Capillary displacement extraction using surfactant-based washing techniques

By

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Abstract

In this study, the use of surfactants and solvents to promote capillary displacement of bitumen from aged oil sands & fine particles and of lipids from microalgae was explored. The surfactant-based washing fluid was used to reduce the interfacial tension to facilitate the removal of oil by inertial and shear forces. For most of the extractions, the amount of oil recovered can be estimated considering the effect of inertial forces on the emulsification of oil. Larger solvent to substrate ratios produced thicker films that were easily removed. Using surfactant-only extraction was not sufficient to remove bitumen from oil sands or fines. The extraction of bitumen from fines was more challenging than oil sands due to their smaller particle size. The surfactant-solvent systems performed better than water-solvent systems for low solvent to substrate ratios. For microalgae, recoveries of up to 70% of transesterifiable lipids were achieved with extended surfactants only and up to 82% with a conventional surfactant-cyclohexane system.
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1. Introduction

1.1 – Crude and vegetable oil

Oil is a vital source of energy for the world and despite the growth in alternative energy sources, it will remain critical to the world’s energy needs for many more years. Oil is globally used for energy in a variety of key sectors such as transportation, space heating, power generation, agriculture etc. In addition, its components are used in the manufacturing of chemical products such as plastics, detergents, cosmetics, paints and even medicines [1].

The oil industry is a major contributor to Canada’s economy as the oil and gas companies make up roughly between 20 and 30% of the value of the Toronto Stock Exchange (TSX). These companies make up approximately 5% of Canada’s Gross Domestic Product (GDP) [2]. Millions of Canadians are affected by the petroleum industry, either through employment or ownership in shares, RRSPs and mutual funds [2]. Approximately 97% of Canadian oil reserves are unconventional oil sands reserves and are usually extracted using unconventional technology such as bitumen mining and in situ extraction [2]. The amount of oil in the Canadian oil sands is estimated to be close to 1.8 trillion barrels [2]. According to Natural Resources Canada a capital expenditure of $54 billion was made by the oil and gas extraction industry in 2008 [2].

According to the Canadian Energy Research Institute (CERI) the costs of primary recovery is about $30.32/barrel [3]. Steam Assisted Gravity Drainage (SAGD) is $47.57/barrel, while the price estimated by the Alberta government for SAGD extracted oil is between $50 and $80/barrel [4].

Oil crops and seeds are another source that is vastly used for oil production. Only 5 to 6% of the world production of oil crops is used for seeds and animal feed, while about 8% is
used for food [5]. The rest of the 86 to 87% is processed into oil [5]. Different kinds of oils are obtained by crushing the seeds using press methods or by solvent extraction methods [5]. Some of the most common crops used to obtain oil include sunflower seeds, olives, palm-kernel seeds, corn, peanuts, rapeseed, sesame seed etc [5]. These oils are commonly used as cooking oil or ingredients in other products such as margarine [5].

Vegetable oil has also emerged as an alternative to petroleum in some aspects [6]. Biodiesel produced from vegetable oil is highly preferable over diesel obtained from petroleum due to its low net CO$_2$ emissions and cost effectiveness [6]. Even though it is not yet commercially available in most places, the work done with vegetable oil has shown that it can be a promising source of fuel especially in the transportation sector [6]. However, the cost of production of one liter of biodiesel from vegetable oil is about $0.85, which is much higher than conventional diesel or gasoline and as a result uneconomical at this point [6].

1.2 – Methods of heavy oil extraction and the case of oil sands.

Oil sands are a mixture of sand, water, clay and bitumen. It takes large amounts of resources, particularly energy and water, to transform the bitumen trapped inside the complex mixture of sand, water and clay into crude oil [7]. Currently, in the oil and gas industry two methods are commonly used for bitumen extraction from oil sands, open pit mining (that requires large quantities of hot water), and steam assisted gravity drainage processes (SAGD) [8]. The purpose of adding hot water or steam is to reduce the viscosity of the bitumen to be able to extract it [8].

In open pit mining the source of bitumen is first identified, the area is then cleaned and overburden is removed to ensure the smooth and continuous recovery of oil sands [8]. Firstly the
oil sands ore is collected from the ground and sent to a crushing facility [8]. After crushing the ore, hot water is added so the viscosity of bitumen can be reduced and the now liquid bitumen along with the water and some solids can be pumped to the extraction plant [8]. The slurry of sand, clay, bitumen and water is further mixed with hot water at the extraction plant in a large separation vessel [8]. Settling takes place over time in the settling vessel via gravity and causes the slurry components to separate [8]. In the settling vessel, the solids including the sand, clay and rocks settle to the bottom, while the bitumen froth rises to the surface [8]. Bitumen froth contains bitumen, clay and trapped water and requires further treatment [8].

The technique used to extract bitumen from depths of more than 130m is called steam assisted gravity drainage (SAGD) [8]. SAGD is the most popular in-situ (or in-place) technique which is able to economically recover up to 55-60% of bitumen [8]. In this technique, two horizontal wells that are parallel to each other are drilled such that one is slightly higher than the other [8]. The upper well is called the injection well and works as a steam chamber that is used to continually inject steam into the ground [8]. As the temperature rises, bitumen becomes more fluid, and due to gravity, flows to the lower (production) well [8]. The condensed water and the bitumen is then pumped to the surface and sent to an upgrader facility [8].

The conditions of the extraction process determine the extraction recovery, as well as the degree of clay dispersion [9]. Clay dispersion is the most crucial factor in determining tailings’ properties [9]. As the energy input into the extraction process is increased, the recovery for a given ore type also increases [9]. In general, the extraction process conditions are defined by the thermal (process temperature), mechanical (mixing/pipelining), and chemical (process aids) conditions used to extract the oil [9]. The processability (how hard or how easy it is to process the ore) depends on a combination of extraction conditions and ore properties [9]. Hydrocarbon
and fines (clay) content in the ore are two of the most important ore properties that influence processability [9]. The characterization of hydrocarbon and clay properties forms the foundation of the oil sands extraction and heavy oil research [9]. These fundamental processability factors have to be optimized to maintain the economic and environmental sustainability of the oil sands and heavy oil industries [9].

The purpose of froth treatment is to reduce the water and solid content in bitumen before sending the bitumen to the upgrading processes. The froth treatment is achieved in the froth treatment vessel via the addition of solvent (dilutent) and heat to reduce the viscosity of bitumen [8]. Naphtha is most commonly used as the diluent in the oil and gas industry. However, some companies such as Shell have started adopting newer technologies that require the use of paraffinic solvents (more environmentally friendly) as the diluent [10]. The paraffinic solvent froth treatment (PSFT) is a relatively new method of bitumen froth treatment. PSFT helps achieve lower levels of water and solids in the produced bitumen [10]. The PSFT process precipitates asphaltene (complex polyaromatic/polycyclic hydrocarbons that contribute to the high viscosity of bitumen) from bitumen, resulting in lower viscosity bitumen [10].

At the end of the froth treatment process (with conventional or paraffinic naphtha), a mixture of clay, water, sand and traces of bitumen combined with process chemicals, known as tailings, are pumped out to setting ponds, while the recovered bitumen is sent for upgrading [8]. The bitumen obtained from conventional froth treatment is a dense and viscous substance that has to be upgraded for it to be transported through the pipelines, and to be used as the feed in refineries [8]. The product of paraffinic froth treatment is much less viscous so it requires considerably less diluent to pump the bitumen through pipelines [8].
According to studies performed by Gray et al. at the University of Alberta, solvent-based extraction of bitumen from oil sands would be greatly beneficial as dry, compactable tailings would be produced, reducing the consumption of water and eliminating the need for settling ponds [11]. For this solvent process to be feasible, a high recovery of solvent and bitumen from sand and fines, and producing bitumen free of fine solids are essential [11]. Nikakhtari et al. reported that cyclohexane had good solvent properties such as low toxicity and low boiling point (enabling easy recovery via vaporization) along with low solids content in the produced bitumen [11]. The studies showed that the migration of fine solids into produced bitumen during the cyclohexane extraction depended on the water and fines content of the ore. The migration increased with the fines content of the ore [11]. Also, when water was removed from the ore more fines migrated because they were no longer bound by the capillary forces of the water phase [11]. However, when too much water was added, fines migrated with emulsified water. Under the most favorable conditions the fine solids that migrated into the bitumen are more hydrophobic than the average material in the ore [11].

Oil extraction from various sources such as oil sands, tailings (wastes produced during bitumen processing) and biological sources such as algae or seeds depends on overcoming the forces entrapping the oil on the particles. This entrapment is a result of the high interfacial tension between the oil and the other particles surrounding the oil. Since the interfacial tension is high, the oil naturally stays attached to the surrounding particles and does not separate on its own. Thus, the key to extracting oil is by overcoming the interfacial tension forces by applying external forces. These external forces that can overcome the interfacial tension forces include shear, inertial, and buoyancy forces [12]. Previously done work by Quraishi et al. and Kiran et al. has shown that surfactants help lower the bitumen-water interfacial tensions by up to three orders
of magnitude [12,13]. Surfactants are amphiphilic compounds with a hydrophobic tail group and a hydrophilic head group [13]. Surfactants can help achieve significantly better separation and more efficient extraction of oil [12].

Studies performed at Cenovus Energy Inc. have produced preliminary evidence of the cost-effectiveness of using a surfactant-steam process (SSP) [14]. SSP requires tiny amounts of surfactant co-injected with steam to improve oil recovery from steam-assisted gravity drainage (SAGD) wells [14]. This process highly depends on interfacial tension (IFT) reduction, reservoir rock wettability, oil relative permeability enhancement, and in-situ emulsification [14]. SSP is expected to result in oil recovery rate acceleration, lower steam-to-oil ratio (SOR) (i.e. lower water and energy usage and lower water treatment costs) and enhanced ultimate oil recovery [14]. Similarly a significant enhancement can be expected if the SSP is combined with other steam-solvent processes [14]. In particular, these studies performed by Zeidani et al at Cenovus present a scientific approach to surfactant selection for SSP, describes the conditions in which the surfactants need to be deployed within the reservoir, and also predicts the potential synergies with mixtures of different classes of surfactants [14]. Experiments performed using selected surfactants on Canadian oil sands illustrated an increase in the incremental oil recovery factor (RF) in the range of 6-16% [14]. SSP simulations were conducted for one of the surfactants that were tested in the lab and its results showed that this surfactant on average accelerated the oil rate by 15% in the initial 30 months of SSP operation, increased the ultimate oil RF by 10%, and reduced the cumulative steam-to-oil ratio (CSOR) by almost 11% relative to a SAGD base case [14]. It is evident that if SSP is successfully developed and employed, the use of surfactant would surely make the operations more environmentally friendly as well as improve the economics of in-situ oil sands recovery [14].
Currently extraction techniques such as the hot water extraction and SAGD are highly energy intensive. Heat is added for prolonged periods to increase the temperature of large volumes of water in both processes. In addition, heat is added in the froth treatment stage to enhance the separation of solids and water from the solvent-diluted bitumen [8].

