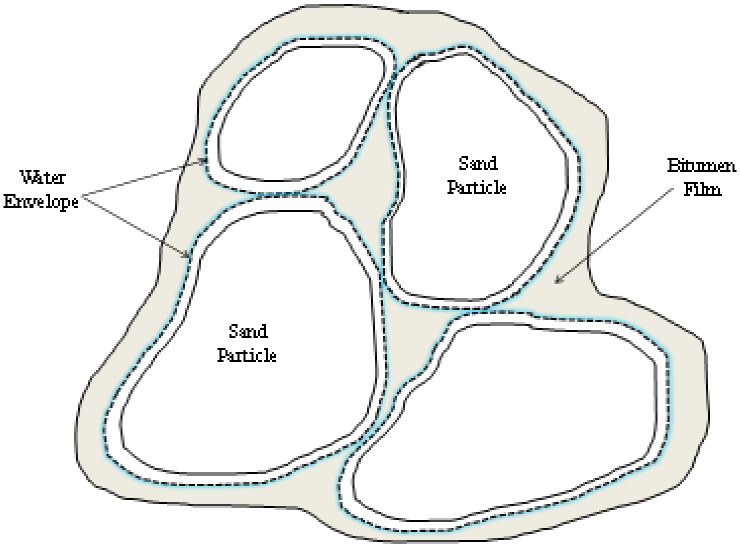


Figure 2.2: Arrangement of typical oil sand particles

The bitumen contained in the oil sands is a naturally occurring, viscous mixture of hydrocarbons. At room temperature, it behaves like cold molasses and is very hard to flow (Government of Alberta 2009c). The bitumen must be upgraded to crude oil than can be refined into common products like gasoline, kerosene, or gas oil (Oil Sands Discovery Centre). On average, bitumen consists of 83.2% of carbon, 10.4% of hydrogen, 0.94% of oxygen, 0.36% of nitrogen, and 4.8% of sulphur. It also contains small traces of nickel, iron and vanadium (Oil Sands Discovery Centre).

Currently, bitumen is extracted from oil sand by one of two methods: surface mining followed by a water extraction process or by in-situ methods. The next section will introduce surface mining and the water extraction process. In-situ methods will not be discussed further since the SFE technique described in this thesis would be applied to surface mined oil sand and not in-situ.

2.2 Surface Mining and the Water Extraction Processes

The current commercial hot water process is based on the original work of Dr. Karl A. Clark that produced more than 90% bitumen recovery with caustic (NaOH) hot water at approximately 85°C and at a pH of around 8.5 (Clark and Pasternack 1932). Figure 2.3 is a schematic of a typical commercial water extraction process plant.

The oil sands ore is transported by giant trucks from the mine to the crushers, where the oil sand lumps are broken down. Then, the crushed oil sand is sent to rotating conditioning drums and is well mixed with water and caustic (NaOH). In the conditioning drums, the slurry (50-60 wt% oil sand) is conditioned to pH 8.0-8.5 and 41-53°C temperature (Chow et al. 2008). A hydro-transport line is used to pump the slurry to the primary separation cells. During hydro-transportation, the bitumen is separated from the water and sand particles in a process called ablation (Fiscor 2009).

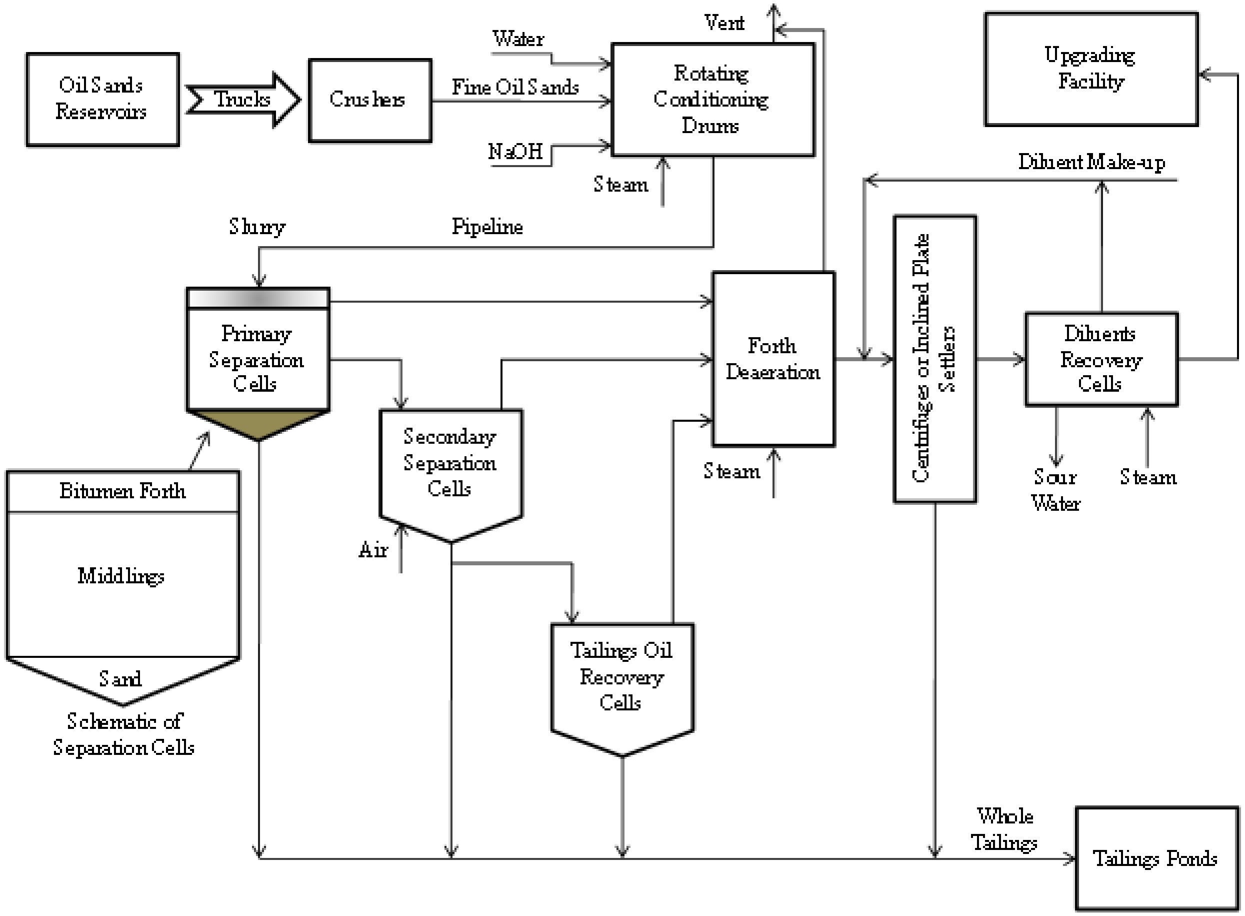


Figure 2.3: **Schematic of a typical commercial hot water process plant (adapted from Chalaturnyk et al. 2002)**

The primary separation cells are cone-bottom vessels where gravity and flotation separation occurs. In order to control the temperature of slurry and promote bitumen flotation, steam is pumped into these separation cells. In the separation cells, the slurry separates into three parts: the froth, the middlings and the coarse solids. The coarse solids settle to the bottom of the primary separation cells and are called tailings. These tailings contain 55 wt% solids (sand, clay, and fine particles), 44% water, and 1% residual bitumen, and are hydraulically transported to and deposited in tailings ponds (Chalaturnyk et al. 2002). The froth floats to the top of the primary separation cell and is a mix of water, air, solids and bitumen (60% bitumen, 10-15% solids, and 25-30% water) (Chow et al. 2008; Fiscor 2009). It is sent to the froth deaeration where more steam is introduced to reduce the viscosity of bitumen. Since the froth contains most of the bitumen, after the froth deaeration, it is subjected to a solvent extraction process to further separate water and solids from the bitumen. In this solvent extraction process, the bitumen is washed with a light hydrocarbon solvent, typically naphtha (Chow et al. 2008). In order to further separate residual water and solids from the bitumen, the froth is diluted with naphtha and passed through centrifuges, or inclined plate settlers. Finally, the froth is passed through diluent recovery cells where diluent (naphtha) is recycled, and the bitumen is sent to upgrading facility. The tailings produced from the froth treatment and tailings from other treatment processes (i.e. solids from primary and secondary separation cells, and tailing oil recovery cells) are discharged to tailings ponds.

The middlings are a blend of water, sand, bitumen, and clay. These middlings go into secondary separation cells (also called scavenger cells) to extract additional bitumen. Large amounts of air are introduced to these secondary separation cells to promote bitumen flotation. The froth produced in this process is subjected to froth treatment. Tailings oil recovery cells are used to recover residual oils in the tailings from secondary separation cells. The froth in these cells is also sent to froth treatment.

From the water extraction process described above, it can be seen that large amounts of water are needed in the extraction process. Actually, recovering one barrel of bitumen in surface mined oil sand operations needs approximately 12 barrels of water. During the process, 70% of water is recycled, but there is a net use of four barrels of water per barrel of bitumen production (Mikula et al. 2008). In Alberta, most of water used by oil sands industries is drawn from Athabasca River. In 2007, the licensed fresh water from Athabasca River for oil sands operation was 445 million m^3, which is equal to the annual water needs for a city with three million people (Alberta Environment 2007).

It can also be seen that tailings are a waste product of the water extraction process, and these tailings contain toxic compounds, naphthenic acids, PAHs, phenolic compounds, ammonia-ammonium, and heavy metals such as mercury and iron (Allen 2008). In the last 40 years, oil sands industries have produced approximately 1 billion cubic meters of tailings (IHS CERA Inc. 2009), and the oil sands industries directly discharge these tailings into tailings ponds. These tailings ponds not only occupy large amounts of land, but also bring some serious environmental threats, such as the migration of pollutants through the groundwater system and the risk of leaks to the surrounding soil and surface water (National Energy Board 2006).

Because of the drawbacks of the water extraction process, the oil sands industries are looking for other technologies that can (Alberta Chamber of Resources 2004):

- increase bitumen recovery amount and recovery rates;
- produce higher extraction efficiency with lower costs;
- be applied in any regions with any geological conditions;
- reduce the tailings production and GHG emissions; and
- reduce the fresh water usage and natural gas consumption.

2.3 The Concepts of Supercritical Fluids and Supercritical Fluid Extraction

This section introduces the concepts of SCFs and SFE and also gives the critical properties of some common supercritical solvent.

2.3.1 The concept of Supercritical Fluid

A pure component will become a SCF when its temperature and its pressure are above the critical temperature (T_C) and critical pressure (P_C). For a certain substance, P_C is the highest pressure at which an increase in temperature can convert this substance from the liquid state to the gas state. Similarly, T_C is the highest temperature at which the substance can convert from the gas state to the liquid state by increasing the pressure (Hedrick et al. 1992).

Table 2.1 lists the critical temperatures and pressures for a number of substances.

Table 2.1: Critical Properties for Various Supercritical Solvents (McHugh and Krukonis 1994)

Solvent	Critical Temperature (°C)	Critical Pressure (MPa)
CO_2	31.1	7.38
Ethane	32.3	4.88
Ethylene	9.3	5.04
Propane	96.7	4.25
Propylene	91.9	4.62
Cyclohexane	280.3	4.07
Isopropanol	235.2	4.76
Benzene	289.0	4.89
Toluene	318.6	4.11
P-Xylene	343.1	3.52
Chlorotrifluoromethane	28.9	3.92
Trichlorofluoromethane	198.1	4.41
Ammonia	132.5	11.28
Water	374.2	22.05

Based on Table 2.1, most hydrocarbons have a P_C below 5MPa with the exception of Ethylene. Some light hydrocarbons, such as ethylene and ethane, have a T_C in the range of ambient temperature (5°C - 35°C), however, cyclic aliphatics and aromatics have higher critical temperatures, close to 300°C. Because of their molecular structure, ammonia and water are polar and have strong hydrogen bonding, which causes them to have high critical temperatures or pressures. As compared to most of the compounds listed in Table 2.1, CO_2 has a moderate T_C and a slightly elevated P_C.

The guidelines for choosing ideal SCFs for extraction include (McHugh and Krukonis 1994):

- stable chemical properties, not corrosive and non-reactive
- moderate critical temperature, with the best condition being a critical temperature close to ambient temperature or typical operating temperature

- low critical pressure which will reduce costs on compression of the supercritical solvent
- high purity, strong solvent power, and reusable
- easy to obtain or produce, inexpensive, no toxicity (especially for some food or drug processes) and odor, environmentally acceptable.

Considering all of the requirements for an ideal SCF, it is not difficult to understand that why CO_2 is the most popular SCF. CO_2 is non-polar, and it has relatively low critical parameters (T_C=31.1°C, P_C=7.38MPa). This colorless, odorless fluid is also relatively inert, inexpensive, reusable, non-toxic and available in high purity (Casas et al. 2007).

The main limitation of SC CO_2 is its limited ability to dissolve polar analytes even at very high densities (Levy et al. 1993). Mobile phase selectivity and solubilizing power can be enhanced by the addition of polar organic compounds, known as modifiers, to the primary SCF phase (Levy et al. 1993). Depending on the situation, if the maximum solvent power of the primary SCF phase is not high enough to extract the components of interest, such as polar or high molecular weight compounds, then higher solubilizing power can be achieved by adding a modifier. The use of modifiers may also be necessary to overcome the physical or chemical attractions of the target solute with the sample matrix (Levy et al. 1993).

2.3.2 Comparison of the Properties of Gases, Liquids, and SCFs

The uniqueness of a SCF lies in some of its properties. Table 2.2 compares some of the properties of gases, liquids, and SCFs.

Table 2.2: Comparison of Typical SCF , Liquid, and Gas Properties (Savage et al. 1995)

	Liquid	SCF	Gas
Density (g·cm^{-3})	1	0.1-0.5	10^{-3}
Viscosity (Pa·s)	10^{-3}	10^{-4}-10^{-5}	10^{-5}
Diffusivity (cm^{2}·s^{-1})	10^{-5}	10^{-3}	1

From Table 2.2, it can be seen that the density of a SCF is hundred times greater than that of gases, but is similar to the density of liquids. On the other hand, the viscosity of a SCF is very similar to that of gas, which is much smaller than that of liquid. The diffusivity of SCF is between that of a gas and a liquid. Therefore, based on the data above, the SCF has the advantages of both gases and liquids. Like liquids, SCFs can dissolve more solute than gases, but they also has excellent fluidity and diffusivity; these gas-like transport properties make SCFs able to penetrate into a solid matrix more readily (McHugh and Krukonis 1994). SCFs exhibit physico-chemical properties intermediate between those of liquids and gases (Brunner 1994).

Another unique property of a SCF is the variation of its density as a function temperature and pressure. Figure 2.4 shows the density behaviour of a pure component in the vicinity of its critical point.

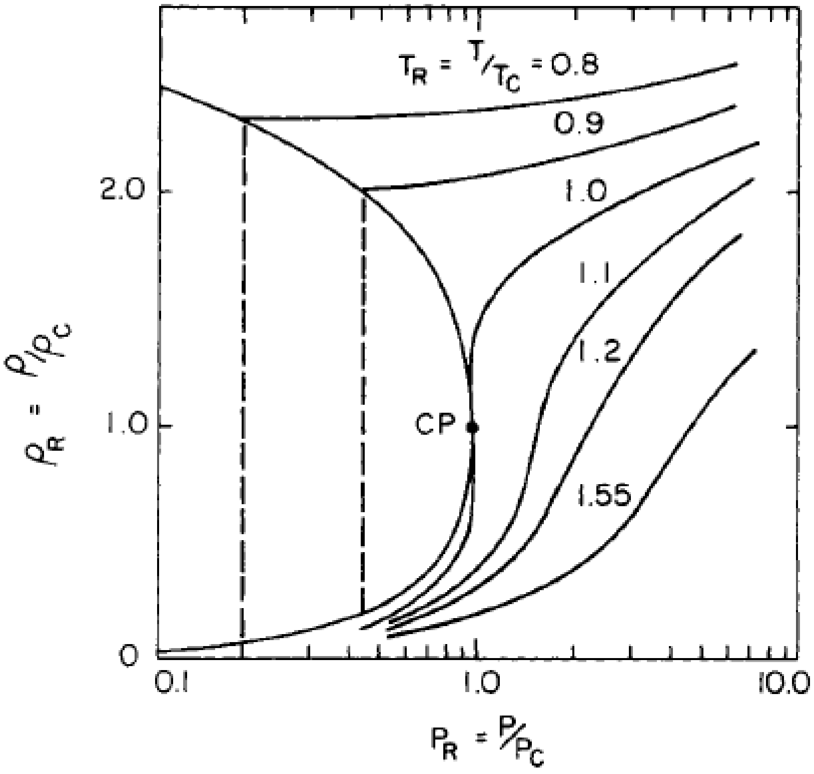


Figure 2.4: Variation of the Reduced Density (ρ_R) of a Pure Component in the Vicinity of its Critical Point (taken from McHugh and Krukonis 1994)

For a reduced temperature ($T_R = T/T_C$) range of 0.9-1.2 and at reduced pressure ($P_R = P/P_C$) greater than 1.0, the reduced density ($\rho_R = \rho/\rho_C$) of the solvent can change from gas-like values of 0.1 to liquid-like values of 2.5. As the reduced densities become liquid-like, the SCF begins to act as a liquid solvent. However, as the T_R is increased to 1.55, the SCF density decreases and in order to obtain liquid-like densities, the reduced pressures must be increased to at least as high as 10 (McHugh and Krukonis 1994). The curve corresponding to a T_R of 1 is the most interesting curve, since the slope of the curve near the critical point is close to vertical. This slope indicates that near the critical point, even very small changes of pressure will cause large changes in the solvent density. By operating in the critical region, the pressure and temperature can be used to regulate density, an important parameter in the solubility of solutes in SCFs.

Figure 2.5 describes the solubility behavior of solid naphthalene in supercritical ethylene.

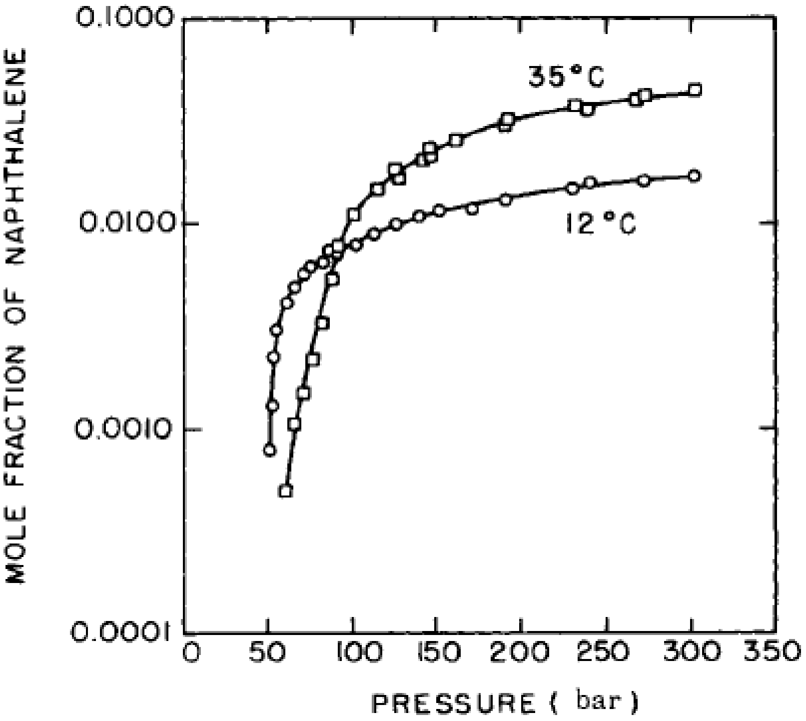


Figure 2.5: Solubility Behavior of Solid Naphthalene in Supercritical Ethylene (taken from McHugh and Krukonis 1994)

The melting temperature of solid naphthalene is 80.2°C, and the critical temperature and critical pressure of ethylene are 9.3°C and 50.5bar. At a temperature of 12°C (T_R=1.01), the solubility of solid naphthalene in supercritical ethylene increases quite dramatically as the pressure is increased to 50bar, essentially the critical pressure of ethylene. At pressures below 50bar, naphthalene solubility is extremely low, as would be expected for the solubility of a solid in a gas. At pressures much greater than about 250bar, the solubility of naphthalene in ethylene reaches a limiting value of about

7mole%. The solubility behavior along this isotherm is closely related to the variation in the ρ_R of ethylene depicted in the reduced isotherm at 1.0 in Figure 2.4. Note that the 12°C isotherm has the same characteristic shape as the reduced density isotherm at 1.0 in Figure 2.4. This example suggests that the SCF solvent strength is related to solvent density, and it is the interactions between solvent and solute molecules that determine how much solute dissolves in the SCF solvent (McHugh and Krukonis 1994).

2.3.3 Supercritical Fluid Extraction and Examples of its Application

The phenomena and behaviour of SCFs is unique and attractive and research about SCFs and their applications dates back to the 1800's. The first literature report, where SCF dissolved a large amount of relatively non-volatile materials, was published over 130 years ago (Hedrick et al. 1992). Researchers began to use SCFs to do extractions i.e. SFE. The SFE technology has developed very rapidly and is being used in more and more fields, such as the food and natural products industry, pharmaceutical industry, environmental processes, and the oil and gas industry. In food and natural products industry particularly, some applications have been commercially successful and have given rise to numerous variations and improvements, which have also been developed on an industrial scale. The first commercial SFE was performed in Germany in 1978 by Hag A.G (Palmer and Ting 1995) for the decaffeination of coffee beans. Later, in the food and natural products industry, more and more interesting applications used SC CO_2 for performing extractions such as extracting carotenoids from carrots (Sun and Temelli 2006); extracting polyphenolic compounds from grape skin (Chafer et al. 2005); extracting 2-dodecylcyclobutanone from ground beef (Gadgil et al. 2005).

Conventional pharmaceutical processing involves extensive use of organic solvents as either antisolvents for recrystallizing drugs from solutions, as reaction media in the synthesis of drugs, or as extracting agents for selectively isolating drugs from solid matrices (Bala et al. 1997). Health concerns caused by some of these solvents such as methylene chloride (Geens et al. 2007) by way of either environmental emissions and/or trace residues in the product have propelled research efforts aimed at developing "environmentally benign" processing techniques that either eliminate or significantly reduce pollution at the source (Bala et al. 1997). Because of the characteristics of SCFs, they are utilized more and more in the pharmaceutical industry. The formation of drug particles (Fages et al. 2004; Pathak et al. 2006a), using SC CO_2 either as a solvent or con-solvent and the "clean" synthesis of drug compounds using SC CO_2 as a reaction medium (Weinstein et al. 2004; Yamini et al. 2001), hold immense appeal for large-scale application in the pharmaceutical industry. Another useful application is using SCF technology to enhance drug delivery (Del Valle and Galan 2005; Pathak et al. 2006b; Shekunov et al. 2006).

Typical methods for sample preparation of environmental samples usually involve liquid-solid extraction with an organic solvent often followed by both clean-up and preconcentration stages (Barnabas et al. 1994). These methods are time consuming and costly in the amount of solvent required. Greater concern over the disposal of such toxic organic solvents and their effect on the environment has led to a move towards a cleaner extraction method (Barnabas et al. 1994). SFE has some advantages which make it an excellent environmental sample extraction method. The first one is that it requires far less time to achieve extraction and uses a fraction of the solvent (Janda et al. 1993). The second one is that the typical solvent used is CO_2 and the positive properties of CO_2 (non-toxic, high purity, low cost, and mild critical parameters) lead SFE to be a green, clean, and economic extraction method. The last one is that solvation characteristics of SCFs altered by changing either the pressure or temperature of the fluid, allows SCFs to extract target analytes selectively from a mixture.

There are many studies about treating environmental samples and remediating soil using SFE (Laitinen et al. 1994; Li et al. 2003; Librando et al. 2004; Lin et al. 2001; Morselli et al. 1998; Nagpal and Guigard 2005; Saldana et al. 2005; Zaragoza et al. 1998; Zhou et al. 2004). The matrices covered include soils and related materials, liquids and some biological samples. The analytes that have been extracted from these matrices are typical of those which are of environmental concern and include metals, pesticides, polychlorinated biphenyls, dioxins, PAHs**,** petroleum hydrocarbons and aliphatic hydrocarbons.

2.4 Supercritical Fluid Extraction of Bitumen and Heavy Oil

The work described in this thesis will discuss the use of SFE to extract bitumen from oil sand. Some research has already been done to study the extraction, upgrading and fractionation of bitumen and heavy crude oils using SCFs. Different types of supercritical solvents such as ethane, propane, pentane, water and CO_2 have been tested. The following sections will summarize some of these studies.

2.4.1 Supercritical Fluid Extraction with Carbon Dioxide

CO_2 is commonly used as a SCF. CO_2 is a colorless, odourless, non-toxic fluid that, when used in solvent extraction processes, is much more environmentally acceptable as compared to some organic solvents. CO_2 is also a relatively inert, inexpensive gas, available in high purity. CO_2 is non-polar, has a relatively low critical pressure (7.4MPa) and low critical temperature (31.1°C), close to ambient temperature. All of these advantages make CO_2 a popular SCF.

Table 2.3 summarizes some of the previous studies that used CO_2 as the SCF to extract bitumen and heavy oils from various feed material. The extraction conditions (pressure and temperature) and the types of feed material are also included in Table 2.3.

The research presented in Table 2.3 focused on extracting hydrocarbons from crude oils and bitumen using SC CO_2. Of the research listed in Table 2.3, only the studies by Rose et al. (2000) and Al-Marzouqi et al. (2007) investigated the extraction of bitumen or crude oil from a solid matrix (bitumen-sand mixture and soil spiked with crude oil). The other studies were extractions of hydrocarbons from a liquid matrix (bitumen and crude oil). The pressure in the studies presented in Table 2.3 ranged from as low as 7.6MPa to as high as 30.9MPa. The observations of effect of pressure from all research were consistent: an increase in pressure increased extraction yields (Al-Marzouqi et al. 2007; Deo et al. 1992; Guiliano et al. 2000; Hwang et al. 1995; Hwang and Ortiz 2000; Liu et al. 1999; Rose et al. 2000). All of these studies subjected known amount of feed material (i.e. crude oil, bitumen, or heavy oil) to a SFE experiment. Hwang and Ortiz (2000) and Al-Marzouqi (2007) calculated the extraction efficiency by using the weight losses of the sample during the SFE divided by the weight of initial feed. The remaining studies in Table 2.3 defined the extraction yield as a percentage of the cumulative extracted hydrocarbons from the initial feed.

Table 2.3: Summary of research investigating the use of SC CO_2 to extract hydrocarbons

Feed Material	Modifier(s)	Extraction Pressure (MPa)	Extraction Temperature (°C)	Reference
Crude Oil	None	7.6,10.3,17.2, 24.0 and 30.9	30.85, 37.85, 65.85 and 92.85	Deo et al. (1992)
Bitumen	None	10.3, 17.2, 24.0 and 30.9	93.85	Deo et al. (1992)
Hexadecane Crude oil	None	10.3 and 17.2	38	Hwang et al. (1995)
Jiangsu crude oil	None	15-25	55, 65and 75	Liu et al. (1999)
Asphaltenes from Bal 150 Crude Oil	toluene and dichloromethane	13,15, 20 and 30	40 and 50	Guiliano et Al. (2000)
McElroy crude oil	toluene, methanol, hexane and isoprpyl alcohol methanol/toluene, isopropanol/toluene LAH	8.1, 10.1 and 12.2	35 30-100	Hwang and Ortiz (2000)
Peace River bitumen-sand mixture	None	7.6-17.2 10.0,15.0 and 12.2	34-55 32 and 38	Rose et al. (2000)
UAE Soil spiked with crude oil	None	8-12 20-30	40-60 100-140	Al-Marzouqi et al. (2007)

The increase in pressure increases the density of SC CO_2 at a fixed temperature. Since the solvent power of SC CO_2 increases with density, the increase of pressure improves the solvent power of SC CO_2 and more hydrocarbons are extracted.

The effect of temperature on the extraction yield however is more complex. Some studies observed that the extraction yield decreased with temperature (Al-Marzouqi et al. 2007; Hwang and Ortiz 2000; Rose et al. 2000). This trend was explained by the fact that an increase in temperature reduces the density of SC CO_2 and consequently decreases the solvent power of SC CO_2. Deo et al. (1992), on the other hand, tested the SFE of crude oil at a constant pressure 10.3MPa and at three temperatures: two temperatures (30.85 and 37.85°C) near the critical temperature of CO_2 (31.1°C) and one temperature (65.85°C) far from the critical temperature of CO_2. The extract yields at the two low temperatures were almost the same and were much higher than that at the high temperature (Deo et al. 1992). Deo et al. (1992) explain that the lower yield at high temperature is due to two reasons. One reason was that the phase behavior shifted from liquid-liquid-like system to a liquid-vapour-like system. In a liquid-liquid-like system, the CO_2 is a liquid, with a relative high density and can be mixed very well with the matrix. However, in a liquid-vapour-like system the density of SC CO_2 is much lower and the surface area of vapour solvent is much smaller and cannot be well mixed. The other reason of the lower yield at high temperature was the significant decrease of the density of SC CO_2 at high temperature (Deo et al. 1992). Some studies suggest that at low temperatures ranging from 30 to 100°C (Hwang and Ortiz 2000) and 40 to 50°C (Guiliano et al. 2000), the effects of temperature on the extraction yield are small. Liu et al. (1999) suggest that the temperature has two opposite effects on the solubility of oil components. One effect was that higher temperature improved the volatility of oils and made the oil components diffuse more easily into the SC CO_2. The opposite effect was that the higher temperature reduced the density of SC CO_2 and caused the solvent power of SC CO_2 to decrease. For the temperature range studied by Liu et al. (1999), the solubility of oil in SC CO_2 at the higher temperature (75°C) was higher than the solubility at the lower temperature (55°C). For example, with the same pressure 10MPa and these two different temperatures, the solubility of oil in SC CO_2 at 75°C was $2.9 cm^3 \cdot g^{-1}$, and at 55°C was $2.19 cm^3 \cdot g^{-1}$. Therefore, Liu et al. (1999) believe that the effect of temperature on the oil volatility was more significant than the effect of temperature on the CO_2 density (Liu et al. 1999).

Most of the studies presented in Table 2.3 concluded that the extraction yield increased with increased solvent density (Deo et al. 1992; Hwang et al. 1995; Hwang and Ortiz 2000; Liu et al. 1999; Rose et al. 2000), but some studies mention other factors that should be considered. Rose et al. (2000) discovered that the extract yield increased with pressure and decreased with temperature. Therefore, they concluded that the extraction yield was solvent density related. In the study of Deo et al. (1992), they compared the reduced densities and the extraction yields of sub-critical and SC CO_2. Based on the observations, Deo et al. (1992) concluded that the pure solvent density was not the only factor that governed the extraction yield. For example, two sets of experimental conditions were used to extract bitumen from crude oil with SC CO_2: 23.85°C and 10.3MPa (sub-critical condition), and 37.85°C and 17.2MPa (supercritical condition). The reduced densities were 2.22 and 2.19 respectively, but the extraction yield of the experiment at 37.85°C and 17.2MPa was higher. This observation clearly reflected that although the pure solvent density was higher, the extraction yield was lower (Deo et al.

1992). Another example was that when doing SFE on crude oil at a constant pressure 10.3MPa and two different temperatures (23.85°C and 37.85°C), the lower reduced density 1.77 at higher temperature, which was close to the critical temperature of CO_2, produced higher extraction yield. They concluded that the proximity of the extraction temperature to the critical temperature of solvent also enhanced the oil solubility and hence the extraction yield (Deo et al. 1992).

Al-Marzouqi et al. (2007) suggest that the viscosity of the SC CO_2 is another key factor that affects the extraction efficiency when extracting hydrocarbons such as crude oil from solid matrices. The viscosity reflects the ability of the SC CO_2 to diffuse into the solid matrix, with a lower viscosity enabling the SCF to diffuse more easily and rapidly into the matrix. Al-Marzouqi et al. (2007) suggest that in the vicinity of the critical point of CO_2, the density of the fluid plays key role in the extraction, but at higher pressures, the effect of viscosity was more important than that of density. At higher pressures, kinematic viscosity, which was a combined effect of viscosity and density, was used to analyze these complex effects. Al-Marzouqi et al. (2007) stated that increasing the kinematic viscosity caused a decrease in the mass transfer coefficient, so an extraction at conditions where the fluid had a lower kinematic viscosity resulted in a higher mass transfer coefficient and hence a larger extraction efficiency. In most of their observations, larger kinematic viscosity corresponded to higher extraction efficiency (Al-Marzouqi et al. 2007).

The studies in Table 2.3 reported not only the extraction yields but also investigated the quality of the extracted compounds as a function of extraction time. Hwang et al. (1995) examined the extracts using gas chromatography-mass spectrometry

(GC-MS) and looked at how the carbon number distribution of the extracted hydrocarbons changed as a function of time. Hwang et al. (1995) discovered that the weight percentage of lighter hydrocarbons (i.e. low carbon numbers) in the extracted compounds that were extracted in the earlier periods was higher and the carbon distribution curve was shift to heavier hydrocarbons (i.e. higher carbon numbers) as the extraction progressed (longer extraction time) (Hwang et al. 1995). The color of the earlier extracts were darker, and further analysis by GC-MS suggested that earlier in the extraction, more naphthenic and aromatic compounds and less paraffinic compounds were extracted (Hwang et al. 1995). By using simulated distillation, Deo et al. (1992) also found that the light hydrocarbons were extracted in earlier stages and heavier ones were extracted in later stages (Deo et al. 1992). Deo et al. (1992) also noted that the heavier hydrocarbons were extracted at higher pressure. Al-Marzouqi et al. (2007) also used GC analysis to study the extracted hydrocarbons, and found that the carbon number increased with increasing pressure. At low temperature and pressure (8MPa, 40°C), the carbon number of the heaviest hydrocarbons extracted was C_{17}. Large amount of hydrocarbons heavier than C_{11} were left in the residual soil sample. However, under higher pressure and temperature conditions (30MPa, 120°C) heavy hydrocarbons up to C_{31} were extracted and only few hydrocarbons remained in the extracted soil sample. At low temperature and low pressure, SC CO_2 could only extract gasoline range hydrocarbons (C_1 to C_{11}), while at high pressure and high temperature condition, even intermediate (diesel up to C_{22}) and heavy hydrocarbons (up to C_{31}) could be extracted by SC CO_2 (Al-Marzouqi et al. 2007).

By analyzing the average molecular weights (AMW) of the extracts, Liu et al. (1999) found that the AMW of the extracts at 55°C and 8.95MPa and at 75°C and 16.10MPa were similar (205g·mol^{-1} and 210g·mol^{-1}, respectively) and that the effect of temperature and pressure on the AMW of the extracts was small. Compared to the AMW of the crude oil (384g·mol^{-1}), the AMW of the extracts was much smaller (Liu et al. 1999). Using boiling point curves, Rose et al. (2000) studied the composition of the extracts. The results show that in the range of experimental temperatures and pressures studied, the compositional variations of the extracted hydrocarbons were small (Rose et al. 2000). Two boiling point curves of different extracts that were obtained at two different experimental pressures (7.3 and 15.0MPa) were almost identical. Rose et al. (2000) did some comparative extractions using supercritical ethane (SC ethane), both with the same operating conditions and the same reduced density as with SC CO_2. After comparing the results with that of extracts from SC ethane, Rose et al. (2000) concluded that using ethane not only recovered six times more extracts, but also a larger range of hydrocarbons could be extracted using SC ethane as compared to SC CO_2. The influence of experimental conditions on the composition of extracts extracted by SC CO_2 is negligible (Rose et al. 2000).

Hwang and Ortiz (2000) and Guiliano et al (2000) investigated the use of modifiers with SC CO_2. Hwang and Ortiz (2000) carried out extractions with modifiers (methanol, toluene, hexane and isoprpyl alcohol), mixtures of modifiers (methanol + toluene, isopropyl alcohol + toluene) and a modifier consisting of a light aromatic hydrocarbon mixture (LAH). By comparing the extraction efficiencies and the compositions of extracts from extractions with or without modifier(s), Hwang and Ortiz

(2000) found out that adding modifier(s) not only increased the density and polarity of the SC CO_2, but also resulted in the extraction of a wider range of hydrocarbons and greater amounts of intermediate (diesel) and heavy hydrocarbons (Hwang and Ortiz 2000). When using CO_2 alone, very little amount of hydrocarbons heavier than C_{22} were extracted. However, when using CO_2 and 10% methanol, some heavy hydrocarbons up to C_{30} were extracted (Hwang and Ortiz 2000). A LAH was used as a modifier in the work of Hwang and Ortiz (2000). Because LAH contains light aromatic hydrocarbons such as toluene, xylenes, and other alkyl benzenes, it provided extraction efficiencies as high as 94.3% but at a lower cost as compared to other pure modifiers (Hwang and Ortiz 2000).

Other advantages of using chemically modified CO_2 include:

- much higher extraction efficiency was obtained with a smaller volume of CO_2 when modifiers were used (Hwang and Ortiz 2000);
- less asphaltenes remained in the extracted samples (Hwang and Ortiz 2000); and
- heavier *n*-alkanes and more highly branched and complex cyclic alkanes were extracted when using modified SC CO_2 as compared to pure SC CO_2 (Guiliano et al. 2000).

2.4.2 Supercritical Fluid Extraction with Ethane

Ethane is another popular SCF because of its mild critical pressure and temperature. The critical temperature and critical pressure of ethane are 32.2°C and 4.88MPa, respectively (Rose et al. 2000). As compared to CO_2, ethane not only recovers more oil, but also extracts a wider range of hydrocarbon constituents (Rose et al. 2000).

Table 2.4 summarizes some of the research that investigated the use of ethane as a supercritical solvent to extract hydrocarbons (bitumen and crude oil) from different matrices.

Table 2.4: Summary of research investigating the use of SC ethane to extract hydrocarbons

Feed Material	Modifier	Extraction Pressure (MPa)	Extraction Temperature (°C)	Reference
Cold Lake oil sand	None	4.9	60	Lim et al. (1995)
Peace River bitumen-sand mixture	None	7.3-15.0	47	Rose et al. (2000)
Peace River Bitumen-sand mixture	None	7.3-15.0	37-92	Rose et al. (2001)
Crude oil tank bottom sludge	None	10 and 17.2	35 and 65	Ávila-Chávez et al. (2007)

Lim et al. (1995) did three dimensional scaled physical modeling experiments. Cold Lake oil sand was subjected to cyclic stimulation with sub-critical and supercritical ethane. Lim et al. (1995) compared the bitumen production rates (cycle bitumen production volume divided by the cycle time) and found that by using supercritical ethane (SC ethane) 30% recovery was reached in 13 hours, 3 hours earlier than unheated ethane (Lim et al. 1995). The viscosity and Conradson carbon residue (CCR) of the extracted hydrocarbons from each experiment were analyzed. CCR is a standard petroleum industrial coking test for determining the coke forming tendency of petroleum liquids (Wiehe 2008). The results show that although the bitumen production rate and recovery by SC ethane were higher than sub-critical ethane, the quality of produced bitumen was lower that is, both the viscosity and the CCR were higher (Lim et al. 1995).

Table 2.4 shows three studies with SC ethane extraction: two studies on a Peace River Bitumen-sand mixture (Rose et al. 2001; Rose et al. 2000) and one study on crude oil tank bottom sludge (Ávila-Chávez et al. 2007). Although all three studies were conducted at different pressures and temperatures, the conclusions of the effects of temperature and pressure of all three studies were similar. The extraction yield increased with pressure and decreased with temperature (Ávila-Chávez et al. 2007; Rose et al. 2001; Rose et al. 2000). At higher pressure and lower temperature conditions, the extraction behaved like a liquid-liquid extraction, and the higher attractive forces caused the solubility of the hydrocarbons in a liquid solvent was much higher than the solubility of the hydrocarbons in a vapor solvent. So Rose et al. (2000) concluded that the pure solvent density largely controlled the extraction yield of bitumen-SC ethane system (Rose et al. 2000). Ávila-Chávez et al. (2007) also found that the extraction yield increased with the density of solvent and the highest yield of extracted hydrocarbons (58.5%) was obtained at the highest SC ethane density (Ávila-Chávez et al. 2007). In addition to temperature and pressure, Ávila-Chávez et al. (2007) tested the effects of other factors such as solvent flow rate and extraction time. Ávila-Chávez et al. (2007) tried higher flow rate (5cm^3·min^{-1}) with constant extraction time (150min) and longer extraction time (292min) with constant flow rate (1cm^3·min^{-1}), the yield of extracted hydrocarbons of these two conditions were higher than the yield of extracted hydrocarbons with a flow rate of 1cm^3·min^{-1}and 150min extraction time. Therefore, Both higher flow rate with constant extraction time and longer extraction time with constant flow rate could increase the yield of extracted hydrocarbons (Ávila-Chávez et al. 2007).

Rose et al. (2000) also performed experiments to determine if the extraction of bitumen from sand was controlled by thermodynamic equilibrium or mass-transfer resistance. Rose et al. (2000) changed the contact time between the SC ethane and bitumen by doing SFE with different amounts of bitumen-sand mixture and solvent flow rates but keeping the same pressure and temperature. However, the extraction results were independent of the amount of bitumen and solvent flow rate, therefore the bitumen-solvent contact time had little influence on the mass extracted (Rose et al. 2000). These results indicated that, when exiting the extractor, the SC ethane was saturated with the soluble hydrocarbons, indicating that the system had reached thermodynamic equilibrium.

For the studies in Table 2.4, different methods were used to determine the compositions and quality of extracted bitumen. The viscosity and CCR was used by Lim et al. (1995) to investigate the quality of the extracted hydrocarbons. Rose et al. (2000) compared the boiling curve of hydrocarbons extracted under different conditions of pressure or temperature and concluded that the hydrocarbons extracted at higher pressure or lower temperature was consistently heavier than that extracted at lower pressure or higher temperature. With lower temperature and higher pressure, not only more hydrocarbons were recovered, but a larger range of hydrocarbons (in terms of carbon number) was also obtained (Rose et al. 2000). In a follow-up study, Rose et al. (2001) observed that the viscosity of extracted hydrocarbons increased with pressure and decreased with temperature. After a SARA (saturate, aromatic, resin and asphaltene) analysis on the extracts, Rose et al. (2001) found that there were no asphaltenes in the hydrocarbons extracted by SC ethane and that the resin content of the extracted material was much lower than in the bitumen feed. At higher pressure and lower temperature, the aromatic fraction of the extracted hydrocarbons increased. The SC ethane selectivity for the saturate fractions was much higher than for resin and aromatic fractions (Rose et al. 2001). SARA analysis was also performed on samples taken at different time of extraction (samples obtained during intervals 1 and 4) but since there was little difference, the effect of extraction time on the composition of the extracted hydrocarbons was considered negligible (Rose et al. 2001).

In order to determine the quality of the extracted hydrocarbons, Ávila-Chávez et al. (2007) analyzed and compared the contents of the treated and untreated Isthmus crude oil tank bottom sludge (COTBS). Ávila-Chávez et al. (2007) observed that 95% of total petroleum hydrocarbons were extracted by SC ethane and that the asphaltenes content of SC ethane extracted sample of the COTBS was higher than the untreated COTBS (Ávila-Chávez et al. 2007). The extracted hydrocarbons were composed of saturates (58 % by mass) and aromatics (38% by mass). By studying the compositional results of the recovered hydrocarbon fraction extracted from the Isthmus COTBS and comparing the content of total petroleum hydrocarbons, asphaltenes, and metals in the untreated and treated (extracted with SC ethane) Isthmus COTBS, Ávila-Chávez et al. (2007) found that SC ethane not only extracted bitumen but also extracted part of the iron, nickel, vanadium, and sulphur content present in the original Isthmus COTBS. Hence, Ávila-Chávez et al. (2007) concluded that compared to the original matrix, the extracted hydrocarbons were upgraded by SC ethane (Ávila-Chávez et al. 2007).

Rose et al. (2000) carried out experiments under the same experimental conditions using different supercritical solvents (CO_2 and ethane). The SC ethane extracted much more hydrocarbons than SC CO_2. The solubility of bitumen in SC CO_2 also increased with pressure and decreased with temperature. The influence of operating conditions (pressure and temperature) had a negligible impact on the composition of bitumen extracted by SC CO_2. With the same operating conditions (47°C and 12.2MPa) but using SC ethane rather than SC CO_2, the change in the composition of the extract was greater with SC ethane than with SC CO_2 and the flexibility to control the composition of the extract was greater when ethane was used as the solvent. When extractions were performed with both SC CO_2 and SC ethane at the same reduced density, SC ethane extracted more hydrocarbons (Rose et al. 2000). Since SC ethane extracted more hydrocarbons and a wider range of hydrocarbons than SC CO_2, the observations indicate that SC ethane is a better solvent than SC CO_2 to extract complex hydrocarbons such as bitumen.

2.4.3 Supercritical Fluid Extraction with Propane

Some researchers have investigated propane as supercritical solvent, which has a critical temperature of 96.7°C and a critical pressure of 4.3MPa. Table 2.5 summarizes studies that have investigated the use of supercritical propane (SC propane) for the extraction of bitumen, bitumen-derived liquid, and petroleum vacuum-distillation residuum.

Deo et al. (1992) did SFE experiments on bitumen-derived liquid and native bitumen with SC propane and studied the influence of pressure and temperature on the extraction efficiency. The results showed that, at a constant temperature, the extraction efficiency increased with the extraction pressure. The other four studies in Table 2.5 also concluded that the extraction efficiency increased with the pressure (Deo and Hanson 1994; Han et al. 1998; Kim et al. 1997; Subramanian and Hanson 1998).

Table 2.5: Summary of research investigating the use of SC propane to extract hydrocarbons

Feed Material	Modifier	Extraction Pressure (MPa)	Extraction Temperature (°C)	Reference
Bitumen-derived liquid	None	5.5, 10.3 and 17.2	37.85, 106.85 and 134.85	Deo et al. (1992)
Bitumen	None	10.3 and 17.2	65.85 and 106.85	Deo et al. (1992)
Bitumen	None	5.5, 10.3 and 17.2	65.85, 106.85 and 148.85	Deo and Hanson (1994)
Petroleum vacuum-distillation residuum	None	5.5,10.3 and17.2	65.85, 96.85, 106.85 and 168.85	Kim et al. (1997)
Bitumen from Fengcheng District	None	4.4-8.6	108, 115 and 125	Han et al. (1998)
Four bitumens	None	5.6, 10.4 and 17.3	65.85,106.85 and 168.85	Subramanian and Hanson (1998)

Different researchers had different opinions about the effects of extraction temperature on the extraction efficiency. Both Han et al. (1998) and Subramanian and Hanson (1998) stated in their studies that the extraction yield decreased with the increasing temperature. However, Deo et al. (1992) observed that the most effective extractions from which more hydrocarbons were extracted occurred in the vicinity of the critical temperature of propane (Deo et al. 1992). Although Deo and Hanson (1994) concluded that at a constant pressure, the influence of the three temperatures tested (65.85, 106.85 and 148.85°C) was very limited, comparing with a lower temperature (65.85°C), higher extraction yield was produced at higher temperature which was 106.85°C (Deo and Hanson 1994).

Since both Han et al. (1998) and Subramanian and Hanson (1998) found that the extraction efficiency increased with pressure and decreased with temperature, it was suggested that the extraction yield was governed by the pure solvent density. However, Deo et al. (1992) pointed out that at 10.3MPa and 65.85°C (reduced density of 2.64), the extraction yield from the native bitumen at this condition was lower than the extraction yield at 17.2MPa and 106.85°C, (a lower reduced density of 2.44). The higher extraction yield at a lower reduced density was also observed in the extraction of bitumen-derived liquid. Therefore, Deo et al. (1992) suggest that the extraction yield is not only governed by the pure solvent density.

Deo and Hanson (1994) observed that a higher temperature produced higher extracts yield, and suggest that the higher temperature increased the volatility of the bitumen in the feed sample and this improvement offset the negative effect of the decrease in propane density. Accordingly, Deo and Hanson (1994) thought that the SFE of bitumen was controlled by a complex interplay of pure solvent density and bitumen volatility (Deo and Hanson 1994). From the experiment results of Kim et al. (1997), at a constant pressure 10.3MPa, when the temperature increased from 65.85°C to 106.85°C, the density of propane dropped from $0.4728 g\cdot cm^{-3}$ to $0.3825 g\cdot cm^{-3}$, but the yields of deasphalted oils (DAO) were almost the same (40.3% and 40.8%).

Deo et al. (1992) did carbon-number distributions of the first, middle and the last extracts from the native bitumen, and observed that the later extracts were heavier than the earlier ones. Furthermore, analyzing the effect of pressure on the carbon-number distributions of the extracts revealed that heavier compounds were extracted under higher pressure conditions (Deo et al. 1992). Deo and Hanson (1994) and Han et al. (1998) also observed the same trend. Although the composition of the extracts was different from that of original bitumen-derived liquid, the bitumen-derived liquid acted as a single component in the extractions and the pressure, temperature and the extraction time had no effects on the composition of the extracts (Deo et al. 1992).

Deo and Hanson (1994) also analyzed the residual fractions produced by the extraction process. The asphaltene content of residual fractions were largely higher than that of original feed sample and increased with extraction pressure. The highest extraction yield condition (106.85°C and 17.2MPa) produced a residual fraction with the highest asphaltene content. As the extraction pressure increased, more of saturates and aromatics were extracted and more resins were left in the residual fractions (Deo and Hanson 1994). Because all the hydrogen to carbon ratios (H/C) of the residual fractions were lower than that of original bitumen, the residual fractions were more polar than original bitumen. The H/C ratios of the residual fractions decreased with pressure, and the lowest H/C ratio was obtained at 106.85°C, which also produced the highest extraction efficiency (Deo and Hanson 1994).

Deo and Hanson (1994) also stated that some of the lighter compounds played a role in the amount of asphaltenes in the supercritical solution. During the SFE process, the SC propane extracted the lighter compounds and therefore the ability of the supercritical solution to dissolve the asphaltenes was decreased and the asphaltenes accumulated in the residual fraction (Deo and Hanson 1994). However, after the SFE process, the H/C ratio of residual fraction was lower than that of the original bitumen, which indicated that the residual fractions are more polar that the original bitumen. There are two ratios that are varied after SFE process, one is the ratio of high to low molecular weight species (told from H/C ratio) and the other one is the ratio of polar to non-polar compounds. Deo and Hanson (1994) thought that these two ratios control the mutual solubility of compounds in complex petroleum mixture, but only extraction of lighter components will not cause more asphaltenes left in the residual fractions. Therefore, Deo and Hanson (1994) concluded that the polar to non-polar compounds ratio was another factor that affected the asphaltene solubility in the solution and this factor was even more important than the depletion of light components.

Kim et al. (1997) did SC propane extractions on petroleum vacuum-distillation residuum. Different extraction conditions were tested to determine the effects of pressure and temperature on the yields of extracted deasphalted oils. In the experiments, at a constant temperature (106.85°C) as the extraction pressure was increased from 5.5 to 17.2MPa, both the densities of propane and the extraction yields were increased. The propane densities were raised from 0.2585g·cm^{-3} to 0.4416g·cm^{-3}, and the extraction yields were increased from 20.3% to 51.1% (Kim et al. 1997). Therefore, Kim et al. (1997) concluded that the extraction yield was affected by the density of propane and increased with extraction pressure. However, with a constant pressure (10.3MPa), three different temperatures were tested. Two temperatures (65.85 and 106.85°C), which were near the critical temperature of propane, produced almost the same extraction yield even with different density of propane (0.4728 and 0.3825g·cm^{-3} respectively). At a higher temperature (168.85°C), because of the reduce of propane density, the extraction yield was relatively low (Kim et al. 1997).

Han et al. (1998) performed experiments to study the vapor-liquid phase equilibria of a SC propane-Fengcheng bitumen system. Under all experimental conditions of this study, the effects of pressure and temperature on viscosity were not significant. Han et al. (1998) found that the densities and viscosities of propane-saturated bitumen were significantly lower than that of gas-free bitumen, which meant dissolution of propane in the bitumen could reduce the density and viscosity of the Fengcheng bitumen. Han et al. (1998) found that at higher pressure (more than 7.5MPa) and lower temperature (at 108°C) the SC propane had very strong ability to extract the components from bitumen. The AMW of the extracts was lower than that of the original bitumen, implying that the components extracted by SC propane are lighter and the molecule structures are simpler than the original bitumen (Han et al. 1998).

Subramanian and Hanson (1998) did a series of SFE experiments on bitumens from four Uinta Basin (Utah) oil sand deposits using SC propane. The four deposits are Whiterocks (WR), Asphalt Ridge (AR), PR Spring (PRS) and Sunnyside (SS). In addition to the experimental conditions of pressure and temperature, the natural physical and chemical properties of these 4 bitumens had an impact on the extraction efficiency (Subramanian and Hanson 1998). The yields of extract from the four bitumens decreased with an increase in their asphaltene content, specific gravity, viscosity and Conradson carbon numbers. Furthermore, the highest yield (45% by mass) was achieved at the highest solvent density with WR bitumen, which has the lowest asphaltene content, specific gravity, viscosity and Conradson carbon number. The light part of extracts were obtained in the early stages of extraction; the extracted components obtained later in the extraction were heavier (Subramanian and Hanson 1998).

Different from Deo and Hanson (1994), Subramanian and Hanson (1998) used a modified SARA analysis to determine the saturate, aromatic, resin and asphaltene contents of the original bitumen, the extracts and the residual fractions. The asphaltene contents of the residual fractions were much higher than those of the original bitumen and no asphaltenes were found in the extracts (Subramanian and Hanson 1998). Subramanian and Hanson (1998) suggest that no asphaltenes were extracted by SC propane because of the interaction between resins and asphaltenes, with the resins keeping the asphaltenes soluble in the original bitumen. After SFE, these resins were extracted by SC propane and found in the extract. Without these resins, the asphaltenes precipitated and were trapped in residual fractions (Subramanian and Hanson 1998). By doing elemental analyses, Subramanian and Hanson (1998) found that the H/C ratios of the residual fractions were much lower than those of the original bitumen and this was attributing to the preferential removal of saturated compounds relative to aromatics and resins during the extraction process leaving the residual fractions more unsaturated. The extracted hydrocarbons were much lighter than the original bitumen and the volatility of the extracted hydrocarbons were higher than the original bitumen, so Subramanian and Hanson (1998) concluded that the extracted hydrocarbons were significantly upgraded during the SFE process.

2.4.4 Supercritical Fluid Extraction with Pentane

Pentane has a low critical pressure (3.37MPa), but has a relatively high critical temperature of 196.6°C. Table 2.6 provides a summary of some of the research investigating the extraction of crude oil using supercritical pentane (SC pentane) to extract hydrocarbons.

Table 2.6: Summary of research investigating the use of SC pentane to extract hydrocarbons

Feed Material	Modifier(s)	Extraction Pressure (MPa)	Extraction Temperature (°C)	Reference
Middle Eastern tar sands	benzene, acetone, and ethanol	6-10.6	246.85-411.85	Demirbas (2000)
Vacuum residue of domestic Dagang crude oil	None	4-6	150-220	Zhao et al. (2003)

Demirbas (2000) performed SFE experiments on Middle Eastern tar sands using SC pentane and modifiers (benzene, acetone, and ethanol). The mixture of SC pentane and benzene (at a volume ratio of 1 to 1) at 441.85°C produced the highest extraction yield (24.3% on dry mass basis). The most polar solvent mixture (SC pentane with a mixture of benzene and ethanol) produced the lowest extraction yield (Demirbas 2000). By comparing the higher heating values (HHVs) of treated tar sand and original tar sand, Demirbas (2000) found that the HHVs of treated tar sand were lower than that of original tar sand and the HHVs of extracts obtained with SC pentane and benzene mixture was the lowest one. These result suggest that part of the extractable materials and combustible compounds were extracted by the SC pentane and, of the modifiers tested, the most effective modifier was benzene (Demirbas 2000).

In the study of Zhao et al. (2003), temperature, pressure and mass ratio of solvent to oil feed (S/O ratio) were three key factors that affected the yield and quality of extracts. In a resin separator, the extracts were further separated into two fractions by heating, producing one light phase of deasphalted oil (DAO) and one heavy phase of resin. Zhao et al. (2003) found that DAO yield increased with pressure and decreased with temperature. The DAO yield decreased as temperature increased and above 170°C, the yield of DAO dropped dramatically (Zhao et al. 2003). Zhao et al. (2003) also observed that the DAO yield reached 85% when the SC pentane density was $0.484g\cdot cm^{-3}$, and the DAO yield only was 0.035% when the density reduced to $0.181g\cdot cm^{-3}$. These results suggested that the density of SC pentane is a good indicator of its solvating power (Zhao et al. 2003). The carbon residue is coking precursor and heavy metals are poisons to catalysts for further upgrading processes. Zhao et al. (2003) observed that the carbon CCR content in the DAO or DAO+resin increased and the Ni (nickel) removal rate decreased as the DAO yield or extracts (DAO+resin) yield increase. Hence, when the yield was high, the quality of DAO and resin was poor. Zhao et al. (2003) also found that, for a given deasphalting system, there was an optimal S/O ratio that not only produced good DAO and resin quality, but also reduced the solvent usage (Zhao et al. 2003).

2.4.5 Supercritical Fluid Extraction with Water

Water has both a high critical temperature and critical pressure (Tc=374.2°C, Pc= 22MPa) and extraction studies using supercritical water can use temperatures as high as 500°C. A temperature this high may change the properties of the bitumen. For example, high molecular weight compounds in oil sand may decompose to form smaller molecular weight compounds (Meng et al. 2006) and these changes may influence the extraction efficiency. Table 2.7 represents some research using supercritical water (SC water) to extract hydrocarbons from oil sand.

Table 2.7: Summary of research investigating the use of SC water to extract hydrocarbons

Feed Material	Modifier	Extraction Pressure (MPa)	Extraction Temperature (°C)	Reference
Athabasca oil sands	CO and toluene	14-24.5	400	Berkowitz and Calderon (1990)
Tumuji oil sand	None	20, 25 and 30	20-500	Meng et al. (2006)

Berkowitz and Calderon (1990) performed extractions on two samples of Northern Alberta's Athabasca oil sands with SC water. In their experiments, the feed materials were continuously swept by metered steam. The volume of steam that sweep the autoclave in 1min is called sweep rate (unit is mL steam/min). It is also can be called flow rate. From their results, the pressure, sweep rates and solvent to modifier ratios almost had no effect on the extract yields. However, if the steam can sweep the sample more effectively, higher extract yield could be produced. For example, higher extracted yields were obtained when the sample was placed in porous thimbles rather than on a set of plates. Therefore, a better sweep efficiency might generate higher extract yields (Berkowitz and Calderon 1990). Extractions at pressures above 21MPa promoted the formation of coke from residual bitumen, but did not improve the extract yields. By doing the class analyses of early stage extracts from extractions at 400°C and 14MPa with water only, Berkowitz and Calderon (1990) found that large amounts of heavy asphaltenes converted to resins, aliphatic and aromatic hydrocarbons (Berkowitz and Calderon 1990).

Berkowitz and Calderon (1990) studied the effects of two kinds of modifiers. An experiment using a water/toluene mixture at 24.5MPa produced similar extract yields at 14MPa without toluene, but some polar materials were transferred to lighter aliphatic and aromatic hydrocarbons when toluene was used as a modifier (Berkowitz and Calderon

1990). Just like toluene, the presence of CO did improve the extract yield, but after doing the class analyses of the extracts, the "bitumen+heavy oil" fraction contained larger amount of hydrocarbons at the expense of precursor asphaltenes than extracts obtained from extractions with water only. This observation and why extraction with CO largely reduced the coke yields at a high temperature (400°C) could be attributed to the hydrogen that provided by a chemical reaction: $CO+H_2O \rightarrow CO_2+H_2$. CO also ameliorated the extract composition by significantly shifting the polar and aromatic hydrocarbons to aliphatic hydrocarbons (Berkowitz and Calderon 1990).

Meng et al. (2006) carried out a series of experiments on Tumuji oil sand from Inner Mongolia with SC water. In order to test the effect of temperature, the extraction vessel was heated from room temperature to 500°C. Before 210°C, the extract flow was negligible. The extract formation rate increased with temperature and it reached a peak value at 390°C. After 390°C, as the temperature was further increased, the extract formation rate started to decrease. Meng et al. (2006) suggest that the balance of two opposite effects of temperature on the extraction led to these results. The dielectric constant of water increased with increased temperature, increasing the solubility of heavy organic substances in SC water. Furthermore, as the temperature increased, some large molecular weight compounds in the oil sand decomposed to form smaller molecular weight compounds. These two reasons led to an increase in the extract formation rate. An opposite effect was that the water density decreased with increasing temperature which resulted in a decrease in the amount of extracted bitumen from the oil sand. At 390°C, these two opposite effects balance each other, so a maximum extraction yield was observed (Meng et al. 2006).

The solubility of hydrocarbons in supercritical water increases with pressure, so high pressures help the supercritical water extraction of hydrocarbons from oil sand. Meng et al. (2006) fractionated the extract into oil, asphaltene, and preasphaltene. The oil was further divided into saturates, aromatics, and resins. An increase in pressure would cause more asphaltene and preasphaltene to form. The fraction of saturates in the extracted oil decreased with pressure while the aromatics percentage increased with pressure (Meng et al. 2006). Meng et al. (2006) found that when the pressure increased, the temperature corresponding to the maximum extract formation rate would shift to a lower value, so extraction could be carried out at lower temperature and higher pressure condition (Meng et al. 2006).

By analyzing the composition of extracts, the saturate fraction of the extract was higher than that of the bitumen in the oil sand and the fraction of asphaltenes and preasphaltenes was lower, suggesting that SC water extracts more saturates from the bitumen in the oil sand. Because both the H/C ratio and the contents of C and H in the extract were higher than those of the bitumen originally present in the oil sand sample, the extract contained more hydrogen-rich components and less relatively large molecular weight compounds than the bitumen in the oil sand (Meng et al. 2006).

All the studies included in this section are about SFE experiments of bitumen and heavy oils using different SCFs, such as SC CO_2, SC ethane, SC propane, SC pentane and SC water. Almost all the studies have the same opinion about the impact of extraction pressure on the extraction yield, which is that the extraction yield increased with extraction pressure. The effects of extraction temperature and supercritical solvent density are complex and the conclusions from different studies are different. In addition to the effects of extraction conditions, some studies also examined the properties of the extracts and the residuals using different analytical methods. In summary, all of these studies proved that hydrocarbons can be extracted from various types of feed material using SFE.

Chapter 3 Materials and Methods

This chapter will introduce the materials and methods used in this study. Hydrocarbons in the oil sands were extracted by SCF extraction. Dean-Stark extraction was used to determine the composition of the oil sand before and after SFE. Gravimetric analysis and Dean-Stark results were used to determine the extraction efficiency. Both the system setup and the procedures for SFE and Dean-Stark are discussed in this chapter. A 2^3 factorial design was used for experiments and allowed the investigation of the impacts of some important experimental factors such as pressure, temperature and mixing rate on the extraction efficiency. The factorial design will also be discussed in this chapter.

3.1 Experimental Materials:

There are various materials used for both the SFE and Dean-Stark extractions in this research. These materials can be divided into three groups.

- oil sands
- reagents and other materials
- apparatus for SFE and Dean-Stark extraction

3.1.1 Oil Sands

Three different oil sands were used as the feed material in this research and details are provided in Table 3.1. Syncrude oil sand and Suncor oil sand were obtained from other research groups on the Department of Civil and Environmental Engineering, ARC oil sand (Average Grade Athabasca Oil Sand) was purchased from the Alberta Research Council sample bank in May 2009. Since the Syncrude oil sand was received several years ago, some early stage preliminary screening experiments were carried out with this oil sand. The ARC oil sand was purchased more recently and it is used for the second stage of preliminary experiments and for formal experiments. The Suncor oil sand was used for select experiments to compare the results to results obtained with ARC oil sand.

The composition (oil, water and solid content) of all three oil sands were determined by Dean-Stark extraction.

Table 3.1: Details of oil sands used in this research

Name	Supplier	Storage	Received Year
ARC Oil Sand	Alberta Research Council sample bank (Edmonton, Alberta, Canada)	Walk-in Freezer -4°C	2009
Syncrude Oil Sand	N A*	Walk-in Cooler 4°C	2003
Suncor Oil Sand	N A	Walk-in Freezer -4°C	2006

***** *N A* - Not available

3.1.2 Reagents and Laboratory Materials

The reagents and laboratory materials used for SFE and Dean-Stark extraction are listed in Table 3.2 and 3.3 respectively. Included in these tables are the quality details and suppliers of the reagents and laboratory materials.

Table 3.2: List of reagents and other materials used in SFE

Name	Properties	Supplier
CO_2	Grade 3 (bone dry)	Praxair (Mississauga, Ontario, Canada)
Fisherbrand Glass Beads	Solid	Fisher Scientific (Ottawa, Ontario, Canada)
Fisherbrand Glass wool	Silane-treated	Fisher Scientific (Ottawa, Ontario, Canada)
Fisherbrand Economical Glass EPA vials	40mL, silicone septa	Fisher Scientific (Ottawa, Ontario, Canada)

Table 3.3: List of reagents and other materials used in Dean-Stark extraction

Name	Properties	Supplier
Toluene	HPLC grade	Fisher Scientific (Ottawa, Ontario, Canada)
Whatman Extraction Thimbles	Double and single thickness	Fisher Scientific (Ottawa, Ontario, Canada)
Whatman GD/X 25mm Disposable Syringe Filters	Pore size 0.45µm	Fisher Scientific (Ottawa, Ontario, Canada)
BD Brand Disposable Luer-Lok Syringes	Without Needles 20cc	Fisher Scientific (Ottawa, Ontario, Canada)
Whatman Binder-Free Glass Microfiber Filters	Diameter 15 cm, Retention 1.5µm	Fisher Scientific (Ottawa, Ontario, Canada)

3.1.3 Supercritical Fluid Extraction System Setup

In this research, the extraction vessel is a laboratory high pressure bolted-closed stirred batch reactor purchased from Autoclave Engineers (Erie, Pennsylvania, USA) (Autoclave Engineers 1998). Figure 3.1 displays a picture of the SFE system.

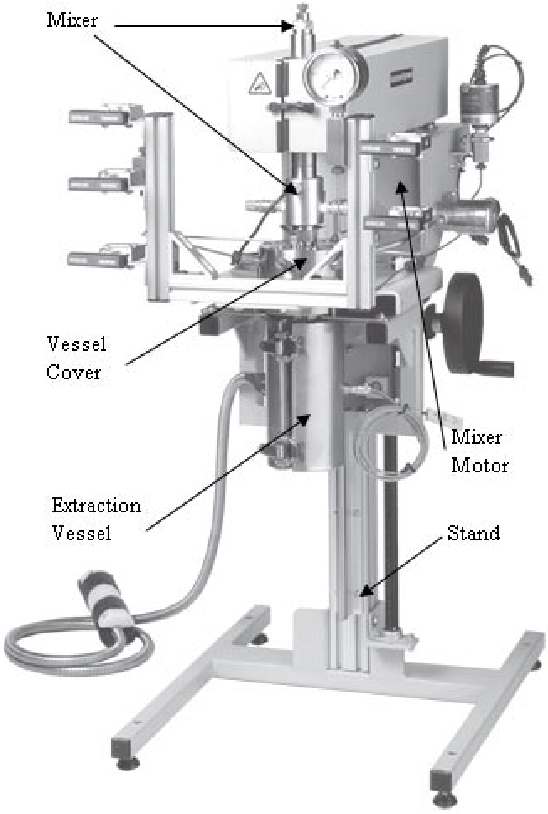


Figure 3.1: Supercritical Extraction System (adapted from Autoclave Engineers 1998)

The extraction vessel itself is a pressure vessel made of 316 stainless steel and the body can be removed from the lid without disassembling the pressure connections. The capacity of the vessel is 300 cm^3 and its operating pressure is as high as 34.3MPa at 510ºC (Autoclave Engineers 2006a). Figure 3.2 shows the vessel body with dimensions. A heating jacket surrounds the outside of the vessel and controls and maintains the temperature during the extraction.

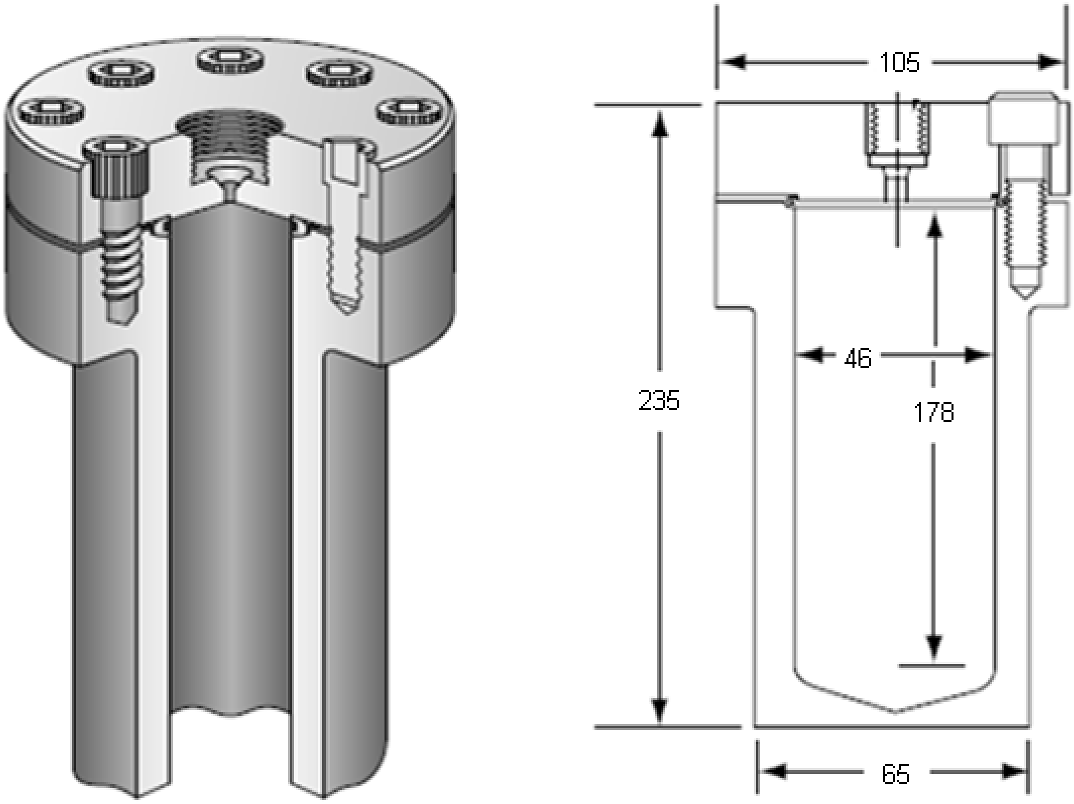


Figure 3.2 Diagram of extraction vessel (all dimensions are in mm)

The system is also equipped with a MagneDrive® mixer. As shown in Figure 3.3, there are two exchangeable impellers for the MagneDrive® mixer: a helical blade impeller (purchased from PRECIMAX, Edmonton, Alberta, Canada) and a pitched blade impeller (purchased from Autoclave Engineers, Erie, Pennsylvania, USA). The agitator is mounted to the drive shaft of a MagneDrive® mixer that has a maximum speed of 3300 rpm and a maximum torque of 0.79N·m. A belt is used to transfer the mixing power from a 0.37kW (1/2HP), 120V DC motor to the mixer. The speed of the motor is controlled electronically and monitored with magnetic sensors within the MagneDrive®.

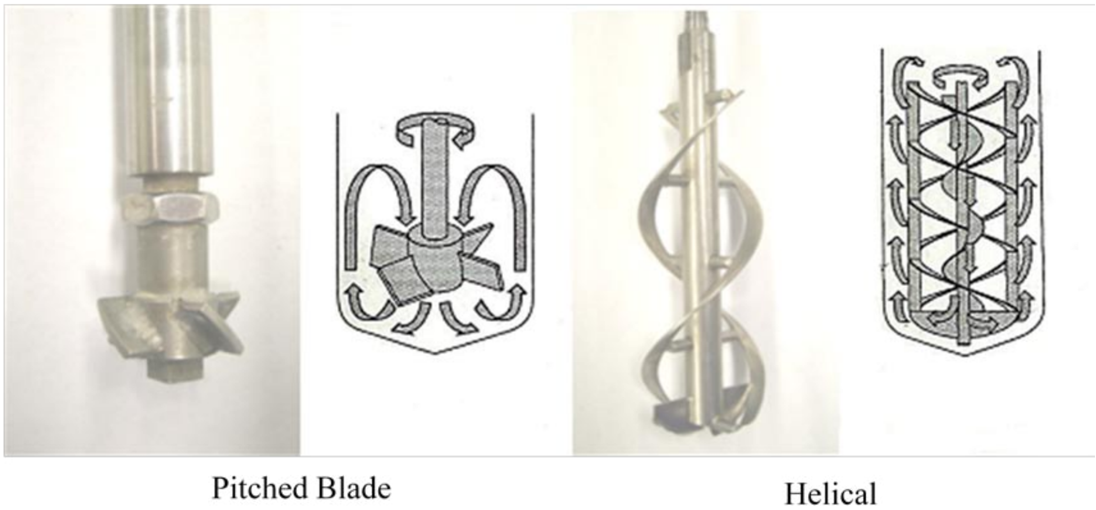


Figure 3.3: Photos (left) and schematic (right) of the two impellers (adapted from Autoclave Engineers 2006b)

The stainless steel vessel cover (Figure 3.4) is fixed to the stand. It has several connections, but only three (the inlet, outlet and safety vent) are used in this particular set up, as shown in Figure 3.4. When attached to the cover, the inlet and outlet are the entrance and exit of the high pressure vessel, respectively.