Government regulations have tightened to reduce the use of clean water in oil sands [15]. The Canadian oil sands are perceived as having poor environmental performance. Oil sands operators have improved the productivity of freshwater, but the units of water used from the Athabasca river makes up most of the water used in the processes and for every unit of bitumen 2.5 units of water is used from the Athabasca river [16]. Also, the solvent that is most commonly used in oil sands is Naphtha, which is a toxic compound. Extensive naphtha usage increases the environmental and health risks significantly [17]. Long time exposure to naphtha poses significant health risks [17]. Hence, it is important to continue to explore processes that would significantly reduce the energy and water usage along with the health and environmental risks. Based on all the studies performed with surfactant based washing techniques it is evident that using a surfactant may reduce the interfacial tension significantly and enhance bitumen recovery which would result in lower water usage. Also, injecting a solvent along with the surfactant based washing technique would reduce the bitumen viscosity greatly by diluting it and help achieve high bitumen recovery. To resolve the issue of solvent toxicity a paraffinic solvent such as cyclohexane could be used. Therefore, injecting a combination of a surfactant based fluid along with a paraffinic solvent could prove to be very beneficial in reducing water, solvent, and energy consumption to a great extent.
1.3 – Methods of vegetable oil extraction

In the case of vegetable oils, the substrates for oil extraction include nuts, seeds and algae. A common method for extracting oil from seeds involves pressing the seed to force the oil to flow out of the seed [18]. An expeller press is one of the common types of presses used. It is a screw-type machine that presses oil seeds through a caged barrel-like cavity [18,19]. This kind of pressing results in friction and high temperatures. The oil seeps through small openings that do not allow seed fiber solids to pass through [18,19]. However, the expeller processing is unable to extract all of the oil as significant amount remains trapped inside of the cake leftover after pressing [18,19]. Another press method is the hydraulic press method which yields the best quality of oil among the popular commercial press methods. Sesame seeds and olives are widely used as substrates for hydraulic press. Because the hydraulic press does not involve the friction and heat associated with the screw press, the produced oil is referred to as cold pressed or virgin oil [19]. In the case of hydraulic presses the seeds are crushed and the paste is spread on fiber disks stacked on top of each other and placed into the press [20]. These disks are then put on a hydraulic piston, forming a pile. A pressure of up to 400 atm is applied on the disks [20,21]. To facilitate separation of the liquid phases, water is run down the sides of the disks to increase the speed of percolation [20, 21]. The liquids are then separated via decantation or centrifugation [20, 21].

Another common method used to extract oil from oilseeds is solvent extraction. Solvent extraction methods use large volumes of solvent and long extraction times to remove oil from seeds. Developments in the solvent extraction process have resulted in an extraction technique known as accelerated solvent extraction. In this accelerated extraction, a solvent is pumped into an extraction chamber containing the seeds, which is then brought to an elevated temperature and
pressure. Within minutes the extract is transferred from the heated chamber to a standard collection vessel and the entire extraction process is repeated with low solvent consumption [22]. In solvent extraction, the first step is the grinding of the seeds. The ground seed or cake is then purged or washed with a petroleum distillate (hexane is most commonly used), which releases the oil from the oilseeds [23]. The solvent is then flashed off by heating the oil/solvent mixture in a sealed chamber at 100˚C. This process should theoretically leave no solvent in the oil but analysis has shown that traces of hexane can remain in the finished oil [23]. The majority of vegetable oils in the market are solvent-extracted oils [23].

Problems with the solvent extraction process include toxicological and environmental safety issues, and for the case of rapeseed processing, the low quality of rapeseed oil extracted [24]. Kostic et al have shown that extraction parameters such as extraction temperature and seed to solvent ratio have an impact in the extraction of oil [25]. The oil yield was directly related to the seed to solvent ratio and it improved by a factor of 1.012 to 1.027 for every 10˚C rise in temperature [25]. One important substrate characteristic for solvent extraction of seeds is that seeds should have low moisture (water) content such as 2.5g/100g in order to achieve high extraction efficiencies [25].

Another biofuels prospect that has been looked into intensively in recent times is microalgae. Microalgae are unicellular species found in water systems and their sizes range from a few microns to a few hundreds of microns. Microalgae contain reasonably high level of oil content and can be grown in different environments including an open raceway pond or a sewage plant. The triglycerides in the microalgae can be converted to biofuels through chemical or biochemical processes. Microalgae with reasonably high oil content in dry biomass and fast growth rate are the most suitable for producing biodiesel. Once the lipids are extracted from the
biomass using different methods, other value-added products such as protein and carbohydrates can also be extracted. Then, the waste algal mass is disposed or sent to become fertilizer [36].

Lipid extraction from algae has also been successfully performed via solvent extraction of dry algae. According to studies performed by Dastidar et al. the maximum biodiesel yield from algae was obtained using simultaneous extraction and esterification using hexane as a solvent [26]. The group of Webley, using mixtures of alcohols as polar organic solvents, reported lipid extraction from wet microalgal concentrate [27]. It was observed that the lipid extraction efficiency increased with an increase in the speed of agitation, the extraction temperature and the degree of cellular disruption [27]. However for most conditions the extraction efficiency was close to 30%-50% and only one experiment reached 80% extraction, when the water content in the alcohol solution was the lowest, at 6 vol% [27]. The authors further explained that for the extraction of wet algae it is important that the mixture of alcohols and water remained monophasic to maintain the level of 30%-50% extraction. The authors also discussed that high extraction efficiency from wet algae is very important for the economics of algal oil because it removes the need for the energy-intensive step of drying the algae [27].

Even though solvent extraction is the most effective among the commercial extraction techniques for oilseeds and algae, it has several disadvantages. One major disadvantage is the flammability of the extraction solvent, which means that strict precautions have to be taken to avoid fires and minimize explosion risk in the extraction facilities. Due to the clean air act of 1990 the oilseed processing industry is under pressure to switch from commonly used volatile solvents such as hexane to low or non-volatile solvents such as alcohol or water [28]. High energy requirement for solvent recovery and drying are also major disadvantages [28]. With the mechanical press extraction techniques the costs are lower initially due to lower investments but
the extraction efficiencies are significantly lower than that of solvent-extraction. In addition, the power requirements for the mechanical press methods are considerably higher than any other process and the wear and tear on the equipment results in higher maintenance costs [29]. Hence, it is important to explore methods for the extraction of lipids from algae and oilseeds that would reduce the environmental risks, lower the energy costs and improve extraction efficiency. Another interesting prospect could be the use of surfactant-based solvent systems for the extraction of oil, as used for oil sands but in this case from a biomass substrate.

1.4 – Surfactants in oil extraction processes.

The reason for using surfactants in oil extraction processes are three-fold, they reduce the surface tension of the aqueous extraction phase [30], facilitating the penetration into the porous structure of the substrate to be extracted, they modify the wettability of the surface of the substrate to facilitate the transport of water and displaced oil [30, 31] and finally they reduce the interfacial tension between the aqueous phase and the oil, allowing the displacement of the oil from the porous media. If one uses sufficiently high surfactant concentration, the oil can be solubilized into micelles.

One of the most efficient methods to use surfactants in oil recovery is via the formulation of microemulsions. Microemulsions are surfactant-oil-water (SOW) systems that exist in thermodynamic equilibrium. The aqueous phase can include of salt and/or other species, and the oil phase is generally a mixture of hydrocarbons and olefins [31]. Microemulsion systems can be classified into three categories known as Winsor Type I, II, and III microemulsions [32]. In Type I, the oil is solubilized in micelles present in the aqueous phase, while in Type II water is
solubilized in reverse micelles present in the oil phase. In Type III, both the water and oil are
solubilized in a bi-continuous structure [32]. Increasing surfactant hydrophobicity, salt content or
the polarity of the oil phase induce a transition from Winsor Type I to Type III to Type II [33]. In
the Type III region ultralow-low interfacial tensions are often obtained, which are very important
for developing oil extraction processes based on aqueous surfactant solutions [33]. The
combination of conditions that produce Type III microemulsions with the lowest interfacial
tension are often referred as the optimal formulation conditions. Such optimal formulation
conditions can be determined using the semi-empirical hydrophilic-lipophilic-difference (HLD)
framework [13]. For systems that involve ionic surfactants, the HLD equation is:

\[ HLD = \ln(S) - k \times EACN + Cc - c_T(T-25^\circ C) \] (1.1)

A negative value of HLD means that the SOW system is hydrophilic and oil-swollen
micelles (Type I systems) are formed [13]. Positive values of HLD mean that the SOW system
forms water-swollen reverse micelles [13]. When HLD=0 the surfactant is at its optimal
formulation, for producing middle phase (Type III) microemulsions and ultralow interfacial
tensions at the oil-water interface [13]. The term \( \ln(S) \) in equation 1.1 accounts for the effect of
ionic strength in the aqueous solution (S, expressed as equivalent g NaCl/100 mL of aqueous
solution) [13]. The term \( EACN \) stands for equivalent (linear) alkane carbon number, and is a
measure of the hydrophobicity of the oil phase [13]. For n-hexane, for example, \( EACN = 6 \). The
term \( Cc \) is known as the characteristic curvature of the surfactant [13]. Positive \( Cc \) values are
associated with more lipophilic surfactants, and negative \( Cc \) values are associated with more
hydrophilic surfactants [13]. \( T \) in equation 1.1 stands for the temperature of the system [13]. The
parameters \( k \) and \( c_T \) are constants that depend on the structure of the surfactant, but are close to
0.16 and 0.01°C\(^{-1}\) for most ionic surfactants [13].
Kiran et al. used the HLD framework to study the phase behavior of bitumen-solvent microemulsions, and quantified the EACN of bitumen, asphaltenes and deasphalted bitumen, as well as the Cc of asphaltenes and naphthenates [13]. As oils, asphaltenes have low EACN values, reflecting the polar nature of these polyunsaturated aromatic bitumen compounds [13]. As surface-active material, asphaltenes were found to be hydrophobic species that lead to the formation of water-in-oil emulsions [13]. Naphthenates, particularly sodium naphthenates, are highly hydrophilic compounds that result in the formation of oil-in-water emulsions [13]. Based on calculations performed using parameters such as the characteristic curvature, temperature deviation etc. in the HLD equation it was found that bitumen-water systems produce water-in-oil emulsions, while in the presence of naphthenates these systems produce oil-in-water emulsions [13].

The use of surfactant-based washing fluids is beneficial in the case of oil spills and can be very advantageous in bitumen recovery from oil sand ores as well. Methods have been developed by Quraishi et al. [12] to extract bitumen using surfactant-based washing fluids from bitumen-coated sand. Figure 1.1 provides the interfacial tension of their formulations with toluene, as a function of the sodium dihexyl sulfosuccinate (ionic surfactant, SDHS) concentration [12]. The critical microemulsion concentration (CµC), i.e. the minimum surfactant concentration required to form a microemulsion phase, was found to be 3000 ppm at optimal salinity (3g NaCl/100ml) [12]. Quraishi et al. [12] observed that very low interfacial tensions produced substantial increases in oil recovery from bitumen-coated sand, when compared to the recoveries obtained with water [12]. The team also reported that increasing the solvent to bitumen ratio brought about substantial increase in bitumen recovery, mainly because of the reduction in the viscosity of the oil [12].
Experiments conducted by Chang and co-workers have shown approximately 74 to 100% removal of polycyclic aromatic hydrocarbons from sand using sodium dodecyl sulfate (SDS), while the recoveries obtained with water ranged between 30 to 80% [34]. The experiments conducted by Quraishi et al. using 3000 ppm SDHS solutions have shown bitumen recoveries over 90% from sand-bitumen systems [12]. However, the use of surfactants in the extraction of bitumen from aged oil sands and bitumen-coated clay was not evaluated by Quraishi et al.

The oil-particle-water separation process is governed by interfacial phenomena at three different interfaces i.e. the oil/particle interface, the water/particle interface, and the water/oil interface. This separation can occur via roll up/roll back, snap-off/emulsification, or solubilization [35]. According to Quraishi et al. “In roll up, if the surface is initially non-wetting, once the three phase contact line is formed; the oil film recedes until it detaches from the surface” [12]. The roll up/roll back mechanism is related to the work of adhesion which is a function of the interfacial tension between the oil and washing fluid, and the contact angle.

**Figure 1.1:** Interfacial tension of solvent (toluene) and washing fluid versus the surfactant concentration at its optimal salinity (3g/100ml) in deionized water (Adapted from the work of Quraishi et al) [12]
between the oil and solid particle [12]. Emulsification or snap-off takes place when the surface tension forces between the oil drop and the particle surface are less than the gravitational or external hydrodynamic forces applied [12]. In this case the contact angles are smaller and thus complete detachment does not occur. Snap off is related to the work of cohesion of the oil [12].

Solubilization can be explained as the phenomenon of dissolving the hydrophobic oil into the surfactant micelles [12]. This type of separation can achieve complete removal of oil, but then requires additional processes to separate the oil from the micelles [12]. Snap-off seems like the most efficient way of optimizing oil removal, while using lower surfactant concentrations and energy usage than solubilization [12]. Figure 1.2 illustrates the above mentioned mechanisms.