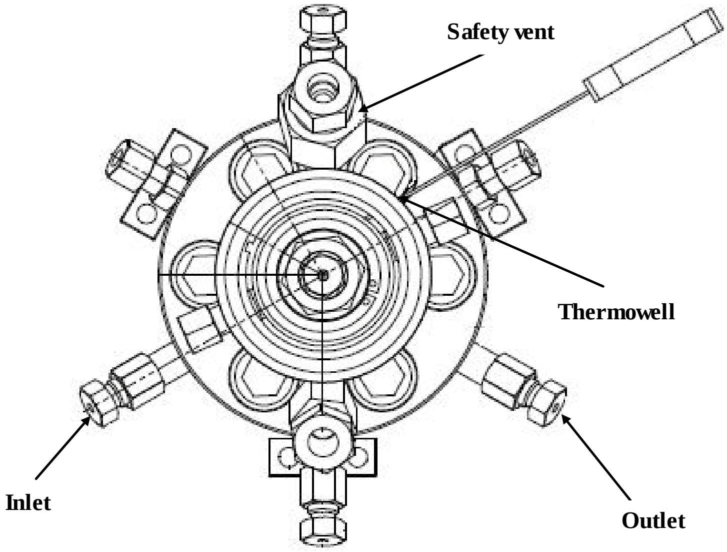
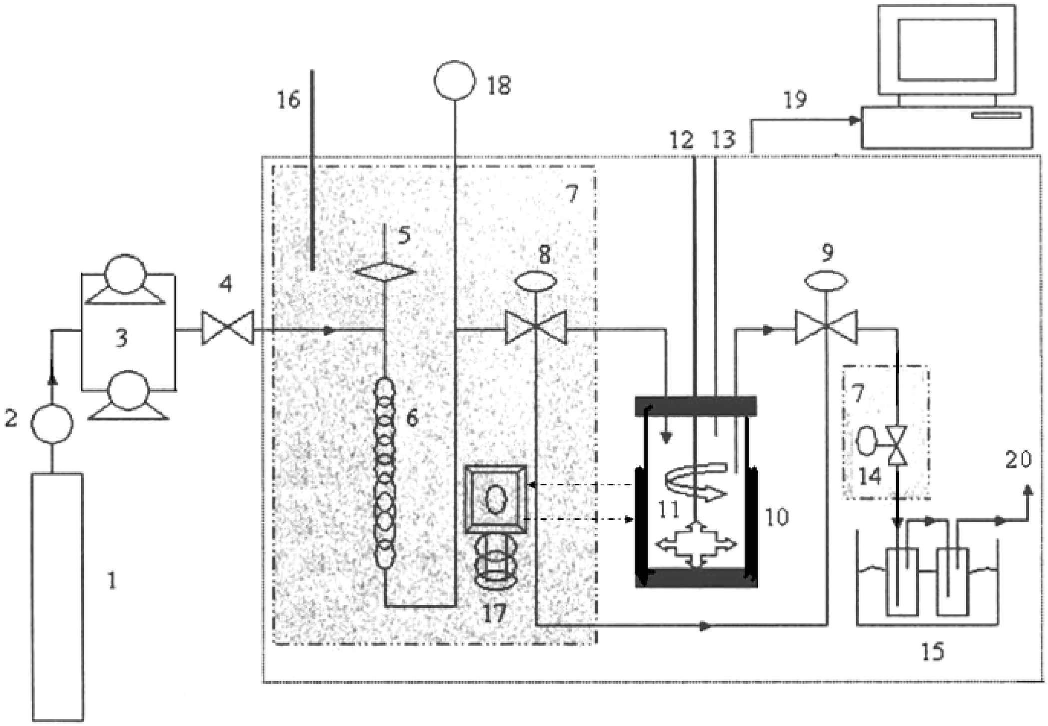


Figure 3.4: Schematic of extraction vessel cover (top view) (adapted from Street 2008)

Figure 3.5 provides a schematic of SFE apparatus, which is shown in Figure 3.6. The suppliers of some of the main components are listed in Table 3.4.



Legend:

1. CO_2 cylinder
2. Filter
3. Syringe pumps
4. Check valve
5. Pressure relief valve
6. Preheating coil
7. Hot water bath
8. Inlet valve (three way valve)
9. Outlet valve (three way valve)
10. Heating jacket
11. Extraction vessel
12. Impeller and MagneDrive® mixer
13. Thermocouple
14. Metering Valve
15. Sample vials and ice water bath
16. Thermometer
17. Water heating circulator
18. Pressure transducer
19. Data acquisition
20. CO_2 vent to fume hood

Figure 3.5: Schematic of SFE system

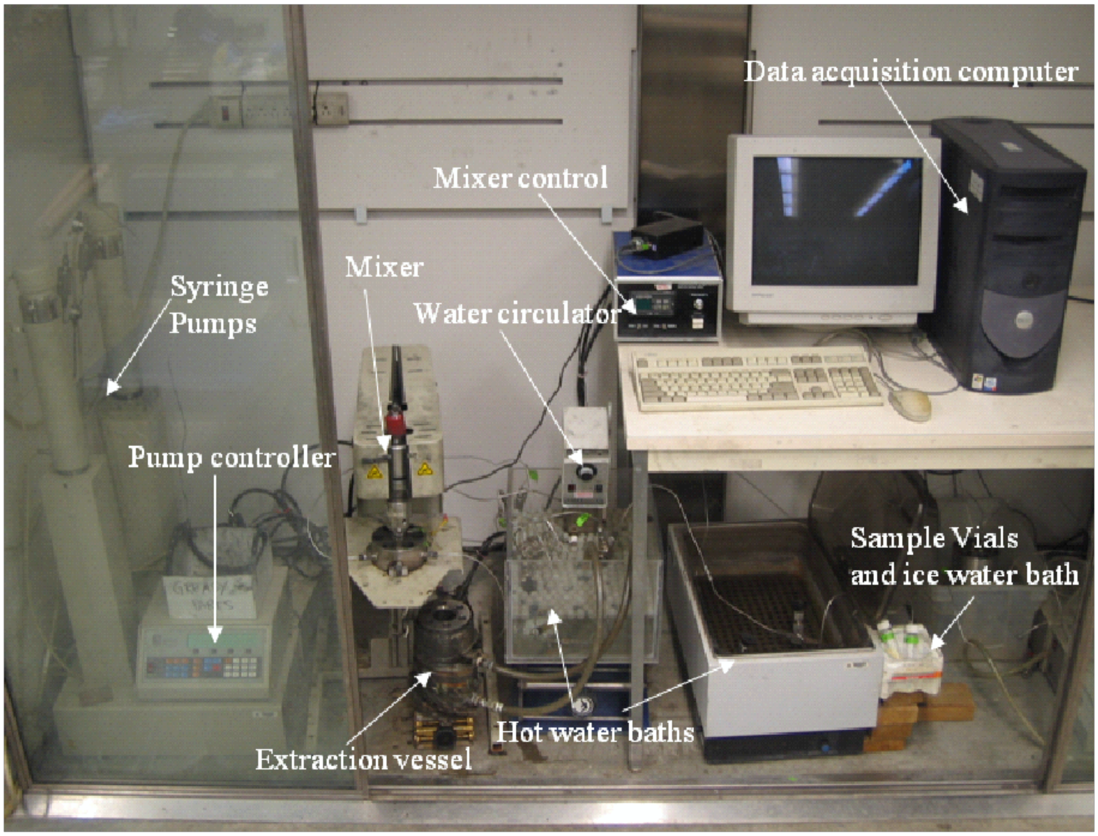


Figure 3.6: Photo of the laboratory-scale batch scale SFE setup

Table 3.4: List of the laboratory-scale SFE system components and their suppliers (the number in bracket corresponds to the legend in Figure 3.5)

Name	Property	Supplier
Filter (2)	0.5µm	Swagelok (NUPRO)
ISCO syringe pumps (3)	Model 500D	Teledyne ISCO
Check Valve (4)	Model SS-4CA150	Swagelok (NUPRO)
Pressure relief valve (5)	Model SS-4R3A with Spring R3A-F	Swagelok(NUPRO)
Hot water bath (7)	Isotemp	Fisher
Three-way ball valves (8 and 9)	SS-83XKS4	Swagelok
Extraction vessel (11)	300mL	Autoclave Engineers (Division of Snap-tite)
Metering valve (14)	Model SS-31RS4	Swagelok(NUPRO)
MagneDrive® mixer (12)	II, Series 0.75	Autoclave Engineers (Division of Snap-tite)
Thermocouple (13)	YSI 406	Labcor Technical Sales Inc.
Water heating circulator (17)	Model 002-4175	Fisher
Pressure transducer (18)	Omega PX 502	Omega

The following describes the SFE system and its operation. The numbers provided in bold refer to the components in Figure 3.5.

When the CO_2 exits the cylinder (**1**), it is first filtered by a 0.5μm filter (**2**). Then, two ISCO 500D syringe pumps (**3**), which work in parallel, compress the CO_2 to desired pressure. The two pumps are cooled by a circulating refrigerated water system. In order to prevent high pressure CO_2 from flowing back into the pumps and potentially damaging the pumps, a check valve (**4**) is placed between the extraction vessel and the pumps. A pressure relief valve, which is set to a cracking pressure of 27.6MPa, is also used to ensure that the pressure cannot increase to an unsafe level in the SFE system. The compressed CO_2 is preheated by a preheating coil (**6**) that is placed in a hot water bath (**7**). Then, the CO_2 flows into the extraction vessel. There are two three-way valves which control the CO_2 in and out of the extraction vessel. One is the inlet valve (**8**) and the other is the outlet valve (**9**). The extraction vessel is surrounded by a heating jacket (**10**) to control and maintain the temperature of the extraction vessel. The water that circulates through the heating jacket comes from the hot water bath and is pumped by a heating water circulator (**17**). A thermometer (**16**) is also place in the hot water bath to measure the water temperature. Mixing of the extraction vessel contents is provided by the impeller and the MagneDrive® mixer (**12**). CO_2 exiting the extraction vessel then passes through the outlet valve (**9**) to the metering valve (**14**) and through two sample vials (**15**).

The metering valve allows the CO_2 to depressurize to atmospheric pressure. The pressure drop can cause the metering valve to freeze, so the metering valve is placed in a second hot water bath (**7**) to prevent freezing. Any material present in the CO_2 is collected in the sample vials and then the CO_2 is vented to the laboratory fume hood (**20**).

A thermocouple (**13**) inside the vessel and a pressure transducer (**18**) attached to the inlet line are used to monitor the temperature and pressure in the extraction vessel and the SFE system. Finally, data is collected using a data acquisition system (**19**) and a program written in Lab View 5.1 (National Instruments, Austin, Texas, USA).

3.1.4 Dean-Stark Extraction Setup

Both the composition of the oil sands before and after SFE are determined by Dean-Stark extraction. This method divides oil sand into three parts: solids (on a dry basis), water, and bitumen. Figure 3.7 and 3.8 show the Dean-Stark extraction setup. All glassware, except for the condenser, was manufactured by the Glass shop in the Department of Chemistry at the University of Alberta.

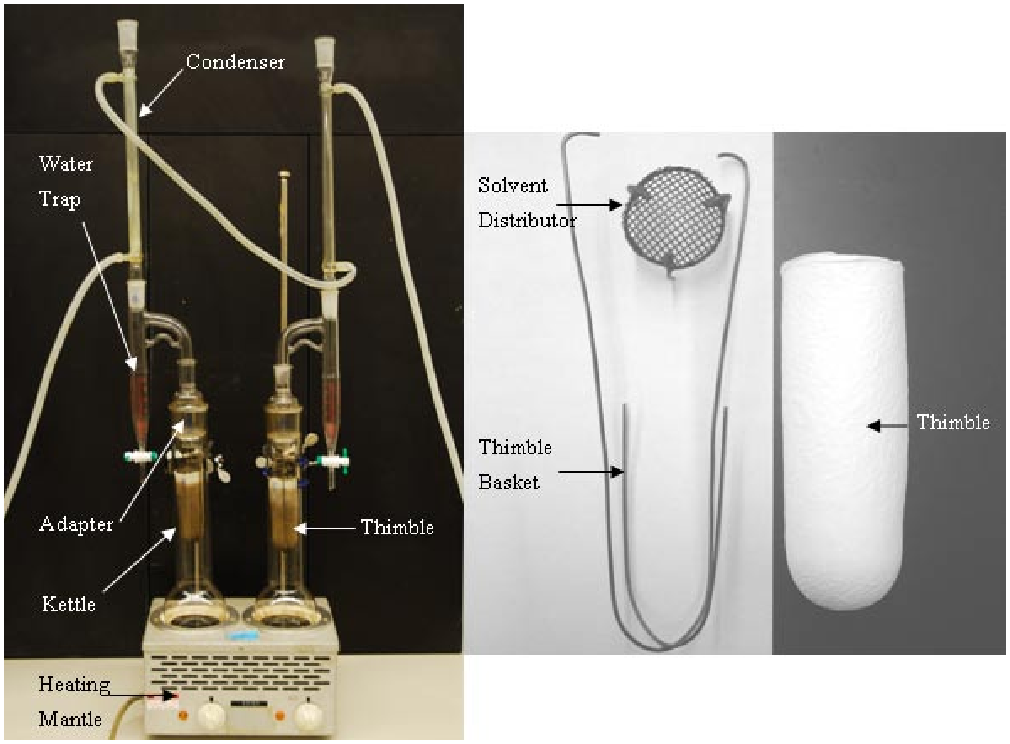
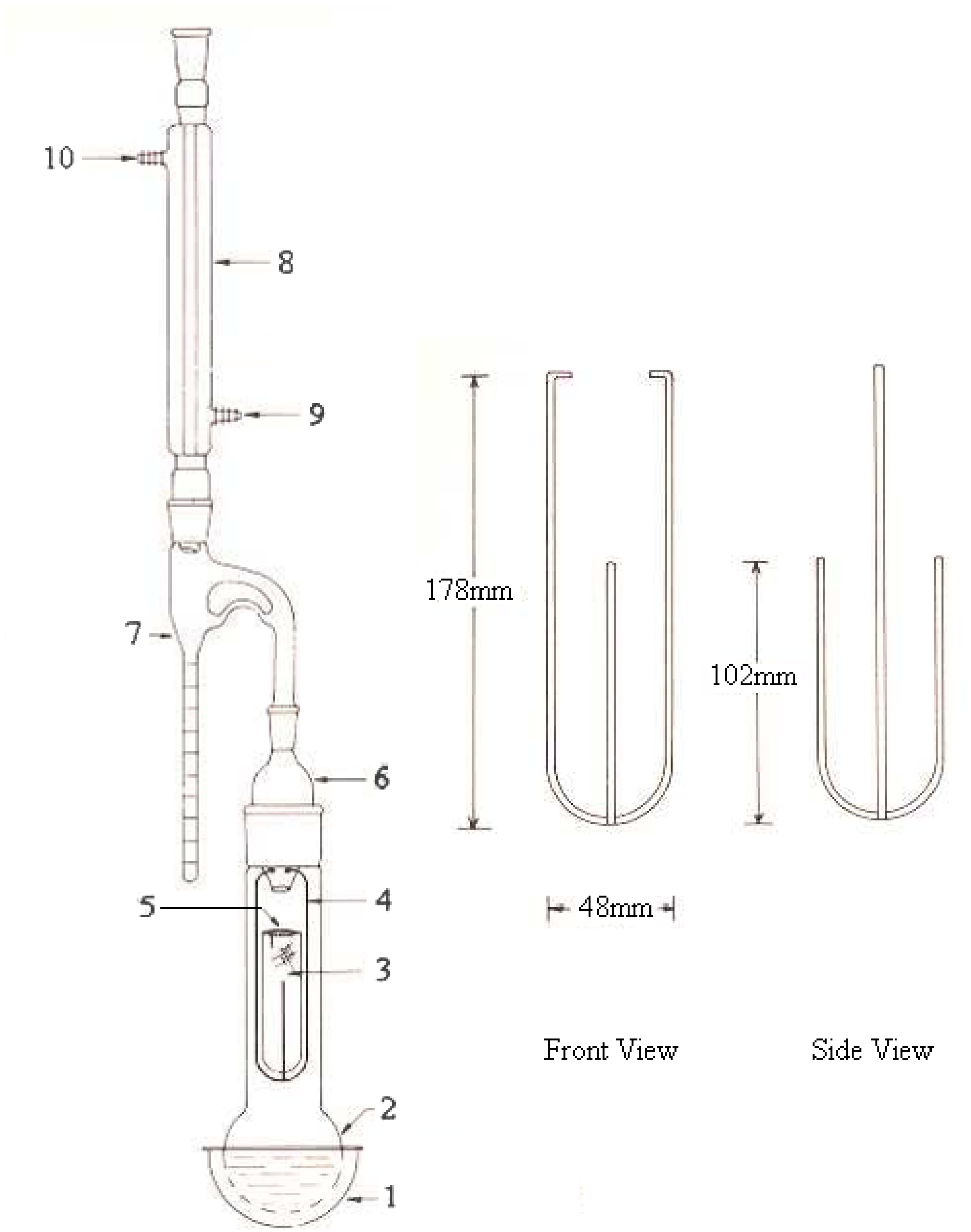


Figure 3.7: Photo of Dean-Stark extraction system and extraction thimble



Legend:

1. Heating Mantle
2. Kettle
3. Extraction Thimble
4. Thimble Basket
5. Solvent Distributor
6. Adapter
7. Water Trap
8. Condenser
9. Cooling Water Entrance
10. Cooling Water Exit

Figure 3.8: Schematic of Dean-Stark extraction system and thimble basket (adapted from Syncrude Canada Limited 1979)

The following describes the Dean-Stark extraction system, with the numbers provided in bold referring to the components in Figure 3.8.

During a Dean-Stark extraction, the system is assembled as shown in Figure 3.7. A sample (oil sand before or after SFE) is placed in the thimble that is covered by a solvent distributor (**5**) and supported by a thimble basket (**4**). The toluene in the kettle (**2**) is heated by a heating mantle (**1**). When the temperature of toluene is above its boiling point (110.6°C), the toluene evaporates. When the toluene vapour reaches the thimble, it heats the water in the sample and dissolves hydrocarbons in the sample. Since the temperature of toluene vapor is higher than the boiling point of water (100°C), the water vaporizes and rises with the toluene vapour. The vapours exit the kettle, pass through the adapter (**6**) and the water trap (**7**) and finally arrive in the condenser (**8**). The water vapour and toluene vapour are cooled by the cold water circulating in the condenser (entering at (**9**) and exiting at (**10**)). When the vapours are cooled, they become a liquid again and the liquid falls into water trap. Water and toluene are immiscible and since water is heavier than toluene, water forms a layer at the bottom of the trap. When the water trap is full, the toluene refluxes back into the thimble, through the sample and back into the kettle. This process is repeated for several hours (approximately three hours) to ensure that all water and hydrocarbons are removed from the sample.

3.2 Experimental Methods

This section describes the procedures used for preparing raw oil sands subsamples, and for carrying out a SFE experiment and a Dean-Stark extraction. The Dean-Stark extraction is used to determine the hydrocarbon (i.e. bitumen) content of the oil sand before and after SFE. The results of the Dean-Stark extraction are used to determine the extraction efficiency of the SFE experiment.

3.2.1 Subdivision of Bulk Oil Sand Samples

In order to make sure that the oil sand samples used for SFE and Dean-Stark extraction are as uniform as possible, the bulk oil sand samples were homogenized and subdivided into smaller samples (approximately 50 grams) for each experiment. The method to subdivide the bulk sample was based on the method of (Syncrude Canada Limited 1979) and can be summarized as follows:

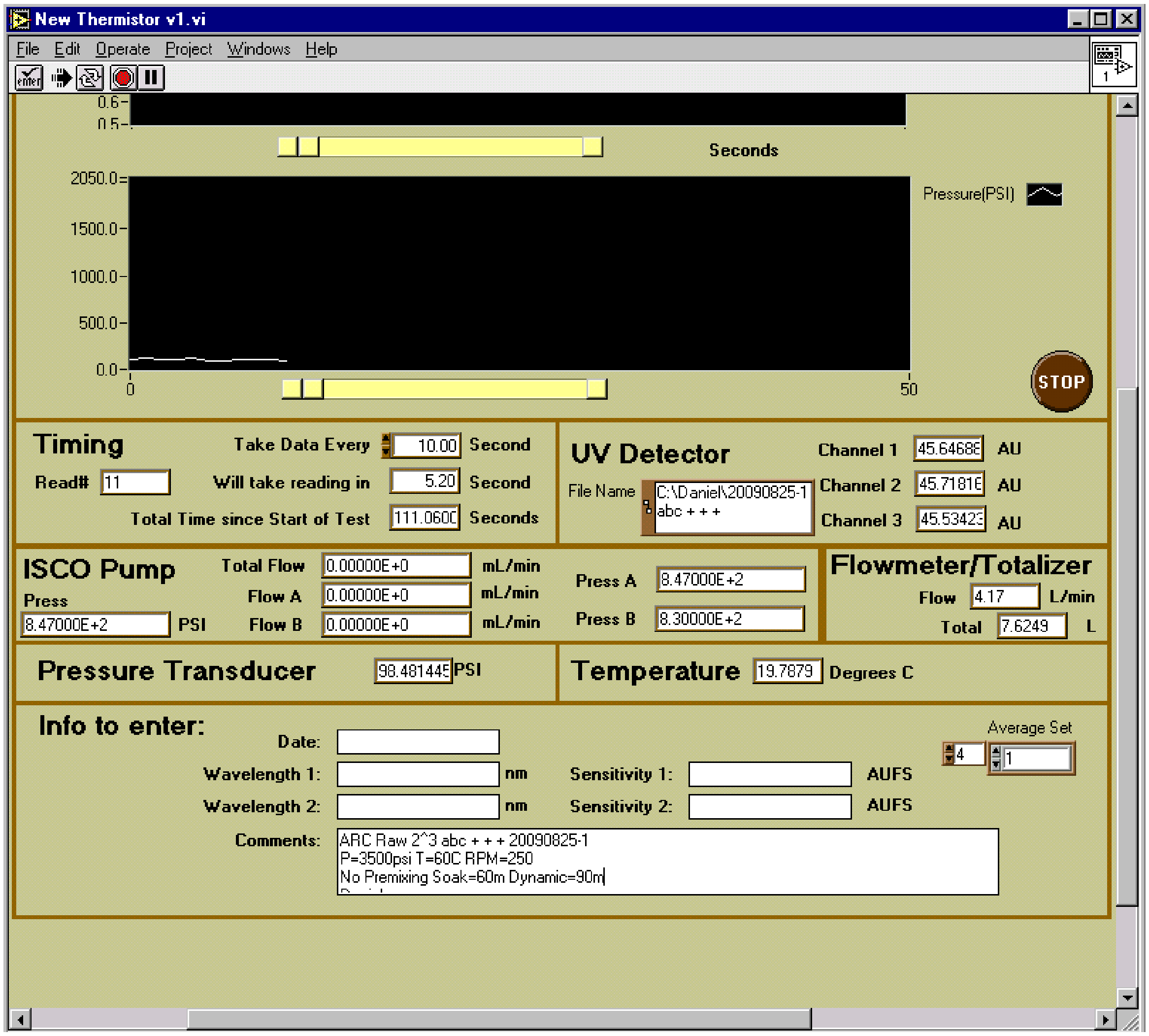
1. Place the bulk oil sand sample in a bowl. Remove all stones that are greater than 6 mm in any dimension.
2. Chop the oil sand into small pieces, then agitate the whole sample and chop again. Repeat the chopping and agitating processes until all oil sands particles are less than 6 mm in any dimension.
3. Transfer the oil sand into a tightly closed jar. Shake and homogenize the jar well, then store the jar in the freezer.

3.2.2 Supercritical Fluid Extraction Procedure

Extracting hydrocarbons from oil sand using supercritical CO_2 is the main part of this research. The general procedure for a SFE experiment can be summarized as follow:

1. Turn on the circulating refrigerated water system and set to a temperature of 4°C to cool the two syringe pumps.

2. Fill the sample vials with 2 layers of glass beads and glass wool. Using the analytical balance (Mettler-Toledo International Inc., Columbus, Ohio, USA), determines the initial mass of the sample vials.
3. Weigh approximately 50 grams of homogenized subdivided oil sand sample using the analytical balance and transfer into the extraction vessel.
4. Attach the extraction vessel to the cover using the six bolts provided. Tighten with a small wrench first, then with a torque wrench. The specific bolt tightening sequence suggested by Autoclave Engineers is 25, 35, and then 42ft-lbs.
5. Fill the water bath with hot water. Turn on the heating water circulator to heat the water and circulate the hot water through the extraction vessel's heating jacket.
6. Turn on the pumps and compress the CO_2 to the desired experimental pressure.
7. Open the data acquisition program and start collecting the experimental data and monitoring the experimental conditions. During the entire extraction process, the software records experimental data every 10 seconds. Figure 3.9 is a screen shot of the program window, showing all the monitored experimental data. This data includes: time (in seconds), total flow rate and individual pump flow rate (in $mL \cdot min^{-1}$); individual pressure and vessel pressure (in psi); and vessel temperature (in °C). A file containing all of the experimental data is created by the software and it can be opened and analyzed using Microsoft Excel®. It should be noted that the data for the UV detector and Flowmeter/Totalizer were not used in this research.



Timing
Take Data Every 10.00 Second
Read# 11
Will take reading in 5.20 Second
Total Time since Start of Test 111.0600 Seconds

UV Detector
File Name C:\Daniel\20090825-1abc + + +
Channel 1 45.64688 AU
Channel 2 45.7181E AU
Channel 3 45.53423 AU

ISCO Pump
Press 8.47000E+2 PSI
Total Flow 0.00000E+0 mL/min
Flow A 0.00000E+0 mL/min
Flow B 0.00000E+0 mL/min
Press A 8.47000E+2
Press B 8.30000E+2

Flowmeter/Totalizer
Flow 4.17 L/min
Total 7.6249 L

Pressure Transducer 98.481445 PSI

Temperature 19.7879 Degrees C

Info to enter:
Date:
Wavelength 1: nm
Wavelength 2: nm
Sensitivity 1: AUFS
Sensitivity 2: AUFS
Average Set 4 1
Comments:
ARC Raw 2^3 abc + + + 20090825-1
P=3500psi T=60C RPM=250
No Premixing Soak=60m Dynamic=90m

Figure 3.9: LabView data acquisition software control screen

8. If premixing is needed, turn on the mixer and premix the material before pressurizing the extraction vessel. After the desired time period has passed, switch the inlet valve (three-way valve) to the inlet direction that allows pressurized CO_2 to enter the extraction vessel. Once the extraction vessel is at the desired pressure, the static extraction period begins. The pressurized CO_2 is then heated to the desired experimental temperature and becomes a SCF (SC CO_2). Throughout the static extraction period, the outlet valve (three-way valve) is closed and the SC CO_2 remains in the vessel (no CO_2 flows out of the vessel).

9. During the static period, the hot water bath that keeps the metering valve from freezing is filled with hot water, and the two sample vials are connected to the system. The first sample vial is for extract collection and will be changed every 15min during the dynamic extraction period. The second sample vial collects any extract not removed in the first vial and it will remain in place until the end of the experiment.
10. At the end of static extraction period, the outlet valve is opened and the dynamic extraction period begins. The SC CO_2 carrying the extracted hydrocarbons, flows out of the vessel and through the metering valve. After leaving metering valve, the SC CO_2 is depressurizing to gaseous CO_2 and the CO_2 can no longer solubilise the hydrocarbons, so the hydrocarbons precipitate and are collected in the sample vials. Finally, the CO_2 is vented to the fume hood.
11. During the dynamic extraction, sample vials are changed every 15min. In addition, the experimental conditions (pressure, temperature and flow rate) are recorded by the data acquisition system and are also used to guide the adjustment of all the equipment. The metering valve is adjusted frequently to maintain a relatively constant flow rate. The temperature of the water bath is also monitored to keep the temperature in the extraction vessel constant. Periodically, the pumps must be refilled to ensure sufficient CO_2 for the dynamic extraction.
12. When the dynamic extraction is complete, the inlet valve is closed and no more CO_2 flows into the extraction vessel. However, with the outlet and metering valves still open, the remaining CO_2 in the extraction vessel leaves the vessel and the vessel depressurizes. When the pressure reading is approximately 100psi, the

depressurization of the extraction vessel is considered complete. Both the inlet and outlet valves are then switched to the bypass line and the pump is run for about 0.5min. During this bypass process, clean SC CO_2, which comes directly from the pump and bypasses the extraction vessel, carries out any hydrocarbons that remain in the system. These hydrocarbons, as well as any hydrocarbons from the depressurization process, are collected in a sample vial labelled “Remaining”.

13. When depressurization and bypass is complete, all the valves are closed; pumps and water baths are turned off; the computer, mixer and refrigeration system are shut down. The extraction vessel is opened and the treated oil sand is collected for analysis by Dean-Stark extraction.
14. The sample vials are weighed after the experiment is complete. The sample vials are then left open to the atmosphere so that any collected water can evaporate and so that any CO_2 can degas. The mass of the vials are monitored until the mass stabilizes (approximately 2 to 3 weeks) and the final mass of collected hydrocarbons is recorded.

3.2.3 Dean-Stark Extraction Procedure

The Dean-Stark extraction is used to determine the composition of the oil sands before and after SFE. In this research, the Dean-Stark extraction is modified from (Syncrude Canada Limited 1979) and the method allows the determination of the amount of water, dry solids, and bitumen in a sample. The following describes the methodology for a Dean-Stark extraction:

1. Insert 3 rolled Kimwipes into each new extraction thimble. Let each thimble sit in a clean marked beaker. Put the beaker and thimble in the drying oven (120ºC) for at least 1 hour. Then let them cool down to room temperature (approximately 20ºC) in a desiccator. Weigh and record the mass of the thimble plus beaker.
2. Transfer the sample (homogenized oil sand sample or treated oil sand) into the thimble. Weigh the beaker, thimble and sample to determine the mass of the sample.
3. Add approximately 200mL toluene to the kettle. Cover the thimble with the solvent distributor. Place the thimble in support basket and attach the basket to the adapter. Assemble the apparatus as shown in Figure 3.7 and ensure all connections are vapour tight.
4. Turn on the heating mantle and adjust the heating to maintain a reflux rate such that the toluene does not overflow the thimble. Since the refluxed toluene dissolves the hydrocarbons in the sample and brings them through the thimble, the color of the solvent drops from the thimble is brown. As the extraction continues, since less hydrocarbons remain in the sample, the color of the solvent drops will get lighter. When the water level in the water trap is no longer changing and the solvent drops coming out of the thimble are colorless, it is assumed that all the water has been collected in the water trap and all the hydrocarbons have been extracted from the sample. Some small particles can go through the pores of the thimble, but it is assumed that all solids of the sample are trapped in the thimble. At this point, the extraction is assumed to be complete, and the heating mantle can be turned off.
5. Allow the liquids in the water trap and kettle to cool to room temperature. Using a graduate cylinder, estimate the volume of water in the trap to the nearest 0.01mL.

Disassemble the apparatus, put the thimble back into the marked beaker and dry in the drying oven (120ºC) for at least three hours. Transfer the solution from the kettle to a 250mL volumetric flask. In order to ensure that no hydrocarbons are lost, rinse the kettle with clean toluene and pour the rinsed liquid into the 250mL volumetric flask. Bring the flask to volume with pure toluene.

6. Take more than 10mL of the solution from the flask and put it into a syringe. Filter that solution through a Whatman GD/X 25mm Disposable Syringe Filter (nominal pore size of 0.45µm) to remove any small particles that may have escaped from the thimble.
7. Superpose 2 Whatman Binder-Free Glass Microfiber Filters together and weigh them on the balance. Using a pipette transfer exactly 5mL of filtered solution and spread it evenly onto the 2 microfiber filters. Put the 2 filters in the fume hood and wait until all toluene is evaporated and only the hydrocarbons remain on the two pieces of filter paper. Figure 3.10 provides photos of the clean filter paper and the hydrocarbons on the filter paper after the toluene has evaporated. Weigh the filter paper again to determine the mass of hydrocarbons in 5mL of solution. The total mass of hydrocarbons in the sample is determined by multiplying this number by 50.
8. Take the thimble and beaker out of the drying oven and cool them to room temperature in the desiccator. After cooling, weigh and determine the mass of solids present in the sample.

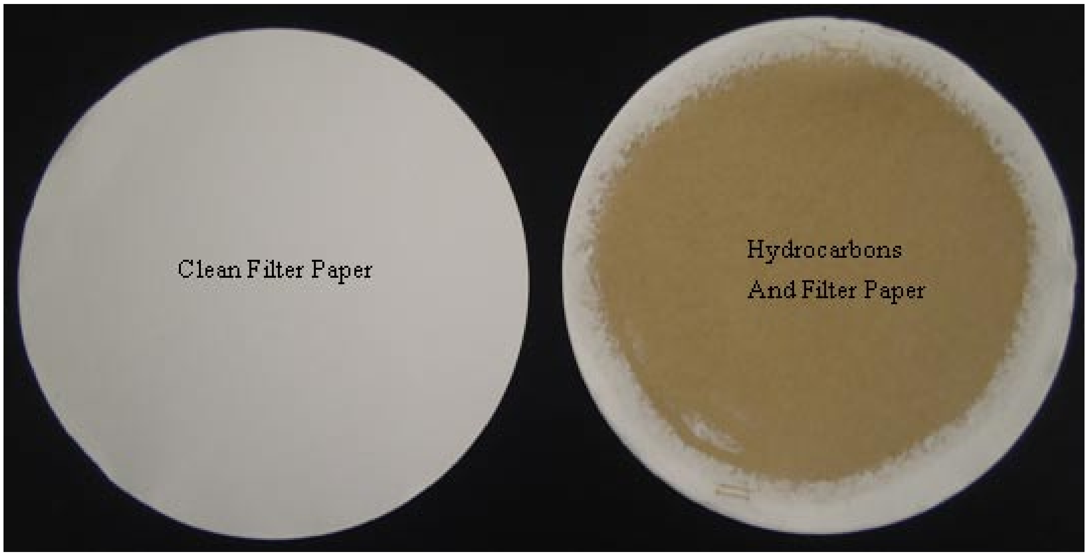


Figure 3.10: Photo of clean and hydrocarbons contaminated filter paper

3.3 Experimental Design

In this study, preliminary experiments were carried out to determine which experimental factors seem to influence the extraction efficiency when performing the SFE of oil sands. Then three experimental factors were subject to a 2^3 factorial design to study the significance of their impact on the extraction efficiency. This section introduces the basic concepts of the 2^3 factorial design.

3.3.1 General Description of the 2^3 Factorial Design

Factorial design is the most useful and most efficient tool for experiments that involve the study of the effects of two or more factors (Montgomery 2001). For a factorial design, all possible combinations of the levels of the factors can be investigated in each complete trial or replication of the experiment. Just as in this research, some experiments have to study the joint effect of the factors or, otherwise called the interaction of the factors. The factorial design can also compare the effect of the interaction with the effect of the main factors. Factorial design also evaluates the effects of a factor at several levels of the other factors and produces conclusions about the importance of each model term (factor or interaction of factors). An advantage of factorial design is that the produced conclusions are valid over a range of experimental conditions (Montgomery 2001).

One of the most important common cases of factorial design has k factors and each factor has two levels. A complete replicate of this design contains 2^k observations, so it is called 2^k factorial design (Montgomery 2001). In this research, three factors were studied and two levels ("high" and "low") were assumed for each factor. This type of experiment is called 2^3 factorial design.

3.3.2 The 2^3 Factorial Design Used in This Study

In order to apply this 2^3 factorial design, three assumptions are made (Montgomery 2001):

(1) All the factors are fixed.

(2) The designs are completely randomized.

(3) The usual normality assumptions are satisfied.

When the high level and low level of the three factors of interest are determined, all three factors are fixed. All experiments are performed in random order. By doing this, the environment (i.e. the equipment, lab room temperature, CO_2 quality, etc) of each run is as uniform as possible. At the same time, the randomization reduces the bias of one particular factor and brings down the error only to instrumental errors. The last assumption is verified by the residual analysis.

Since this factorial design investigates three factors and each factor has two levels, there are eight treatment combinations. These treatment combinations are written in standard order as *(1), a, b, ab, c, ac, bc,* and *abc*. Each symbol not only represents one observation out of the eight, but also corresponds to a particular treatment combination. Table 3.5 is a design matrix of a typical 2^3 factorial design. In the design matrix, the capital letters A, B and C represent three factors, with the “0” and “1” denoting the low level and high level of these factors, respectively. For example, the treatment combination of all three factors at their low level is labelled as *(1),* the symbol *a* represents the treatment combination when only factor A is at high level, and similarly, *abc* represents the observation that is performed when all three factors are at their high level. Thus, this design matrix summarizes all 8 treatment combinations of a 2^3 factorial design.

Table 3.5: Design matrix of a typical 2^3 factorial design

Labels	A	B	C
(1)	0	0	0
a	1	0	0
b	0	1	0
ab	1	1	0
c	0	0	1
ac	1	0	1
bc	0	1	1
abc	1	1	1

In this study, for each treatment combination, three replicates were performed, for a total of 24 experiments. As mentioned previously, these 24 experiments must be run in random order so that the experimental design is considered as a completely randomized design and so that the experimental environment is uniform for each run. Table 3.6 shows all 8 treatment combinations and the run order of every experiment.

Table 3.6: Run order of 24 experiments in this study

Labels	A	B	C	Replicate 1	Replicate 2	Replicate 3
(1)	0	0	0	8	24	9
a	1	0	0	23	2	14
b	0	1	0	13	1	20
ab	1	1	0	5	4	12
c	0	0	1	19	18	7
ac	1	0	1	11	3	17
bc	0	1	1	10	6	22
abc	1	1	1	21	15	16

3.3.3 Calculating the Extraction Efficiency

One of the most important results of every experiment is the extraction efficiency. There are two methods used in this study to calculate extraction efficiencies. In the first method, the gravimetric method, the extraction efficiency is determined using the total mass of the extracted hydrocarbons collected divided by the theoretical bitumen content in the oil sand before SFE. Because of some drawbacks of gravimetric method, which will be discussed more in Chapter 4, the analysis of the 2^3 factorial design and the discussion of the experimental results are based on a second method to calculate extraction efficiencies which uses the data from Dean-Stark extraction. Extraction efficiencies calculated by the gravimetric method are used only for comparison purposes.

Calculating the extraction efficiency using the results from the Dean-Stark extraction involves performing Dean-Stark extraction on oil sands before and after SFE. Dean-Stark extraction on the oil sands prior to SFE provides the amount of bitumen and the amount of dry solids initially present in the sample. Dean-Stark extraction on the SFE treated oil sands provides the amount of bitumen and dry solids remaining in the treated oil sands. The initial bitumen mass in the oil sand is calculated from the Dean-Stark results on the initial (untreated) oil sand and knowing the dry solids remaining after Dean-Stark of the treated sample i.e. the initial bitumen mass is equal to the ratio of the bitumen to dry solids in the initial (untreated) oil sand multiplied by the dry solids content of the treated sample. The amount of bitumen extracted is then determined by subtracting the remaining bitumen mass from the initial bitumen mass. The extraction efficiency is then determined by dividing the amount of bitumen extracted by the initial amount of bitumen present in the sample that is corresponding to the amount of dry solids in the treated sample. The relevant equations and sample calculations are included in Appendix A.

3.3.4 Analysis of Results from the 2^3 Factorial Design Experiments

After the extraction efficiencies of all experiments and the replicates are obtained, the data is subjected to an ANOVA statistic analysis. The first step is estimating the factor effects. A change in the level of a factor or interaction will cause a change in response. It could be positive or negative, and its value may be large or small. This change in response is defined as the effect of this model term (a factor or interaction) (Montgomery 2001). Based on the effect of every factor, the sum squares, mean squares and the F_0 values can be calculated. Finally, the *P*-value of each factor or interaction is calculated by Microsoft Excel®.

In a statistic analysis of a typical engineering test, in order to determine whether the factor or interaction has effect on the experiment results, the corresponding *P*-value is compared with a specified value α called level of significance (Montgomery 2001). For a typical engineering test, the level of significance (α) usually is set at 0.05 (5%). If the *P*-value is larger than 0.05, the model term corresponds to this *P*-value has no effect on the experiment results. After all the *P*-values are checked, the conclusion of statistical analysis about the model terms is made and the significance of each model term is determined.

Chapter 4 Results and Discussion

This section presents both the results of the preliminary experiments and of the formal experiments of this research. The effects of factors of interest on the extraction efficiency and some meaningful observations are also discussed in detail.

4.1 Characterization of Oil Sands

In order to determine the composition of the oil sands in terms of bitumen, water and solids content, the three oil sands were analyzed by Dean-Stark extraction. The Dean-Stark extraction divides the oil sand into three main components: bitumen, water and dry solids, expressed as a percentage of the total mass on a dry solids basis. The theory of this dry solid basis standard is that in the raw oil sand, the mass of bitumen and water corresponding to certain mass of dry solid should be constant. The advantage of this expressing the composition on a dry solids basis is that, no matter how much oil sand sample is subjected to Dean-Stark extraction, as long as the mass of dry solid contained in the analyzed sample is measured, the corresponding masses of bitumen and water in the oil sand before SFE can be calculated.

To measure the composition of oil sand before SFE, homogenized subdivided oil sand samples were used. After doing several Dean-Stark extractions, the average composition of the oil sands before SFE is calculated and these data are provided in Table 4.1. The raw data from Dean-Stark extractions on the ARC oil sand are presented in Appendix B. In all Dean-Stark extractions performed to characterize the oil sands, the recovery was greater than 98.8%.

Table 4.1: Composition of the three oil sands used in this study

Oil sand type	Composition (% mass)			Number of samples
	Solid	Bitumen	Water	
ARC Oil Sand	85.0±0.35	10.1±0.25	4.9%±0.14	5
Syncrude Oil Sand	86.3±0.15	13.6±0.13	0.1%±0.02	3
Suncor Oil Sand	86.5±0.19	8.3±0.27	5.2%±0.30	3

From Table 4.1, it appears that the bitumen content of Syncrude oil sand is the highest and that it also contains the least amount of water. In addition, the water content is much less that the water content typical for oil sand, ranging from 3 to 6wt% (Chalaturnyk et al. 2002). Since the Syncrude oil sand was several years old and stored in a walk-in cooler at 4°C, water may have evaporated and therefore this composition likely does not reflect the composition of the fresh oil sand. The mineral (solids) content of all three oil sands are in the typical range for oil sands, that is, between 84 to 86 wt% (Chalaturnyk et al. 2002).

The Syncrude oil sand was only used for preliminary experiments. The ARC oil sand was purchased from the Alberta Research Council sample bank in May 2009. The ARC oil sand was the feedstock for some preliminary extractions and was used for most extractions in this study. The Suncor oil sand was used for a final set of experiments, to determine the effect of oil sand ore type on the extraction of bitumen from oil sands at a given set of experimental conditions.

4.2 Summary of SFE Experiments Performed

In order to test the feasibility of using SC CO_2 to extract hydrocarbons from oil sand and to determine some of the factors that have significant impacts on the extraction, a number of preliminary experiments were carried out. Then, based on the results of these preliminary experiments, a formal experimental program was designed using a two to the three (2^3) factorial design.

Some preliminary experiments used the Syncrude oil sand as the feed material for the extractions and tested the effects of experimental factors such as temperature, static extraction period, dynamic extraction period and mixing rate on the amount of bitumen extracted from the oil sand. Some SFE experiments were also performed on an oil sand slurry (a 1:1 mass ratio of Syncrude oil sand and water). The impacts of an additive were also studied.

A second set of preliminary experiments used ARC oil sand and focused on determining the effects of impeller type, mixing rate, and premixing on the extraction efficiency.

The results of the preliminary experiments identified three experimental factors to be studied as part of the formal experiments. The formal experiments followed a 2^3 factorial design and investigated the effects of pressure, temperature, and mixing rate on extraction efficiency. All other experimental conditions were maintained constant that is a 60min static period followed by a 90min dynamic extraction period with no premixing and mixing using the helical impeller during the extraction.

For the formal experiments, 8 different treatment combinations were tested (different pressure, temperature or mixing rate). Each experiment was tested in triplicate for a total of 24 trails. Each experiment yielded a value of extraction efficiency. As described in Section 3.3.3, the extraction efficiency was calculated by determining the hydrocarbon content before and after SFE using Dean-Stark extraction.

4.3 Data Collected for All Supercritical Fluid Extraction Experiments

For all extractions conducted in this research, LabView 5.1 data acquisition software was used to record the pressure at the pump, the CO_2 flow rate from the pumps, the pressure just before the extraction vessel and the temperature inside the extraction vessel. All data was recorded every ten seconds. This section presents and discusses the collection of these experimental data. A sample of the output from this data acquisition software is provided in Appendix C.

4.3.1 Pressure Data

The pump controller measures the pressure of the two pumps (Pump A and Pump B), and the pressure transducer measures the pressure just before the extraction vessel. All pressure data is recorded by the data acquisition software. Figure 4.1 shows the pressure data from a typical SFE experiment.

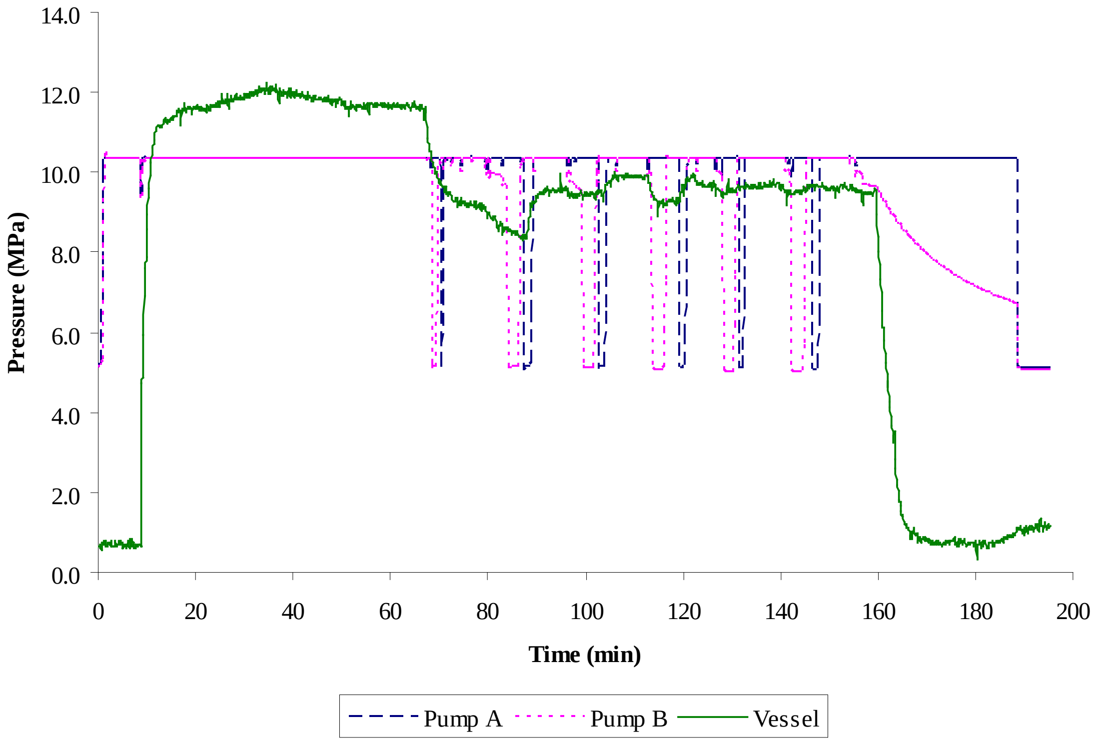


Figure 4.1: Pressure data for a typical SFE experiment at 10.3MPa and 60°C

As shown in Figure 4.1, in the first 2min, when the pumps are turned on, the pressure of Pumps A and Pump B increase from 5.2MPa (the CO_2 cylinder pressure) to the desired extraction pressure of 10.3MPa. At about 9min, when the vessel inlet valve is opened, the vessel pressure increases to approximately 11.5MPa. Because Pump A and Pump B try to pressurize the vessel, there is a slight decrease in the pressures of these pumps. Once the extraction vessel is pressurized, the static period begins: the vessel outlet valve is closed, and no CO_2 flows out of the vessel. From Figure 4.1, it can be seen that during the static period, the vessel pressure is higher than the pump pressure. The possible reason for this is that there appears to be an offset in the pressure transducer of approximately 0.8MPa, as can be seen at the beginning of the experiment. Before opening the valve to the pressure vessel, the pressure transducer should read atmosphere pressure, but from Figure 4.1, it can be seen that at the beginning the pressure reading is approximately 0.9MPa and it is much higher than the atmosphere pressure (0.1MPa). Therefore, the offset in the pressure transducer is approximately 0.8MPa.

At approximately 70min, the dynamic extraction period begins and the vessel outlet valve and metering valve are opened. The metering valve is adjusted to maintain the desired flow rate. During this adjustment, the pressure in the extraction vessel drops while the pump pressure remains at the desired experimental pressure. It is possible that the vessel pressure is lower than the pump pressure due to leaks in the system or due to the high flow rate at the metering valve that does not allow a higher pressure to be maintained in the vessel. Throughout the dynamic extraction period, the vessel is continuously supplied with high-pressure CO_2 from one of the two pumps. When the CO_2 in one pump runs out, that pump is stopped and refilled. At the same time, the second pump continues to maintain the pressure in the vessel. After the first pump is refilled and pressurized, it begins to flow. The change in pressure of the pumps reflects this pump refilling process.

At approximately 160min, the dynamic extraction period is stopped, the inlet valve is closed and the CO_2 inside the vessel is allowed to flow out in order to depressurize the vessel. The vessel pressure quickly drops during this depressurization. The pumps are still at pressure since they are continually supplying high pressure CO_2 through the bypass line to remove any remaining hydrocarbons in the system.

4.3.2 Temperature Data

Figure 4.2 provides the temperature profile of a typical extraction. A thermistor probe placed inside the extraction vessel monitors the temperature of the vessel and all temperature data is recorded by the data acquisition software.

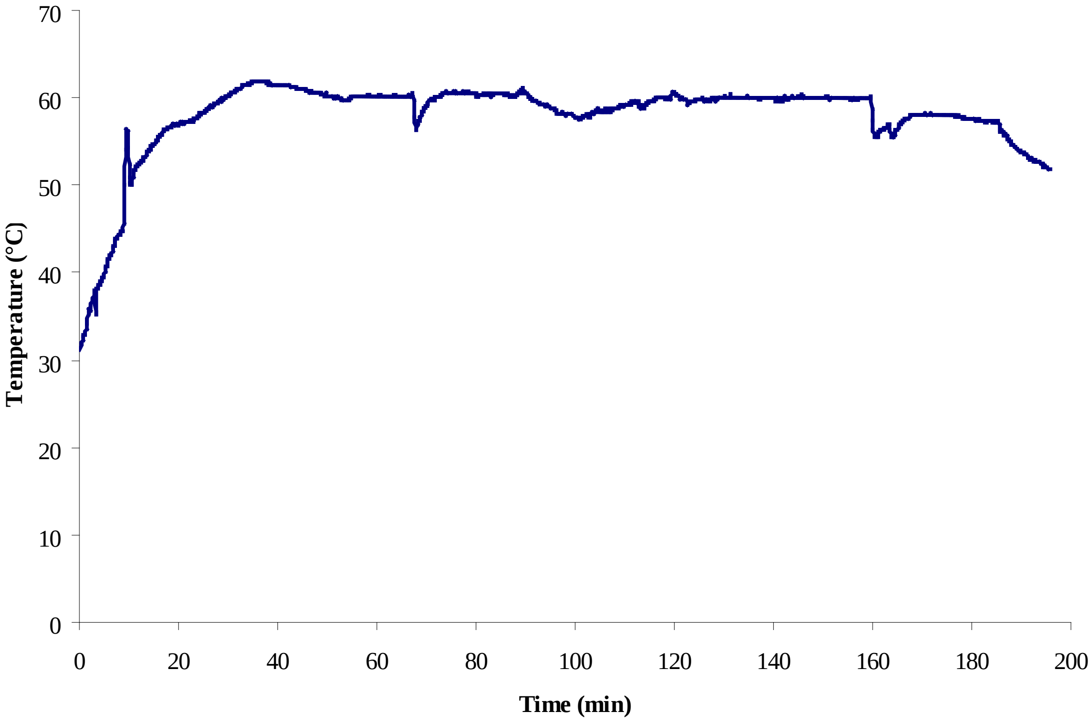


Figure 4.2: Temperature data for a typical SFE experiment at 10.3MPa and 60°C

When the extraction vessel is connected to the extraction system, hot water is circulated through the vessel heating jacket which controls the temperature in the extraction vessel. After approximately 10min, the vessel reaches a temperature of about 48°C. Then, the inlet valve is opened to begin the static period and warm CO_2 (CO_2 which was heated in the preheating coil) pressurizes the vessel. A slight increase in temperature is observed during this pressurization but then the temperature drops to the value prior to pressurization. The temperature then continues to increase and reaches the desired temperature at about 30min.

At about 70min, the dynamic extraction period begins. As some high temperature CO_2 flows out the vessel, the vessel temperature decreases slightly. During the dynamic extraction, the temperature is maintained at the desired temperature (60°C). When the dynamic extraction is over, no more CO_2 enters the vessel and the vessel starts depressurizing. The temperature also starts dropping. At the end of the extraction, the circulator is turned off, and no water is circulated through the heating jacket, so the temperature in the vessel drops. Based on Figure 4.2, during the static extraction period and dynamic extraction period, the average temperature of the vessel is 60±1°C. In fact, for different extraction conditions, the accuracy of the vessel temperature is ±1°C (i.e. 32±1°C, 40±1°C and 60±1°C).

Table 4.2 presents the density of SC CO_2 at different temperatures and pressures (NIST 2010). Table 4.2 shows that the difference in density caused by 1°C is minimal. Given that the uncertainty in the temperature is small and given that this uncertainty appears to have little effect on the density of the SC CO_2, it was assumed that the small fluctuation in temperature (±1°C) would not affect the experiment results.

Table 4.2: The density of SC CO_2 at different temperature and pressure (unit g·mL^{-1})

	31°C	32°C	33°C	59°C	60°C	61°C
10.3MPa	0.7692	0.7589	0.7481	0.3187	0.3117	0.3052
24.1MPa	0.9131	0.9088	0.9045	0.7825	0.7775	0.7724

4.3.3 Carbon Dioxide Flow Rate Data

The pump controller also measures the flow rate from each pump. Since the pumps are cooled to 4.0°C using a circulating refrigerated water system, the flow rate is measured at 4.0°C and at the experimental pressure. Figure 4.3 presents the flow rate data as measured by the pump controller for the same experiment as depicted in Figure 4.2.

The first peaks that appear at approximately 2min correspond to the flow necessary to pressurize the short length of tubing that connects the pumps to the extraction vessel inlet valve. At approximately 10min, the inlet valve is opened and compressed CO_2 flows into the vessel. After the vessel is pressurized, the static period begins. The flow is zero since there is no flow during this period (the extraction vessel outlet is closed).

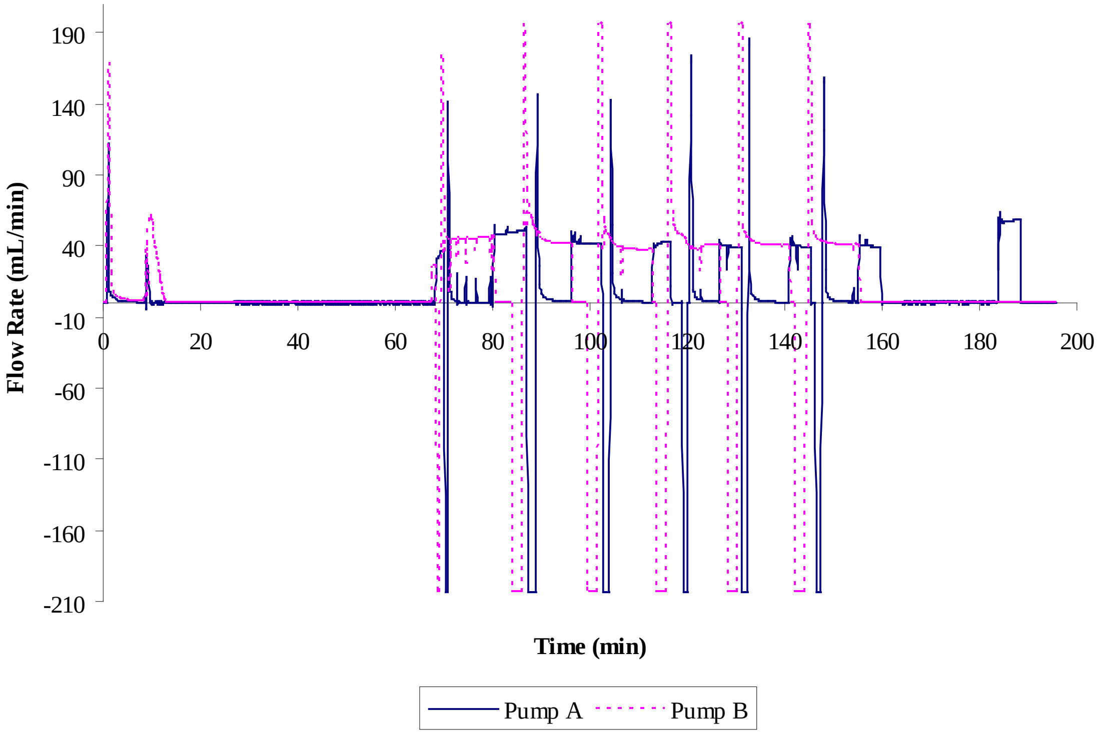


Figure 4.3: Flow rate data for a typical SFE experiment at a flow rate of approximately 40mL·min^{-1}

Once the extraction vessel outlet valve and metering valve are opened, the dynamic extraction period begins. The two pumps supply CO_2 at a flow rate determined by the metering valve. During the dynamic extraction, when one pump is empty, it will stop and refill with CO_2. On the pump controller, this refilling process registers as a negative flow (-204mL·min^{-1}). After the pump is refilled, it will go back into service and will register a high positive flow for a short period of time. Throughout the dynamic extraction, Pump B is the primary pump while Pump A is a backup pump that runs when Pump B is refilling. Pump B always runs with a flow rate of approximately 40mL·min^{-1}, which was the desired flow rate for this experiment. For the experiments at an extraction pressure of 10.3MPa, the flow rate was approximately 38.23g·min^{-1} (based on a density of 0.9558g·mL^{-1} at 4°C and 10.3MPa (NIST, 2010)). However, for the experiments at higher pressure, the flow rate was approximately 40.83g·min^{-1} (based on a density of 1.021g·mL^{-1} at 4°C and 24.1MPa (NIST, 2010)).

At about 160min, when the dynamic extraction is finished, the inlet valve is closed, and therefore there is no flow from pumps. After the vessel is depressurized, the pumps are turned on again and CO_2 flows through the bypass line and purges any hydrocarbons that may have remained in the lines between the vessel and the sample vials.

The flow rate through the vessel and the SFE sample vials is controlled by adjusting the metering valve. Since the SC CO_2 is depressurized at the metering valve, despite the fact that the metering valve is placed in a hot water bath, sometimes it can freeze or plug. During the dynamic extraction process, the metering valve is adjusted frequently to maintain a constant flow rate through the SFE system.

4.4 Analysis of the Preliminary SFE Experiments

Before the design of the 2^3 factorial design experiments, preliminary experiments were performed to test the SFE system and to confirm the feasibility of extracting hydrocarbons from oil sands by SC CO_2. The most important objective of the preliminary experiments was to identify experimental factors to be tested in the formal experiments. The following sections will discuss the preliminary experiments. Since different types of oil sands were used and since the methods of analysis were being developed, the preliminary experiments of this research can be divided into two sets, a first set and a second set.

4.4.1 First Set of Preliminary Experiments Carried out on Syncrude Oil Sand

In the first set of preliminary experiments, the Syncrude oil sands ore was tested. As mentioned previously, this oil sand was received in 2003 and was stored in a walk-in cooler at 4°C. Since this oil sand was old, some water had already evaporated and the properties of this oil sand were different than those of fresh oil sand.

In the first set of preliminary experiments, the extraction efficiency was determined by the gravimetric method. The gravimetric method uses the mass of hydrocarbons collected and compares this mass to the initial amount of hydrocarbons present in the sample. The extraction efficiency is determined by dividing the mass collected by the initial mass. The mass of the collected hydrocarbons was measured at least three times. The first mass (m_1) was measured after the extraction was complete. A second mass (m_2) was determined after the sample vials of collected hydrocarbons were allowed to sit overnight. The third mass (m_3), also referred to as the final mass, was determined at least two weeks later, when the mass of the extracts had stabilized. The mass was considered stable when it no longer fluctuated more than 0.0001g. It was assumed that once the mass was stable, any water present in the extracts had evaporated. The sample raw data of hydrocarbon masses (m_1, m_2 and m_3) are provided in Appendix D. For these preliminary experiments, the extraction efficiency from the gravimetric method was calculated by using final mass (m_3) divided by the bitumen content in the feed before SFE experiment, which was determined by the mass of the feed before SFE multiplied by the bitumen percentage of Syncrude oil sand (13.6% as provided in Table 4.1).

Table 4.3 and 4.4 summarize the results of the first set of preliminary experiments. Experiments shown in Table 4.3 were performed on oil sand alone. Table 4.4 presents the results of extractions performed on water slurries of oil sand or on water slurries of oil sand with an additive. It should be noted that in Table 4.4, m_4 is the mass of the extracts determined 15min after the sample vials were disconnected from the SFE system. It was assumed that after 15min, the CO_2 in the sample vials is degassed, so m_4 was assumed to represent the total mass i.e. the mass of water and mass of hydrocarbons extracted by SC CO_2. The mass m_3 represents the mass of the extracted hydrocarbons after approximately four weeks. Since water was extracted in the experiments with slurries, at least four weeks was required for the mass of the extracts to stabilize. It was assumed that once the mass stabilized, any water present in the extracts had evaporated.

The premixing period of the extractions in Table 4.3 was 10min. All of the extractions in Table 4.4 were conducted at 24.1MPa and 40°C with 10min of premixing at 110rpm and a static and dynamic period of 60min and 90min, respectively.

Table 4.3: Summary of the results of the first set of preliminary SFE experiments on Syncrude oil sand

Experiment	Mass of Oil sand	Pressure	Temperature	Mixing Rate	Static Period	Dynamic Period	Mass of Extracts			Extraction Efficiency
	(g)	(MPa)	(°C)	(rpm)	(min)	(min)	m_1 (g)	m_2 (g)	m_3 (g)	%
1	50.322	24.1	40	110	60	90	3.1348	3.0174	2.9685	43.4%
2	50.163	24.1	40	110	60	90	2.8988	2.8016	2.5775	37.8%
3	50.050	24.1	***60***	110	60	90	2.8761	2.6485	2.5178	37.0%
4	50.181	24.1	***60***	110	60	90	2.9190	2.6393	2.4816	36.4%
5	50.170	24.1	40	110	***90***	90	2.4732	2.1903	2.1383	31.3%
6	50.180	24.1	40	110	***90***	90	2.3363	2.2285	2.1846	32.0%
7	50.299	24.1	40	110	60	***120***	3.1835	2.8222	2.7981	40.9%
8	50.102	24.1	40	110	60	***120***	3.2621	3.0842	3.0014	44.0%
9	50.036	24.1	40	***250***	60	90	2.6395	2.6335	2.6312	38.7%
10	50.005	24.1	40	***250***	60	90	2.6420	2.5553	2.5264	37.1%

m_1 is the mass of the extracts determined after completion of the extraction experiment.
m_2 is the mass of the extracts determined after approximately 12 hours (overnight).
m_3 is the mass of the extracts determined after a minimum of 2 weeks after completion of the experiment.

Table 4.4: Summary of the results of the first set of preliminary SFE experiments on Syncrude oil sand slurry or oil sand slurry with additive

Experiment	Mass of Oil sand	Mass of Water	Mass of Additive	Mixing Rate	Mass of Extracts			Extraction Efficiency
	(g)	(g)	(g)	(rpm)	m_4 (g)	m_1 (g)	m_3^* (g)	%
11	50.102	50.653	None	110	3.6921	3.5791	0.9606	14.1%
12	50.296	49.975	None	110	3.5884	3.4348	0.9965	14.6%
13	50.445	49.754	None	110	2.9160	2.8111	0.5082	7.4%
14	50.074	49.909	None	110	3.4905	3.3887	0.6043	8.9%
15	50.136	50.116	None	110	3.4714	3.3677	0.6603	9.7%
16	50.418	50.116	9.8989	110	3.9079	3.7430	1.5854	23.1%
17	50.387	49.635	10.0352	110	4.2553	4.0900	1.8410	26.9%
18	50.139	49.610	None	***250***	10.506	10.337	2.4483	35.9%
19	50.295	49.351	None	***250***	9.6971	9.5142	1.7124	25.0%

* Large amounts of water are extracted and it takes almost 4 weeks for the mass to stabilize. Therefore m_3 is the extract mass that was determined at least 4 weeks later.

m_4 is the mass of extracts determined 15min after the sample vial was disconnect from the SFE system.

One of the objectives of this research was to identify the experimental conditions that could produce the highest extraction efficiency. Most of the published work suggests that the extraction yield increases with extraction pressure (Al-Marzouqi et al. 2007; Deo et al. 1992; Guiliano et al. 2000; Hwang et al. 1995; Hwang and Ortiz 2000; Liu et al. 1999; Rose et al. 2000), Therefore, all preliminary experiments were tested at the highest pressure obtainable with the laboratory bench-scale apparatus used in this work, that is 24.1MPa. Other extraction conditions tested in the early stages of the preliminary experiments include temperature, static extraction period, dynamic extraction period, mixing rate additive and modifier. Premixing is the mixing time after the vessel is attached to the SFE system and before the introduction of the SC CO_2 into the vessel. Premixing was fixed at 10min and allowed the oil sand or the oil sand slurry to be well mixed.

From Table 4.3, the extraction efficiencies for Experiments 1 and 2 (duplicates) are 43.4% and 37.8%, respectively. These two experiments were carried out at a pressure of 24.1MPa, a temperature of 40°C, and a mixing rate of 110rpm. The static extraction period and dynamic extraction period were 60min and 90min, respectively. This set of experimental conditions (extraction conditions of Experiments 1 and 2) was the first tested condition of the study and is considered as the initial extraction condition.

As seen in Table 4.3, Experiments 3 and 4 were tested at a higher temperature (60°C). The extraction efficiencies were slightly lower than for Experiments 1 and 2. Some previous studies also observed that the extraction yield decreased with increasing temperature (Al-Marzouqi et al. 2007; Hwang and Ortiz 2000; Rose et al. 2000), and these studies explained that an increase in temperature reduces the density of SC CO_2 and therefore causes a decrease in the solvent power of SC CO_2. Deo et al. (1992) did SFE experiments of crude oil at a constant pressure (10.3MPa) and at three different temperatures (30.85, 37.85 and 65.85°C). The two lower temperatures (30.85 and 37.85°C) gave almost the same extraction yield, while the extraction yield at the higher temperature (65.85°C) was much lower. Deo et al. (1992) suggest two reasons for the lower yield at high temperature. One reason was that the phase behaviour shifted from liquid-liquid-like system to a liquid-vapour-like system. In the liquid-liquid-like system, the liquid like CO_2 has a higher density and can be well mixed with the feed. However, in the liquid-vapour-like system, the vapour like CO_2 has a much lower density and it could not mix well with crude oil. The second reason for the lower yield at higher temperature was the significant decrease of density of SC CO_2 at high temperature (Deo et al. 1992).

As shown in Table 4.5 and for all the extractions in this research, most of the hydrocarbons (more than 75%) are collected in the first 15min of the dynamic extraction. In order to explain this trend, the mechanism of how hydrocarbons are extracted by SC CO_2 from a solid matrix must be understood. According to Madras et al. (1994), hydrocarbons first desorb from the solid matrix (oil sands particles). This desorption consists of three consecutive mass-transport steps: (1) intraparticle diffusion of the hydrocarbons from the interior to the outer surface of the particle; (2) mass transfer of the hydrocarbons from the outer surface of the particle into the bulk mobile phase (SCF phase); (3) bulk transport of the hydrocarbons in the mobile phase (Madras et al. 1994). During the static period, no SC CO_2 is flowing through the vessel and therefore hydrocarbons are not carried out of the vessel. The hydrocarbons will dissolve into the SC CO_2 until solubility is reached or until no more hydrocarbons are available to dissolve into the SC CO_2. When the dynamic phase begins, the SC CO_2 containing hydrocarbons flows out of the vessel and the hydrocarbons are collected. As the dynamic phase continues, less and less hydrocarbons are collected, either due to the fact that sufficient time is not allowed to reach solubility in the vessel or due to the fact that less and less hydrocarbons are available to dissolve into the flowing SC CO_2.

In order to determine if the static period was sufficient time to allow the available hydrocarbons to dissolve into the SC CO_2, longer static periods were tested in Experiments 5 and 6, i.e. 90min as opposed to 60min in Experiments 1 and 2. The extraction efficiencies for Experiments 5 and 6 were of the same order or less than that of Experiments 1 and 2. Table 4.5 is a comparison of final masses (m_3 as defined in Table 4.3) of Experiments 1, 2, 5 and 6 over the different extraction periods. The mass of hydrocarbons collected over the period 70-90min includes the mass of hydrocarbons extracted during the bypass process. Figure 4.4 presents the cumulative mass of extracted hydrocarbons as a function of cumulative mass of CO_2 for Experiments 1, 2, 5 and 6. It can be seen that for all four extractions, almost more than 75% of hydrocarbons are collected in the first 15min of dynamic extraction period, and the mass of hydrocarbons collected in the first 15min with longer static extraction period (90min) is less than that with 60min static extraction period. Although one would expect that the longer static extraction should lead to more or as many hydrocarbons being extracted, the different behaviour observed here may be due to the heterogeneous nature of the oil sands and the hydrocarbons they contain. The hydrocarbons are a complex mixture and one sample of oil sands may contain heavier hydrocarbons that are less likely to desorb and dissolve in the SC CO_2 than the hydrocarbons found in another sample. In addition, the solid matrix (oil sands) is a complex matrix that may be different from one experiment to the next, despite efforts to homogenize the oil sands. Both the nature of the hydrocarbons and of the oil sands may explain the difference observed. In any case, a longer static extraction period did not increase the extraction efficiency.

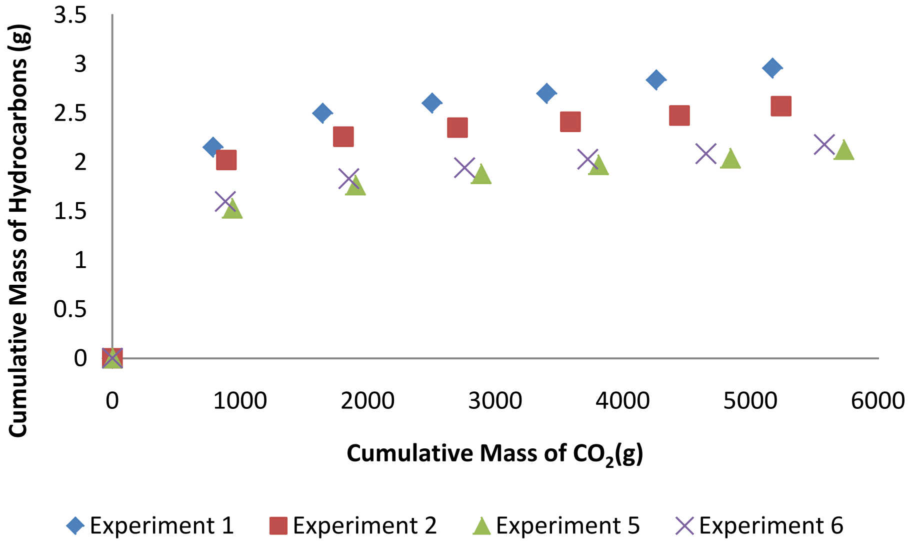


Figure 4.4: The relationships between cumulative mass of extracted hydrocarbons and cumulative mass of CO_2 for Experiments 1, 2, 5 and 6

Table 4.5: Comparison of the mass of hydrocarbons extracted as a function of time Experiments 1, 2, 5 and 6

Experiments	0-15 min	15-30 min	30-45 min	45-60 min	60-75 min	75-90 min	Carryover	Total	Extraction Efficiency	% of extracted hydrocarbons*
1	2.1518	0.3459	0.1034	0.0981	0.1375	0.1202	0.0116	2.9685	43.4%	72.5%
2	2.0212	0.2375	0.0920	0.0594	0.0642	0.0954	0.0077	2.5775	37.8%	78.4%
5	1.5274	0.2367	0.1147	0.0918	0.0667	0.0874	0.0137	2.1383	31.3%	71.4%
6	1.5966	0.2330	0.1112	0.0869	0.0563	0.0936	0.0070	2.1846	32.0%	73.1%

* % calculated from the mass of hydrocarbons extracted in the first 15min divided by the total mass of hydrocarbons extracted.

After 90min of dynamic extraction, there are still some hydrocarbons left in the SFE treated sample (approximately 20 to 30%), so a longer dynamic extraction period was investigated in Experiments 7 and 8 (i.e. 120min instead of 90min). Table 4.6 compares the results of Experiments 1 and 2 with the results of Experiments 7 and 8. The mass values in Table 4.6 are m_3 as defined in Table 4.3. The mass values m_{90min} and m_{120min} are total masses of hydrocarbons collected after 90min and 120min, respectively. It should be noted that the m_{90min} of Experiments 7 and 8 do not include the mass of hydrocarbons extracted during the bypass process. Figure 4.5 presents the relationships between the cumulative mass of extracted hydrocarbons and cumulative mass of CO_2 for Experiments 1, 2, 7 and 8.

Table 4.6 Comparison the results of Experiments 1, 2, 7, and 8

Experiments	m_{90min} (g)	Extraction Efficiency at 90min	m_{120min} (g)	Extraction Efficiency at 120min
1	2.9685	43.4%	NA	NA
2	2.5775	37.8%	NA	NA
7	2.6908	39.3%	2.7981	40.9%
8	2.9159	42.8%	3.0014	44.0%

NA: not applicable.

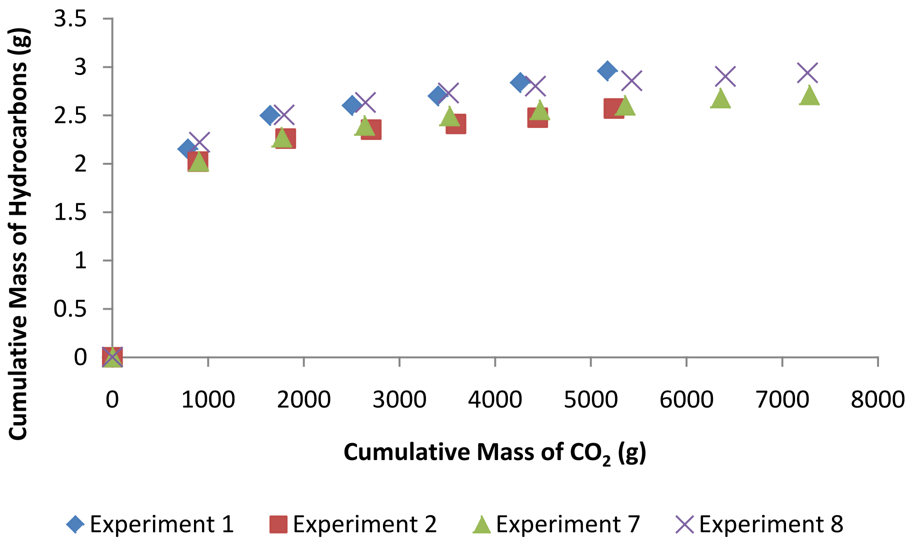


Figure 4.5: The relationships between cumulative mass of extracted hydrocarbons and cumulative mass of CO_2 for Experiments 1, 2, 7 and 8

From Table 4.6, it can be seen that, with a longer dynamic extraction period, more hydrocarbons are extracted and higher extraction efficiencies are achieved. However, the mass of hydrocarbons and the extraction efficiencies at the end of Experiments 1 and 2 and at 90min for Experiments 7 and 8 were similar. Furthermore, for all four experiments a majority of the hydrocarbons (approximately 2.8 grams) were extracted in the first 90min. Based on the result in Table 4.6 and Figure 4.5, performing 30min of additional dynamic extraction and using approximately 2000g of additional CO_2 to extract approximately 0.1 gram of additional hydrocarbons does not seem valuable if one considers the time and economics of the process.