![Figure 1.2: Mechanisms of oil removal from solid surfaces (Adapted from Acosta and Quraishi et al) [35]](image)

Quraishi et al used the Weber number (ratio of inertial to surface tension forces) to determine the drop size of the oil removed during the extraction process [12]:
\[ We = \frac{\rho v^2 d_p}{\gamma} \quad (1.2) \]

where \( \rho \) is the density of the fluid, \( v \) is the velocity of the fluid, \( d_p \) is the diameter of the drop, and \( \gamma \) is the interfacial tension between the oil and the aqueous phase. If the Weber number is greater than a certain critical value, then the drops are unstable and break into smaller droplets. A review by Walstra of the critical Weber number as a function of the ratio between the viscosity of the dispersed phase and the continuous phase shows that for viscosity ratios between 0.01 and 10, the critical Weber number is around 1 [36]. For viscosities greater than 10 and smaller than 0.01 the critical Weber number is substantially larger [12].

Using the HLD framework, combined with the net-average-curvature (NAC) model, the interfacial tension, viscosity and density of the surfactant formulation can be calculated [12]. These formulation properties can then be integrated with capillary curves. The capillary curve portrays the fraction of total fluid volume in an aquifer occupied by NAPL for a given capillary number [12]. Capillary curves are characteristic for a given soil, with a given contaminant and a given surfactant formulation [12]. Changes in the viscosity of the oil or the surfactant solution, or heterogeneities in the permeability of the aquifer could change these curves [12]. The capillary number indicates the ratio between the viscous or shear forces that tend to stretch or spread the oil and the interfacial forces that tend to keep the oil trapped in small pores:

\[ Ca = \mu \cdot v / \gamma \quad (1.3) \]

where \( \mu \) is the viscosity of the surfactant solution, \( v \) is the velocity of the solution in the pore, and \( \gamma \) is the interfacial tension between the surfactant solution and the NAPL phase [12].

The mechanisms of roll up/roll back and snap-off/emulsification discussed above for bitumen and crude oil removal from particles, can also apply to the removal of oil from
microalgae. Microalgae are unicellular species with sizes ranging from a few microns to a few hundreds of microns. Microalgae contain reasonably high levels of oil and can be grown in different environments, including open raceway ponds [37]. The triglycerides in the microalgae can be converted to biofuels through chemical or biochemical processes [37]. Microalgae with reasonably high oil content in dry biomass and fast growth rate are the most suitable for producing biodiesel [37]. Once the lipids are extracted from the biomass using different methods, other value-added products such as protein and carbohydrates can also be extracted. Then, the waste algal mass can be used as fertilizer [37].

The role of surfactants in oil seed extraction is to reduce the interfacial tension (IFT) between the aqueous extracting phase and oil in crushed seed. IFT reduction promotes the snap-off, roll-up, and oil liberation mechanisms and hence promotes the oil extraction. Extended surfactants can be very useful in reaching low interfacial tensions with the triglycerides found in vegetable oils. Extended surfactants are surfactants containing groups of intermediate polarity, such as polypropylene oxides or block copolymers of propylene oxides and ethylene oxide, inserted between the hydrocarbon tail and hydrophilic head group [38]. Due to their unique molecular structure, the surfactant is stretched out further into both the oil and aqueous phases, providing a smoother transition between the hydrophilic and lipophilic regions of the interface, which provides a more suitable environment for solubilizing the hydrophilic and lipophilic molecules [38]. Using a surfactant based process such as this is beneficial as it avoids the use of organic solvents, while achieving greater than 80% corn oil recovery with low surfactant and salt concentrations [38].

It has been found from previous work by Sabatini et al. that extended surfactants containing an intermediate-polarity spacer such as polypropylene oxide in between the
hydrophilic head and the hydrocarbon tail are known to result in superior solubilization and low interfacial tension, though they exhibit slow solubilization and emulsion separation kinetics [32]. Extended surfactants have low critical micelle concentration (CMC) and critical microemulsion concentration (CµC) compared with other surfactants, which allows one to obtain ultralow interfacial tensions using low surfactant concentration, below 1 g/L [39,40]. The unique structure of these extended surfactants allows them to achieve ultralow IFT with a wide range of oils, including highly hydrophobic oils using ppm levels of these surfactants [32,39,40]. Also, despite the relatively large molecular weight of these surfactants, they are water-soluble and can be formulated in relatively high electrolyte concentration while avoiding surfactant precipitation [39,40]. Because of these characteristics, the use of extended surfactants in the extraction of triglycerides from biomass such as algae has great potential and has been explored by other researchers [39,40].

1.5 – Hypothesis and objectives

The purpose of this project is to examine the hypothesis that capillary displacement - the use of aqueous surfactant solutions to reduce the surface tension forces holding the oil to the substrate - can be used to improve (reduce solvent and/or water and/or energy usage) the extraction of oil from oil sands, clay (fines from oil sands) and from microalgae.

The key objective of this work is to evaluate the recovery of the oil phase from bitumen-coated clay, oil sands ores, and wet algae using capillary displacement. The separation of bitumen from oil sand using capillary displacement was evaluated as a function of solvent to bitumen ratio and it was compared to solvent-only extraction and water-only extraction. The separation of bitumen from clay using capillary displacement was evaluated as a function of solvent volume fraction (in aqueous emulsion) and compared to solvent-only and water-only
extraction. For the extraction of bitumen from oil sands and from clay, the effect of substrate aging and centrifugation (used to separate the particle-oil-water system) was evaluated. For the extraction of microalgae, extended surfactants (no solvent) and combinations of surfactants and solvents were used to carry out the capillary displacement studies.

The following section in this paper show the effectiveness of the capillary displacement extraction using surfactant based washing fluid on aged oil sands and bitumen-coated clay, while section three illustrates the effectiveness of this technique on lipid extraction from microalgae. This technique for the oil sands and bitumen-coated clay was evaluated by testing varying solvent: bitumen ratios, solvent only and washing fluid only systems and by comparing extractions obtained using DI water as the washing fluid to extractions obtained using the surfactant based fluid. Also, the residual solvents leftover in the solids after the extractions was estimated. In addition, the effect of eliminating centrifugation from the extraction process was also tested. For the microalgae systems the technique was evaluated by testing different solvent to dry biomass ratios, using extended surfactant based washing fluid in the absence of solvents to achieve extraction and by estimating the residual solvent leftover in the biomass.
2. Capillary displacement of aged oil sands and bitumen-coated clay

2.1 – Introduction

In recent years a lot of work has been done to develop newer extraction technologies that can help resolve or minimize the issues associated with the oil and gas industry. Pathak et al., for example, tested a new technology where bitumen recovery is achieved via hot solvent injection [41]. In this process the solvent is co-injected with steam or into a pre-heated reservoir. The purpose of this study was to test the performance of paraffinic solvents such as propane and butane in bitumen recovery at elevated temperatures [41]. N-solv Corporation has been working on the development of a process which uses no water and 85% less energy than Steam Assisted Gravity Drainage (SAGD) [42]. In this process, heated propane vapor is injected at moderate pressures into the gravity drainage chamber [42]. The vapor flows from the injection well to the colder part of the chamber and condenses, delivering fresh solvent to the bitumen extraction interface [42]. The use of an aliphatic solvent preferentially extracts the valuable components in the bitumen while leaving behind the problematic components such as asphaltenes [42]. Although this technique upgrades the oil’s API from 8 (raw bitumen) to between 13 and 16 API, non-condensable gases are released from the bitumen and accumulate in the reservoir if no special measures are taken [42]. Nikakhtari et al. also evaluated solvent-only, ex-situ extraction of bitumen from oil sands, finding that bitumen recoveries greater than 94% could be achieved when using 300 grams of cyclohexane (over three separate stages) to treat 100 grams of “fresh” oil sand containing approximately 13% bitumen [11]. This would represent a solvent to bitumen ratio of around 23. Although such solvent-only process would accomplish the goal of producing “dry” tailings, the large solvent demand would also call for large solvent process facilities and large amounts of energy utilized in the distillation/recovery of the solvent during the process.
Yang et al. explored the use of a hybrid technology that combines water and solvent (naphtha, toluene and cyclohexane), and they were able to extract 70 to 80\% of bitumen from weathered sand using 100 g of solvent to treat 100 g of weathered oil sand at 50°C, resulting in solvent to bitumen ratios of about 6 to 10 \cite{43}. For Yang et al., the addition of surfactant to the aqueous solution produced only minor increases in oil recovery, but better separation of particles. In this work, the use of solvent and aqueous surfactant solutions is also explored. The difference is that the surfactant solution has been optimized to produce ultralow interfacial tension with the mixture of solvent and bitumen to promote the capillary displacement of oil from the particles. The approach was initially used by Quraishi et al. to remove bitumen from beach sand coated with bitumen \cite{12}. It is expected that this technique would be effective in removing bitumen from fine (clay) particles of oil sands and from aged oil sands that are known to be difficult to extract using conventional hot water extraction processes. We also expect the capillary displacement technology to reduce the solvent to bitumen requirements, which would reduce the energy and infrastructure required to separate the solvent from the extracted bitumen.

Previous work by Hirasaki et al. has shown that the extraction of bitumen from ores having high clay content is much more difficult in comparison to systems with low clay content \cite{44}. These researchers also reported that illite and kaolinite are the most common type of clays found in oil sands. Vu et al. reported that oil sand ores also consist of hydrophobic and hydrophilic solids and that the more hydrophobic the solids (oil-coated clays), the lower the bitumen recovery and the bitumen froth quality \cite{45}.

In addition to fine particles, weathering or aging of the crude oil coating particles can substantially decrease the effectiveness of surfactant-based recovery of oil \cite{46}. The effect of aging on the rheological properties of bitumen has been explored \cite{47}. The results obtained from
that study showed that aging increases the solid-like behavior of bitumen (elastic solid) under shear [47]. The processes impacting the rheological properties of the bitumen include oxidation, loss of volatile components and exudation (migration of oily components from bitumen into the aggregate) [47]. The chemical changes due to aging include formation of carbonyl compounds and sulfoxides, transformation of generic fractions, and increases in the amount of large molecules, molecular weight and polydispersity [47]. Aging of bitumen also has an impact on the tendency of bitumen droplets to coalesce [47]. It has been observed by the Syncrude Canada’s Research Centre that when the bitumen ages for even a few hours its ability to coalesce with other droplets to form larger ones decreases [48].

In the first part of this work, Athabasca oil sands aged for two years was washed with a combination of solvent (toluene and cyclohexane) and a solution of 3000 ppm SDHS capable of producing ultralow interfacial tension with these solvents, using various solvent to bitumen ratios [12]. A similar set of experiments was carried out in the second part of this work with bitumen-loaded kaolinite as a substrate. For the kaolin systems, the effect of aging was also considered. Oil removal from aged oil sand of 85% or more was obtained using solvent to bitumen ratios of 1 and at room temperature when coupling the extraction with a centrifugation step. Water-solvent systems (no surfactant) could also achieve similar removal as long as solvent to bitumen ratios of 2 or larger were achieved. These results were interpreted using the film emulsification (snap-off) theory of Quraishi et al. [12] that predicts the experimental trends and the importance of using surfactants to reduce the residual solvent content in the particles. The same theory also explained the results obtained with kaolin-bitumen systems where large solvent to bitumen ratios, ranging between 10 and 20, are required to obtain more than 90% bitumen removal due to the large surface area per unit of mass of kaolin.
2.2 – Materials and methods

Anhydrous toluene (99.8%), sodium chloride (99.5%), cyclohexane (>99%) and sodium dihexylsulfosuccinate (SDHS ≈ 80% in water) were purchased from Sigma-Aldrich Canada. Deionized water (conductivity <4mS/cm) was used to prepare all the aqueous solutions.

Oil sand samples used for the experiments were donated by Syncrude Canada Ltd, and aged for two years at room temperature in a 5 gallon pail covered with an air-permeable lid. Figure 2.1 presents the cumulative particle distribution (area-weighted) obtained after analyzing 20X micrographs (obtained with an Olympus BX-51 microscope) of toluene-washed oil sand using imageJ version 1.48. The Sauter ($d_{32}$) diameter was determined to be 68 µm.

Coker fed bitumen (CFB), used to produce bitumen-coated kaolin, was donated by Syncrude Canada Ltd. Kaolin was purchased from Sigma Aldrich Canada. Figure 2.1 also includes the cumulative particle distribution (area-weighted) for kaolin obtained after analyzing a 50X micrographs of kaolin particles dispersed in toluene. The Sauter ($d_{32}$) diameter of kaolin was determined to be 3.9 µm.

![Graph showing particle size distribution of kaolin and oil sands](image)

Figure 2.1 Area-weighted particle size distributions of kaolin and oil sands.
Washing fluids

The surfactant concentration and salinity used in the preparation of the surfactant-based washing fluid was kept constant at 3000 ppm and 3g NaCl /100ml respectively for toluene, according to the composition identified by Quraishi et al. [12] as producing ultralow interfacial tensions with toluene (EACN =1). For cyclohexane, two different salinities i.e. 3g NaCl/100ml and 4.3g NaCl/100ml were used to account for the larger EACN of cyclohexane (EACN=3) [49]. To this end, 0.3g of SDHS, and the required mass of NaCl (3g or 4.3g, as required) were diluted with DI water to a volume of 100 ml. The solution was mixed in a multi-tube vortex-mixer at 3200 RPM for 5 minutes. Deionized water with no salt or surfactant added was also used as alternative washing solution.

Washing Experiments

For the washing experiments, 1g of the oil sand samples were placed in 20ml scintillation vials. The samples were then mixed with the solvent and the washing fluid. Toluene and cyclohexane were used as model solvents, cyclohexane for its low toxicity and high volatility, and toluene for its high affinity to the asphaltenic compounds of bitumen.

For oil sand washing experiments, solvent to bitumen (mass) ratios of 0.26:1 to 2.6:1 were evaluated. The mass of bitumen in the ores was obtained prior to the experiments via total organic carbon (TOC) analysis of the oil sand. The TOC analysis was carried out using a Total organic carbon analyzer by Shimadzu – Solid sampler (SSH) – 5000 A equipped with a solid sampler analyzer. The average of ten oil sand samples tested in the TOC analyzer provided a bitumen content of 15% (by mass) in the oil sand. The solvent: bitumen ratios were calculated as follows:
The prescribed volume of solvent was first added to 1g samples, then the samples were mixed in a multi-tube vortex mixer set at 3200 RPM for 10 seconds. The washing fluid was then added to the samples, then the entire system as mixed in the multi-tube vortex mixer at 3200 RPM for 3 minutes. The mixing time and speed of the multi-tube vortex mixer were the same as those found optimal by Quraishi et al. when washing bitumen-coated sand [12]. After mixing, the samples were allowed to sit for two hours to achieve separation via gravity settling. The purpose of the gravity settling was to let the solids and water, i.e. the heavier phases settle by gravity, while the diluted bitumen layer (solvent and bitumen) floated on top. Following gravity settling separation, the samples were centrifuged for 15 minutes at 2700 RPM to achieve complete separation of the oil layer. Figure 2.2 provides a schematic of the process.

![Schematic representation of the solvent-surfactant based washing protocol.](image)

**Figure 2.2**: Schematic representation of the solvent-surfactant based washing protocol.

For oil sands, one additional experiment was carried out, the extraction of bitumen using only the surfactant solution, without the addition of solvent. To mitigate the high viscosity of bitumen in the absence of solvent, these solvent-free extractions were carried out at 80°C. To
this end, 1g of oil sand was placed in 20 ml scintillation vials, along with the washing solution. The samples were then placed in a water bath that was heated to about 80˚C for one hour. After heating, the samples were mixed for 3 minutes in a multi-tube vortex mixer at 3200 rpm, and then placed on the bench (room temperature) for two hours at room temperature to undergo gravity settling. The samples were then centrifuged at 2700 rpm for 15 minutes.

Kaolin washing experiments were conducted in a similar fashion to those explained above except that kaolin had to be loaded with bitumen, and required larger solvent to bitumen ratios. The typical bitumen content in oil sands ores ranges between about 5 to 15% [8]. To be consistent with the bitumen loading in the oil sands used in this work, kaolin was contaminated with 15% bitumen. To this end, 25g of kaolin was mixed with 7.5g of a 50:50 (w/w) toluene-bitumen mixture. The dilution of bitumen with toluene was essential to ensure a homogenous bitumen coating. A pipette was then used to evenly coat the batch of kaolin with the toluene-bitumen mixture. Once the batches were evenly coated, they were placed in a fume hood to evaporate the toluene. The bitumen-coated clay system was aged for 6 months (unless otherwise specified) before washing. Figure 2.3 illustrates the bitumen coating protocol.

**Figure 2.3:** Schematic representation of the bitumen coating protocol
For the bitumen-kaolin experiments, the case of solvent-only extraction was explored using toluene and cyclohexane as model solvents. For combinations of solvent-aqueous washing solutions, toluene was used as the solvent. Toluene volume fractions in liquid (aqueous washing solution+ toluene) of 0, 0.25, 0.5, 0.75 and 1 were evaluated. Total liquid volumes of 2, 3, 4, 5, 6 and 8 ml were considered. Toluene was first added to 1g of bitumen-coated kaolin and the sample was mixed in a multi-tube vortexer at 3200 RPM for 10 seconds. After that, the washing solution was added to the samples. The samples were then mixed further in the multi-tube vortexer at 3200 RPM for 3 minutes. Once the mixing of the samples was completed, they were allowed to sit for 24 hours to achieve separation via gravity settling. Following gravity settling, the samples were centrifuged for 30 minutes (unless otherwise specified) and at 2700 RPM (unless otherwise specified). Table 1 and table 2 represent the different solvent: bitumen ratios and solvent fractions explored for the oil sands and the clay-bitumen cases respectively:

Table 2.1: Different solvent: bitumen ratios tested for oil sands extractions

<table>
<thead>
<tr>
<th>Solvent amount (ml)</th>
<th>Washing fluid amount (ml)</th>
<th>Bitumen content in oil sands (%)</th>
<th>Solvent: bitumen ratio</th>
<th>Sample mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
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<tr>
<td>Solvent amount (ml)</td>
<td>Washing fluid amount (ml)</td>
<td>Total liquid volume used (ml)</td>
<td>Bitumen content in oil sands (%)</td>
<td>Solvent: bitumen ratio</td>
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<td>6</td>
<td>15</td>
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Oil recovery

Toluene was carefully added to the liberated oil phase layer on the top of the liquid phase to dilute the bitumen even further. A dilution factor of 82 was used for each of the samples. The solvent was slowly added using a plastic pipette directly into the liberated bitumen phase to ensure that no solvent came into contact with the cleaned solid particles settled at the bottom of the vial. Further dilution was required to reduce the viscosity of the liberated oil phase, thereby making it easier to handle for analysis. Then, 40μl of the diluted liberated bitumen phase was added to 3ml of solvent in a quartz cuvette using a gastight 100μl syringe (Hamilton Company). Such high dilution factors were essential to reduce the magnitude of the absorbance values of the liberated bitumen phase. The absorbance of the diluted bitumen-solvent mixture was then measured in a Pharmacia LKB ultrospec plus spectrophotometer at a wavelength of 400nm, consistent with the method of Quraishi et al. [12]. The absorbance of this “treated sample” was compared to the absorbance of a “clean sample” prepared by diluting 0.15 g of bitumen (as if all the bitumen was liberated) in enough toluene to produce the same dilution ratio as the treated sample. Figure 2.4 summarizes the protocol used to measure bitumen recovery. The percentage of bitumen recovery was calculated as:

\[
\% \text{ Bitumen Recovery} = \frac{\text{Absorbance treated sample}}{\text{Absorbance clean sample}} \times 100
\]  

(2.2)
2.3 Results and Discussion

Bitumen recovery from aged oil sands

Figure 2.5 presents the recovery of bitumen from aged oil sand as a function of the toluene to bitumen ratio when the aged sand was washed with the 3000ppm SDHS at 3% salinity (Toluene-SDHS) and when the aged sand was simply washed with DI water and toluene (Toluene-Water). For solvent to bitumen ratios larger than 1, the recovery of bitumen is greater than 85%, and adding the surfactant to the aqueous phase makes no difference in bitumen recovery. On the other hand, when the solvent to bitumen ratio is less than 1, the Toluene-SDHS system produced better recoveries than the toluene-water system, although for both washing solutions the recovery is relatively low.
Figure 2.5: Bitumen recovery from aged oil sand as a function of toluene to bitumen mass ratio. The SDHS solution was prepared with 3000 ppm SDHS and 3g NaCl/100 mL. The water system corresponds to DI water. Total liquid to oil sand ratio: 4 ml/g.

To understand the experimental trends in Figure 2.5, the film emulsification model of Quraishi et al. [12] was employed. According to that model, the addition of solvent produces an oil + solvent mixture that coats the surface of the particle. The initial film thickness can be estimated by dividing the volume of the oil (bitumen+ solvent) mixture by the area of the particle. Upon mixing, and as long as the inertial forces are greater than the shear forces, part of the film will emulsify. The diameter of the emulsified drop ($d_e$) of bitumen + solvent mixture can be calculated using the critical Weber number ($We_c$) [36], according to:

$$d_e = \frac{\gamma \cdot We_c}{\rho \cdot v^2}$$  \hspace{1cm} (2.3)
where $\gamma$ is the interfacial tension of the washing solution with the mixture of bitumen + solvent, $\rho$ is the density of the continuous phase, and $v$ is the velocity of the fluid. The interfacial tension for toluene-bitumen mixtures with the SDHS solution of Figure 2.5 has been reported to be 0.02 mN/m, and the interfacial tension of toluene-bitumen mixtures with DI water is on the order of 20 mN/m [12]. The velocity of the fluid ($v$) was estimated by Quraishi et al. using a momentum-averaged value for a fluid rotating inside a vial: $v = 0.667 \cdot 2 \cdot \pi \cdot R \cdot f$. R is the radius of the vial (1.1 cm for the scintillation vials used in this work), and $f$ is the mixing frequency (3200 rpm). For all the systems evaluated in this work, this means a velocity of 2.5 m/s. The value of $W_e$ depends on the ratio between the viscosity of the dispersed phase and the continuous phase, and for the viscosity ratios of 0.1 to 1, the value of the critical Weber number ranges from 0.3 to 1 [36]. A value of $W_e = 0.35$ was used to calculate $d_e$ with Equation 2.3. The film emulsification theory is based on the premise that the film will emulsify as long as the thickness of the film is greater than the diameter of the emulsified drop, which translates to assuming that the mechanisms that break drops also apply to the breakup of films. This means that at steady state the thickness of the film is equal to $d_e$, and the bitumen recovery can be estimated as:

$$\% \text{ Bitumen recovery} = (1 - d_e/t_i) \cdot 100\% \quad (2.4)$$

where $t_i$ is the initial thickness of the film. To confirm that inertial forces dominate the emulsification of the oil, the Reynolds number of the drop should be greater than 1 [12]:

$$Re_d = \frac{d_e \cdot \rho \cdot v}{\mu} \geq 1 \quad (2.5)$$
where $\mu$ is the viscosity of the continuous phase. If the value of $d_e$ calculated from Equation 2.3 produces a Reynolds number less than one, then the value of the $d_e$ should be calculated using Equation 2.5, setting the value of the Reynolds number equal to 1.