A higher mixing rate will not only provide better contact between the oil sands and SC CO_2, but it may also break down the oil sands into finer particles, consequently, increasing the surface area of the oil sands particles and facilitating diffusion of bitumen from the particle into the bulk supercritical fluid. In order to test the impacts of higher mixing rate on the extraction efficiency, Experiments 9 and 10 were carried out with a high mixing rate (250rpm). The extraction efficiencies were 38.7% and 37.1%, and the final mass of hydrocarbons extracted was 2.6312 grams and 2.5264 grams. It was hard to conclude, based on the results, if higher mixing rate increased or decreased the extraction efficiency, so it was decided that the mixing rate would be one of the parameters in the formal experiments.

Table 4.4 summarizes the extractions that were carried out on an oil sand slurry. The oil sand slurry is a mixture of oil sand and deionized water at a mass ratio of 1:1. The pressure, temperature and premixing time of extractions in Table 4.4 were fixed at 24.1MPa, 40°C and 10min, respectively. The static extraction period and dynamic extraction period were set at 60min and 90min, respectively. Experiments No. 18 and 19 tested the impacts of higher mixing rate.

The oil sand slurry contained a lot of water, and during the SFE, some water was extracted by the SC CO_2. Thus, the mass determined after extraction (m_1) in Table 4.4 was higher than that of Table 4.3. Four weeks later, after the extracted water had evaporated, the mass of extracted hydrocarbons became stable (m_3). All the final masses of SFE on oil sand slurry with low mixing rate (Experiments 11, 12, 13, 14, and 15) are less than 1 gram, and the extraction efficiencies were from 7.4% to 14.6%, much less than that of initial condition on dry oil sand. Some studies suggest that the dissolution of water into SC CO_2 can increase the polarity of the CO_2 and therefore the solubility of non-polar hydrocarbons in the SC CO_2 decreases (Akgerman and Yeo 1993; Laitinen 1999). For the slurries experiments of this study, the “shielding” effect of water is perhaps a explanation for the lower extraction efficiencies from slurries. Some studies state that water is quite immiscible with SC CO_2, so it acts as a mass transfer barrier that limits the penetration of SC CO_2 into the porous feed material (Camel et al. 1993; Laitinen 1999). Becnel and Dooley (1998) suggest that the diffusion in liquids (i.e. water) is slower than in SCFs (i.e. SC CO_2), so water in the pores of the solid matrix may increase the diffusional limitations. In another study, Hawthorne et al. (1993) found that some organic components may be trapped between the solid matrix and the water layer that coats the solid matrix and making them contact with SCF much harder (Hawthorne et al. 1993). All these negative effects of water may cause the lower extraction efficiency obtained in the slurry experiments.

In Experiments 16 and 17, oil sand, water and approximately 10g of additive were added to the extraction vessel before the vessel was attached to the SFE system. The additive is an inert substance that does not react with hydrocarbons and SC CO_2. When the additive was added to the slurries (Experiments 16 and 17), the final mass and extraction efficiencies increased slightly but were still not as good as the extraction efficiencies of dry oil sand extractions in Table 4.3.

Experiments 18 and 19 in Table 4.4 tested a higher mixing rate on the oil sand slurry. The mass of hydrocarbons collected immediately after the extraction (m_1) was as high as approximately 10 grams, but the final mass (m_3) was less than 2.5 grams. From this result, it can be seen that, as compared to the lower mixing rate, a higher mixing rate (250rpm) resulted in more water being extracted from the oil sand slurry. The extraction efficiencies of these two extractions were 35.9% and 25.0%, respectively, much higher than extraction efficiencies with lower mixing rate (less than 15%). This observation indicates that increasing the mixing rate can influence the extraction efficiency of SFE on oil sand slurry, therefore the mixing rate was considered as an important experimental factor. With a higher mixing rate greater than 250 rpm, the extraction system would shake tremendously, so the upper limit of the mixing rate for this study was 250rpm.

A lot of water was extracted from the slurry, so almost all the extract masses determined after the extraction (m_1) of Table 4.4 were larger than those in Table 4.3. However, after the extracted water is evaporated, nearly all the final masses were smaller than those of Table 4.3, and the extraction efficiencies of the extractions in Table 4.4 were less than those in Table 4.3. Therefore, the formal experiments of this research focused on extractions from oil sands with no added water.

Based on the results in Table 4.3 and 4.4, even under the same experimental conditions, the final masses of the gravimetric method are not very consistent. But using this method to test the equipment, check the feasibility of SFE, and choose some experimental factors to study in further detail is reasonable.

The gravimetric method used in this study is very straightforward, but it also has some drawbacks. The first one is the loss of hydrocarbons. Although in this research a separate vial was used to collect the hydrocarbons from the vessel during the vessel depressurizing process and from the outlet lines during the bypass flushing, some extracted hydrocarbons were lost from the sample collection and leaking of the system. Another drawback is that during the extraction, some water is also extracted by SC CO_2 and collected in the sample vials. After the extraction, the vials are left for some time to allow the water to evaporate. If the time period is not long enough, some water will be counted as extracted hydrocarbons and if the time period is too long, some volatile hydrocarbons may be lost. These two drawbacks affect the mass of the hydrocarbons extracted and therefore affect the accuracy of the extraction efficiency calculation by the gravimetric method.

4.4.2 Second Set of Preliminary Experiments Carried Out with ARC Oil Sand

In consideration of the difference in the properties of old and fresh oil sands and the disadvantages of the gravimetric method, the second set of preliminary experiment used fresh ARC oil sand as the feed material and the Dean-Stark extraction for analysis and extraction efficiency calculations. The ARC oil sand was purchased from the Alberta Research Council sample bank in May 2009 and stored in a walk-in freezer (-4°C).

Sample calculations for extraction efficiency are provided in Appendix A. Calculating the extraction efficiency using data from the Dean-Stark analysis rather than the gravimetric analysis offers the advantage of not being influenced by water being extracted with bitumen or hydrocarbons being lost or ineffectively collected during the SFE extraction.

Previous studies have stated that the extraction efficiency and the solvating power of SC CO_2 are solvent density-related (Deo et al. 1992; Hwang et al. 1995; Hwang and Ortiz 2000; Liu et al. 1999; Rose et al. 2000), and some studies also have found out that the extraction efficiency is decreased with the increasing of temperature (Al-Marzouqi et al. 2007; Hwang and Ortiz 2000). Deo et al. (1992) even mentioned that the proximity of the extraction temperature to the critical temperature enhanced oil solubility in SC CO_2. Hence, in this set of preliminary experiments, a lower temperature condition (32°C) just above the critical temperature of CO_2 was tested. It was also considered that 15min was enough time for the residual CO_2 to degas from the sample vials, so the mass of the extracts collected are measured 15min after the vials are removed from the SFE system. The mass m_4 is considered as the mass of the extracted water plus the mass of extracted hydrocarbons. Other experimental factors such as pressure, static and dynamic extraction periods are kept at 24.1MPa, 60min and 90min, respectively.

Some experiments (Experiments 28, 29, 30, and 31) examined the influence of higher mixing rate. Experiments 29 and 34 used a new kind of impeller (Pitched Blade Impeller) for mixing. Four experiments (Experiments 32, 33, 34, and 35) were carried out on oil sand slurry. In the end, some extractions were performed without premixing.

Table 4.7 summarizes the results of these second set of preliminary experiments which were carried out using fresh ARC oil sand. Although the extraction efficiency was calculated using data from Dean-Stark extraction, the extraction efficiency calculated by the gravimetric method is provided for comparison purposes.

Table 4.7: Summary of results of the second set of preliminary SFE experiments on ARC oil sand

Experiment	Mass of Oil Sand	Mass of Water	Impeller Type	Mixing Rate	Premixing Period	Mass of Hydrocarbons Extracted			EE from Gravimetric Method	Extraction Efficiency
	(g)	(g)		(rpm)	(min)	m_4^* (g)	m_1 (g)	m_3 (g)	%	%
20	50.083	N A	Helical	90	10	3.2151	3.1866	1.9505	38.6%	42.8%
21	50.104	N A	Helical	90	10	3.7198	3.6568	2.0485	40.5%	39.1%
22	50.060	N A	Helical	90	10	3.0165	2.9661	2.0329	40.2%	42.3%
23	50.069	N A	Helical	90	10	3.4485	3.4015	1.8678	36.9%	42.0%
24	50.084	N A	Helical	***250***	10	3.0266	2.9810	2.1287	42.1%	N M
25	50.063	N A	***Pitched Blade***	***250***	10	2.7962	2.7450	2.4892	49.2%	N M
26	50.055	N A	Helical	***250***	10	2.8214	2.8133	1.6504	32.6%	N M
27	50.189	N A	Helical	***250***	10	2.6019	2.5678	1.6805	33.2%	N M
28	50.111	50.051	Helical	90	10	1.7881	1.7042	0.6423	12.7%	N M
29	50.160	49.9161	Helical	90	10	1.7834	1.6652	0.6687	13.2%	N M
30	50.007	49.703	***Pitched Blade***	90	10	1.6562	1.4170	0.2820	5.6%	N M
31	50.114	49.933	Helical	90	***0***	1.1741	1.1021	0.5130	10.1%	N M
32	50.178	N A	Helical	90	***0***	2.7280	2.4003	2.1566	42.6%	47.3%
33	50.209	N A	Helical	90	***0***	2.0618	2.0419	1.8410	36.3%	44.2%
34	49.969	N A	Helical	90	***0***	2.8168	2.7739	2.1813	43.2%	42.3%
35	50.128	N A	Helical	90	***0***	2.8367	2.8121	1.9982	39.5%	42.8%
36	50.069	N A	Helical	90	***0***	2.8525	2.8343	1.9628	38.8%	N M

* m_4 is the extract mass determined 15min after the sample vials are removed from the SFE system. N M means that the value was not measured.

First, the effects of mixing rate were tested with ARC oil sand (Experiments 20 to 24, 26 and 27 in Table 4.7). The ARC oil sand contains much more water than the Syncrude oil sand and is much stickier. The helical impeller does not touch the bottom of the extraction vessel, and there is a small space between the edge of the impeller and the extraction vessel. During the extraction, the impeller pushed the oil sand against the wall and the bottom of the vessel. After extraction, when the vessel was removed from the extraction system, a layer of oil sand was formed on the wall and at the bottom of the vessel. The surface of the oil sand layer is shiny, and beneath the surface and inside the layer, there appeared to be some oil sand that did not come into contact with SC CO_2.

A pitched blade impeller was therefore tested in Experiment 25. The space between the blade and the vessel bottom was much larger, so a very thick layer of oil sand was formed at the bottom of the vessel after the extraction. Therefore, the helical impeller was seemed to be better than the pitched blade impeller at mixing the oil sands throughout the vessel.

Some experiments (Experiments 28 to 31) also were carried out with an ARC oil sand slurry. Approximately 50 grams of oil sand and 50 grams of water were added to the vessel. After 10min of premixing, the oil sand and water were well mixed. The extraction efficiencies for hydrocarbons from the ARC oil sand slurry, as determined by the gravimetric method, were less than 14%, and the clarity of water and sand in the treated ARC oil sand slurry were not as good as that of the treated Syncrude oil sand slurry. Figure 4.5 provides photos of the treated slurries. The water and sand in the treated Syncrude oil sand slurry (left) was very clean and the sand settled well. However, the treated ARC oil sand slurry was still sticky and did not settle well. This difference may be because of the differences of initial water contents of two oil sands and the texture (i.e. clay content and types of clays) differences of these two oil sands.

Figure 4.6: The photos of treated oil Syncrude oil slurry (left) and fresh ARC oil sand slurry (right)

It was hypothesized that the decreased extraction efficiencies may be due to the fact that the oil sand is “stickier” and that it forms agglomerated particles or layers on the vessel bottom and vessel wall during the extraction. It was also believed that these agglomerated particles or layers were formed during the premixing stage.

In order to test the effect of premixing on the extractions from ARC oil sands and ARC oil sands slurries, some experiments (Experiments 32 to 35) were performed without premixing. In these experiments, the sample of oil sand was placed in the vessel and the vessel was quickly attached to the SFE system. The SC CO_2 was the introduced and mixing was started. The results of these experiments are provided in Table 4.7 and are also presented in Table 4.8 for comparison purposes. Experiments with no premixing lead to a slightly higher extraction efficiency than the experiments with premixing. Visually, the oil sand formed smaller and thinner layers at the bottom or on the wall of the vessel. Based on these results, no premixing was used in the formal experiments.

Table 4.8: The comparison of results from extractions with 10min premixing and no premixing

10min premixing				No premixing			
Experiments	Final Mass (g)	EE from Gravimetric Method	Extraction Efficiency	Experiments	Final Mass (g)	EE from Gravimetric Method	Extraction Efficiency
24	1.9505	38.6%	42.8%	36	2.1566	42.6%	47.3%
25	2.0485	40.5%	39.1%	37	1.8410	36.3%	44.2%
26	2.0329	40.2%	42.3%	38	2.1813	43.2%	42.3%
27	1.8678	36.9%	42.0%	39	1.9982	39.5%	42.8%
Average	1.9749		41.5%	Average	2.0443		44.2%

4.4.3 Summary of Preliminary Experiments

By performing the two sets of preliminary experiments, the operation of the SFE system was tested and the feasibility of using SC CO_2 to extract hydrocarbons from oil sand was demonstrated. Furthermore, not only were the three factors to be tested determined (pressure, temperature and mixing rate), but some experimental conditions other than these three factors were also fixed. Consequently, it was concluded that the formal experiments would use ARC oil sand. The impeller to be used was the helical impeller. There would be no premixing and the static extraction and dynamic extraction periods would be 60min and 90min, respectively.

4.5 Formal SFE Experiment Discussion

4.5.1 The Statistic Analysis of This Research

The three factors of interest of the formal experiments are extraction pressure, extraction temperature, and mixing rate. The pressure is Factor A: the high level and low level of this factor are set at 10.3MPa and 24.1MPa respectively. Factor B represents temperature with the high level of 60°C and low level of 32°C. The mixing rate is Factor C, and the high and low levels are 250rpm and 90rpm, respectively. All the other experimental factors and conditions of each experiment were fixed. The static period and dynamic period were set at 60min and 90min respectively. Only the helical impeller was used and no premixing was used in any formal experiments. The flow rate was set at $40\text{mL}\cdot\text{min}^{-1}$ and efforts were made to keep the flow rate as stable as possible.

For every extraction, all three factors (pressure, temperature and mixing rate) are rising from certain values, such as cylinder pressure, room temperature, and 0rpm. After each experiment, all three factors are set back to these values. Therefore, the high level and low level of these three factors are determined. Thus, the first assumption that the factors of interest are fixed is satisfied. To increase the accuracy, three replicates are applied. Since all 24 experiments are performed in random order, the experimental design is considered as a completely randomized design and the experimental environment is uniform for each run.

Table 4.9 summarizes all the treatment combinations and experimental results. The extraction efficiencies presented in Table 4.9 were calculated using the data from the Dean-Stark analysis according to the method shown in Appendix A.

Table 4.9: Results of supercritical fluid extraction experiments from the 2^3 factorial design

Experiment	Experimental Conditions			Extraction Efficiency				Deviation	
Labels	Pressure (MPa)	Temperature (°C)	Mixing Rate (rpm)	Replicate 1	Replicate 2	Replicate 3	Average	Standard Deviation	Relative Standard Deviation
(1)	10.3	32	90	33.3%	34.5%	35.0%	34.3%	0.89%	2.61%
a	24.1	32	90	38.5%	39.8%	38.5%	38.9%	0.75%	1.92%
b	10.3	60	90	5.34%	4.26%	4.46%	4.69%	0.57%	12.2%
ab	24.1	60	90	48.6%	48.2%	47.1%	48.0%	0.79%	1.65%
c	10.3	32	250	30.5%	28.2%	30.0%	29.6%	1.19%	4.02%
ac	24.1	32	250	45.4%	44.0%	45.0%	44.8%	0.74%	1.66%
bc	10.3	60	250	2.05%	1.88%	1.94%	1.96%	0.09%	4.37%
abc	24.1	60	250	51.7%	49.3%	50.2%	50.4%	1.21%	2.40%

From Table 4.9, the highest extraction efficiency is obtained when the experimental conditions are such that all three factors are set at the high level. The lowest extraction efficiency is obtained at low pressure, high temperature and high mixing rate. The results from the 2^3 factorial design analysis are presented in Table 4.10. Equations that are used to calculate the effect estimate and sum of squares of each model term (factor or interaction of factors) are shown in Appendix E. The percent contribution is the ratio of the sum of squares of each factor or the interaction of factors divided by the total sum of squares. It is commonly used as an estimate of the relative importance of each model term.

Table 4.10: Effect estimate summary for the 2^3 factorial design

Factor	Effect Estimate	Sum of Squares	Percent Contribution
A	27.92%	46.77%	63.17%
B	-10.62%	6.76%	9.13%
C	0.21%	0.00%	0.00%
AB	17.96%	19.35%	26.14%
AC	3.92%	0.92%	1.25%
BC	-0.36%	0.01%	0.01%
ABC	-1.35%	0.11%	0.15%
Pure Error		0.11%	0.16%
Total		74.03%	

Therefore, based on Table 4.10, the most important model term is the pressure (Factor A). The interaction of pressure and temperature (Factor AB) is not as important as pressure, but it still plays a significant role. Temperature (Factor B) is the third most important model term and has some influence on the experiment results. Compared to these three model terms (i.e. pressure, temperature and their combined interaction), the effects of the other factor and factor combinations are relatively small.

The relative importance of each model term is approximately evaluated by the percentage contribution. Often *P*-values and an analysis of variance are used to better confirm the importance of the model term. Appendix F shows all the calculation results of the 2^3 factorial design and Table 4.11 is an analysis of variance table of this 2^3 factorial design.

Table 4.11: Analysis of variance for the 2^3 factorial design

Source of Variation	Sum of Squares	Degree of Freedom	Mean Squares	F_0	*P*-Value
A	46.77%	1	46.77%	6518.1	2.541E-22
B	6.76%	1	6.76%	942.49	1.1929E-15
C	0.00%	1	0.00%	0.36768	5.5277E-01
AB	19.35%	1	19.35%	2696.9	2.8822E-19
AC	0.92%	1	0.92%	128.69	4.6252E-09
BC	0.01%	1	0.01%	1.1008	3.0969E-01
ABC	0.11%	1	0.11%	15.2497	1.2602E-03
Error	0.11%	16	0.01%		
Total	74.03%	23			

Equations for calculating the mean square and F_0 are represented in Appendix E. The *P*-value is the smallest level of significance and in this research it is computed by Microsoft Excel®. For a typical engineering test, each *P*-value is compared with a specified value α, which is called level of significance. If the *P*-value is larger than α, the conclusion that the model term, which corresponds to this *P*-value, has no effect on the experiments results can be made. For a typical engineering test, α equal to 0.05 (5%) is usually satisfied.

From Table 4.11, the *P*-values of model term C and BC are much larger than 0.05, so, statistically speaking, the mixing rate and the interaction of temperature and mixing rate have no effect on the extraction efficiency. Since the *P*-values of A, B and AB are extremely small, pressure, temperature and the interaction of these two factors significantly affect the extraction efficiency. Although the *P*-values of AC and ABC are less than 0.05, they are much larger than those of A, B and AB. Statistically, it can be said that C and BC are not important, but their interactions with A have some effects, indicating that the effects of AC and ABC are a result of A. On the other hand, A and AB are significant model terms, but the importance of their interactions with C is weak. Thus, C reduces the significance of the other model terms. Combining the results of Table 4.10 and 4.11, it can be concluded that pressure, temperature and the interaction of these two factors significantly affect the extraction efficiency. The mixing rate and the interaction of temperature and mixing rate have little to no influence on the extraction efficiency. The effects of AC and ABC interactions are negligible.

Before the conclusions from this statistic analysis are adopted, the adequacy of this 2^3 factorial design must be verified. The two assumptions i.e. (1) the factors are fixed, (2) the design is completely randomized, must be satisfied. The last assumption implies that all the observations are from a large normally distributed population. A normal probability plot of the residuals verifies this assumption, and the residual analysis is an extremely useful diagnostic tool to check the adequacy of the statistic model (Montgomery 2001). Residuals are the differences between the observations and the estimated extraction efficiencies (Montgomery 2001). From the analysis of variance, the effects of the model terms that have a *P*-value less than 0.05 are A=27.92%, B=-10.62%, AB=17.96%, AC=3.92%, and ABC=-1.35%. The average of the all extraction efficiencies of the 24 experiments is 31.57%. The estimated extraction efficiency can be calculated by

$$\hat{y} = 31.57\% + (\frac{27.92\%}{2})x_1 + (\frac{-10.62\%}{2})x_2 + (\frac{17.96\%}{2})x_1x_2 + (\frac{3.92\%}{2})x_1x_3 + (\frac{-1.35\%}{2})x_1x_2x_3$$

When all the three factors are at the low level ($x_1=x_2=x_3=-1$), the estimated efficiency is

$$\hat{y} = 31.57\% - (\frac{27.92\%}{2}) - (\frac{-10.62\%}{2}) + (\frac{17.96\%}{2}) + (\frac{3.92\%}{2}) - (\frac{-1.35\%}{2}) = 34.53\%$$

Table 4.12 represents the calculated residuals for all observations, and Figure 4.6 and 4.7 are the residuals plots for this 2^3 factorial design.

Table 4.12: Residuals for all observations

Labels	x_1	x_2	x_3	Estimated Efficiency	Residuals 1	Residuals 2	Residuals 3
(1)	-1	-1	-1	34.53%	-1.27%	-0.07%	0.48%
a	1	-1	-1	39.22%	-0.68%	0.58%	-0.75%
b	-1	1	-1	4.61%	0.73%	-0.35%	-0.15%
ab	1	1	-1	47.91%	0.72%	0.32%	-0.81%
c	-1	-1	1	29.93%	0.52%	-1.73%	0.05%
ac	1	-1	1	44.49%	0.88%	-0.55%	0.52%
bc	-1	1	1	2.03%	0.02%	-0.15%	-0.09%
abc	1	1	1	50.49%	1.22%	-1.16%	-0.29%

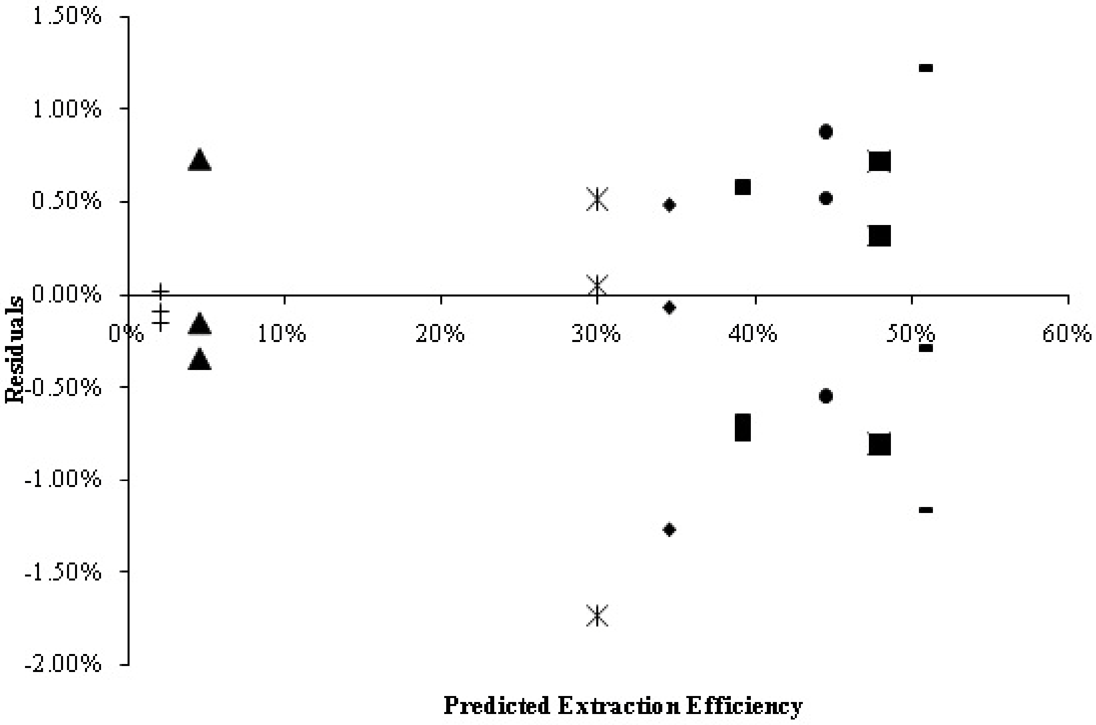


Figure 4.7: **Residuals versus predicted extraction efficiency**

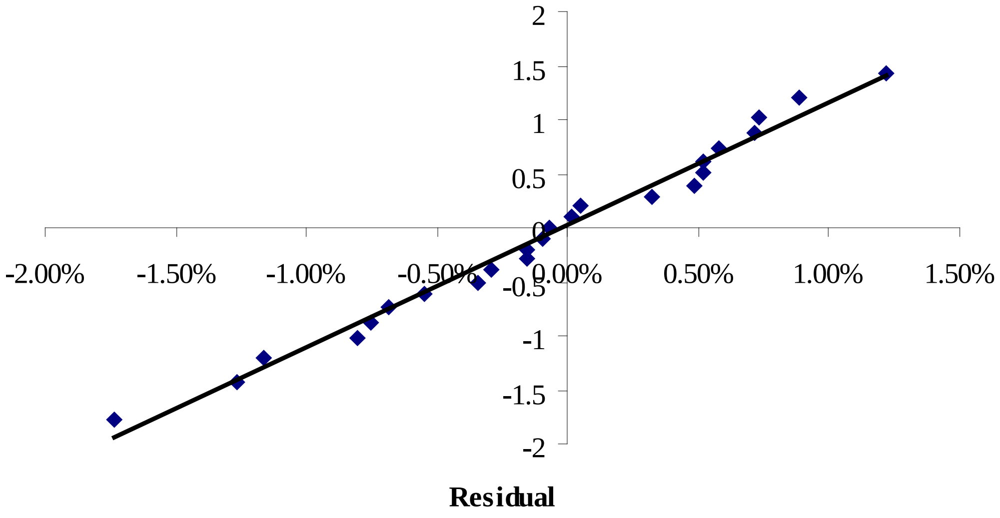


Figure 4.8: **Normal probability plot**

From Figure 4.7 all residuals are distributed on both sides of x-axis, so this plot is appropriate. Figure 4.8 is a normal probability plot of the residuals. Since almost all of the residuals are linearly distributed, the normality assumptions are satisfied. The adequacy of the 2^3 factorial design is therefore confirmed and the conclusions from this model are reliable.

4.5.2 The Analysis of Experimental Factor Effect

Effect of pressure

Previous studies have also highlighted the effect of pressure (Factor A) on the SFE efficiency, suggesting that the extraction efficiency increases with the pressure (Al-Marzouqi et al. 2007; Deo et al. 1992; Guiliano et al. 2000; Hwang et al. 1995; Hwang and Ortiz 2000; Liu et al. 1999; Rose et al. 2000). The effect of pressure on the extraction efficiency shown in this research agrees with the published data and is similar to that of all reviewed papers. Table 4.13 presents the average extraction efficiency as a function of pressure at constant temperature.

Table 4.13: Comparison of the average extraction efficiency as a function of pressure at constant temperature

Temperature (ºC)	Pressure (MPa)	Extraction Efficiency at 90rpm	Extraction Efficiency at 250rpm	Density ($g \cdot mL^{-1}$)	Viscosity (μPa·s)
32	10.3	34.3%	29.6%	0.7589	64.177
32	24.1	38.9%	44.8%	0.9088	93.582
60	10.3	4.69%	1.96%	0.3117	24.873
60	24.1	48.0%	50.4%	0.7775	67.893

From the results in Table 4.13, it is obvious that at all temperature conditions, an increase in pressure will cause an increase in the extraction efficiency. When the temperature is near the critical temperature of CO_2, an increase in pressure from 10.3MPa to 24.1MPa increases the average extraction efficiency from 4.68% to 15.2%. At the high temperature condition, the same pressure increase causes the extraction efficiencies to increase from less than 5% to over 48%. Thus, the effect of pressure at high temperature is much larger than that at a temperature just above the critical temperature of CO_2. This large increase in extraction efficiency as a function of pressure at the higher temperature is likely related to the density behaviour of SC CO_2 which will be discussed later.

Effect of temperature

The effect of temperature (Factor B) is more complex. Table 4.14 compares the average extraction efficiency as a function of temperature at constant pressure.

Table 4.14 Comparison of the average extraction efficiency as a function of temperature at constant pressure

Pressure (MPa)	Temperature (°C)	Extraction Efficiency at 90rpm	Extraction Efficiency at 250rpm	Density (g·mL^{-1})	Viscosity (μPa·s)
10.3	32	34.3%	29.6%	0.7589	64.177
10.3	60	4.69%	1.96%	0.3117	24.873
24.1	32	38.9%	44.8%	0.9088	93.582
24.1	60	48.0%	50.4%	0.7775	67.893

Some studies suggest that an increase in temperature reduces the extraction efficiency (Al-Marzouqi et al. 2007; Hwang and Ortiz 2000; Rose et al. 2000). In this work, based on the results in Table 4.14, at the lower pressure (10.3MPa), the extraction efficiencies decrease with temperature. However, at a higher pressure (24.1MPa), the extraction efficiencies increase slightly with temperature. When the pressure is kept at

10.3MPa, the extraction efficiencies at 32°C are approximately 30% higher than that of high temperature condition (60°C), which are less than 5%. This observation is the same as that of Deo et al. (1992), who performed SFE experiments on crude oil with CO_2. Deo et al. (1992) tested four different temperatures (23.85, 30.85, 37.85 and 65.85°C) at a constant pressure 10.3MPa and found that the extraction efficiencies of the three temperatures near the critical temperature were much higher than that of the high temperature (Deo et al. 1992). Actually, the temperature has two opposite influences on the extraction efficiency. For example, lower temperature reduces both density and viscosity of the CO_2. Lower density decreases the solubility of hydrocarbons in the CO_2, consequently, causes a negative influence on extraction efficiency. However, low viscosity allows the CO_2 to more easily diffuse into the oil sand, so it has a positive influence on the extraction efficiency. These two opposing effects cause the complexity of the effect of temperature, and they will be discussed in detail lately.

Effect of mixing rate

Table 4.15 shows the effect of mixing rate (Factor C) on the extraction efficiency.

Table 4.15 The comparison of average extraction efficiency at different mixing rates

Mixing Rate (rpm)	Pressure (MPa)	Temperature (°C)	Average Extraction Efficiency
90	10.3	32	34.3%
250	10.3	32	29.6%
90	24.1	32	38.9%
250	24.1	32	44.8%
90	24.1	60	48.0%
250	24.1	60	50.4%
90	10.3	60	4.69%
250	10.3	60	1.96%

From Table 4.15, it can be seen that the effect of mixing rate on the extraction efficiency is not large. This conclusion matches the conclusion about mixing rate from the 2^3 factorial design. However, this conclusion is only applicable to this research, over the mixing rate range (90-250 rpm) studied and using the helical mixer. Hwang et al. (1995) investigated a mixing rate as high as 2500 rpm. If higher mixing rates were tested, perhaps the effect of mixing rate would not be negligible.

Effect of density

The density of SC CO_2 is related to the pressure and temperature. An increase of pressure will cause the increase of density of SC CO_2 at a fixed temperature. An increase of temperature at a fixed pressure will cause a decrease in the density of SC CO_2. Therefore, density can be considered as the combination or interaction of pressure (Factor A) and temperature (Factor B) that is Factor AB. Figure 4.9 provides a graph of the extraction efficiency as a function of SC CO_2 density.

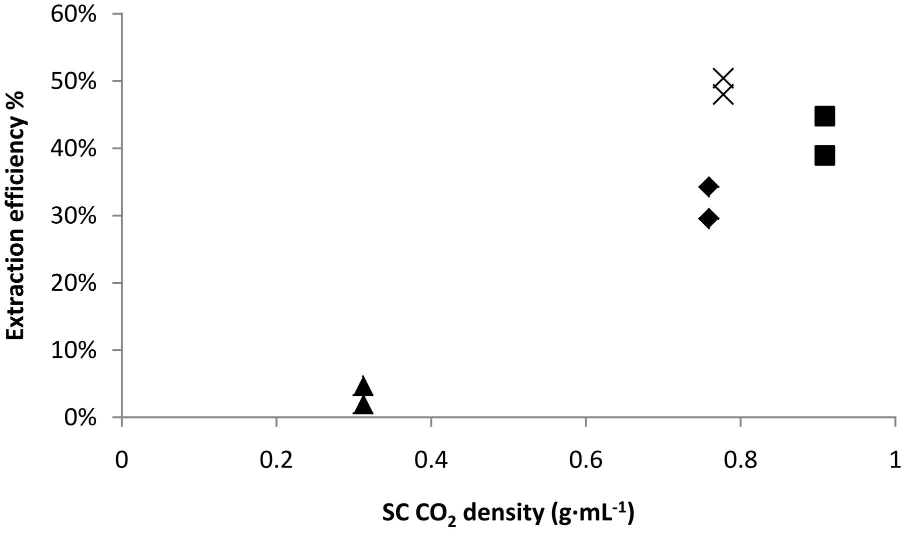


Figure 4.9: Extraction efficiencies as a function of SC CO_2 density

Many studies state that the pure solvent density controls the extraction efficiency (Deo et al. 1992; Hwang et al. 1995; Hwang and Ortiz 2000; Liu et al. 1999; Rose et al. 2000). From Figure 4.9 it can be seen that, in this research, the low SC CO_2 density produced lower extraction efficiency, and higher SC CO_2 density produced higher extraction efficiency. However, the highest extraction efficiency was not produced by the highest SC CO_2 density.

According to Al-Marzouqi et al. (2007), another key factor that must be considered when extracting a compound from a solid matrix is the SC CO_2 viscosity. The ability of SC CO_2 to penetrate the solid matrix is inversely proportional to the viscosity of the solvent (Al-Marzouqi et al. 2007). Both the density and the viscosity are increased with pressure and decreased with temperature. Al-Marzouqi et al. (2007) also investigated the relationship between kinematic viscosity and extraction efficiency and suggested that the kinematic viscosity and the mass transfer coefficient have an inversely proportional relationship, so higher extraction efficiencies could be obtained with higher mass transfer coefficients and lower kinematic viscosity. However, the highest extraction efficiency was obtained with a kinematic viscosity of $8.12\times10^{8} m^{2}\cdot s^{-1}$ (Al-Marzouqi et al. 2007). If the density and viscosity are known, the kinematic viscosity is calculated by the follow equation.

$$\nu = \mu / \rho \qquad \text{Equation 4.1}$$

where

ν = kinematic viscosity ($m^{2}\cdot s^{-1}$)

μ = absolute or dynamic viscosity ($kg\cdot(m\cdot s)^{-1}$)

ρ = density ($kg\cdot m^{-3}$)

Table 4.16 provides the average extraction efficiencies as a function of density, viscosity and kinematic viscosity. All values of density, viscosity and kinematic viscosity are obtained from NIST (NIST 2010).

Table 4.16: The average extraction efficiency, density, viscosity and kinematic viscosity for each experimental condition

Labels	Pressure (MPa)	Temperature (°C)	Mixing Rate (rpm)	Average Extraction Efficiency	ρ ($g\cdot mL^{-1}$)	μ (μPa·s)	$\nu\times10^8$ ($m^2\cdot s^{-1}$)
(1)	10.3	32	90	34.3%	0.7589	64.177	8.46
a	24.1	32	90	38.9%	0.9088	93.582	10.3
b	10.3	60	90	4.69%	0.3117	24.873	7.98
ab	24.1	60	90	48.0%	0.7775	67.893	8.73
c	10.3	32	250	29.6%	0.7589	64.177	8.46
ac	24.1	32	250	44.8%	0.9088	93.582	10.3
bc	10.3	60	250	1.96%	0.3117	24.873	7.98
abc	24.1	60	250	50.4%	0.7775	67.893	8.73

From Table 4.16, it can be seen that at the lower temperature condition, the increase in pressure causes the density of SC CO_2 to increase from 0.7589$g\cdot mL^{-1}$ to 0.9088$g\cdot mL^{-1}$, with a relatively small increase in extraction efficiency (from 34.3% to 38.9% and from 29.6% to 44.8%). However, at the higher temperature condition, as the pressure increases from 10.3MPa to 24.1MPa, the density of SC CO_2 more than doubles. Thus, the extraction efficiency increases greatly (from 4.69% to 48.0% and from 1.96% to 50.4%). As mentioned previously, the effect of pressure at a high temperature is much larger than that at a temperature just above the critical temperature of CO_2. This large increase in extraction efficiency is due to the large increase of SC CO_2 density at the higher temperature condition caused by the increase in pressure.