The solid line in Figure 2.5 was produced using the film emulsification model assuming that oil sand particles are spheres with a diameter of 68 µm (Sauter diameter, required to calculate the area of the particles), and interfacial tension is 0.02 mN/m, corresponding to the SDHS formulation. The dashed line in Figure 2.5 was produced using the same protocol, but with an interfacial tension of 20 mN/m, characteristic for toluene-diluted bitumen with water. These predicted lines are consistent with the experimental data for solvent to bitumen ratios greater than 1. At first, it seems counterintuitive that although there are three orders of magnitude difference in the interfacial tension with the SDHS formulation and with DI water, there is almost no difference in the fraction of oil recovered. A closer look at the predictions from the film emulsification model reveals that even though Equations 2.3 and 2.4 would have predicted substantially more oil removal for the SDHS system, the problem is that those $d_e$ values would have produced very low Reynolds numbers. In fact, for interfacial tensions lower than 7.5 mN/m, further reduction in interfacial tension would not have made a difference in the fraction of oil removed. For solvent to bitumen ratios lower than 1, the film emulsification model predicts greater differences between the SDHS and DI water washing solution, which are also observed in the experiments. However, the decrease in oil recovery obtained in the experiments was more pronounced than that predicted by the model. The reason is likely associated with the fact that at low solvent to bitumen ratios the bitumen-solvent mixture is more viscous and more difficult to remove [12]. This viscosity ratio was not considered in the film emulsification model, although adjustments to the critical Weber number could partially account for this observation.
The recovery obtained in Figure 2.5 could be compared with that obtained by Yang et al. where 1 part of aged oil sand was washed at 50°C with 1 part of toluene and 1 part of water, producing close to 95% bitumen recovery [43]. The solvent to bitumen ratio used by Yang et al. was close to 10, considering that the bitumen content in the oil sand was 10.4%. In Figure 2.5, the system with SDHS can extract 90% of bitumen using only a toluene to bitumen ratio of 1 and at room temperature.

Figure 2.6 presents the recovery of bitumen with SDHS and water as washing formulations, and using cyclohexane as solvent. The solid and dashed lines show the predicted extraction with the film emulsification model for the SDHS and water washing solutions. The results obtained with cyclohexane were close to those obtained with toluene, which are consistent with the predictions of the film emulsification model. This is also consistent with the findings of Yang et al. who obtained 85% bitumen removal with cyclohexane and water at 50°C [43]. The fact that cyclohexane and toluene removed bitumen in a similar fashion suggests that there is no concern of asphaltene precipitation, or if that asphaltenes precipitated during the extraction, they were suspended in the solvent, which is consistent with the observations of Pereira et al. [50]. One of the issues with the film emulsification model used is that it assumes complete dissolution of the bitumen in the solvent. It is true for the case of toluene but cyclohexane and bitumen are not perfectly miscible and there is some asphaltene precipitation that takes place. However, with cyclohexane the asphaltene precipitation is not as pronounced as some of the other paraffinic solvents such as Heptane or pentane. Therefore, that is another factor which if considered can result in the modification of the emulsification model to predict the cyclohexane and other paraffinic solvent extractions more accurately.
Figure 2.6: Bitumen recovery from aged oil sand as a function of cyclohexane to bitumen mass ratio. The SDHS solution was prepared with 3000 ppm SDHS and 3 g NaCl/100 mL. The water system corresponds to DI water. Total liquid to oil sand ratio: 4 ml/g.

The residual solvent content in the washed particles is an important parameter because it indicates the need for a post-extraction process to recover or remove the residual solvent from the particles. Due to analytical limitations (residual solvent content was too low - less than 5% - for our solvent balance method), we are not able to report a residual solvent content. However, it is possible to estimate what the value of residual solvent content would be assuming that the residual film on the particle has a solvent to bitumen ratio composition equivalent to the solvent to bitumen ratio used to wash the sample, such that the recovery of bitumen also applies to the recovery of solvent. Therefore, the estimated residual solvent content would be:

\[
\% \text{ residual solvent} = \frac{m_{\text{solvent}}(1 - \% \text{ recovery})}{m_{\text{sand}} + (m_{\text{bitumen}} + m_{\text{solvent}})(1 - \% \text{ recovery})} \cdot 100% \quad (2.6)
\]
Figure 2.7 presents the estimated solvent content as a function of the bitumen to solvent ratio when using toluene and cyclohexane as solvents, and SDHS and water as washing solutions. The predicted values from the film emulsification theory are also included as a comparison.

![Graph showing solvent content vs solvent to bitumen ratio](image)

**Figure 2.7:** Estimated residual solvent content on sand (Equation 2.6) as a function of the solvent to bitumen mass ratio when using toluene and cyclohexane as solvents, corresponding to the systems of Figures 2.5 and 2.6, respectively.

To assess the accuracy of the estimate from Equation 2.6, consider that although Yang et al. reported a 74% recovery of bitumen, they were able to recover 92% of naphtha, suggesting that the residual mixture of oil + solvent on the particle was more concentrated in bitumen than the extracted mixture [43]. Using 74% recovery, Equation 2.6 would have produced an estimate of 18% residual bitumen, but 92% recovery would produce an estimate of 7% residual solvent,
which is the value reported by Yang et al. Therefore, the estimated values of residual solvent in
Figure 2.7 are more representative of the upper bound value of that residual solvent.

According to Figure 2.7, the combination of surfactant and solvent produces a reduction in
residual solvent, particularly at low solvent to bitumen ratios. The reason for this difference is
the improved recovery obtained with surfactants at low solvent to bitumen ratios. In the case of
cyclohexane, the residual solvent content remains in the range of 1 to 2% even at high
cyclohexane to bitumen ratios. The residual solvent values of Figure 2.7 are substantially lower
than the 7% reported by Yang et al., but they are still large compared to current Canadian
guidelines for residual petroleum hydrocarbon residues in soils for industrial sites, that range
between 0.03% to 0.3%, depending on the volatility of the residue [51]. Considering that the
emulsified film model predicts residual solvent values below 1% with the use of surfactants, it is
conceivable than an optimized set of process conditions (e.g. higher fluid velocity) and suitable
surfactant solution could produce residual total petroleum hydrocarbons that would approach
Canadian guidelines. However, it is likely that a post-treatment process might be necessary to
remove the residual solvent.

Solvent-free extraction

The use of solvent not only brings up the issue of residual solvent on the soil, but it also
requires dedicated facilities that can handle flammable solvents. In order to avoid the use of
solvents altogether, a set of tests were conducted with SDHS formulations and without solvent.
To partially reduce the viscosity of bitumen, the experiments were carried out at 80°C. Figure
2.8 presents a picture of five vials, all of which correspond to 1g of oil sand treated with 4 ml of
a solution of 3000 ppm SDHS with 3 g NaCl/100 ml for 1 hour, then mixed for 3 minutes. The
brownish appearance of the aqueous phase suggests that a fraction of bitumen was emulsified or that small bitumen-coated particles were dispersed in the aqueous phase. However, this emulsified / dispersed oil eventually settled, leaving the aqueous phase clear, with no measurable oil removal. Therefore, based on these observations it is clear that for aged oil sands, the use of solvent is important. The presence of the solvent impacts three aspects of the process, first the solvent reduces the viscosity of bitumen, second, it reduces the density of the bitumen-solvent mixture facilitating the separation by gravity of the emulsified film, and third it makes the film on the particle thicker, thus facilitating its emulsification.

**Figure 2.8**: Vials containing 1g of aged oil sand and 4 ml of 3000 ppm SDHS solution with 3 g NaCl/100 ml after heating for 1h at 80°C, and 3 minutes of vortex-mixing at 3200 rpm.

*Gravity settling vs. centrifugation*

The bitumen recoveries presented in Figures 2.5 and 2.6 were obtained after subjecting the systems to gravity settling, followed by centrifugation at 2700 rpm. From an operational point of view, these are extreme conditions that although possible for field operations, require
substantial capital and maintenance costs. Ideally, a separation like this would be achievable under gravity settling alone. Figure 2.9 shows pictures of the separation achieved after 2 hours of gravity settling with aged oil sand extracted with cyclohexane and SDHS washing solution at solvent to bitumen ratios ranging from 0.27 (far left) to 2.1 (far right). Evidently, a significant amount of bitumen can be extracted using gravity settling.

![Figure 2.9: Separation after 2 hours of gravity settling using cyclohexane and SDHS washing solution.](image)

Figure 2.9: Separation after 2 hours of gravity settling using cyclohexane and SDHS washing solution.

Figure 2.10 shows the bitumen recoveries obtained using only gravity settling with cyclohexane and SDHS washing solution. Without centrifuging the entire system, the extraction is significantly lower than the extractions obtained when centrifugation is used. For solvent to bitumen ratios of 1, less than 60% bitumen is recovered for the 1xG case. Even at solvent to bitumen ratios as high as 3 the bitumen recoveries obtained are less than 70%. One potential question that arises is whether one needs to centrifuge the entire system, or if separating the particles first and then centrifuging the oil-water emulsion would suffice. That question was not explored within this work, but it is relevant to mention that Yang et al. obtained 85% removal.
with cyclohexane after centrifuging the oil-water emulsion solvent only. There is, therefore, room to improve the separation of oil-particles and water for these systems in a manner economical and feasible for field deployment.

**Figure 2.10**: Bitumen recovery from oil sand using a cyclohexane-SDHS solution at room temperature, followed by centrifugation or gravity settling.

**Bitumen recovery from bitumen-coated kaolin.**

*Solvent-only extraction*

Figure 2.11 shows the adsorption isotherm (25°C) obtained when a mixture of solvent (toluene or cyclohexane) and bitumen are set in contact with clean kaolin. To obtain the adsorption isotherm, the initial and final concentrations (after 24 hours) of bitumen were determined using the spectrophotometric method at 400 nm. The y-axis in Figure 2.11 indicates the grams of bitumen adsorbed per gram of kaolin and the x-axis the concentration of bitumen in the solvent at equilibrium.
Figure 2.11: Adsorption isotherm (25°C) for clay-bitumen system using toluene and cyclohexane as solvents. The trendlines represent the Freundlich isotherm fits.

The isotherms of Figure 2.11 were analyzed using three adsorption models, Langmuir, Freundlich, and Langmuir-Freundlich. For both isotherms, Langmuir produced the lowest correlation coefficient ($R^2$) and Langmuir-Freundlich produced the largest, but only marginally better than the Freundlich isotherm. Figure 2.11 only includes the power law fits corresponding to the Freundlich isotherm. From Figure 2.11 it is clear that toluene produces less bitumen adsorption than cyclohexane. This might be explained by the fact that the asphaltenes in bitumen have a higher affinity for toluene than for cyclohexane. Marczewski and Szymula evaluated the adsorption isotherm of asphaltenes, from a toluene solution, on kaolinite and also determined that the Freundlich isotherm was more accurate than the Langmuir isotherm to describe the adsorption of asphaltenes [52]. To compare the adsorption of bitumen with that of asphaltene, one should compare the adsorption obtained with 1000 ppm bitumen (Figure 2.11) with that of
150 ppm of asphaltenes (obtained by Marczewski and Szymula), considering that Athabasca bitumen contains close to 15% asphaltenes [13]. Marczewski and Szymula determined that when the concentration of asphaltene in toluene was 150 ppm, the adsorption was 16 mg asphaltene/g kaolin, close to the value of 20 mg bitumen/g kaolin in Figure 2.11 for 1000 ppm of bitumen in toluene. This comparison suggests that most of the bitumen adsorbed on kaolin corresponds to asphaltene adsorption.

An increase in bitumen adsorption would result in a decrease in bitumen recovery. Because of the larger adsorption obtained with cyclohexane, the rest of the studies on bitumen-coated kaolin focused on the use of toluene as a model solvent. Although this decision was driven by the interest in establishing a baseline for maximum bitumen recovery, eventual application of solvent-extraction technologies should concentrate on the use of more environmentally friendly solvents.

The Freundlich adsorption isotherm can be used to predict the recovery of bitumen from kaolin, considering the mass balance of bitumen:

\[
m_{bi} = C_b \cdot V_s + (K_f C_b^n) m_k
\]  

(2.7)

where \( m_{bi} \) is the initial mass of bitumen in kaolin, \( C_b \) is the concentration of bitumen in equilibrium with the adsorbed bitumen, \( V_s \) is the volume of the solvent (including the dissolved bitumen), \( K_f \) and \( n \) are the Freundlich adsorption constant and exponent, respectively; and \( m_k \) is the mass of kaolin (not including bitumen) in the system. Solving equation 2.7 (using the Freundlich constants in Figure 2.11) for a given mass of bitumen-coated kaolin with a given volume of solvent produces the estimated value of bitumen concentration in the solvent \( C_b \), and once this value is known, the recovery can be estimated as \( C_b \cdot V_s / m_{bi} \). Figure 2.12 presents the
estimated values of bitumen recoveries with cyclohexane and toluene as a function of the solvent to bitumen ratio, as well as the experimentally determined recoveries obtained with toluene.

Figure 2.12: Bitumen recovery from bitumen-coated kaolin using solvent-only extraction, as a function of the solvent to bitumen ratio. The estimated values for toluene and cyclohexane extraction were obtained after implementing the mass balance of bitumen (Equation 2.7).

The estimated bitumen recovery with toluene in Figure 2.12 tends to be larger than the experimental values for ratios of 20 or less, but is comparable at higher ratios. The recovery of bitumen from kaolin is low compared with the 90% obtained from oil sands using solvent-only extraction [11], likely due to the large specific area of kaolin, amenable for bitumen adsorption.

Combined solvent + washing solution extraction

Figure 2.13 presents the extraction of bitumen from bitumen-coated kaolin as a function of the solvent to bitumen ratio, using a combination of toluene and water or SDHS solution.
Figure 2.13 includes the extraction predicted from the film emulsification model with the same parameters used with oil sands, except for a particle size of 3.8µm (Sauter diameter of kaolin).

![Figure 2.13: Bitumen recovery from bitumen-coated kaolin as a function of toluene to bitumen mass ratio. The SDHS solution was prepared with 3000 ppm SDHS and 3g NaCl/100 ml. The water system corresponds to DI water. Total liquid to solid ratio: 4 ml/g.](image)

According to Figure 2.13, the extraction of bitumen with a combination of toluene and SDHS solution produces substantially better recovery than the combination of toluene and water at solvent to bitumen ratios close to 5. This difference is explained by the film emulsification model and the reason is that only at solvent to bitumen ratios of 5 or larger the film is thick enough to be emulsified in the absence of surfactants.

At solvent to bitumen ratios larger than 11, water and SDHS produce similar recoveries, and increasing the ratio only produce similar or lower bitumen recoveries. To understand this observation is important to note that when using 4ml of liquid (washing solution +solvent) to
extract 1g of bitumen-coated kaolin, solvent to bitumen ratios larger than 11 correspond to volume fractions of toluene of 50% or more in the liquid. This means that solvent to bitumen ratios larger than 11 produce water emulsions in a continuous toluene phase. The highest solvent ratio in Figure 2.13 corresponds to toluene-only extraction. When the continuous phase of the emulsion is the solvent, the most likely scenario is that the particles are in direct contact with the solvent, in which case the extraction should be predicted with the adsorption isotherm (Figure 2.12) and not with the film emulsification model. At a solvent to bitumen ratio of 11, Figure 2.12 (solvent-only extraction) shows that the experimental bitumen recovery is close to 50%, whereas Figure 2.13 shows that for the same solvent ratio, the extraction in the presence of SDHS (or water for that matter) is close to 70%. The question is, therefore, why introducing the aqueous phase would increase the fraction of bitumen recovery. The answer is likely associated with a previous report that water interferes with the adsorption of asphaltenes on metal oxides, likely because metal oxides have a greater affinity for water than for asphaltenes [53].

To further explore the issue of oil and water continuity in the emulsion, SDHS-toluene washing experiments were repeated using liquid volumes of 2 and 6 ml. Figure 2.14 presents the bitumen recoveries obtained with those systems as a function of the solvent to bitumen ratio. For each total liquid volume, there are five points corresponding to toluene volume fractions in the liquid of 0, 0.25, 0.5, 0.75 and 1.0. One feature common to all the systems of Figure 2.14 is that at low solvent to bitumen ratios, they tend to approach the recovery predicted by the film emulsification model, but they reach a maximum recovery at a 0.5 volume fraction of toluene in the liquid, corresponding with the inversion point of the emulsion. From this observation one can conclude that in order to extract more bitumen, it is important to use solvent to bitumen ratios
close to 20, but ensuring that the volume fraction of toluene in the emulsion is less than 50% to ensure that the aqueous solution is the continuous phase of the emulsion.

Figure 2.14: Bitumen recovery from bitumen-coated kaolin as a function of toluene to bitumen mass ratio obtained with total liquid to solid ratios of 2, 4, and 6 ml/g kaolin. All the aqueous phases were prepared 3000 ppm SDHS and 3g NaCl/100 mL. The SDHS-toluene extraction of aged oil sands only required solvent to bitumen ratios of 1 to 2 to produce bitumen recoveries greater than 80%. In Figure 2.14, only systems with solvent to bitumen ratios of 20 or greater (in continuous aqueous phase) can produce oil recoveries greater than 80%. The reason for this pronounced difference is explained by the difference in particle size. The Sauter diameters of aged oil sand and kaolin are 68 µm, and 3.8 µm, respectively. The area per volume of spheres is estimated as $6/diameter$, which means that the specific area of kaolin is nearly 20 times the specific area of oil sands. This also means that to produce bitumen+ solvent films with equivalent thickness, 20 times more solvent is required for kaolin than for oil sands.
The residual solvent on kaolin can be estimated using Equation 2.6, assuming that the bitumen recovery also applies to solvent recovery. Figure 2.15 presents a summary of this estimated residual solvent as a function of the toluene to bitumen ratio, for SDHS-toluene extracted kaolin with a liquid to solid ratio of 4 ml/g. Figure 2.15 also includes values of solvent recoveries calculated on the basis of toluene balance after measuring the volume of toluene + bitumen recovered at the end of the extraction.

\[ \text{Equation 2.6} \]

**Figure 2.15**: Estimated residual solvent on kaolin (Equation 2.6) as a function of toluene to bitumen ratio when using toluene-SDHS washing solution, and a liquid to solid ratio of 4 ml/g.

According to Figure 2.15, the values of residual toluene estimated from bitumen recoveries (bitumen balance) are close to the values of toluene recoveries (toluene balance). Both set of estimated residual solvents show that with increasing solvent to bitumen ratio, the residual solvent on kaolin increases. The residual solvent on kaolin in Figure 2.15 is substantially larger than the maximum levels of residual petroleum hydrocarbons (PHC) of 0.03% to 0.3%.
recommended by the Canadian Council of Ministers of Environments (CCME) for soils in industrial sites [51]. In fact, for solvent to bitumen ratios greater than 5, according to Figure 2.15 one leaves more solvent in the particle than the initial bitumen content. This means that an additional process of solvent recovery would be necessary to make sure that most of the solvent can be reused in the process.

The film emulsification model produced a reasonable prediction of the residual solvent for solvent to bitumen ratios of 11 or less, corresponding to systems where the washing emulsion is continuous in the aqueous SDHS solution. According to the film emulsification model, the reason for such high residual solvent is the large surface area to volume ratio of kaolin particles. The residual film thickness is 0.4 microns, which is difficult to emulsify. An alternative mechanism to remove this residual film is to take advantage of shear forces to induce complete film de-coating. Quraishi et al. have shown that film de-coating can be achieved if the capillary number \( Ca = \frac{\mu v_p}{\gamma} \) of the particle – calculated using the relative velocity of the particle \( (v_p) \) with respect to the surrounding fluid - is greater than 1 [12]. Using the estimations of Quraishi et al., the capillary number for the kaolin particles washed with SDHS and toluene is 0.03. To increase the capillary number to values greater than one, there are three potential options: increase the viscosity of the washing fluid by two orders of magnitude, decrease the interfacial tension by two orders of magnitude (to values of \( 10^{-4} \) mN/m), or increase the velocity of the particle by about two orders of magnitude (mixing speeds in the order of \( 10^5 \) rpm). These conditions for film de-coating (analogous to film roll-up) are difficult to attain. It is possible, however, that a combination of strategies could achieve film de-coating, which could be an area for future studies.
Effect of aging on bitumen recovery from kaolin

Figure 2.16 shows the comparison on bitumen recovery from 3 and 6 month old bitumen-coated kaolin samples using liquid to solid ratios of 2 ml/g and 4 ml/g. It is apparent that more bitumen was recovered with samples aged for 3 months, and these recoveries, at least for systems continuous in the aqueous phase, were close to those predicted by the film emulsification model. The negative impact of aging is associated with the fact that during the aging process bitumen is exposed to air, leading to oxidation and loss of volatile components, which impact the rheological properties of bitumen, and bitumen binding to the substrate [47]. Accelerated aging tests on oil sands extracted using the hot water process, show that subjecting fresh oil sands to 60°C air for three days reduce the oil recovery from 90% to less than 50% [54].

Figure 2.16: Bitumen recovery from bitumen-coated kaolin as a function of toluene to bitumen ratio obtained with total liquid to solid ratios of 2 and 4 ml/g kaolin, for kaolin aged for 6 months (baseline scenario) and for 3 months. All the aqueous phases were prepared 3000 ppm SDHS and 3g NaCl/100 mL.
Gravity settling versus centrifugation

Figure 2.17 illustrates the comparison between the separation obtained via gravity settling and the separation obtained via a combination of gravity settling and centrifugation. It is clear from Figure 2.17A that after gravity settling, very poor separation was achieved. In fact, for toluene fractions of 0.5 and below stable emulsions were observed. On the other hand, when combining gravity settling and centrifugation, a better separation was achieved (Figure 2.17B).

![Figure 2.17: Pictures of bitumen-coated kaolin extracted with liquid to solid ratio of 4 ml/g using toluene and SDHS solution with toluene volume fractions in the liquid of (from left to right) of 0, 0.25, 0.5, 0.75 and 1.0 after (A) gravity settling, and (B) centrifugation.](image)

Since the clay particles do not agglomerate as easily as the sand particles to form larger aggregates, the settling process for clay is much slower. Hence, due to the slow settling of the particles sufficient separation could not be obtained at a force of 1G. As a result a higher G-force is thus required to achieve the separation.

To optimize the G force, bitumen recovery was evaluated as a function of the centrifugation speed for the system prepared with a toluene volume fraction of 0.5 in the liquid
mixture with the SDHS formulation, using 4 ml/g of liquid to solid ratio, and bitumen-coated kaolin aged for six months. Seven different centrifugation speeds were tested. Table 2.1 shows the bitumen recoveries obtained at each of the different centrifugation speeds after 30 minutes of centrifugation. From Table 2.1 is evident that at approximately 440 RPM or 20.6 G-force, maximum bitumen recovery is obtained. At 440 RPM a recovery of 71.5% was obtained. Centrifuging at higher speeds would result in higher energy costs, but the bitumen extraction would not improve significantly.

**Table 2.3**: Optimized centrifugation speed required to obtain the best possible bitumen recovery

<table>
<thead>
<tr>
<th>Toluene Fraction</th>
<th>Total Volume</th>
<th>Centrifuging time (min)</th>
<th>Centrifuge speed (rpm)</th>
<th>G-Force</th>
<th>% Bitumen Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4</td>
<td>30</td>
<td>100</td>
<td>1.1</td>
<td>28.3</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>30</td>
<td>240</td>
<td>6.1</td>
<td>30.3</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>30</td>
<td>340</td>
<td>12.1</td>
<td>32.2</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>30</td>
<td>440</td>
<td>20.6</td>
<td>71.5</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>30</td>
<td>600</td>
<td>38.3</td>
<td>70.2</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>30</td>
<td>2100</td>
<td>469.2</td>
<td>71.0</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>30</td>
<td>2700</td>
<td>775.7</td>
<td>67.8</td>
</tr>
</tbody>
</table>

To optimize the centrifugation time, the parameters used to produce Table 2.1 were set constant except that centrifugation times of 5, 10, 15, 20, 25 and 30 minutes were evaluated with a constant centrifugation speed of 440 RPM. Table 2.2 shows the bitumen recoveries obtained.
From table 2.2 the results suggest that a centrifugation time interval required to obtain the best possible bitumen recovery is 10 minutes at a speed of 440 RPM.