According to Table 4.16, the density and absolute viscosity of CO_2 at 60°C, 10.3MPa are 0.3117g·mL^{-1} and 24.873 μPa·s respectively. The extraction efficiencies of this experimental condition are less than 5%. With the same temperature, when the pressure rises to 24.1MPa, the density and viscosity increase to 0.7775g·mL^{-1} and 67.893μPa·s, respectively, and the average extraction efficiency is more than 48%. With the constant high temperature condition, an increase of pressure causes an increase of viscosity, suggesting that it is more difficult for the CO_2 to diffuse into the matrix. However, a higher extraction efficiency is produced because of the increase in CO_2 density. It is clear that at the high temperature condition of this research, the extraction efficiencies are controlled by the density of SC CO_2 and not by the viscosity.

Based on Table 4.16, when the extraction pressure is set at 10.3MPa, the increase in temperature from 32°C to 60°C decrease both the density of CO_2 from 0.7589g·mL^{-1} to 0.3117g·mL^{-1} and the absolute viscosity of CO_2 from 64.177μPa·s to 24.873μPa·s. The extraction efficiency of the lower viscosity and lower density condition is much lower than at the high viscosity and high density condition. Therefore, the largely decreased extraction efficiencies indicate that at the low pressure condition, the extraction efficiencies are mainly influenced by the pure solvent density. On the contrary, at the high pressure (24.1MPa) and 32°C, density and viscosity are as high as 0.9088g·mL^{-1} and 93.582μPa·s, respectively. When the pressure remains constant but the temperature increases to 60°C, the density and viscosity are reduced to 0.7775g·mL^{-1} and 67.893μPa·s, respectively. The relatively lower density and lower viscosity condition produces slightly higher extraction efficiencies. This phenomenon reveals that at the high pressure conditions of this study, the impact of absolute viscosity is stronger than that of

SC CO_2 density. Al-Marzouqi et al. (2007) showed similar results in their research, and found that, in the vicinity of the critical point of CO_2, the density was the main factor, but at higher pressure conditions, the effect of viscosity was more important than that of density (Al-Marzouqi et al. 2007).

The conclusion about kinematic viscosity of this work is different from that of Al-Marzouqi et al. (2007). In their study, the kinematic viscosity was used to reflect the effects that were observed at high pressure condition. For 20MPa and 25MPa, Al-Marzouqi et al. (2007) tested three temperatures 100, 120 and 140°C. As the temperature increased, the kinematic viscosity increased and caused the extraction efficiency to decrease with temperature (Al-Marzouqi et al. 2007). In this research, at 24.1MPa, the increase of temperature from 32°C to 60°C causes the kinematic viscosity to decrease from $10.3\times10^{8}\text{m}\cdot\text{s}^{-1}$ to $8.73\times10^{8}\text{m}\cdot\text{s}^{-1}$. Therefore, the extraction efficiency increases with temperature. The lowest extraction efficiency (1.96%) corresponds to the lowest kinematic viscosity ($7.98\times10^{-8}\text{m}\cdot\text{s}^{-1}$), and the highest extraction efficiency (50.4%) is obtained at a moderate kinematic viscosity ($8.73\times10^{-8}\text{m}\cdot\text{s}^{-1}$).

From the above discussion and the conclusions of the 2^3 factorial design experiments, the properties of SC CO_2 are largely and simultaneously affected by temperature and pressure, and this complex effect can be considered as the interaction of pressure and temperature (AB). In this design, the high pressure and high temperature conditions (ab and abc) produced higher extraction efficiencies.

4.5.3 Comparison of Dean-Stark and Gravimetric Analysis to Determine Extraction Efficiency

As described previously, two methods can be used to determine the extraction efficiency: the Dean-Stark analysis or the gravimetric method. Although the Dean-Stark method was chosen for the 2^3 factorial design experiments, the masses of the hydrocarbons collected were still determined and therefore an extraction efficiency based on the gravimetric method was determined and was compared to that determined using the Dean-Stark analysis. The results of the calculations are provided in Table 4.17. The last column of Table 4.17 is the mass of water left in the treated oil sand sample corresponding to 42.2309 grams of dry solid.

Table 4.17: Results of formal experiments from gravimetric method

Replicate Number	Pressure (MPa)	Temperature (°C)	Mixing Rate (rpm)	m_1 (g)	m_2 (g)	m_3 (g)	Recovery (%)	EE from Gravimetric Method	EE from Dean-Stark Analysis	Mass of Residual Water (g)
1	10.3	32	90	2.0527	1.9440	1.5209	91.6%	29.8%	33.3%	0.44
2				1.8631	1.8316	1.5715	85.6%	31.0%	34.5%	0.36
3				1.6522	1.6095	1.3105	89.5%	25.8%	35.0%	0.62
1	24.1	32	90	3.9178	3.8714	3.2998	78.6%	64.8%	38.5%	0.52
2				3.4937	3.4348	2.1970	95.9%	43.2%	39.8%	0.62
3				2.6884	2.5940	1.9478	93.6%	38.2%	38.5%	0.63
1	10.3	60	90	0.12710	0.10815	0.08160	94.8%	1.60%	5.34%	0.40
2				0.10538	0.10227	0.08105	91.3%	1.59%	4.26%	0.19
3				0.23508	0.21261	0.17178	93.7%	3.39%	4.46%	0.18
1	24.1	60	90	4.0769	3.9104	2.5197	90.0%	49.5%	48.6%	0.00
2				4.1897	4.1030	3.3759	89.0%	66.3%	48.2%	0.17
3				3.5292	3.4877	2.2717	87.6%	44.6%	47.1%	0.11
1	10.3	32	350	1.3686	1.3394	1.2234	75.8%	24.1%	30.5%	0.44
2				1.3360	1.2996	1.0132	77.0%	19.9%	28.2%	0.82
3				1.4051	1.3586	1.1243	84.1%	22.1%	30.0%	0.48

1				2.9407	2.8841	2.1497	91.3%	42.4%	45.4%	0.50
2	24.1	32	250	2.8241	2.7675	1.9733	89.7%	38.8%	44.0%	0.60
3				2.9252	2.8770	1.9633	91.1%	38.6%	45.0%	0.64
1				0.3312	0.2790	0.2099	94.6%	4.12%	2.05%	0.25
2	10.3	60	250	0.2431	0.2282	0.1121	95.1%	2.20%	1.88%	0.20
3				0.1469	0.1425	0.1301	89.9%	2.55%	1.94%	0.43
1				3.3485	3.2833	2.4252	91.6%	47.8%	51.7%	0.05
2	24.1	60	250	3.3720	3.3270	2.4040	89.1%	47.2%	49.3%	0.01
3				3.8778	3.8113	2.4264	91.0%	47.8%	50.2%	0.16

Table 4.17 includes the final mass of hydrocarbons, the extraction efficiencies determined from the Dean-Stark analysis and gravimetric method, the recovery percentage from Dean-Stark Extraction of the initial oil sand sample before SFE, and the mass of residual water. From the recovery percentages reported in Table 4.17 all the extraction recovered more the 75% of the initial oil sand sample before SFE.

Although the gravimetric method has disadvantages as discussed previously, its results can be used to check the extraction efficiency calculated from the Dean-Stark extraction. It is assumed that the ARC oil sand is well mixed and homogenous, so the initial bitumen content in the oil sand before SFE is the mass of oil sand sample multiplied by 10.1% (see Table 4.1). The extraction efficiency is the ratio of the bitumen collected and this initial mass of bitumen. The trend of the extraction efficiencies determined by the gravimetric method roughly matches those determined by the Dean-Stark extraction, so the extraction efficiencies obtained from Dean-Stark extraction seem reasonable. With the exception of some extractions, almost all the extraction efficiencies determined by the gravimetric method are less than those determined using the Dean-Stark extraction.

Figure 4.10 is the comparison of the mass of hydrocarbons extracted based on Dean-Stark results versus the mass of hydrocarbons extracted based on gravimetric analysis.

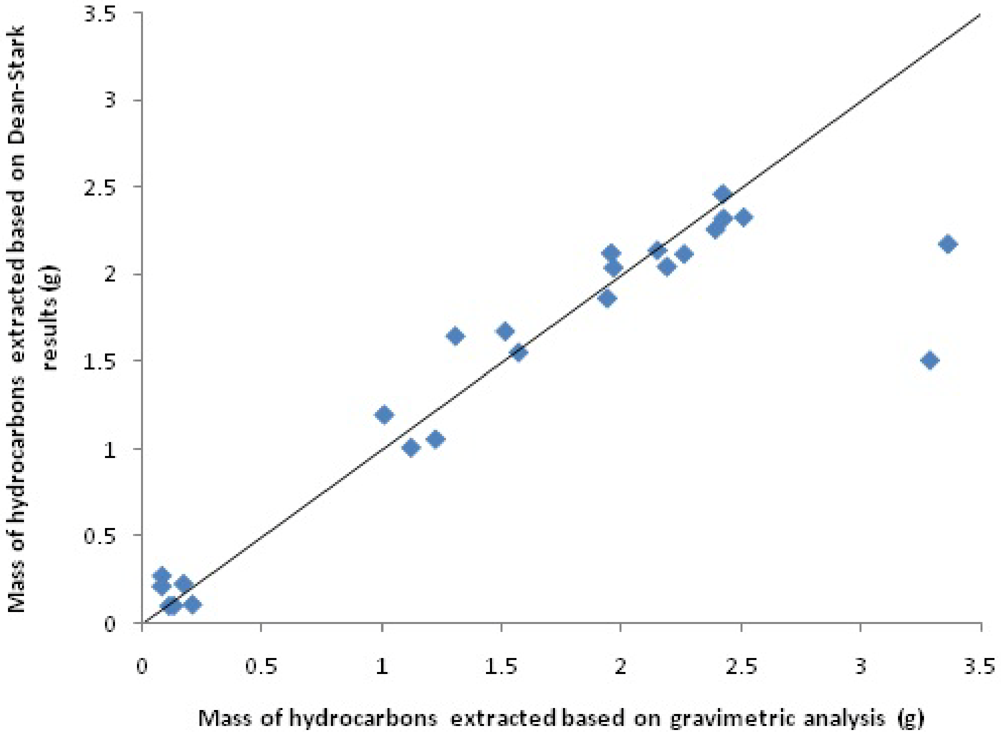


Figure 4.10 Comparison of the mass of hydrocarbons extracted based on Dean-Stark results versus the mass of hydrocarbons extracted based on gravimetric analysis

From this figure, it can be see that the gravimetric method does not consistently over-predict or under-predict the mass of hydrocarbons extracted. This result suggests that the errors due to either loss of hydrocarbons or extraction and collection of water are equally contributing to uncertainty in the gravimetric method.

The relative differences between the two extraction efficiencies (the highlighted values in Table 4.17) of the two extraction conditions (b: high temperature and bc: high temperature and high mixing rate) are large, whereas the absolute values of these extraction efficiencies are small (less than 5.5%). These observations reveal one disadvantage of the Dean-Stark extraction. As mentioned in Section 3.2.3, the mass of bitumen left in the treated oil sand sample is that of the mass of bitumen on the filter paper after toluene evaporation multiplied by 50. The mass of bitumen on the filter paper is determined by determining the mass difference of filter paper before spreading the 5mL of solution and after the evaporation of toluene. If an error occurs during the weighing process, this error will be magnified by 50 times in the final extraction efficiency calculation. For some extractions, this error is relatively small. However, for others, this error is may be much larger. This error may be due to incomplete evaporation of toluene from the filter paper or adsorption of moisture from the air to the filter paper.

The high pressure, high temperature, and high mixing rate condition (abc) produced the highest extraction efficiency. Appendix G shows the Dean-Stark extraction results of the three abc replicates. At this condition, the properties of SC CO_2 are favourable for good extraction but also, under these conditions, the properties and the physical condition of the oil sand to allow better extraction of hydrocarbons. The better extraction efficiency can be qualitatively observed by looking at the treated oil sand samples. The oil sands prior to treatment and some oil samples after SFE treatment have a strong hydrocarbon odour. Oil sands treated at high pressure, high temperature and high mixing rate do not have this characteristic odour. Unlike treated oil sand samples from other experimental conditions, the treated oil sands at this condition form no layer or a very thin layer in the extraction vessel and the average particle size of the treated oil sands is smaller than that of other treated oil sand samples. Figure 4.12 shows the kettles after the solutions of toluene and bitumen are poured out.

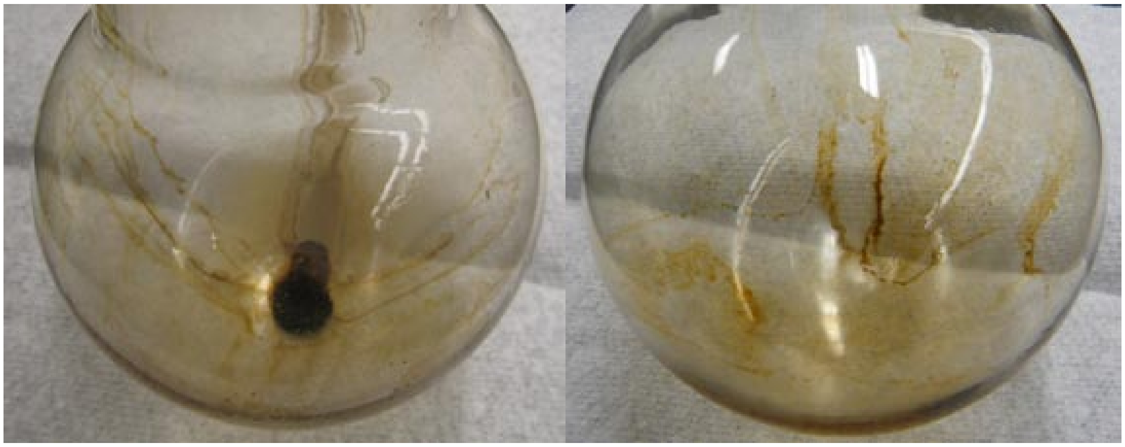


Figure 4.11: Photos of residue left in kettles (left – kettle after Dean-Stark extraction of sample treated at abc condition; right – kettle after Dean-Stark extraction of sample treated at another set of conditions)

It can be seen clearly that some fine particles are sitting on the bottom of the kettle (left). These fine particles are so fine that they pass though the pores of the Dean-Stark thimbles.

In order to test the effect of the oil sands type on the extraction efficiency, three SFEs were carried out on Suncor oil sand under high pressure, high temperature, and high mixing rate condition. Table 4.18 summarizes the results of these three extractions.

Table 4.18: Summary of three SFE results on Suncor oil sand under abc condition

Experiment	Mass of Extracts (g)			Extraction Efficiency (%)		Mass of Residual Water (g)
	m_1	m_2	m_3	Gravimetric Method	Dean-Stark Extraction	
abc 1	3.4847	3.4226	2.0757	51.4%	55.3%	0
abc 2	3.6153	3.5623	2.0916	51.8%	54.2%	0
abc 3	3.5131	3.4382	2.0984	51.9%	55.2%	0
Average	3.5377	3.4744	2.0886	51.7%	54.9%	0

m_1 is the mass of the extracts determined after completion of the extraction experiment.
m_2 is the mass of the extracts determined after approximately 12 hours (overnight).
m_3 is the mass of the extracts determined after a minimum of 2 weeks after completion of the experiment.

The data in Table 4.18 shows that the extraction efficiencies on Suncor oil sand under the best condition are around 55%. Referring to the last column there is no water left in the treated oil sand, so all water is extracted by SC CO_2. Some fine particles were also observed in the kettle during the Dean-Stark extraction of the SFE treated sample.

Chapter 5 Conclusions and Recommendations

5.1 Conclusions

With the global oil demand growing rapidly and with conventional oil reserves that may not be able to meet this demand, more and more attention is focusing on unconventional oil resources. Alberta's oil sands are one of the largest and attractive unconventional oil resources. Traditional methods to recover the bitumen from oil sands (surface mining and in-situ methods) have some disadvantages, such as high GHG emissions and high water usage so new technologies are currently being investigated to lower these negative environmental impacts.

This study investigated bench-scale SFE experiments as a method to extract bitumen (or hydrocarbons) from oil sands. SFE is an environmental friendly, non-aqueous technology and in this study, uses SC CO_2 as the SCF. SC CO_2 is a popular SCF because of its ideal physical and chemical properties.

Preliminary experiments revealed testing the feasibility of extracting hydrocarbons from oil sands by SC CO_2. The effects of some experimental factors (i.e. temperature, mixing rate, static period, dynamic period, type of impeller and premixing) on the extraction efficiency were also studied in the preliminary experiments. Based on the experiments conducted, it appears that a static period longer than 60min did not increase the extraction efficiency. A longer dynamic period (120min) did slightly increase the mass of hydrocarbons extracted by SC CO_2, but considering the large amount of additional CO_2 used to extract little additional hydrocarbons, a dynamic period of more than 90min was not considered of value. When preliminary experiments were performed on ARC oil sands, layers of oil sand were formed on the walls of the extraction vessel during the premixing and extraction stages. A higher mixing rate, the use of a helical impeller, and the removal of the premixing stage decreased the formation of these layers. Based on the results of the preliminary experiments, three factors (pressure, temperature and mixing rate) were chosen for further testing in the formal experiments.

The formal experiments adopted a statistical experimental design method called 2^3 factorial design. Two levels of each factor (a high level and a low level) were tested. The results (extraction efficiencies) of all the experiments were subjected to the statistical analysis. After this analysis, it was concluded that the most important model terms were the pressure, the temperature and the interaction of pressure and temperature. The mixing rate and other interactions of temperature, pressure and mixing rate are considered to have a negligible effect on the extraction efficiency.

The observations of this study show that the extraction efficiency increases with the pressure. Because at higher temperatures, the density change caused by the change in pressure is much larger than that at a lower temperature, the effect of pressure at high temperature is much larger than that of a temperature just above the critical temperature of CO_2.

The effect of temperature is complex, because the temperature affects the extraction efficiency in two opposite ways. Both the density and the viscosity of SC CO_2 decrease with temperature. Unlike density, a lower viscosity leads to a higher extraction efficiency, since a lower viscosity allows the SC CO_2 to more easily penetrate the solid matrix (oil sand). At the lower pressure condition, the density and viscosity of SC CO_2

decreased with temperature, and the extraction efficiency was lower. However, at the higher pressure condition, although the density and viscosity of SC CO_2 decrease with temperature, the extraction efficiency increased significantly. The results suggest that, at the low pressure condition, the extraction efficiencies are mainly influenced by the pure solvent density, while at the high pressure condition, the impact of viscosity is stronger than that of SC CO_2 density.

The effect of the density of SC CO_2 on the extraction efficiency i.e. that a higher SC CO_2 density produced a higher extraction efficiency, agrees with the conclusions from previous studies, but the highest extraction efficiency of this study was not produced by the highest SC CO_2 density.

The highest extraction efficiencies (approximately 50% for the ARC oil sand and approximately 55% for the Suncor oil sand) were obtained at the high pressure, high temperature, and high mixing rate condition. At this condition, the density of SC CO_2 is high and the oil sand is effectively broken down into fine particles to allow better extraction of the hydrocarbons.

5.2 Recommendations

1. The extraction efficiency was calculated using both the gravimetric method and the results of the Dean-Stark extraction. The gravimetric method has some drawbacks and therefore the Dean-Stark method was the preferred method for extraction efficiency calculation. The Dean-Stark analysis also suffers from a limitation when the difference in the mass of the filter paper is determined. Any uncertainty on this mass difference is multiplied by 50. A better method of weighing the filter is necessary that will allow a

more stable mass to be determined. Alternatively, another method to determine the bitumen content in the toluene after Dean-Stark extraction, rather than the filter paper method, would be desirable.

2. In this study, efforts were made to homogenize the oil sand before the experiments. The results of the preliminary and formal experiments suggest that perhaps the oil sands were not fully homogenized. A better, more effective homogenization method would be desirable.

3. In this study, the mixing rate ranged from is 90 to 250 rpm, and the effect of mixing rate was not significant. However, in the future studies, if the SFE system is improved and a higher mixing rate can be achieved, a higher mixing rate should be tested, and perhaps additional experiments with higher mixing rates may show that the mixing rate is significant.

4. Due to equipment limitations, the results of this study are based on mass analysis. In future studies, the properties of the extracted hydrocarbons should be analyzed by GC-MS, simulated distillation, AMW or SARA analysis. These analyses would allow further discussion and conclusions on the benefits (selectivity and potential upgrading) of using SC CO_2 for extracting hydrocarbons from oil sand.

Chapter 6 References

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Appendices

Appendix A- Sample Calculation of Extraction Efficiency

M_D is defined as the mass of dry solid in the treated oil sand sample after SFE. M_R is the mass of residual bitumen remain in the treated oil sand sample after SFE. M_S is the mass of bitumen in the subdivision that corresponds to M_D amount of dry solid.

In the ARC oil sand before SFE there are 5.04047 (M_{AB}) grams of bitumen and 2.44 grams of water that corresponds to 42.2309 (M_{AD}) grams of dry solid. These values are calculated form Appendix B- The Dean-Stark extraction results of ARC oil sand. The extraction efficiency of experiment abc 1 is represented as follow. The dry solid mass (M_D) and the residual bitumen mass (M_R) that determined from Dean-Stark extraction are 39.8515 grams and 2.297 grams, respectively. M_R is the mass of bitumen on the filter paper times 50. Equation A.1 and A.2 show the calculations of the mass of bitumen in the subdivision that is corresponding to the amount of dry solid (M_S) and extraction efficiency (EE).

$$M_S = \frac{M_D \times M_{AB}}{M_{AD}} \qquad \text{Equation A.1}$$

$$EE = \frac{M_S - M_R}{M_S} \times 100\% \qquad \text{Equation A.2}$$

Substituting the values into these two equations, the M_S and EE of experiment abc 1 can be calculated.

$$M_S = \frac{M_D \times M_{AB}}{M_{AD}} = \frac{39.8515 \times 5.04047}{42.2309} = 4.7565(g)$$

$$EE = \frac{M_S - M_R}{M_S} \times 100\% = \frac{4.757 - 2.300}{4.757} \times 100\% = 51.7\%$$

Appendix B- The Dean-Stark Extraction Results of ARC Oil Sand Before SFE

Sample ID	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Beaker+Thimble (g)	79.6349	79.5919	118.2195	69.3674	70.3345
Beaker+Thimble+Raw Oil Sand (g)	129.4548	129.5416	168.636	119.4246	120.4945
Beaker+Thimble+Solid (g)	121.8658	121.5949	160.6765	111.7295	112.591
Water (ml)	2.44	2.43	2.58	2.36	2.40
Filter (g)	2.32148	2.30741	2.31043	2.42629	2.41995
Filter+Bitumen (g)	2.41957	2.41038	2.41511	2.52671	2.51821
Sample Total Mass (g)	49.8199	49.9497	50.4165	50.0572	50.16
Solid Total Mass (g)	42.2309	42.0030	42.457	42.3621	42.2565
Bitumen in 5 ml Solution (g)	0.09809	0.10297	0.10468	0.10042	0.09826
Bitumen Total Mass (g)	4.9045	5.1485	5.234	5.021	4.913
Water Total Mass (g)	2.44	2.43	2.58	2.36	2.4

Appendix C - Sample Raw Data of Output from SFE System

Experiment Date: August 24, 2009
Experiment Condition: Pressure 1500psi Temperature 60°C Mixing Rate 90rpm
Static Period 60min Dynamic Period 90min

No.	Time (Sec)	Vessel Pressure (psi)	Pump A Pressure (psi)	Pump B Pressure (psi)	Vessel Temperature (°C)	Pump Flow A (mL·min^{-1})	Pump Flow B (mL·min^{-1})
0	11.1	748	748	738	31.27919	0	0
1	21.04	756	756	749	31.74522	0	0
2	30.93	757	758	750	31.9214	0	0
3	40.81	758	758	751	32.33554	0	0
4	50.81	759	759	751	32.63404	0	0
5	60.7	1007	1116	773	32.93484	112.169	130.719
6	70.58	1433	1452	937	33.17716	26.458	170.12
7	80.53	1493	1492	1183	33.60492	9.577	125.225
8	90.52	1498	1499	1523	34.16201	7.807	22.824
9	100.41	1501	1500	1499	34.538	5.236	14.722
10	110.4	1500	1500	1502	35.30146	4.613	9.201
11	120.29	1500	1500	1501	35.75417	3.846	6.838
12	130.29	1500	1500	1500	35.62426	3.272	5.971
13	140.17	1501	1501	1501	36.27847	3.423	4.901
14	150.12	1500	1500	1500	36.67669	2.568	4.809
15	160	1500	1500	1500	36.94462	2.322	4.151
16	171.1	1500	1500	1500	37.3503	2.115	3.795
17	180.98	1500	1500	1500	37.76062	1.951	3.501
18	190.98	1500	1500	1500	37.89845	1.787	3.289
19	200.87	1500	1500	1500	35.10913	1.717	3.07
20	210.81	1500	1500	1500	38.1062	1.617	2.908
21	220.7	1500	1500	1500	38.17572	1.504	2.732
22	230.58	1500	1500	1500	38.38512	1.419	2.561
23	240.47	1500	1500	1500	38.52541	1.363	2.421
24	250.46	1500	1500	1500	38.66626	1.301	2.301
25	260.35	1500	1500	1500	38.8786	1.22	2.156
26	270.29	1500	1500	1500	38.94967	1.189	2.054
27	280.07	1500	1500	1500	39.23539	1.142	1.961
28	291	1500	1500	1500	39.45123	1.079	1.845
29	300.67	1500	1500	1500	39.74112	1.048	1.753
30	310.39	1500	1500	1500	40.03347	0.99	1.677
31	320.06	1500	1500	1500	40.47669	0.958	1.616
32	330.99	1500	1500	1500	40.77539	0.915	1.547
33	340.76	1500	1500	1500	41.15248	0.889	1.468
34	350.48	1500	1500	1500	41.3045	0.858	1.391
35	360.15	1500	1500	1500	41.53381	0.816	1.351
36	370.15	1500	1500	1500	41.76469	0.793	1.302
37	380.03	1500	1500	1500	41.91949	0.731	1.257

38	391.18	1500	1500	1500	42.23125	0.722	1.192
39	401.07	1500	1500	1500	42.46699	0.704	1.15
40	411.07	1500	1500	1500	42.86362	0.66	1.108
41	420.95	1500	1500	1500	43.10388	0.637	1.075
42	430.95	1500	1500	1500	43.42697	0.618	1.019
43	440.84	1500	1500	1500	43.67137	0.589	0.997
44	450.56	1500	1500	1500	43.83532	0.56	0.948
45	460.23	1500	1500	1500	44.00008	0.532	0.915
46	471.16	1500	1500	1500	44.24879	0.541	0.874
47	480.82	1500	1500	1500	44.41565	0.506	0.838
48	490.76	1500	1500	1500	44.41565	0.503	0.808
49	500.54	1500	1500	1500	44.58336	0.455	0.781
50	510.26	1500	1500	1500	44.66754	0.45	0.771
51	521.14	1500	1374	1360	44.83656	6.503	8.478
52	530.91	1513	1503	1502	45.00645	-4.307	3.47
53	540.64	1439	1438	1424	45.69506	33.144	38.528
54	550.41	1508	1474	1457	50.07027	21.922	8.588
55	560.13	1511	1509	1493	54.00381	26.264	42.033
56	571.01	1501	1502	1487	56.3608	2.378	62.323
57	580.84	1498	1498	1500	56.1167	0.749	60.641
58	590.51	1502	1501	1502	54.34593	-1.145	57.003
59	600.34	1500	1502	1500	52.34827	1.063	53.471
60	610.34	1497	1497	1501	50.98207	0.601	48.799
61	620.22	1501	1500	1500	50.37125	-1.24	43.89
62	630.11	1502	1502	1501	50.07027	-0.293	40.967
63	640	1498	1498	1501	50.47223	0.563	36.542
64	651.2	1500	1500	1502	50.98207	-0.522	32.09
65	661.14	1499	1501	1501	51.50042	1.246	28.109
66	671.03	1497	1497	1501	51.71021	0.483	24.102
67	680.92	1500	1500	1500	52.02759	-0.985	20.761
68	690.8	1500	1502	1501	52.241	1.141	18.025
69	700.69	1498	1498	1501	52.45591	0.441	15.038
70	710.63	1501	1500	1500	52.45591	-1.073	11.552
71	720.52	1498	1501	1501	52.45591	1.249	8.192
72	730.51	1499	1498	1500	52.56392	0.437	5.73
73	740.4	1501	1501	1502	52.67231	-0.734	3.31
74	750.18	1498	1498	1500	52.89026	1.202	0.91
75	761.11	1500	1500	1500	52.78109	-0.313	-0.066
76	770.77	1501	1501	1500	52.89026	-0.315	-0.248
77	780.61	1499	1500	1500	52.99981	0.639	-0.187
78	790.27	1499	1499	1500	53.2201	0.468	-0.134
79	801.2	1500	1500	1500	53.33083	-0.085	-0.092
80	811.09	1500	1500	1500	53.55352	0.085	-0.083
81	820.92	1500	1500	1500	53.66547	0.209	-0.279
82	830.59	1500	1500	1500	53.89061	0.149	-0.112
83	840.31	1500	1500	1500	53.89061	0.157	-0.163
84	850.31	1500	1500	1500	54.00381	0.158	-0.034
85	860.08	1500	1500	1501	54.11742	0.17	0.233
86	871.01	1500	1500	1500	54.46083	0.153	0.254

87	880.68	1500	1500	1500	54.57616	0.139	0.159
88	890.4	1500	1500	1499	54.57616	0.166	-0.221
89	900.07	1500	1500	1500	54.69193	0.125	0.05
90	911	1500	1500	1500	54.80814	0.152	0.199
91	920.67	1500	1500	1500	55.04191	0.146	0.123
92	930.39	1500	1500	1500	55.15947	0.143	0.11
93	940.05	1500	1500	1500	55.15947	0.109	0.11
94	950.98	1500	1500	1500	55.5149	0.137	0.191
95	960.65	1500	1500	1500	55.5149	0.14	0.13
96	970.65	1500	1500	1500	55.5149	0.127	0
97	980.59	1500	1500	1500	55.75418	0.12	-0.162
98	990.48	1500	1500	1500	55.75418	0.097	-0.173
99	1000.36	1500	1500	1500	55.87454	0.133	0.001
100	1010.25	1500	1500	1500	56.2385	0.145	-0.148
101	1020.08	1500	1500	1500	56.1167	0.114	0.128
102	1030.96	1500	1500	1500	56.3608	0.108	0.248
103	1040.68	1500	1500	1500	56.48359	0.128	0.02
104	1050.45	1500	1500	1499	56.48359	0.108	-0.204
105	1060.18	1500	1500	1500	56.48359	0.145	-0.066
106	1071.05	1500	1500	1500	56.73069	0.107	0.047
107	1080.77	1500	1500	1500	56.60689	0.167	0.081
108	1090.77	1500	1500	1500	56.73069	0.13	0.13
109	1100.77	1500	1500	1500	56.73069	0.099	0.11
110	1110.65	1500	1500	1500	56.73069	0.138	0.134
111	1120.54	1500	1500	1500	56.73069	0.12	0.11
112	1130.43	1500	1500	1500	56.97983	0.131	0.139
113	1140.37	1500	1500	1500	56.97983	0.102	0.105
114	1150.25	1500	1500	1500	56.97983	0.108	0.073
115	1160.14	1500	1500	1500	56.855	0.127	-0.001
116	1171.13	1500	1500	1500	56.97983	0.102	-0.055
117	1181.01	1500	1500	1500	56.97983	0.124	0.021
118	1191.06	1500	1500	1500	56.97983	0.11	0.112
119	1200.95	1500	1500	1500	56.855	0.103	0.081
120	1210.95	1500	1500	1500	56.97983	0.115	0.057
121	1220.94	1500	1500	1500	57.10517	0.1	0.065
122	1230.94	1500	1500	1500	57.23103	0.125	-0.035
123	1240.94	1500	1500	1500	57.10517	0.09	-0.027
124	1250.93	1500	1500	1500	57.23103	0.107	-0.013
125	1260.93	1500	1500	1500	57.10517	0.105	0.07
126	1270.93	1500	1500	1500	57.23103	0.118	-0.05
127	1280.92	1500	1500	1500	57.23103	0.077	-0.116
128	1290.92	1500	1500	1500	57.23103	0.107	-0.074
129	1300.91	1500	1500	1500	57.35743	0.095	-0.021
130	1310.91	1500	1500	1500	57.35743	0.109	0.085
131	1320.91	1500	1500	1500	57.35743	0.106	0.076
132	1330.9	1500	1500	1500	57.23103	0.086	-0.012
133	1340.9	1500	1500	1500	57.35743	0.116	-0.128
134	1350.9	1500	1500	1500	57.48435	0.084	0.027
135	1360.89	1500	1500	1500	57.35743	0.106	0.147

136	1370.89	1500	1500	1500	57.35743	0.078	0.023
137	1380.89	1500	1500	1500	57.48435	0.102	-0.062
138	1390.88	1500	1500	1500	57.48435	0.089	0.098
139	1400.88	1500	1500	1500	57.61182	0.099	0.197
140	1410.93	1500	1500	1500	57.61182	0.067	0.147
141	1420.93	1500	1500	1500	57.73982	0.096	0.097
142	1430.92	1500	1500	1500	57.86837	0.099	0.174
143	1440.92	1500	1500	1500	57.99747	0.076	0.14
144	1450.81	1500	1500	1500	58.12713	0.028	0.148
145	1460.58	1500	1500	1500	58.25735	0.178	0.052
146	1470.41	1500	1500	1500	58.12713	0.188	0.009
147	1480.19	1500	1500	1500	58.25735	0.122	-0.202
148	1491.18	1499	1500	1500	58.38814	0.168	-0.091
149	1501.01	1500	1499	1500	58.25735	0.067	0.001
150	1510.79	1500	1500	1500	58.38814	0.087	0.004
151	1520.78	1500	1500	1500	58.65144	0.035	0.043
152	1530.78	1500	1500	1500	58.5195	-0.108	0.06
153	1540.77	1500	1500	1500	58.78395	0	0.019
154	1550.77	1500	1500	1500	58.78395	0.038	0.143
155	1560.77	1500	1500	1500	58.78395	-0.022	0.006
156	1570.76	1500	1500	1500	58.78395	0.184	0.084
157	1580.76	1499	1500	1500	59.18506	0.37	-0.046
158	1590.76	1500	1499	1500	59.05076	-0.112	-0.168
159	1600.75	1500	1500	1500	58.91706	-0.183	-0.107
160	1610.75	1499	1499	1500	59.05076	0.453	0.156
161	1620.75	1500	1500	1500	59.18506	-0.576	0.081
162	1630.8	1499	1500	1500	59.31997	0.919	-0.006
163	1640.79	1499	1498	1500	59.31997	-0.797	0.124
164	1650.68	1502	1501	1500	59.45548	-1.012	0.001
165	1660.46	1498	1499	1500	59.45548	1.659	-0.134
166	1670.29	1500	1500	1500	59.45548	-0.471	0.044
167	1680.07	1499	1500	1500	59.59161	0.714	0.02
168	1690.17	1500	1500	1500	59.59161	-0.647	0.065
169	1700.17	1498	1500	1500	59.72837	1.449	0.058
170	1710.16	1499	1498	1500	59.59161	-0.834	0.012
171	1720.16	1502	1501	1500	59.86575	-0.875	-0.112
172	1730.16	1498	1498	1500	60.00376	1.628	0.006
173	1740.15	1497	1497	1500	59.86575	0.327	0.064
174	1750.15	1501	1500	1500	60.00376	-1.267	0.07
175	1760.15	1501	1502	1500	60.00376	0.315	-0.055
176	1770.14	1497	1497	1500	60.00376	0.768	0.007
177	1780.14	1501	1501	1500	60.14242	-1.099	0.032
178	1790.14	1501	1502	1500	60.14242	-0.068	-0.053
179	1800.13	1497	1497	1500	60.28172	1.179	0.071
180	1810.24	1500	1498	1500	60.28172	-0.858	0.016
181	1820.24	1502	1501	1500	60.42167	-0.635	-0.084
182	1830.23	1498	1498	1500	60.42167	1.297	-0.015
183	1840.23	1500	1499	1500	60.56229	-0.807	0.066
184	1850.22	1502	1502	1500	60.56229	-0.277	0.013