**Table 2.4**: The optimization of the centrifugation time

<table>
<thead>
<tr>
<th>Toluene Fraction</th>
<th>Total Volume (ml)</th>
<th>Centrifugation speed (RPM)</th>
<th>Centrifugation time (min)</th>
<th>Bitumen Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>4</td>
<td>440</td>
<td>5</td>
<td>53.2</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>440</td>
<td>10</td>
<td>72.1</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>440</td>
<td>15</td>
<td>63.9</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>440</td>
<td>20</td>
<td>65.9</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>440</td>
<td>25</td>
<td>69.0</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>440</td>
<td>30</td>
<td>70.4</td>
</tr>
</tbody>
</table>

Although a G force of 20G is easily obtainable with a simple hydrocyclone, the fact that the centrifugation time should be 10 minutes suggests that such hydrocyclone should be operated at a high recycle ratio, which means a low throughput in the operation of those units. The conditions for the particle-oil-water separation could be further optimized by an appropriate surfactant formulation that would minimize the stability of the dilute bitumen-water emulsions, as suggested by Kiran [55], reducing the time required for the particle-water separation. Kiran shows that the stability of toluene-SDHS emulsions can change over three orders of magnitude within a relatively narrow range of salinities in the aqueous phase.
3. Capillary displacement of vegetable oil from wet microalgae

3.1 – Introduction.

One of the biggest disadvantages of microalgae as a feedstock for biofuel, compared to conventional crops, is its high water content. Even after a series of mechanical dewatering process, microalgae can contain as much as 80wt% water [56]. This means that in order to dry the algae before extracting the oil with an organic solvent, as much as 4kg of water need to be evaporated for every kg of dry biomass. Considering that the enthalpy of vaporization of water is 2.3 MJ/kg at its boiling point, then as much as 9.2 MJ of heat are required to evaporate the water associated with 1 kg of dry microalgae biomass. This value is relatively large when compared with an estimated heating value of dry microalgae of 14 MJ/kg [57]. This preliminary energy balance calculation does not even account for the energy required to evaporate the organic solvent to remove it form the extracted oil, and eventually condense it for reuse.

Several wet extraction processes have been proposed to avoid evaporating the algae prior extraction. A combination of wet enzyme extraction, followed by hexane addition to collect the liberated oil has been reported to remove up to 49% of the lipids in the algae [58]. Sathish and Sims, using a four stage process involving acid hydrolysis combined with hexane extraction, reported the recovery of 59% of transesterifiable lipids into the organic phase and an additional 17% into a precipitate phase [59]. Halim et al. used a single phase extraction with two solvent mixtures, one was methanol and water, and the other was a mixture of isopropanol, hexane and water [60]. Halim et al. obtained the largest extraction efficiency, of about 80% when extracting wet algae (containing 99.1% water) with a mixture of 94% methanol and 6% water, and using a methanol to dry algae ratio of 1,500 g methanol/g dry algae. The mixtures of isopropanol and hexane produced an extraction efficiency of 30% using similar solvent to algae ratios [60].
Switchable solvents have also been introduced as an alternative wet extraction process for microalgae. These switchable solvents are organic solvent with amino groups that upon exposure to carbon dioxide, form alkyl ammonium bicarbonate salts that are soluble in water. Samori et al. extracted *B. braunii* using 1,8-diazabicyclo-(5.4.0)-undec-7-ene (DBU) with dry and wet algae using solvent/algae ratio ~ 1000 g/g, obtaining neutral lipid yields superior than those obtained with a modified Folch’s extraction procedure [61]. Boyd et al. used N,N-dimethylcyclohexylamine as switchable solvent to extract sonicated (broken) dried *B. Braunii* and achieved a 41% extraction efficiency total lipids with solvent to dry algae ratio of ~ 3 g/g [62]. Du et al. used dipropylamine and ethylbutylamine as switchable solvents to extract fresh and unbroken *Desmodesmus sp.* at solvent to algae ratio ~ 13 g/g, and although they obtained negligible lipid extraction over a 3-min extraction period, they were able to obtain complete extraction after 24 hours of extraction [63]. In these cases, the advantage of using a switchable solvent is that the separation of the solvent from the extracted lipid can be conducted using a simple CO₂ extraction, without the need to evaporate the solvent, and saving energy in the recovery of the solvent. There are however, two problems, first that most of these switchable solvents, even in their hydrophobic form, are still partially soluble in water and toxic, and second, the losses of switchable solvent obtained during the extraction. For example, Boyd et al. determined that in their process they only recovered 84% of N,N-dimethylcyclohexylamine, and considering that their solvent to algae ratio was close to 3, this means losses of about 0.4 g of solvent for each gram of algae produced.

Ideally, the extraction of lipid from microalgae should not require water evaporation or the use of organic solvents. This would eliminate the energy requirements associated with the evaporation of water and the solvent, and the risks and the capital and operational costs
associated with the use of organic solvents, switchable or not. The group of Sabatini introduced a method for the wet extraction of oilseeds using solutions of extended surfactants that can produce ultralow ($\sim 10^{-3}$ mN/m) interfacial tensions that help remove the oil from the seed via capillary displacement [32,64]. According to this method, crushed oil seeds are set in contact with a surfactant solution that can produce ultralow interfacial tensions with the triglycerides in the seed. After mixing at 500 rpm for 30 minutes at room temperature, then the suspension of seed particles and emulsified oil in water was pumped to a solid/liquid centrifuge to remove the solid particles. The emulsion was then send to a continuous liquid/liquid centrifuge operated at 680xG with a residence time of about 150 minutes to remove the oil from the aqueous solution [64]. A total oil extraction of 90% was obtained with peanut oil, although only 86% was free oil recovered with the centrifuge (4% of oil extracted was trapped in the emulsion) [64]. Do and Sabatini further explained that the challenges associated with this process are the separation of the dispersion of solids, oil, and water [64].

Two strategies were evaluated including a single extraction stages by aqueous surfactant solution and two extraction stages, consisting of one aqueous surfactant wash and one de-ionized water wash. In these experiments no solvent was used and the extractions were performed using a solution composed of a 10 carbon based surfactant, sodium chloride and water. It was observed that at the optimum conditions around 90% oil extraction was obtained from both peanut and canola oil using the single stage extraction, while using the two-stage extraction oil recoveries of up to 94% was obtained [50]. In this work, the surfactant-only extraction of Sabatini and collaborators is used along a hybrid method of surfactant and solvent extraction for the extraction of a mixed culture of microalgae produced in pilot scale plants designed to capture CO$_2$ emissions.
3.2 – Materials and methods

Anhydrous toluene (99.8%), sodium chloride (99.5%), extra virgin olive oil, cyclohexane (>99%) and sodium dihexylsulfosuccinate (SDHS ≈ 80% in water) were purchased from Sigma-Aldrich Canada. The extended surfactants Alfoterra 145-8S (CH₃(CH₂)₁₃(CH₂CH₂CHO)₈SO₄Na, 30% solution in water) was donated by Sasol North America (Houston, TX, USA). Other chemicals required for the Folche and transesterification process such as chloroform (≥98%), sodium hydroxide (NaOH) (≥98%), hydrochloric acid (HCl) (37%), methanol (≥99.8%), and methyl tert-butyl ether (MTBE) (≥99.8%) were also obtained from Sigma-Aldrich. Finally, deionized water (conductivity <4mS/cm) was prepared in the laboratory using an ion exchange column. The microalgae samples extracted in this work was a mixed culture donated by Pond Biofuels Canada. Figure 3.1 presents the particle size distribution for the algae (Sauter diameter of 8.2 µm).

Baseline lipid content

To establish the amount of lipid content in the algal biomass the most commonly used and efficient extraction technique i.e. Folche was used. 5g algae were taken in 40ml glass vials. The wet algae samples were then freeze-dried for 24 hours to obtain the dry algal biomass. The dry mass ratio defined as the algal biomass after freeze drying i.e. dry mass/mass of wet algae. The dry mass was obtained measuring the difference in the mass pre and post freeze drying. Followed by freeze drying the Folche extraction technique was used to extract the lipids. The lipids extracted using Folche (Appendix A) were assumed to be 100% of the oil content in algae. In Folche the samples were mixed with a proportional amount of chloroform/methanol (2:1) and then vortexed at 3200 rpm for 30 minutes. The samples were then centrifuged for 20 minutes at
3000 rpm to separate the liquid from the solids. The lipids are assumed to be completely extracted by the chloroform/methanol mixture and they are only present in the liquid phase. The FAME (Appendix B) transesterification was then run on the extracted liquid samples to prepare them for Gas chromatography (GC) analysis (Appendix C) to quantify the lipids [33].

**Figure 3.1:** Area-weighted particle size distribution of the mixed-culture microalgae.

**Solvent-free extraction with extended surfactant**

The washing fluid was prepared by adding 0.1g of the Alfoterra 145-8S surfactant to 100ml of water along with the % salt to be tested i.e. for 7% salinity 7g salt/100ml water. The extended surfactant: dry algae mass ratio used was 6:1 for the extractions. The samples were then mixed at 3200 rpm for 30 minutes in a multi-tube vortexer. Following the mixing the samples were centrifuged for 15 minutes. After centrifugation the samples were allowed to sit for 5 minutes.
and then the liquid phase was extracted using a pipette and disposed, while Folche, FAME and GC was run on the remaining biomass. The lipid content obtained from GC was the amount of oil that remained after the initial extraction i.e. the residual lipid content. To measure the amount of oil extracted the following equation was used:

\[
\% \text{ Lipid extracted} = \frac{\text{Baseline lipid content} - \text{Residual lipid content}}{\text{Baseline lipid content}} \times 100 \quad (3.1)
\]

**Lipid extraction with a combination of surfactant solution and solvent.**

In this case the surfactant used was SDHS and the washing fluid was prepared using 0.3g surfactant and 3% salt in 100ml of water. The solvent used in these extractions was cyclohexane. The tests were performed using cyclohexane 0.25, 0.5, 1 and 2 grams of cyclohexane added to the wet algae suspension (10wt% in water) containing 0.7g of the algae (dry basis). The solvent was added first and the samples were mixed for 10 seconds in a multi-tube vortexer. After that, the surfactant based fluid was added at a washing fluid: dry mass ratio of 6:1 and the samples were mixed in the multi-tube vortexer for 30 minutes at 3200 rpm. In the case of oil sands and bitumen-coated clay three minutes of mixing was enough to achieve extraction but since for algae the lipids are inside the cell just three minutes of mixing would not be enough to get the lipids out. Previously done work by Chan et al. showed that with microemulsions type I, II and IV lipid extraction from algae increases with increasing contact time between the solvent and the lipids [33]. The mixing times tested by Chan et al. included 0.5, 1 and 3 hours respectively [33]. In this case the tests were performed using 0.5 hour as the mixing time but further work could be done in future to look into the extraction efficiencies at longer mixing times. After mixing, the samples were centrifuged at 3000 rpm for 15 minutes and the liquid phase was disposed. Folche, FAME and GC were run on the remaining solids and the GC analysis provided the residual lipid content in the leftover biomass. The amount of oil extracted was measured using Equation 3.1.
3.3 – Results & Discussion

Lipid extraction from algae using extended surfactants

Figure 3.2 presents the glyceride (transesterifiable lipid) extractions for the 145-8S surfactant prepared with 7% and 10% salt (g NaCl/100 ml). The transesterifiable lipid extraction was close to 75% at 10% salinity, and 65% at 7% salinity. These salinities were chosen because they were reported to produce ultralow interfacial tensions of 0.001 mN/m against flaxseed oil, used as a model oil for algae oil (unpublished results obtained by Sheng Xu).

Figure 3.2: Transesterifiable glycerides (measured via FAME) recovery from mixed culture microalgae as a function of cyclohexane to microalgae (dry basis) mass ratio. The SDHS solution was prepared with 3000 ppm SDHS and 3g NaCl/100 ml. The water system corresponds to DI water. Total aqueous phase to solid ratio: 6 ml/g.

The lipid recovery of 65% to 75% is slightly lower than that obtained with extended surfactants for lipids from peanut seed (~ 90%), but still comparable [64]. The problem with this
extraction, however, is that after centrifuging for 15 minutes, there was no evidence of an oil layer that could be extracted from the top of the aqueous phase. The picture on the far left of Figure 3.3 shows the vial after being centrifuged for 15 minutes. Given the low baseline lipid content in the algae (4 wt%) and the liquid to solid ratio of 6 ml/g, even if all the lipid was liberated in the aqueous solution, this would have created an emulsion with less than 1 wt% of oil in the emulsion. This low oil content in the emulsion is very difficult to separate. In the pilot studies of Do and Sabatini, around 0.4 wt% of oil was still trapped in the emulsion when operating the continuous liquid/liquid centrifuge with 150 minutes of residence time [64]. To aid the separation process, the combination of surfactant solution and solvent was employed, similar to system used by Quraishi et al. for the extraction of bitumen from bitumen-coated sand [12], as explained in the next section.