185	1860.22	1498	1498	1500	60.70356	1.457	-0.08
186	1870.16	1499	1497	1500	60.70356	-0.843	-0.042
187	1881.15	1501	1500	1500	60.70356	-1.373	0.115
188	1890.92	1502	1501	1500	60.84552	-1.027	-0.033
189	1900.76	1498	1499	1500	60.84552	1.712	0.079
190	1910.53	1497	1498	1500	60.98814	0.875	0.057
191	1920.31	1501	1500	1500	60.98814	-1.388	-0.112
192	1930.31	1502	1502	1500	61.13146	-0.293	-0.096
193	1940.3	1497	1497	1500	61.13146	0.947	0.14
194	1950.3	1501	1500	1500	61.13146	-1.153	0.099
195	1960.3	1500	1502	1500	61.27547	1.119	0.194
196	1970.35	1497	1497	1500	61.42017	0.898	0.048
197	1980.34	1500	1499	1500	61.42017	-1.248	-0.214
198	1990.34	1502	1501	1499	61.42017	-0.365	-0.242
199	2000.34	1498	1498	1500	61.56558	1.366	-0.102
200	2010.33	1500	1498	1500	61.56558	-0.782	0.077
201	2020.33	1502	1501	1500	61.56558	-0.757	0.143
202	2030.33	1498	1498	1499	61.56558	1.495	-0.194
203	2040.32	1498	1497	1500	61.71171	-0.038	-0.279
204	2050.21	1502	1501	1500	61.71171	-0.859	0.115
205	2060.2	1498	1498	1500	61.56558	1.655	0.086
206	2070.2	1498	1497	1499	61.71171	0.41	-0.249
207	2080.2	1501	1500	1500	61.71171	-1.251	-0.186
208	2090.19	1502	1502	1500	61.71171	-0.757	0.028
209	2100.08	1498	1500	1500	62.00613	1.719	0.205
210	2111.12	1497	1497	1500	61.85856	1.278	0.197
211	2120.9	1500	1500	1500	61.85856	-1.164	-0.097
212	2130.67	1500	1502	1500	62.00613	1.084	-0.198
213	2140.51	1497	1497	1500	61.85856	0.194	-0.22
214	2150.28	1501	1501	1500	61.85856	-0.837	0.025
215	2160.11	1498	1498	1500	62.00613	1.51	0.069
216	2170	1500	1498	1500	62.00613	-0.843	0.183
217	2180.99	1501	1500	1500	61.85856	-1.373	0.107
218	2190.76	1502	1502	1500	62.00613	-0.738	0.016
219	2200.59	1498	1500	1499	62.00613	1.64	-0.256
220	2210.37	1499	1499	1500	61.85856	0.243	-0.051
221	2220.2	1501	1501	1500	61.85856	-0.532	0.014
222	2231.19	1498	1498	1500	61.85856	1.278	0.121
223	2240.96	1500	1500	1500	61.85856	-0.796	0.193
224	2250.8	1501	1502	1500	61.85856	1.026	0.021
225	2260.57	1497	1498	1500	62.00613	1.103	-0.134
226	2270.35	1500	1499	1500	61.71171	-1.339	-0.11
227	2280.18	1502	1501	1500	61.85856	-1.111	-0.178
228	2290.18	1498	1499	1500	61.71171	0.266	-0.174
229	2301.16	1500	1500	1500	61.56558	0.08	-0.162
230	2310.99	1500	1500	1500	61.71171	-0.084	-0.012
231	2320.77	1500	1500	1500	61.56558	-0.222	0.089
232	2330.55	1500	1501	1500	61.56558	0.505	0.112
233	2340.38	1499	1499	1500	61.56558	-0.458	0.007

234	2350.16	1500	1501	1500	61.56558	0.77	0.075
235	2361.14	1498	1498	1500	61.56558	0.795	0.113
236	2370.97	1501	1501	1500	61.56558	-1.061	0.208
237	2380.75	1498	1500	1500	61.42017	1.605	0.03
238	2390.58	1498	1497	1500	61.56558	-0.216	-0.045
239	2400.36	1501	1501	1500	61.56558	-1.122	-0.093
240	2410.35	1500	1502	1500	61.56558	1.004	-0.072
241	2420.13	1497	1497	1500	61.56558	0.574	0.039
242	2431.17	1501	1500	1500	61.42017	-1.24	0.051
243	2440.95	1500	1502	1500	61.56558	1.063	0.017
244	2450.73	1497	1497	1500	61.42017	0.433	-0.023
245	2460.56	1501	1501	1500	61.42017	-1.004	0.078
246	2470.33	1498	1501	1500	61.42017	1.026	-0.031
247	2480.17	1498	1498	1500	61.42017	0.783	-0.077
248	2491.15	1501	1500	1500	61.42017	-1.278	-0.052
249	2500.93	1501	1502	1500	61.42017	0.232	0.038
250	2510.76	1498	1498	1500	61.42017	1.472	0.034
251	2520.54	1500	1498	1500	61.42017	-0.853	-0.052
252	2530.64	1502	1501	1500	61.42017	-0.772	0.009
253	2540.42	1498	1498	1500	61.42017	1.446	0.021
254	2550.36	1500	1498	1500	61.27547	-0.862	-0.002
255	2560.14	1502	1502	1500	61.27547	-0.342	0.001
256	2571.12	1498	1498	1500	61.27547	1.567	-0.004
257	2580.95	1498	1497	1500	61.27547	0.273	-0.003
258	2590.73	1501	1501	1500	61.27547	-0.859	-0.011
259	2600.51	1498	1498	1500	61.27547	1.434	-0.02
260	2610.34	1500	1498	1500	61.27547	-0.844	-0.014
261	2620.12	1502	1502	1500	61.27547	-0.293	-0.012
262	2631.1	1497	1498	1500	60.98814	1.274	-0.029
263	2640.93	1500	1499	1500	61.13146	-0.789	-0.012
264	2651.04	1502	1501	1500	61.13146	-1.038	-0.026
265	2661.03	1498	1500	1500	61.13146	1.575	0.019
266	2671.03	1498	1497	1500	61.13146	0	-0.085
267	2681.03	1501	1501	1500	60.98814	-1.156	-0.092
268	2691.02	1498	1501	1500	60.98814	1.05	-0.132
269	2701.02	1497	1498	1500	60.98814	1.248	-0.097
270	2711.02	1500	1500	1500	60.98814	-0.757	0.033
271	2721.01	1502	1501	1500	60.98814	-0.646	0.057
272	2731.12	1497	1498	1500	60.98814	1.217	0.064
273	2741.12	1500	1500	1500	60.84552	-0.728	-0.063
274	2751.11	1502	1501	1500	60.84552	-0.49	0.035
275	2761.11	1497	1498	1500	60.84552	1.251	-0.074
276	2770.01	1500	1499	1500	60.84552	-1.324	-0.126
277	2780	1502	1502	1500	60.70356	-0.182	-0.114
278	2790	1497	1498	1500	60.70356	1.08	-0.108
279	2800	1501	1500	1500	60.84552	-1.232	-0.092
280	2811.2	1502	1501	1500	60.70356	-0.745	-0.034
281	2821.2	1498	1500	1500	60.70356	1.67	0.057
282	2831.19	1500	1499	1500	60.70356	-0.707	-0.039

283	2841.19	1502	1502	1500	60.70356	-0.429	-0.069
284	2851.19	1498	1498	1500	60.70356	1.506	-0.111
285	2860.08	1500	1500	1500	60.56229	-0.726	-0.104
286	2870.19	1502	1502	1500	60.56229	-0.041	-0.072
287	2880.19	1498	1498	1500	60.56229	1.404	-0.041
288	2890.29	1499	1497	1500	60.70356	-0.802	-0.088
289	2900.29	1501	1501	1500	60.56229	-1.076	-0.007
290	2910.29	1498	1501	1500	60.56229	1.043	0.039
291	2920.39	1498	1497	1500	60.56229	0.814	0.078
292	2930.5	1501	1500	1500	60.42167	-1.354	0.135
293	2940.5	1502	1501	1500	60.42167	-0.989	0.105
294	2950.49	1498	1501	1500	60.42167	1.004	0.034
295	2960.49	1498	1498	1500	60.42167	0.296	-0.047
296	2970.49	1501	1501	1500	60.28172	-0.768	-0.073
297	2980.48	1498	1499	1500	60.56229	1.643	-0.028
298	2990.48	1498	1497	1500	60.42167	-0.243	0.017
299	3000.36	1501	1501	1500	60.28172	-1.126	0.12
300	3010.47	1498	1501	1500	60.28172	1.514	0.026
301	3020.47	1497	1498	1500	60.28172	0.894	-0.06
302	3030.46	1501	1500	1500	60.28172	-1.339	0.146
303	3040.57	1502	1502	1500	60.28172	-0.327	0.038
304	3050.68	1498	1498	1500	60.28172	1.419	0.152
305	3060.67	1500	1498	1500	60.14242	-0.873	0.165
306	3070.67	1502	1501	1500	60.00376	-0.879	0.107
307	3080.67	1498	1501	1500	60.00376	1.487	0.008
308	3090.66	1498	1498	1500	60.14242	0.677	0.166
309	3100.66	1501	1500	1500	60.28172	-1.407	0.201
310	3110.65	1502	1501	1500	60.00376	-1.111	0.166
311	3120.65	1500	1502	1500	60.14242	1.015	0.052
312	3130.76	1498	1498	1500	60.14242	1.183	-0.105
313	3140.75	1500	1498	1500	60.00376	-0.859	-0.056
314	3150.75	1502	1501	1500	60.00376	-1	-0.123
315	3160.75	1499	1501	1500	60.00376	1.008	-0.023
316	3170.74	1498	1498	1500	59.86575	0.955	-0.011
317	3180.74	1501	1500	1500	60.00376	-1.267	-0.055
318	3190.85	1501	1502	1500	59.86575	-0.152	-0.155
319	3200.84	1497	1498	1500	59.86575	1.259	-0.049
320	3210.95	1500	1499	1500	59.86575	-0.819	-0.064
321	3220.84	1501	1502	1500	59.72837	-0.156	0.132
322	3230.83	1498	1498	1500	59.86575	0.909	0.02
323	3240.72	1501	1500	1500	59.86575	-1.248	0.144
324	3250.82	1500	1502	1500	59.72837	1.029	0.184
325	3260.82	1498	1498	1500	59.86575	0.171	0.059
326	3270.82	1502	1501	1500	59.86575	-0.658	-0.152
327	3280.81	1498	1498	1500	60.00376	1.278	-0.171
328	3290.81	1500	1499	1500	60.00376	-0.896	-0.089
329	3300.81	1502	1501	1500	60.14242	-0.764	-0.037
330	3310.8	1498	1498	1500	60.14242	1.396	0.078
331	3320.8	1500	1498	1500	60.14242	-0.888	-0.025

332	3330.8	1501	1501	1500	60.14242	-1.156	-0.042
333	3340.79	1500	1502	1500	60.28172	1.01	-0.061
334	3350.79	1497	1497	1500	60.28172	0.586	-0.031
335	3360.79	1501	1501	1500	60.14242	-1.035	-0.092
336	3370.78	1498	1501	1500	60.14242	1.013	-0.116
337	3380.61	1497	1497	1500	60.28172	0.65	0.03
338	3390.39	1501	1501	1500	60.14242	-0.269	0.064
339	3400.22	1498	1499	1500	60.14242	1.217	0.043
340	3410	1500	1497	1500	60.28172	-0.836	-0.052
341	3421.09	1501	1501	1500	60.28172	-1.122	-0.098
342	3430.93	1500	1502	1500	60.14242	1.041	-0.126
343	3440.7	1497	1498	1500	60.28172	1.046	-0.11
344	3450.48	1500	1499	1500	60.14242	-0.828	-0.023
345	3460.31	1502	1501	1500	60.28172	-0.791	0.004
346	3470.09	1498	1498	1500	60.14242	1.605	-0.042
347	3481.07	1497	1497	1500	60.28172	0.65	0.048
348	3491.18	1501	1500	1500	60.14242	-1.095	-0.092
349	3501.18	1501	1502	1500	60.42167	0.235	-0.061
350	3511.17	1498	1498	1500	60.14242	1.362	0.09
351	3521.17	1500	1498	1500	60.28172	-0.826	0.027
352	3530.01	1500	1502	1500	60.28172	1.047	-0.013
353	3541.11	1498	1498	1500	60.28172	1.4	-0.107
354	3550.88	1500	1500	1500	60.28172	-0.484	0.004
355	3560.66	1499	1500	1500	60.28172	0.73	0.039
356	3570.49	1500	1499	1501	60.14242	-0.74	0.254
357	3580.6	1502	1502	1500	60.28172	-0.673	0.217
358	3590.7	1498	1498	1500	60.14242	1.56	0.078
359	3600.76	1497	1497	1500	60.14242	0.806	0.043
360	3610.86	1501	1499	1500	60.28172	-1.381	0.128
361	3620.86	1502	1501	1500	60.28172	-0.707	0.093
362	3630.85	1498	1500	1500	60.28172	1.598	0.06
363	3640.85	1497	1497	1500	60.42167	0.654	0.075
364	3650.85	1501	1501	1500	60.28172	-1.126	0.052
365	3660.84	1501	1502	1500	60.28172	0.133	0.001
366	3670.84	1498	1498	1500	60.14242	1.248	-0.126
367	3680.84	1501	1500	1500	60.28172	-0.787	0.04
368	3690.89	1502	1501	1500	60.14242	-0.677	0.045
369	3700.88	1498	1499	1500	60.28172	1.583	0.006
370	3710.88	1497	1498	1500	60.28172	0.974	-0.049
371	3720.88	1501	1498	1500	60.14242	-1.358	-0.121
372	3730.93	1502	1501	1500	60.28172	-0.924	-0.041
373	3740.76	1498	1498	1500	60.28172	1.369	-0.135
374	3750.54	1498	1497	1500	60.28172	-0.266	-0.012
375	3760.37	1502	1501	1500	60.28172	-0.894	-0.028
376	3770.15	1498	1498	1500	60.28172	1.411	0.042
377	3780.03	1500	1498	1500	60.28172	-0.879	-0.127
378	3791.07	1501	1500	1500	60.28172	-1.411	-0.162
379	3800.85	1501	1502	1500	60.28172	1.018	-0.001
380	3810.63	1498	1498	1500	60.28172	1.225	0.08

381	3820.46	1501	1500	1500	60.42167	-0.792	0.14
382	3830.34	1501	1502	1500	60.28172	1.021	0.149
383	3840.12	1497	1498	1500	60.28172	1.153	0.194
384	3850.23	1501	1500	1500	60.28172	-1.244	0.14
385	3860.22	1501	1502	1500	60.28172	-0.251	0.115
386	3870.22	1497	1498	1500	60.28172	0.977	0.05
387	3880.22	1501	1500	1500	60.28172	-1.286	-0.092
388	3890.21	1502	1502	1500	60.14242	-0.456	-0.19
389	3900.15	1498	1499	1500	60.28172	0.658	0.003
390	3911.14	1501	1500	1500	60.28172	-1.362	0.117
391	3920.92	1501	1502	1500	60.28172	0.998	0.15
392	3930.8	1497	1498	1500	60.28172	1.05	0.05
393	3940.63	1501	1500	1500	60.28172	-1.286	-0.024
394	3950.41	1500	1502	1500	60.28172	1.052	-0.105
395	3960.24	1497	1497	1500	60.28172	0.509	-0.158
396	3970.29	1501	1501	1500	60.28172	-1.016	-0.097
397	3980.29	1498	1500	1500	60.28172	1.537	-0.081
398	3990.4	1498	1498	1500	60.42167	-0.757	-0.034
399	4000.5	1501	1501	1500	60.28172	-1.122	0.087
400	4010.61	1498	1501	1500	60.28172	1.036	0.027
401	4020.61	1498	1497	1500	60.28172	0.182	0.014
402	4030.6	1501	1501	1500	60.14242	-0.996	0.026
403	4040.6	1498	1500	1500	60.56229	1.685	0.011
404	4050.59	1497	1497	1491	59.72837	0.612	1.948
405	4060.59	1501	1501	1490	57.86837	-0.761	19.844
406	4070.59	1498	1500	1497	56.855	1.605	25.259
407	4080.58	1498	1497	1500	56.48359	0.057	25.859
408	4090.69	1501	1501	1499	56.97983	-0.84	27.044
409	4100.69	1463	1463	757	57.48435	21.18	-204
410	4110.68	1501	1501	746	57.48435	30.592	-204
411	4120.68	1498	1498	742	57.86837	30.952	-204
412	4130.68	1499	1499	743	57.99747	32.134	-204
413	4140.62	1499	1499	744	58.12713	33.107	-204
414	4150.39	1500	1500	745	58.38814	34.294	-204
415	4160.17	1499	1499	746	58.5195	35.057	-204
416	4170.11	1500	1500	851	58.78395	35.902	171.813
417	4181.1	1500	1500	1026	58.91706	36.707	137.851
418	4190.87	1500	1500	1457	59.18506	37.116	39.019
419	4200.71	1499	1501	1494	59.18506	16.948	35.796
420	4210.76	1498	1466	1480	59.31997	-0.034	42.021
421	4220.75	743	744	1500	59.45548	-204	46.641
422	4230.81	746	746	1500	59.72837	-204	46.182
423	4240.86	749	749	1500	59.72837	-204	45.371
424	4250.96	940	984	1499	59.72837	136.199	44.584
425	4260.96	1427	1447	1500	59.86575	22.15	44.356
426	4270.96	1493	1477	1461	60.00376	9.436	8.375
427	4280.95	1508	1505	1489	59.86575	7.781	38.087
428	4290.95	1491	1492	1498	59.86575	4.726	42.642
429	4300.95	1498	1499	1501	60.14242	3.298	44.558

430	4310.94	1500	1500	1499	60.14242	2.437	44.194
431	4320.94	1500	1500	1500	60.14242	1.987	44.015
432	4331.15	1500	1500	1500	60.28172	1.607	44.004
433	4341.15	1500	1500	1500	60.28172	1.357	44.02
434	4351.04	1500	1500	1499	60.28172	1.159	43.884
435	4360.87	1476	1489	1474	60.28172	20.373	33.201
436	4370.65	1501	1504	1489	60.28172	-1.05	46.968
437	4380.48	1501	1501	1500	60.42167	0.159	44.645
438	4390.36	1500	1500	1500	60.42167	0.873	44.35
439	4400.14	1500	1500	1500	60.70356	0.629	44.405
440	4411.13	1500	1500	1500	60.70356	0.585	44.265
441	4420.96	1500	1500	1500	60.70356	0.554	44.149
442	4430.73	1500	1500	1500	60.70356	0.536	44.315
443	4440.62	1500	1500	1499	60.84552	0.503	44.212
444	4450.73	1500	1500	1500	60.70356	0.48	44.53
445	4460.72	1500	1500	1500	60.70356	0.443	44.446
446	4470.72	1466	1470	1453	60.70356	17.74	27.624
447	4480.72	1501	1501	1488	60.56229	-1.031	45.671
448	4490.71	1498	1501	1500	60.56229	1.31	45.056
449	4500.76	1498	1500	1500	60.70356	0.5	44.806
450	4510.76	1500	1500	1500	60.70356	0.339	44.901
451	4520.76	1500	1500	1500	60.70356	0.307	44.73
452	4530.75	1500	1500	1500	60.84552	0.322	44.813
453	4540.75	1500	1500	1501	60.56229	0.276	44.868
454	4550.75	1500	1500	1500	60.70356	0.305	44.838
455	4560.74	1500	1500	1500	60.84552	0.264	44.959
456	4570.85	1500	1500	1500	60.70356	0.263	44.876
457	4580.85	1500	1500	1500	60.70356	0.262	44.894
458	4590.84	1500	1500	1500	60.70356	0.253	44.945
459	4600.95	1495	1506	1486	60.70356	16.332	36.264
460	4610.94	1497	1497	1501	60.70356	0.631	45.754
461	4620.94	1500	1500	1500	60.70356	-0.262	45.523
462	4630.94	1500	1500	1500	60.70356	0.212	45.327
463	4640.93	1500	1500	1500	60.70356	0.154	45.365
464	4650.93	1500	1500	1500	60.84552	0.14	45.368
465	4660.93	1500	1500	1500	60.56229	0.173	45.462
466	4670.92	1500	1500	1499	60.70356	0.174	45.379
467	4680.92	1500	1500	1499	60.70356	0.168	45.488
468	4691.03	1500	1500	1499	60.70356	0.16	45.529
469	4701.02	1500	1500	1500	60.84552	0.135	45.651
470	4711.02	1500	1500	1500	60.70356	0.176	45.632
471	4721.02	1500	1500	1500	60.70356	0.151	45.758
472	4731.01	1500	1500	1500	60.70356	0.158	45.95
473	4741.01	1500	1500	1500	60.70356	0.154	46.039
474	4750.79	1500	1500	1500	60.56229	0.162	46.162
475	4760.62	1500	1500	1498	60.56229	0.157	46.157
476	4770.39	1471	1488	1467	60.70356	18.84	35.317
477	4780.17	1500	1498	1498	60.56229	-1.088	46.938
478	4790.11	1471	1462	1441	60.56229	14.296	23.946

479	4801.1	1505	1501	1496	60.56229	-2.716	47.935
480	4810.1	1502	1501	1500	60.42167	-0.479	48.056
481	4820.1	1467	1484	1424	60.28172	54.716	0
482	4830.1	1497	1497	1440	60.28172	48.053	0
483	4840.09	1500	1500	1444	60.42167	48.068	0
484	4850.09	1500	1499	1445	60.42167	47.855	0
485	4860.09	1500	1500	1445	60.42167	47.904	0
486	4870.08	1500	1500	1444	60.42167	47.872	0
487	4880.08	1500	1500	1443	60.42167	47.851	0
488	4890.08	1500	1500	1442	60.56229	47.853	0
489	4900.07	1500	1500	1440	60.42167	48.044	0
490	4910.07	1500	1500	1439	60.42167	48.113	0
491	4920.07	1500	1500	1438	60.42167	48.129	0
492	4930.17	1499	1499	1437	60.42167	48.284	0
493	4940.17	1500	1500	1436	60.56229	48.446	0
494	4950.16	1500	1501	1436	60.56229	48.642	0
495	4960.16	1500	1500	1435	60.56229	48.624	0
496	4970.16	1500	1500	1434	60.56229	48.783	0
497	4980.15	1457	1474	1397	60.42167	53.73	0
498	4990.15	1498	1498	1404	60.28172	49.741	0
499	5000.15	1500	1500	1406	60.42167	49.606	0
500	5010.14	1500	1500	1407	60.42167	49.652	0
501	5020.14	1500	1500	1407	60.56229	49.64	0
502	5030.14	1500	1500	1408	60.56229	49.655	0
503	5040.13	1500	1500	741	60.56229	49.61	-204
504	5050.24	1500	1500	742	60.56229	49.763	-204
505	5060.24	1500	1500	739	60.56229	49.971	-204
506	5070.23	1500	1500	741	60.56229	49.862	-204
507	5080.23	1501	1500	742	60.56229	49.915	-204
508	5090.22	1500	1500	743	60.56229	50.053	-204
509	5100.22	1500	1500	743	60.56229	50.113	-204
510	5110.27	1500	1500	744	60.56229	50.262	-204
511	5120.27	1500	1500	744	60.56229	50.427	-204
512	5130.27	1500	1500	744	60.56229	50.483	-204
513	5140.26	1500	1500	744	60.42167	50.483	-204
514	5150.26	1500	1500	744	60.56229	50.615	-204
515	5160.25	1500	1500	744	60.56229	50.763	-204
516	5170.36	1500	1500	744	60.42167	50.707	-204
517	5180.36	1501	1500	744	60.56229	50.845	-204
518	5190.35	1500	1500	851	60.42167	50.974	194.329
519	5200.35	1500	1501	1010	60.42167	51.135	167.665
520	5210.35	1474	1487	1425	60.14242	53.487	80.946
521	5220.34	1497	1500	1492	60.28172	19.753	55.374
522	5230.34	750	747	1488	60.42167	-204	69.884
523	5240.34	734	735	1500	60.42167	-204	64.271
524	5250.22	740	741	1500	60.42167	-204	62.192
525	5260	743	743	1501	60.42167	-204	60.885
526	5271.04	744	745	1501	60.28172	-204	59.904
527	5280.82	745	745	1501	60.42167	-204	58.373

528	5290.92	746	746	1501	61.42017	-204	56.657
529	5300.92	746	747	1501	61.71171	-204	54.122
530	5310.92	747	747	1501	62.00613	-204	52.581
531	5320.91	747	747	1500	62.15444	-204	50.894
532	5330.91	748	748	1500	61.85856	-204	49.654
533	5340.79	757	757	1500	61.85856	0	48.411
534	5350.74	914	943	1500	61.56558	146.648	46.995
535	5360.51	1260	1315	1453	61.27547	58.658	50.34
536	5370.29	1472	1490	1498	60.98814	26.298	46.42
537	5380.29	1493	1497	1500	60.84552	12.903	46.129
538	5390.28	1500	1501	1500	60.70356	9.39	45.235
539	5400.28	1500	1500	1500	60.70356	7.102	44.833
540	5410.39	1500	1500	1500	60.56229	5.871	44.555
541	5420.38	1500	1500	1500	60.56229	5.047	44.163
542	5430.38	1500	1500	1500	60.42167	4.428	43.753
543	5440.37	1500	1500	1500	60.28172	3.918	43.455
544	5450.37	1500	1500	1500	60.28172	3.566	43.311
545	5460.37	1500	1500	1500	60.00376	3.236	43.105
546	5470.42	1500	1500	1500	60.00376	2.971	42.823
547	5480.42	1500	1500	1500	59.86575	2.789	42.893
548	5490.41	1500	1500	1500	60.00376	2.593	42.64
549	5500.41	1500	1500	1500	59.86575	2.4	42.632
550	5510.4	1500	1500	1500	59.86575	2.278	42.472
551	5520.4	1500	1500	1500	59.72837	2.149	42.304
552	5530.51	1500	1500	1500	59.72837	2.032	42.384
553	5540.5	1500	1500	1500	59.59161	1.927	42.181
554	5550.5	1500	1500	1500	59.59161	1.828	42.147
555	5560.5	1500	1500	1500	59.59161	1.721	42.046
556	5570.49	1500	1500	1499	59.45548	1.623	41.997
557	5580.49	1500	1500	1500	59.45548	1.558	41.925
558	5590.49	1500	1500	1500	59.31997	1.478	42.056
559	5600.48	1500	1500	1499	59.31997	1.409	41.897
560	5610.48	1500	1500	1500	59.31997	1.342	42.014
561	5620.48	1500	1500	1500	59.31997	1.291	41.786
562	5630.47	1500	1500	1500	59.18506	1.237	42.116
563	5640.47	1500	1500	1500	59.18506	1.177	42.043
564	5650.57	1500	1500	1500	59.18506	1.122	41.888
565	5660.57	1500	1500	1500	59.18506	1.11	41.848
566	5670.57	1500	1500	1500	59.31997	1.051	41.883
567	5680.56	1500	1500	1500	59.18506	1.034	41.844
568	5690.56	1500	1500	1499	59.18506	1.001	41.914
569	5700.56	1500	1500	1500	59.05076	0.954	41.897
570	5710.55	1500	1500	1500	59.05076	0.933	41.905
571	5720.55	1500	1500	1500	59.05076	0.871	41.907
572	5730.55	1500	1500	1500	58.91706	0.874	42.153
573	5740.54	1500	1500	1500	58.91706	0.825	42.122
574	5750.54	1500	1500	1500	58.78395	0.81	42.224
575	5760.54	1500	1500	1499	58.78395	0.792	42.307
576	5770.75	1500	1500	1500	58.78395	0.743	42.383

577	5780.75	1455	1473	1430	58.5195	48.959	0
578	5790.74	1497	1498	1447	58.38814	42.945	0
579	5800.74	1500	1500	1450	58.38814	42.489	0
580	5810.74	1454	1473	1412	58.38814	49.118	0
581	5820.73	1496	1497	1416	58.38814	42.774	0
582	5830.73	1500	1500	1414	58.38814	42.505	0
583	5840.73	1500	1500	1411	58.5195	42.312	0
584	5850.72	1500	1500	1408	58.5195	42.073	0
585	5860.72	1500	1500	1405	58.38814	41.915	0
586	5870.72	1500	1499	1402	58.38814	41.732	0
587	5880.71	1475	1489	1396	58.25735	47.341	0
588	5890.82	1498	1499	1393	58.12713	42.175	0
589	5900.82	1500	1500	1390	58.38814	41.99	0
590	5910.81	1500	1499	1388	58.25735	41.75	0
591	5920.81	1500	1500	1385	58.25735	41.849	0
592	5930.8	1500	1500	1383	58.25735	41.695	0
593	5940.75	1500	1500	1381	58.25735	41.744	0
594	5950.52	1500	1500	1379	58.25735	41.707	0
595	5960.3	1500	1500	751	58.25735	41.598	-200.128
596	5970.13	1500	1500	742	58.12713	41.59	-204
597	5981.12	1500	1499	737	58.12713	41.524	-204
598	5990.89	1500	1500	737	57.99747	41.59	-204
599	6000.72	1500	1500	738	57.99747	41.673	-204
600	6010.89	1500	1499	738	57.99747	41.476	-204
601	6020.88	1500	1500	739	57.86837	41.651	-204
602	6030.93	1500	1500	739	57.86837	41.659	-204
603	6040.93	1500	1500	739	57.73982	41.613	-204
604	6050.93	1500	1500	739	57.73982	41.63	-204
605	6060.92	1500	1500	739	57.73982	41.479	-204
606	6070.92	1500	1500	739	57.86837	41.571	-204
607	6080.92	1499	1500	738	57.86837	41.348	-204
608	6090.91	1500	1500	738	57.99747	41.441	-204
609	6100.91	1500	1499	738	57.99747	41.259	-204
610	6110.91	1499	1500	747	58.12713	41.355	0
611	6120.79	1500	1500	869	58.12713	41.386	196.486
612	6130.79	1500	1500	1036	58.12713	41.256	195.834
613	6140.56	1523	1545	1511	58.12713	20.853	84.569
614	6150.4	1501	1500	1500	58.25735	-0.877	58.883
615	6160.17	745	742	1414	58.12713	-204	38.045
616	6170	738	739	1504	57.99747	-204	53.004
617	6180.99	741	742	1501	58.12713	-204	51.709
618	6190.77	742	743	1500	58.25735	-204	49.92
619	6200.6	743	743	1500	58.38814	-204	49.098
620	6210.38	743	743	1500	58.5195	-204	48.364
621	6220.15	744	744	1500	58.38814	-204	47.418
622	6231.19	744	744	1500	58.65144	-204	46.283
623	6240.97	744	744	1500	58.65144	-204	45.48
624	6251.07	753	753	1500	58.78395	0	44.44
625	6261.07	936	961	1500	58.78395	141.972	43.458

626	6271.07	1286	1340	1500	58.91706	54.636	42.585
627	6281.06	1497	1508	1500	58.91706	20.232	41.92
628	6291.06	1499	1502	1500	58.78395	11.029	41.384
629	6301.06	1501	1501	1500	58.65144	7.431	40.882
630	6311.05	1500	1500	1500	58.65144	6.044	40.435
631	6321.05	1500	1500	1500	58.65144	5.033	40.183
632	6331.05	1500	1500	1500	58.78395	4.307	39.749
633	6341.04	1500	1500	1500	58.65144	3.77	39.516
634	6351.04	1500	1500	1500	58.65144	3.317	39.312
635	6361.04	1500	1500	1500	58.65144	2.96	39.032
636	6371.14	1500	1500	1500	58.91706	2.723	38.772
637	6381.14	1500	1500	1500	58.91706	2.496	38.586
638	6391.13	1484	1474	1452	58.78395	9.166	19.479
639	6401.13	1499	1495	1497	58.65144	0.372	39.712
640	6411.13	1500	1499	1500	58.78395	2.017	38.647
641	6421.12	1500	1500	1500	58.65144	1.845	38.429
642	6431.12	1500	1500	1500	58.91706	1.776	38.143
643	6441.17	1500	1500	1500	58.91706	1.651	38.033
644	6451.17	1500	1500	1500	58.78395	1.588	37.866
645	6461.16	1500	1500	1501	58.91706	1.517	37.776
646	6471.16	1500	1500	1500	58.91706	1.42	37.825
647	6481.16	1500	1500	1500	58.91706	1.615	37.659
648	6490.06	1500	1500	1499	58.91706	1.297	37.52
649	6500.05	1500	1500	1500	59.05076	1.238	37.532
650	6510.05	1500	1500	1500	58.91706	1.172	37.403
651	6520.15	1500	1500	1500	58.91706	1.112	37.456
652	6530.15	1500	1500	1499	59.05076	1.065	37.227
653	6540.15	1500	1500	1500	59.18506	1.008	37.28
654	6550.14	1500	1500	1500	59.18506	0.975	37.204
655	6560.14	1500	1500	1500	59.31997	0.937	37.327
656	6570.14	1500	1500	1500	59.18506	0.878	37.103
657	6580.24	1500	1500	1500	59.31997	0.828	37.085
658	6590.24	1500	1500	1501	59.18506	0.825	37.089
659	6600.13	1500	1500	1500	59.31997	0.783	37.12
660	6610.23	1500	1500	1500	59.31997	0.756	37.119
661	6620.23	1500	1500	1500	59.45548	0.72	37.022
662	6630.23	1500	1500	1500	59.45548	0.696	37.027
663	6640.22	1500	1500	1500	59.45548	0.66	37.051
664	6650.22	1500	1500	1500	59.45548	0.644	37.07
665	6660.21	1500	1500	1500	59.59161	0.622	37.027
666	6670.32	1500	1500	1500	59.59161	0.609	37.034
667	6680.32	1500	1500	1501	59.45548	0.566	37.019
668	6690.31	1500	1500	1500	59.72837	0.555	37.126
669	6700.31	1500	1500	1500	59.72837	0.531	37.046
670	6710.31	1500	1500	1500	59.59161	0.509	37.113
671	6720.3	1500	1500	1499	59.59161	0.483	37.096
672	6730.41	1500	1500	1500	59.72837	0.478	37.28
673	6740.41	1500	1500	1500	59.59161	0.436	37.283
674	6750.4	1500	1500	1500	59.72837	0.464	37.415

675	6760.4	1500	1500	1501	59.72837	0.449	37.453
676	6770.4	1500	1460	1432	59.59161	7.526	0
677	6780.39	1498	1502	1449	59.18506	41.272	0
678	6790.39	1500	1500	1455	59.31997	38.833	0
679	6800.38	1500	1500	1455	59.05076	39.411	0
680	6810.38	1499	1499	742	59.18506	40.068	-204
681	6820.38	1500	1500	739	58.91706	40.765	-204
682	6830.37	1500	1500	734	58.91706	41.279	-204
683	6840.37	1500	1500	733	59.18506	41.512	-204
684	6850.48	1500	1500	733	59.31997	41.622	-204
685	6860.47	1500	1500	734	59.45548	42.003	-204
686	6870.47	1500	1500	734	59.59161	42.256	-204
687	6880.58	1499	1500	734	59.59161	42.302	-204
688	6890.57	1500	1500	734	59.59161	42.545	-204
689	6900.57	1500	1500	734	59.72837	42.673	-204
690	6910.57	1500	1500	733	59.86575	42.642	-204
691	6920.56	1500	1500	733	59.86575	42.663	-204
692	6930.56	1500	1500	733	59.86575	42.81	-204
693	6940.55	1500	1500	733	59.86575	42.92	-204
694	6950.55	1500	1500	732	59.86575	42.845	-204
695	6960.55	1500	1499	742	59.86575	42.908	0
696	6970.65	1500	1500	743	60.00376	42.993	0
697	6980.65	1500	1500	881	60.00376	42.826	196.985
698	6990.65	1500	1500	1059	60.14242	43.064	195.694
699	7000.64	1543	1547	1511	60.14242	12.378	81.011
700	7010.64	1502	1502	1498	60.28172	-1.281	60.382
701	7020.64	1500	1500	1502	60.28172	-0.65	55.538
702	7030.63	1500	1500	1500	60.14242	-0.52	53.562
703	7040.63	1500	1500	1500	60.14242	-0.432	52.067
704	7050.57	1500	1500	1500	60.14242	-0.35	50.962
705	7060.35	1500	1500	1500	60.14242	-0.306	50.382
706	7070.12	1500	1500	1500	60.14242	-0.246	49.478
707	7081.16	1500	1500	1500	60.14242	-0.203	48.872
708	7091.16	1500	1500	1500	60.14242	-0.181	48.567
709	7101.16	1500	1500	1500	60.00376	-0.135	48.092
710	7110.93	1500	1499	1500	60.14242	0.452	47.628
711	7120.77	1501	1498	1500	60.14242	-0.608	47.475
712	7130.54	1501	1501	1500	60.00376	-0.372	47.25
713	7140.32	1498	1499	1500	60.14242	0.73	46.992
714	7150.15	742	743	1500	60.00376	-204	46.715
715	7161.14	745	744	1500	60.14242	-204	46.081
716	7170.91	740	740	1500	60.56229	-204	44.701
717	7180.74	740	740	1500	60.84552	-204	43.362
718	7190.52	740	740	1500	60.70356	-204	42.3
719	7200.35	740	740	1500	60.84552	-204	41.405
720	7210.4	750	749	1500	60.70356	0	40.708
721	7220.51	751	751	1501	60.56229	0	40.101
722	7230.51	752	752	1500	60.42167	0	39.387
723	7240.61	830	852	1500	60.42167	169.088	38.837

724	7250.72	996	1018	1500	60.42167	131.838	38.45
725	7260.83	1390	1432	1461	60.14242	40.922	39.084
726	7270.93	1494	1492	1500	60.00376	8.619	38.022
727	7281.04	1498	1499	1500	60.14242	7.44	37.949
728	7291.14	1501	1500	1500	60.14242	5.531	37.429
729	7300.04	1500	1500	1500	60.14242	4.536	37.408
730	7310.09	1500	1500	1500	60.00376	3.731	37.178
731	7320.2	1500	1500	1499	60.00376	3.13	36.834
732	7330.31	1500	1500	1500	60.00376	2.735	36.905
733	7340.41	1500	1500	1500	60.00376	2.382	36.669
734	7350.52	1500	1500	1500	59.86575	2.105	37.384
735	7360.62	1500	1500	1500	59.45548	1.966	38.081
736	7370.73	1486	1477	1450	59.59161	8.539	21.697
737	7380.78	1497	1494	1498	59.59161	1.162	40.001
738	7390.89	1498	1498	1500	59.72837	1.539	39.514
739	7401	1498	1497	1500	59.72837	1.047	39.767
740	7411.1	1500	1500	1499	59.72837	1.355	39.537
741	7420	1500	1500	1500	59.72837	1.278	39.86
742	7430.11	1500	1500	1501	59.72837	1.223	39.903
743	7440.21	1500	1500	1500	59.86575	1.165	39.871
744	7450.32	1500	1500	1500	59.86575	1.107	40.044
745	7460.37	1500	1500	1500	59.86575	1.044	39.954
746	7470.48	1500	1500	1500	60.00376	0.988	40.105
747	7480.58	1500	1500	1500	60.00376	0.932	40.085
748	7490.69	1500	1500	1500	60.00376	0.915	40.173
749	7500.79	1500	1500	1500	60.00376	0.872	40.005
750	7510.79	1500	1500	1500	60.00376	0.823	40.258
751	7520.57	1500	1500	1500	60.00376	0.799	40.29
752	7530.4	1500	1500	1500	60.00376	0.785	40.114
753	7540.18	1500	1500	1500	60.14242	0.735	40.23
754	7551.16	1500	1500	1500	59.86575	0.698	40.303
755	7561.1	1500	1500	1500	60.00376	0.694	40.296
756	7570	1500	1500	1500	59.86575	0.668	40.599
757	7580.99	1500	1500	1500	60.00376	0.637	40.641
758	7590.76	1500	1500	1499	60.00376	0.609	40.739
759	7600.59	1446	1462	1430	60.00376	44.213	0
760	7610.37	1496	1496	1452	59.72837	40.745	0
761	7620.15	1500	1500	1455	59.72837	40.738	0
762	7631.19	1499	1500	1452	59.86575	40.381	0
763	7640.96	1500	1500	1448	59.72837	40.146	0
764	7650.74	1500	1500	1444	60.00376	40.075	0
765	7660.57	1500	1500	1440	60.00376	40.012	0
766	7670.35	1499	1500	1436	60.14242	39.954	0
767	7680.18	1500	1500	1432	60.00376	39.8	0
768	7690.23	1455	1434	735	60.00376	23.075	-204
769	7700.34	1501	1498	735	59.86575	38.989	-204
770	7710.45	1500	1500	729	60.00376	40.149	-204
771	7720.55	1499	1500	728	60.14242	39.836	-204
772	7730.66	1500	1500	729	60.00376	39.85	-204

773	7740.54	1500	1500	729	60.14242	39.69	-204
774	7750.32	1500	1500	729	60.28172	39.677	-204
775	7760.15	1500	1500	729	60.14242	39.557	-204
776	7771.14	1500	1500	729	60.28172	39.292	-204
777	7781.02	1500	1500	729	60.28172	39.43	-204
778	7790.86	1500	1500	729	60.28172	39.27	-204
779	7800.63	1500	1500	729	60.28172	39.17	-204
780	7810.74	1500	1500	728	60.42167	39.159	-204
781	7820.52	1500	1500	728	60.14242	39.196	-204
782	7830.35	1500	1500	728	60.14242	38.962	-204
783	7840.12	1500	1500	768	60.14242	39.152	196.867
784	7851.11	1499	1499	900	60.28172	38.964	196.944
785	7860.94	1500	1500	1082	60.14242	38.924	195.555
786	7870.72	1510	1504	1550	60.14242	-3.626	95.132
787	7880.55	742	741	1490	60.56229	-204	54.139
788	7890.33	738	738	1500	60.28172	-204	50.827
789	7900.1	738	739	1501	60.28172	-204	49.136
790	7911.14	738	738	1501	60.28172	-204	47.634
791	7920.92	738	738	1500	60.28172	-204	46.631
792	7931.14	738	738	1500	60.28172	-204	45.931
793	7941.13	738	738	1500	60.14242	-204	45.3
794	7950.03	773	807	1500	60.14242	181.745	45.06
795	7960.14	962	986	1500	60.14242	137.108	44.374
796	7970.19	1325	1377	1500	60.14242	50.713	44.051
797	7980.29	1508	1502	1500	60.14242	7.001	43.647
798	7990.4	1501	1499	1500	60.14242	6.609	43.286
799	8000.51	1501	1501	1500	60.28172	5.844	42.989
800	8010.61	1500	1500	1500	60.14242	4.953	42.696
801	8020.72	1500	1500	1500	60.14242	4.084	42.533
802	8030.83	1500	1500	1500	60.28172	3.439	42.18
803	8040.88	1500	1500	1500	60.28172	2.948	42.191
804	8050.98	1500	1500	1500	60.28172	2.606	41.846
805	8061.09	1500	1500	1500	60.14242	2.283	41.566
806	8071.2	1500	1500	1500	60.28172	2.071	41.524
807	8080.09	1500	1500	1500	60.14242	1.924	41.43
808	8090.2	1500	1500	1500	60.42167	1.795	41.286
809	8100.31	1500	1500	1500	60.14242	1.672	41.027
810	8110.41	1500	1500	1500	60.14242	1.561	41.052
811	8120.52	1500	1500	1500	60.14242	1.455	40.816
812	8130.57	1500	1500	1500	60.14242	1.385	40.933
813	8140.68	1500	1500	1500	60.14242	1.276	40.656
814	8150.78	1500	1500	1500	60.14242	1.234	40.569
815	8160.89	1500	1500	1500	60.14242	1.193	40.691
816	8171	1500	1500	1500	60.14242	1.105	40.314
817	8181.1	1500	1500	1500	60.14242	1.058	40.473
818	8190	1500	1500	1500	60.14242	1.027	40.354
819	8200.11	1500	1500	1500	60.28172	0.961	40.261
820	8210.16	1500	1500	1500	60.28172	0.924	40.105
821	8220.26	1500	1500	1500	60.14242	0.878	40.122

822	8230.37	1500	1500	1500	60.00376	0.84	40.09
823	8240.48	1500	1500	1500	60.28172	0.807	40.022
824	8250.58	1500	1500	1500	60.28172	0.782	39.928
825	8260.69	1500	1500	1500	60.14242	0.746	39.968
826	8270.8	1500	1500	1500	60.14242	0.735	40.101
827	8280.85	1500	1500	1500	60.14242	0.669	39.998
828	8290.95	1500	1500	1499	60.14242	0.647	39.898
829	8301.06	1500	1500	1500	60.14242	0.636	40.004
830	8311.17	1500	1500	1500	60.28172	0.606	39.912
831	8320.06	1500	1500	1501	60.14242	0.608	40.007
832	8330.17	1500	1500	1500	60.14242	0.569	39.87
833	8340.17	1500	1500	1500	60.14242	0.549	39.833
834	8350.05	1500	1500	1500	60.28172	0.538	39.795
835	8361.15	1500	1500	1500	60.14242	0.508	39.99
836	8370.98	1500	1500	1498	60.14242	0.491	39.713
837	8380.87	1500	1500	1500	60.28172	0.471	40.002
838	8390.75	1500	1500	1500	60.14242	0.452	40.042
839	8400.64	1500	1500	1500	60.14242	0.457	40.209
840	8410.64	1500	1500	1500	60.14242	0.445	40.355
841	8420.47	1500	1500	1500	60.14242	0.419	40.351
842	8430.35	1500	1500	1500	59.86575	0.405	40.619
843	8440.24	1500	1500	1500	60.14242	0.407	40.666
844	8450.13	1500	1500	1500	60.14242	0.38	40.92
845	8460.07	1487	1498	1449	60.00376	45.99	0
846	8471.16	1500	1500	1457	59.86575	40.595	0
847	8481.05	1500	1500	1456	59.86575	40.252	0
848	8490.94	1500	1500	1451	60.14242	40.178	0
849	8500.82	1460	1477	1412	60.00376	46.306	0
850	8510.71	1497	1498	1411	59.86575	40.472	0
851	8520.65	1500	1500	731	60.00376	40.155	-204
852	8530.65	1500	1500	733	60.14242	39.959	-204
853	8540.75	1500	1500	725	60.42167	40.029	-204
854	8550.64	1454	1433	725	60.14242	23.037	-204
855	8560.53	1502	1499	725	60.00376	38.574	-204
856	8570.3	1500	1500	725	60.14242	40.27	-204
857	8580.25	1500	1500	725	60.00376	39.858	-204
858	8590.13	1500	1500	725	60.14242	39.937	-204
859	8600.02	1500	1500	725	60.14242	39.662	-204
860	8611	1501	1500	725	60.14242	39.71	-204
861	8620.89	1501	1500	725	60.14242	39.612	-204
862	8630.83	1499	1500	724	60.42167	39.536	-204
863	8640.72	1500	1500	724	60.28172	39.329	-204
864	8650.82	1500	1500	724	60.28172	39.25	-204
865	8660.71	1500	1500	723	60.28172	39.378	-204
866	8670.6	1500	1500	733	60.28172	39.242	0
867	8680.48	1500	1500	734	60.14242	39.301	0
868	8690.43	1500	1500	735	60.28172	39.157	0
869	8700.31	1500	1500	831	60.28172	39.095	197.4
870	8710.2	1500	1500	981	60.42167	39.065	196.304

871	8720.09	1500	1500	1440	60.28172	39.029	128.535
872	8730.03	1502	1497	1498	60.28172	-1.898	57.498
873	8741.12	1500	1500	1500	60.56229	-0.636	50.69
874	8751.01	1500	1500	1501	60.28172	-0.527	48.795
875	8760.9	1500	1500	1500	60.42167	-0.435	47.611
876	8771	1500	1500	1500	60.28172	-0.346	46.624
877	8781	742	739	1500	60.28172	-204	45.771
878	8790.88	737	737	1500	60.14242	-204	45.21
879	8800.77	732	732	1500	60.28172	-204	44.634
880	8810.71	732	732	1500	60.28172	-204	44.145
881	8820.6	733	732	1500	60.28172	-204	43.929
882	8830.49	732	732	1500	60.28172	-204	43.344
883	8840.37	732	732	1500	60.28172	-204	43.154
884	8850.26	732	741	1500	60.28172	0	42.821
885	8860.2	742	742	1500	60.14242	0	42.762
886	8870.09	743	743	1499	60.14242	0	42.458
887	8881.18	905	927	1500	60.28172	154.75	42.528
888	8890.19	1064	1126	1500	60.14242	121.016	42.49
889	8900.08	1474	1492	1500	60.28172	23.341	42.21
890	8911.17	1498	1501	1500	60.14242	9.81	41.964
891	8921.06	1501	1501	1500	60.14242	6.389	42.043
892	8930.94	1500	1500	1500	60.14242	5.051	41.821
893	8940.89	1500	1500	1500	60.28172	4.157	41.728
894	8950.77	1500	1500	1500	60.14242	3.477	41.588
895	8960.66	1500	1500	1500	60.14242	2.999	41.46
896	8970.55	1500	1500	1500	60.14242	2.634	41.318
897	8980.49	1500	1500	1500	60.28172	2.358	41.386
898	8990.37	1500	1500	1500	60.14242	2.147	41.227
899	9000.26	1500	1500	1500	60.28172	1.954	41.169
900	9010.48	1500	1500	1500	60.14242	1.799	41.264
901	9020.58	1500	1500	1500	60.14242	1.669	41.055
902	9030.63	1500	1500	1500	60.28172	1.557	40.863
903	9040.74	1500	1500	1500	60.28172	1.465	40.992
904	9050.85	1500	1500	1500	60.42167	1.386	40.879
905	9060.95	1500	1500	1500	60.14242	1.302	40.847
906	9071.06	1500	1500	1500	60.28172	1.258	40.811
907	9081.17	1500	1500	1500	60.14242	1.193	40.722
908	9090.06	1500	1500	1500	60.00376	1.119	40.809
909	9100.17	1500	1500	1500	60.14242	1.07	40.661
910	9110.22	1500	1500	1500	60.28172	1.004	40.614
911	9120.33	1500	1500	1500	60.28172	0.958	40.692
912	9130.54	1500	1500	1500	60.28172	0.916	40.625
913	9140.65	1500	1500	1500	60.14242	0.898	40.454
914	9150.76	1500	1500	1501	60.28172	0.837	40.549
915	9160.86	1500	1500	1500	60.28172	0.83	40.618
916	9170.91	1500	1500	1500	60.14242	0.772	40.516
917	9181.02	1500	1500	1500	60.14242	0.746	40.511
918	9191.13	1500	1500	1500	60.14242	0.713	40.484
919	9200.02	1500	1500	1500	60.14242	-0.064	40.424

920	9210.13	1500	1500	1500	60.28172	0.654	40.464
921	9220.24	1500	1500	1499	60.14242	0.654	40.362
922	9230.34	1500	1500	1499	60.28172	0.604	40.498
923	9240.45	1500	1500	1500	60.28172	0.597	40.595
924	9250.61	1493	1506	1476	60.14242	10.122	36.104
925	9260.72	1498	1501	1501	60.14242	2.127	41.132
926	9270.82	1499	1500	1500	60.14242	0.91	40.921
927	9280.93	1500	1500	1500	60.28172	0.518	40.914
928	9291.04	1500	1500	1500	60.28172	0.464	40.89
929	9301.09	1500	1500	1500	60.14242	0.468	41.081
930	9311.19	1500	1500	1500	60.28172	0.432	41.149
931	9320.09	1456	1473	1435	60.14242	46.485	0
932	9330.2	1497	1498	1452	60.00376	41.083	0
933	9340.19	1500	1500	1454	60.00376	40.61	0
934	9350.08	1500	1500	1453	60.14242	40.49	0
935	9360.02	1500	1500	1450	60.00376	40.303	0
936	9370.18	1500	1499	1447	60.14242	40.122	0
937	9380.29	1500	1499	1443	60.14242	39.879	0
938	9390.4	1500	1499	1440	60.14242	39.823	0
939	9400.5	1496	1768	1411	60.00376	44.126	0
940	9410.61	1495	1502	1405	60.00376	44.312	0
941	9420.72	1500	1500	1406	60.00376	40.655	0
942	9430.77	1500	1500	1405	60.28172	40.142	0
943	9440.87	1500	1500	1405	60.28172	40.035	0
944	9450.98	1500	1500	1404	60.14242	39.97	0
945	9461.09	1500	1500	1403	60.28172	39.876	0
946	9471.19	1501	1500	1402	60.28172	39.707	0
947	9480.09	1500	1500	1401	60.14242	39.843	0
948	9490.09	1500	1500	1401	60.14242	39.728	0
949	9500.19	1500	1500	1400	60.28172	39.677	0
950	9510.08	1500	1500	1399	60.14242	39.647	0
951	9521.17	1500	1500	1399	60.28172	39.675	0
952	9531.06	1500	1500	1398	60.14242	39.459	0
953	9541	1500	1500	1398	60.28172	39.516	0
954	9550.89	1500	1500	1397	60.28172	39.622	0
955	9560.78	1500	1500	1397	60.28172	39.491	0
956	9570.66	1500	1500	1397	60.28172	39.521	0
957	9580.55	1500	1554	1396	60.42167	37.592	0
958	9590.49	1503	1501	1388	59.05076	-1.733	0
959	9600.38	1500	1500	1383	57.61182	-0.629	0
960	9610.48	1500	1500	1379	56.73069	-0.53	0
961	9620.59	1500	1500	1375	56.2385	-0.433	0
962	9630.64	1500	1500	1367	55.99538	-0.36	0
963	9640.75	1500	1500	1361	55.87454	-0.308	0
964	9650.85	1500	1500	1356	55.87454	-0.247	0
965	9660.96	1500	1500	1352	55.87454	-0.209	0
966	9671.07	1500	1500	1348	56.2385	-0.164	0
967	9681.17	1500	1500	1343	56.3608	-0.133	0
968	9690.07	1500	1500	1335	56.73069	-0.123	0

969	9700.18	1500	1500	1330	56.48359	-0.102	0
970	9710.23	1500	1500	1326	56.73069	-0.088	0
971	9720.33	1500	1500	1322	56.60689	-0.064	0
972	9730.33	1500	1500	1318	56.73069	0.05	0
973	9740.27	1500	1500	1311	56.73069	0.15	0
974	9750.16	1499	1499	1306	56.855	-0.074	0
975	9760.05	1500	1500	1301	56.855	0.184	0
976	9771.14	1500	1500	1297	56.855	0	0
977	9781.03	1500	1500	1293	56.97983	0.026	0
978	9790.91	1500	1500	1289	57.10517	0.387	0
979	9800.85	1500	1500	1283	57.23103	-0.215	0
980	9810.74	1501	1500	1278	56.73069	-0.517	0
981	9820.63	1499	1499	1274	56.2385	0.221	0
982	9830.51	1500	1500	1271	55.87454	-0.504	0
983	9840.46	1500	1500	1267	55.75418	0.592	0
984	9850.51	1499	1498	1264	55.87454	-0.625	0
985	9860.61	1502	1501	1261	55.99538	-0.943	0
986	9870.72	1498	1498	1254	56.2385	1.309	0
987	9880.83	1500	1499	1250	56.3608	-0.727	0
988	9890.93	1500	1502	1246	56.60689	-0.068	0
989	9901.04	1497	1498	1243	56.73069	0.985	0
990	9911.15	1500	1500	1240	56.855	-0.534	0
991	9920.04	1500	1502	1238	57.10517	0.961	0
992	9930.09	1498	1498	1235	57.23103	0.186	0
993	9940.2	1501	1501	1232	57.35743	-0.726	0
994	9950.31	1498	1499	1226	57.48435	1.289	0
995	9960.41	1499	1498	1222	57.48435	-0.584	0
996	9970.63	1501	1501	1218	57.61182	-0.981	0
997	9980.79	1498	1501	1215	57.73982	0.997	0
998	9990.9	1498	1498	1212	57.86837	1.095	0
999	10001.11	1500	1500	1210	57.99747	-0.57	0
1000	10010.12	1498	1500	1207	57.99747	0.932	0
1001	10020.23	1499	1498	1205	57.99747	0.125	0
1002	10030.39	1500	1500	1202	57.99747	-1.084	0
1003	10040.49	1501	1502	1196	57.99747	-0.159	0
1004	10050.71	1498	1498	1193	58.12713	0.806	0
1005	10060.87	1500	1500	1190	58.25735	-0.488	0
1006	10070.98	1500	1502	1187	58.25735	0.905	0
1007	10081.08	1498	1498	1185	58.25735	0.365	0
1008	10091.19	1501	1500	1182	58.38814	-0.772	0
1009	10101.08	1499	1502	1180	58.25735	0.831	0
1010	10111.02	1498	1498	1178	58.25735	0.277	0
1011	10120.91	1501	1500	1173	58.38814	-0.768	0
1012	10130.79	1499	1500	1170	58.38814	1.339	0
1013	10140.68	1499	1498	1167	58.38814	-0.415	0
1014	10150.57	1501	1501	1164	58.38814	-0.624	0
1015	10160.51	1498	1499	1162	58.38814	1.267	0
1016	10170.39	1499	1498	1160	58.38814	-0.557	0
1017	10180.28	1502	1501	1158	58.38814	-0.369	0

1018	10190.17	1498	1498	1156	58.38814	0.974	0
1019	10200.05	1499	1498	1153	58.25735	-0.608	0
1020	10210.27	1501	1500	1151	58.38814	-1.016	0
1021	10220.49	1498	1499	1149	58.38814	1.552	0
1022	10230.59	1499	1498	1144	58.38814	0.186	0
1023	10240.75	1501	1500	1141	58.5195	-0.783	0
1024	10250.86	1498	1500	1139	58.38814	1.309	0
1025	10261.08	1498	1498	1136	58.38814	0.738	0
1026	10270.08	1501	1500	1134	58.38814	-0.129	0
1027	10280.19	1498	1500	1132	58.38814	1.297	0
1028	10290.35	1499	1499	1130	58.38814	0.334	0
1029	10300.46	1500	1500	1128	58.38814	-0.477	0
1030	10310.56	1499	1502	1126	58.5195	0.946	0
1031	10320.67	1498	1498	1124	58.38814	0.639	0
1032	10330.89	1500	1500	1122	58.38814	-0.459	0
1033	10340.94	1501	1502	1121	58.38814	0.811	0
1034	10351.04	1498	1498	1116	58.38814	0.662	0
1035	10361.15	1500	1500	1113	58.38814	-0.423	0
1036	10370.05	1500	1502	1111	58.38814	0.82	0
1037	10380.15	1498	1498	1109	58.38814	0.346	0
1038	10390.37	1500	1500	1107	58.25735	-0.548	0
1039	10400.42	1499	1502	1106	58.38814	1.019	0
1040	10410.47	1498	1498	1104	58.25735	0.996	0
1041	10420.47	1500	1498	1102	58.38814	-0.629	0
1042	10430.47	1501	1501	1100	58.38814	-0.654	0
1043	10440.46	1499	1499	1099	58.25735	1.362	0
1044	10450.51	1498	1498	1097	58.38814	0.703	0
1045	10460.62	1500	1499	1095	58.38814	-0.589	0
1046	10470.73	1502	1501	1093	58.25735	-0.494	0
1047	10480.83	1498	1498	1089	58.25735	0.833	0
1048	10490.94	1500	1500	1087	58.25735	-0.536	0
1049	10501.04	1501	1502	1085	58.38814	-0.133	0
1050	10511.15	1498	1499	1082	58.25735	0.856	0
1051	10520.05	1500	1500	1081	58.25735	-0.394	0
1052	10530.16	1499	1502	1079	58.25735	0.876	0
1053	10540.32	1498	1498	1077	58.25735	0.353	0
1054	10550.53	1500	1500	1076	58.25735	-1	0
1055	10560.75	1499	1502	1074	58.38814	0.988	0
1056	10570.91	1498	1498	1073	58.25735	0.772	0
1057	10581.02	1500	1500	1071	58.25735	-0.486	0
1058	10591.12	1502	1501	1070	58.25735	-0.703	0
1059	10600.02	1498	1498	1068	58.25735	1.084	0
1060	10610.24	1500	1499	1067	58.12713	-0.567	0
1061	10620.29	1501	1501	1063	58.25735	-0.947	0
1062	10630.39	1498	1498	1061	58.25735	1.446	0
1063	10640.5	1499	1498	1059	58.12713	-0.537	0
1064	10650.61	1501	1500	1057	58.12713	-0.772	0
1065	10660.71	1498	1499	1056	58.12713	1.179	0
1066	10670.82	1498	1498	1054	58.12713	0.753	0

1067	10680.93	1500	1500	1052	58.12713	-0.323	0
1068	10691.09	1501	1502	1051	58.12713	-0.38	0
1069	10701.19	1498	1498	1050	57.99747	1.206	0
1070	10710.2	1500	1498	1049	58.12713	-0.621	0
1071	10720.31	1502	1501	1047	57.99747	-0.525	0
1072	10730.41	1498	1499	1046	57.99747	1.149	0
1073	10740.52	1500	1499	1044	57.99747	-0.543	0
1074	10750.41	1502	1501	1043	57.99747	-0.422	0
1075	10760.29	1498	1498	1042	57.86837	0.802	0
1076	10770.18	1500	1500	1041	57.99747	-0.507	0
1077	10780.07	1500	1502	1039	57.86837	-0.019	0
1078	10790.01	1498	1498	1036	57.86837	0.601	0
1079	10801.1	1500	1499	1034	57.86837	-0.496	0
1080	10810.11	1499	1502	1033	57.86837	0.886	0
1081	10820.16	1498	1498	1031	57.86837	0.734	0
1082	10830.1	1500	1499	1030	57.86837	-0.58	0
1083	10841.2	1501	1500	1028	57.73982	-1	0
1084	10851.09	1498	1501	1026	57.73982	0.97	0
1085	10860.97	1498	1498	1025	57.73982	0.566	0
1086	10870.86	1500	1500	1024	57.73982	-0.566	0
1087	10880.8	1502	1501	1023	57.86837	-0.323	0
1088	10890.69	1498	1498	1022	57.73982	1.012	0
1089	10900.57	1500	1499	1021	57.73982	-0.427	0
1090	10910.46	1501	1501	1020	57.73982	-0.654	0
1091	10920.35	1498	1500	1018	57.61182	1.404	0
1092	10930.56	1499	1498	1017	57.73982	0.258	0
1093	10940.67	1500	1500	1016	57.61182	-0.323	0
1094	10950.77	1498	1502	1015	57.61182	0.857	0
1095	10960.88	1498	1498	1014	57.61182	0.917	0
1096	10970.99	1499	1498	1013	57.48435	-0.592	0
1097	10981.04	1502	1501	1012	57.61182	-0.536	0
1098	10991.15	1498	1499	1011	57.61182	1.183	0
1099	11000.15	1500	1499	1008	57.61182	-0.501	0
1100	11010.26	1501	1501	1007	57.61182	-0.506	0
1101	11020.37	1498	1498	1005	57.61182	1.05	0
1102	11030.47	1500	1158	1004	57.61182	60.12	0
1103	11040.58	1420	1466	1002	57.61182	23.771	0
1104	11050.74	1477	1492	1001	57.48435	63.51	0
1105	11060.85	1500	1500	1000	57.48435	59.041	0
1106	11070.95	1500	1500	998	57.48435	58.209	0
1107	11081.06	1500	1500	997	57.73982	57.833	0
1108	11091.16	1502	1500	996	57.61182	55.652	0
1109	11100.06	1500	1500	995	57.48435	57.937	0
1110	11111.16	1500	1500	994	57.48435	57.483	0
1111	11121.04	1500	1500	993	57.61182	57.448	0
1112	11130.93	1500	1500	992	57.35743	57.389	0
1113	11140.82	1500	1500	991	57.10517	57.452	0
1114	11150.76	1500	1500	990	56.73069	57.407	0
1115	11160.65	1500	1500	989	56.48359	57.446	0

1116	11170.81	1500	1500	988	56.60689	57.413	0
1117	11180.91	1500	1500	987	56.3608	57.555	0
1118	11191.02	1500	1500	986	56.1167	57.602	0
1119	11201.13	1500	1500	986	55.99538	57.679	0
1120	11210.02	1500	1500	985	56.1167	57.758	0
1121	11220.13	1500	1500	984	55.99538	57.942	0
1122	11230.24	1500	1500	983	55.87454	58.093	0
1123	11240.34	1500	1500	982	55.63431	58.163	0
1124	11250.39	1500	1500	979	55.63431	58.356	0
1125	11260.5	1500	1500	978	55.27748	58.471	0
1126	11270.61	1500	1500	977	55.27748	58.634	0
1127	11280.71	1500	1500	976	55.15947	58.785	0
1128	11290.93	1500	1500	975	55.04191	58.97	0
1129	11301.09	1500	1500	974	54.9248	59.237	0
1130	11311.2	748	747	740	54.80814	0	0
1131	11320.09	744	744	739	54.69193	0	0
1132	11330.2	742	742	738	54.69193	0	0
1133	11340.42	741	741	737	54.57616	0	0
1134	11350.52	741	741	737	54.46083	0	0
1135	11360.63	740	740	736	54.34593	0	0
1136	11370.68	739	739	736	54.23146	0	0
1137	11380.79	740	740	736	54.23146	0	0
1138	11390.89	740	740	736	54.00381	0	0
1139	11401.11	740	740	736	54.00381	0	0
1140	11410.12	740	740	736	54.00381	0	0
1141	11420.28	739	739	735	54.00381	0	0
1142	11430.38	739	739	736	54.00381	0	0
1143	11440.49	740	740	736	53.89061	0	0
1144	11450.6	740	740	736	53.89061	0	0
1145	11460.7	739	739	736	53.77784	0	0
1146	11470.81	739	739	736	53.66547	0	0
1147	11480.86	739	739	735	53.55352	0	0
1148	11490.97	739	738	735	53.55352	0	0
1149	11501.07	739	739	736	53.44197	0	0
1150	11511.18	739	739	736	53.33083	0	0
1151	11520.08	739	739	736	53.2201	0	0
1152	11530.29	739	739	735	53.44197	0	0
1153	11540.4	739	739	736	53.33083	0	0
1154	11550.4	739	739	735	53.33083	0	0
1155	11560.28	738	738	735	53.10976	0	0
1156	11570.17	739	739	735	53.2201	0	0
1157	11580.06	739	739	736	52.99981	0	0
1158	11591.15	739	739	735	53.10976	0	0
1159	11601.09	738	739	735	53.10976	0	0
1160	11610.98	739	739	735	52.99981	0	0
1161	11620.87	738	738	735	52.99981	0	0
1162	11630.75	738	738	734	52.89026	0	0
1163	11640.64	739	739	735	52.78109	0	0
1164	11650.86	738	738	735	52.78109	0	0

1165	11660.96	738	738	735	52.67231	0	0
1166	11671.07	738	738	735	52.56392	0	0
1167	11681.17	738	738	735	52.45591	0	0
1168	11690.07	738	738	735	52.56392	0	0
1169	11700.18	738	738	734	52.45591	0	0
1170	11710.23	738	738	735	52.34827	0	0
1171	11720.34	738	738	735	52.241	0	0

Appendix D - Sample Raw Data of Hydrocarbon Mass from Gravimetric Method

Experiment Date: August 25, 2009
Experiment Condition: Pressure 3500psi Temperature 60°C Mixing Rate 250rpm
Static Period 60min Dynamic Period 90min

Soak	60 min	Dynamic	90 min				
Label	Pressure	Temperature	RPM				
abc	1	1	1				
	3500	60	250				
Mass (g)			Mass of Oil Sand				
beaker		77.2779	(g)	50.08758			
beaker+Oil Sand		127.3645					
beaker+residue		77.27692					
					Mass (g)		
Time(Min)	Before	A 15	A WE	Sep 21	m_1	m_2	m_3
0-15	27.07229	29.56067	29.53306	28.7726	2.48838	2.46077	1.70031
15-30	24.74787	25.14383	25.12463	25.04961	0.39596	0.37676	0.30174
30-45	24.72162	24.88496	24.87053	24.85703	0.16334	0.14891	0.13541
45-60	24.97279	25.06688	25.0633	25.06092	0.09409	0.09051	0.08813
60-75	24.63881	24.68779	24.68724	24.68554	0.04898	0.04843	0.04673
75-90	24.58995	24.64448	24.64501	24.64356	0.04898	0.05506	0.05361
Remaining	21.9765	22.07197	22.07183	22.06845	0.09547	0.09533	0.09195
Carryover	22.41877	22.4321	22.42631	22.42611	0.01333	0.00754	0.00734
				Total	3.34853	3.28331	2.42522

Appendix E - Equations for 2^3 Factorial Design

In the calculation, the italic capital letters represent the effects of the factors, and the italic lowercases indicate the sums of *n* replicates of the same treatment combination. The single capital letters denote the effect of primary factors of interest in the experiment, so they are called main effects. Likewise, the interactions of the factors are represented by the corresponding combination of the capital letters. First, a look at the calculation of main effect *A* should be taken. The effect of *A* when *B* and *C* are at the low level is [*a*-(1)]/*n*. Similarly, the effect of *A* when *B* is at the high level and *C* is at the low level is [*ab*-*b*]/*n*. Analogically, The effect of *A* when *C* is at the high level and *B* is at the low level is [*ac*-*c*]/*n*. Finally, the effect of *A* when both *B* and *C* are at the high level is [*abc*-*bc*]/*n*. Therefore, the average effect of *A* is just the average of these four.

$$A = \frac{1}{4n}[a - (1) + ab - b + ac - c + abc - bc] \qquad \text{Equation E.1}$$

An estimation of the *AB* interaction is the difference between the average *A* effects at the two levels of *B*. One-half of this difference is called the *AB* interaction. The average *A* effect when *B* is at high level is [(*abc*-*bc*)+(*ab*-*b*)]/2*n*. Similarly, the average *A* effect when *B* is at low level is ((*ac*-*c*)+[*a*-(1)]) /2*n*. Hence, the *AB* interaction is

$$AB = \frac{1}{4n}[abc - bc + ab - b - ac + c - a + (1)] \qquad \text{Equation E.2}$$

This value inside the bracket is single-degree-of-freedom contrast that corresponds to the effect (Montgomery 2001). The main concept of statistical analysis is analysis of variance. This analysis of variance divides the total variability into some component parts, such as the variability of each factor, the variability of the interaction of the factors, and the variability of error (Montgomery 2001). The sums of squares are used to estimate the corresponding variability of the component parts. The total sum of squares (SS_T) is used as a measure of overall variability in the data, and it is calculated by Equation E.3. The sum of squares of the effect is the square of the contrast divided by 8*n*. The sum of squares due to error is calculated by subtracting the total sum of squares with all the sums of squares of the factors and interactions. The mean square is the sum of squares divided by degree of freedom (Montgomery 2001). The degrees of freedom of SS_T, SS_X and SS_E are 23 (8*n*-1), 1 (2-1), and 16 (23-7) respectively. Equation E.5 is the test statistic for the hypothesis of no differences in the two means of the high and low levels (Montgomery 2001).

$$SS_T = \sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2}\sum_{l=1}^{n}(y_{ijkl} - \overline{y}_{...})^2 \qquad \text{Equation E.3}$$

$\overline{y}_{..}$ is the average of all the observations.

$$SS_X = \frac{(\text{Contrast}_X)^2}{8n} \qquad \text{Equation E.4}$$

The subscript X represent factors and interactions (*A*, *B*, *ABC*, …)

$$SS_E = SS_T - (SS_A + SS_B + SS_{AB} + ... + SS_{ABC}) \qquad \text{Equation E.5}$$

$$MS = \frac{SS}{\text{Degree of freedom}} \qquad \text{Equation E.6}$$

$$F_0 = \frac{MS_X}{MS_E} \qquad \text{Equation E.7}$$

Appendix F - Sample of 2^3 Factorial Design

Run		A	B	C	Relocate 1	Relocate 2	Relocate 3		Total
1	(1)	-1	-1	-1	33.26%	34.46%	35.01%	(1)	102.74%
2	a	1	-1	-1	38.54%	39.80%	38.47%	a	116.80%
3	b	-1	1	-1	5.34%	4.26%	4.46%	b	14.06%
4	ab	1	1	-1	48.63%	48.23%	47.11%	ab	143.97%
5	c	-1	-1	1	30.45%	28.20%	29.98%	c	88.64%
6	ac	1	-1	1	45.38%	43.95%	45.01%	ac	134.34%
7	bc	-1	1	1	2.05%	1.88%	1.94%	bc	5.88%
8	abc	1	1	1	51.71%	49.32%	50.20%	abc	151.22%

Factor effects	Effect		Contrast	Sums of squares ss=(Contrast)^2/8n		Percent Contribution
A=1/4n*(a-(1)+ab-b+ac-c+abc-bc)	A=	27.92%	335.02%	SSA=	46.77%	63.17%
B=1/4n*(b+ab+bc+abc-(1)-a-c-ac)	B=	-10.62%	-127.39%	SSB=	6.76%	9.13%
C=1/4n*(c+ac+bc+abc-(1)-a-b-ab)	C=	0.21%	2.52%	SSC=	0.00%	0.00%
AB=1/4n*(ab-a-b+(1)+abc-bc-ac+c)	AB=	17.96%	215.49%	SSAB=	19.35%	26.14%
AC=1/4n*((1)-a+b-ab-c+ac-bc+abc)	AC=	3.92%	47.07%	SSAC=	0.92%	1.25%
BC=1/4n*((1)+a-b-ab-c-ac+bc+abc)	BC=	-0.36%	-4.35%	SSBC=	0.01%	0.01%
ABC=1/4n*(abc-bc-ac+c-ab+b+a-(1))	ABC=	-1.35%	-16.20%	SSABC=	0.11%	0.15%
				SST=	74.03%	100.00%
				SSE=	0.11%	0.16%

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F0	P-Value
A	46.77%	1	46.77%	6518.162	2.541E-22
B	6.76%	1	6.76%	942.4945	1.1929E-15
C	0.00%	1	0.00%	0.367682	0.55277753
AB	19.35%	1	19.35%	2696.909	2.8822E-19
AC	0.92%	1	0.92%	128.6863	4.6252E-09
BC	0.01%	1	0.01%	1.100751	0.30969139
ABC	0.11%	1	0.11%	15.24968	0.00126021
Error	0.11%	16	0.01%		
Total	74.03%	23			

Appendix G - The Dean-Stark Extraction Results of Three *abc* Replicates

Sample ID	abc 1	abc 2	abc 3
Beaker+Thimble (g)	69.5858	122.3567	76.3117
Beaker+Thimble+Treated OS (g)	112.1110	163.8060	117.9937
Beaker+Thimble+Solid (g)	109.4373	160.6779	115.0208
Water (mL)	0.05	0.01	0.05
Filter (g)	2.32047	2.37659	2.42865
Filter+Bitumen (g)	2.36641	2.42295	2.47467
Sample Total Mass (g)	42.5252	41.4493	41.682
M_D (g)	39.8520	38.3212	38.7091
Bitumen in 5 mL Solution (g)	0.04594	0.04636	0.04602
M_R (g)	2.300	2.318	2.301
Water Total Mass (g)	0.05	0.01	0.05
M_S (g)	4.757	4.574	4.620
Extraction Efficiency	51.7%	49.3%	50.2%