![Figure 3.3: Pictures of microalgae extraction after 15 minutes of centrifugation. The formulation for Alforterra 145-8S was prepared with 7g NaCl/100 ml. The SDHS solution was prepared with 3000 ppm SDHS and 3g NaCl/100 ml. Total aqueous phase to solid ratio: 6 ml/g.](image-url)
Lipid extraction from algae using solvent-surfactant systems

Figure 3.2 presents the recovery of transesterifiables glycerides (lipids) from the mixed culture algae with mixtures of cyclohexane (solvent) and either water or a solution of 3000 ppm of SDHS and 3 g NaCl/100 ml, capable of producing interfacial tensions of 0.02 mN/m with cyclohexane. The x-axis of Figure 3.2 represents the mass ratio (g/g) of cyclohexane to dry biomass. For the SDHS solution, recoveries of 54% to 82% are achievable with increasing the cyclohexane to algae ratio from 0.35 to 2.8. The most commonly used technique for oil extraction from oilseeds is the solvent extraction technique. Previously done studies done by Ali et al. show that using the organic solvent extraction technique about 90% or more oil can be recovered from flax seeds when the moisture contents as low as 4% [65]. In addition, Goss et al. mentioned in his studies that with the solvent extraction technique about 96% oil can be recovered from Soy bean [66]. For cyclohexane-water extraction, the recovery of lipids remained close to 40% even when using cyclohexane to algae ratio as high as 2.9. From a recovery point of view, the addition of the solvent did not substantially increase the recovery of lipids when compared to the surfactant (alfoterra 145-8S)-only extraction. However, Figure 3.3 illustrates that when using a combination of SDHS and cyclohexane, a clear and easily extractable oil layer can be removed from the top of the aqueous liquid phase. For the extraction with water and cyclohexane, the last two vials in Figure 3.3 do produce a top oil phase, but that oil phase is an emulsion and not a clear oil phase as it was the case with the cyclohexane-SDHS extraction. Unlike oil sands or clay-bitumen the algal lipids are inside the cell and the cells are not coated with the oil to be extracted. However, the cell membrane of algae is made up of phospholipids which are soluble in the solvent and soften up with solvent addition. As the cell membrane softens up the lipids in the cell seep through to the outside and get dissolved in the solvent.
Figure 3.2 also includes the extraction of lipids predicted with the film emulsification model of Quraishi et al. [12]. To this end, equations 2.3 through 2.5 where used as described in Chapter 2, but using the Sauter diameter of 8.2 µm for the algae, and interfacial tensions of 0.02 mN/m for the SDHS formulation (solid line in Figure 3.2) and 20 mN/m for the water-cyclohexane system (dashed line in Figure 3.2). The predictions for SDHS-cyclohexane extractions are relatively close to the experimental values, but the predictions for the water-cyclohexane system are substantially larger than the experimental values. According to the film emulsification model, there should not be any extraction for the surfactant (Alfoterra 145-8S)-only extraction. To explain this apparent disconnection, it is important to consider than the interfacial tension of the extended surfactant (Alfoterra 145-8S) with triglycerides is of the order $10^{-3}$ mN/m, i.e. 20 times lower than the interfacial tension used in the film emulsification model for the SDHS-cyclohexane system. At this ultralow interfacial tension, the Capillary number based on the velocity of the particle relative to the rest of the fluid becomes larger than 1, which according to Quraishi et al. activates a film de-coating mechanism driven by shear that could lead to nearly complete removal of oil [12].

One other important point is the potential residual solvent on the extracted algae. To estimate this value, Equation 2.6 was used, once again, assuming that the recovery of the solvent is equivalent to the lipid extraction. Figure 3.4 presents the estimated residual solvent on the algae as a function of the cyclohexane to algae ratio for the cyclohexane-SDHS and cyclohexane-water extraction. For the cyclohexane-SDHS system, other two values are presented calculated based on solvent recoveries estimated from the volume of solvent obtained at the end of the extraction. The values predicted by the film emulsification model are also included. The estimated residual solvent are substantially large than the initial lipid content in the algae (~4%).
which would mean that for all the systems in Figure 3.4 we are leaving in the algae more solvent than the oil we meant to recover. One must keep in mind, however, that some of that solvent might be simply emulsified in the aqueous phase.

These results suggest that the process of combined solvent-surfactant extraction needs either an additional process to recover the solvent or it requires the use of alternative technologies. In particular, the extraction with Alfoterra 145-8S suggests that if a combined surfactant-solvent extraction could produce interfacial tensions of $10^{-3}$ to $10^{-4}$ mN/m, there is a possibility of nearly complete solvent recovery.

Although the solvent losses might seem excessive, it is important to put this estimate in perspective. For the system of Boyd [62], which uses the lowest solvent to algae ratio among the studies reviewed, assuming that the solvent losses are retained by the algae, then the residual solvent in the algae would be close to 30%, similar to the values presented in Figure 3.4.

Another opportunity to further improve the solvent-surfactant extraction is the use of a switchable solvent instead of cyclohexane, or the use of polar solvents that are reported to produce better extractions than non-polar solvents [Error! Bookmark not defined.]. There is also ample opportunity to optimize the liquid-liquid separation, for example increasing the centrifugation time from 15 minutes to 150 minutes, to simulate the separation time of Sabatini and Do [64].
Figure 3.4: Estimated residual solvent on algae (Equation 2.6) as a function of cyclohexane to algae ratio when using cyclohexane-SDHS and cyclohexane-water extraction. Aqueous phase to solid ratio of 6 ml/g.
4 - Conclusion

In conclusion, it can be said that using the solvent-surfactant system performs significantly better than solvent-water in capillary displacement extraction. The solvent-surfactant system can extract oil entrapped in clay, sand and even microalgae efficiently with significantly low energy usage. The surfactants such as SDHS and the extended surfactants achieve extremely low interfacial tensions which can’t be achieved using just water and as a result the capillary displacement is much easier. In the case of oil sands, the inertial forces are critical in overcoming the surface tension forces and achieving bitumen extraction via capillary displacement. The shear forces do play a role in the case of oil sands but it is not as substantial as the inertial forces. The Weber number is a dimensionless number that efficiently describes the ratio of the inertial forces to the surface tension forces. For systems that have oil entrapped in fine particles such as clay-bitumen the extractions are a little harder and it takes a lot of inertial force to overcome the surface tension forces holding the clay and bitumen together. Hence, the solvent to bitumen ratios required to extract reasonable amount of bitumen from clay-bitumen systems is significantly higher than that required for the oil sands. Also for both the oil sands and clay-bitumen systems centrifugation separation plays a key role in the extraction of bitumen. The separations obtained using 1-g force provides insufficient amounts of bitumen extraction when compared to the industrial standards and hence it centrifugation becomes an essential part of the extraction. Oil sands are predominantly sand and have much lower clay contents and thus the shear and interfacial forces play a significant role in overcoming the interfacial tension. However, applying centrifugation on oil sands helps enhance the bitumen recovery greatly and thus is essential to optimizing bitumen recovery. Also, the presence of a solvent is the key to extraction from both clay-bitumen and oil sands and just using a surfactant based fluid will not
be enough to achieve any bitumen recovery. In addition, the extended surfactants at optimal salinity are quite efficient at extracting lipids from microalgae without the use of any solvents in the system but it is hard to obtain a clear enough oil layer that easily separates from the other algae extracts present in the fluid. However, using a solvent such as cyclohexane along with a surfactant (SDHS) based fluid helps achieve a much clearer separation as well as substantially higher bitumen recoveries than solvent-water systems and even extended surfactant systems. For microalgae as well the surfactant based systems perform much better at oil extraction via capillary displacement than using just water. Hence, it could be concluded that when it comes to extracting oil from entrapped particles such as sand, fines, oilseeds and algae having a surfactant based washing fluid at optimum salinity combined with an organic solvent such as cyclohexane can provide optimum recovery. It is essential to add the solvent to these systems as the oil extraction can only be achieved in the presence of a solvent. The presence of the surfactant helps reduce the interfacial tension significantly and enhance the oil recovery but on its own it does not achieve extraction for oil sands and poor separation for microalgae.
5 – References


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Appendix

Appendix A: Algae Oil Extraction Baseline Establishment – Extraction Using Folche Method

1. Weigh all empty vials
2. Weigh 2g wet algae sample
3. Freeze dry overnight
4. Homogenize the dried algae sample with chloroform/ methanol (2:1) or to a final volume 20 times the volume of the dry mass
5. Place into orbital shaker/vortexer at maximum speed for 20 min
6. Wait for 5 min (prepare for centrifuge)
7. Centrifuge for 20 min
8. Weigh empty 20ml vials and extract the liquid phase (chloroform/methanol) into the 20 ml vial
9. Repeat step 3-8 two more times
10. Wash the solvent (chloroform/methanol) with 0.2 volume (2.4mL for 12 mL solvent) 0.9% wt NaCl solution
11. Vortex at maximum speed for 20 s
12. Centrifuge at low speed (2000rpm) to separate the two phases
13. Remove the upper phase with Pasteur pipets (Top phase contains methanol, water and polar lipids; bottom phase contains chloroform (dichloromethane) and non-polar lipids)
14. Add methanol/water solution (1:1) without mixing the whole preparation (centrifuge if necessary) and remove the upper phase, including the interface
15. Weigh Qorpak bottles and transfer the liquid to those larger bottles for FAME method
16. Evaporate the chloroform phase (containing non-polar lipids) with air (If no N2, use air under fume hood)
17. Weigh the remaining lipids. When mass stopped decreasing, all chloroform was assumed to be evaporated
Appendix B

Derivatize fatty acids (FAME)

1. Dishwashing

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Wash all of glassware needed</td>
<td>Leave glasswares in the acid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>for 2 days</td>
</tr>
<tr>
<td>1.2</td>
<td>Rinse glassware with distilled</td>
<td>Prepare double the amount of</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>the tubes needed for the later</td>
</tr>
<tr>
<td></td>
<td></td>
<td>usage</td>
</tr>
<tr>
<td>1.3</td>
<td>Dry glassware</td>
<td>Leave glasswares in the oven</td>
</tr>
<tr>
<td></td>
<td></td>
<td>at 500°C for 25mins</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Solvent/Compound</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>NaOH</td>
<td>7.5g</td>
</tr>
<tr>
<td></td>
<td>Distilled water</td>
<td>50 ml</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>50 ml</td>
</tr>
<tr>
<td>R2</td>
<td>HCl</td>
<td>14 ml</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>23 ml</td>
</tr>
<tr>
<td>R3</td>
<td>Hexane</td>
<td>200 ml</td>
</tr>
<tr>
<td></td>
<td>Methyl Tert-Butyl</td>
<td>200 ml</td>
</tr>
<tr>
<td></td>
<td>ether</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>NaOH</td>
<td>2.4g</td>
</tr>
<tr>
<td></td>
<td>Distilled Water</td>
<td>200 ml</td>
</tr>
</tbody>
</table>

1. Start water bath at 87°C
2. Make R1

Saponification

1. Add 7.0 ml of R1 to each vial and heat for 5 minutes
2. Vortex for 10s
3. Continue heating for 30 mins

Methylation

1. Cool the tubes
2. Add 14.0 ml of R2 to each vial and heat for 10 mins

Extraction

1. Cool the tubes and add 3.0 ml of R3 to each tube and tumble at maximum speed for 10 mins
2. Extract lower aqueous phase and discard

Base Wash

1. Add 7.2 ml of R4 into each tube and tumble at maximum speed for 5 mins
2. Pipette 2/3 of the organic phase (top phase) for GC test
Appendix C – GC setup

Capillary GC
Instrument : GC5
Column : simplicity 5
Column Length : 30 m x 0.53 mm (1.5um)
Carrier Gas : H2
Flow Rate : 1 mL/min
Split Ratio : 25 mL/min
Temperature : 55
Injection Temp.: 250
Detector 1 : fid 200 (range 1)(att -3)
Detector 2 : N/A