University of Alberta

Role of Bitumen Viscosity in Bitumen Recovery from Athabasca Oil Sands

by

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This thesis is dedicated to my parents.

Abstract

Viscosity, as a fundamental physical property of bitumen, has been studied extensively for the past several decades. By and large, nearly all the bitumen samples used in viscosity measurement were from hot water extraction processes that were further cleaned by solvents. A drawback of this approach is inevitably incomplete evaporation of solvent or losses of light ends of bitumen. Such a gain or loss can have a significant influence on the measured bitumen viscosity. To accurately understand the role of bitumen viscosity in bitumen recovery by water-based extraction processes, viscosity measurement of raw (solvent-free) bitumen is necessary.

In this study, bitumen samples from good ore, artificially weathered good ore, average ore, and naturally weathered poor processing ore were prepared through direct centrifugation method. The viscosity of isolated bitumen at different temperatures and with different solvent (kerosene and naphtha) additions was measured. A correlation between solvent addition and temperature was established via viscosity measurements. Based on correlations established in this study, processability of oil sands was evaluated to identify the critical role of bitumen viscosity.

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Chapter 1 Introduction

Oil sand also known as bituminous sand or tar sand is composed of bitumen (heavy viscous oil), water, sand and clays. The formation of bitumen is believed to relate to the aerobic biodegradation and gradual transformation of lighter crude oil. The widely accepted explanation for the present physical form of bitumen suggests that bitumen being a residual product of the oil, originates from decaying marine creatures over millions of years, through the loss of lighter components (Masliyah and Gray, 2010).

1.1 Overview of Alberta oil sands

Typical composition of an oil sand ore is about 10 wt% bitumen, 85 wt% solids (sands and clays) and 5 wt% water. Takamura (1982) proposed a model for the microscopic structure of Athabasca oil sands. The three components are all intermixed, with a thin 10nm water film between the bitumen and sand particle, see Figure 1.1. For successful recovery bitumen is to be liberated from the sand grains and water matrix.

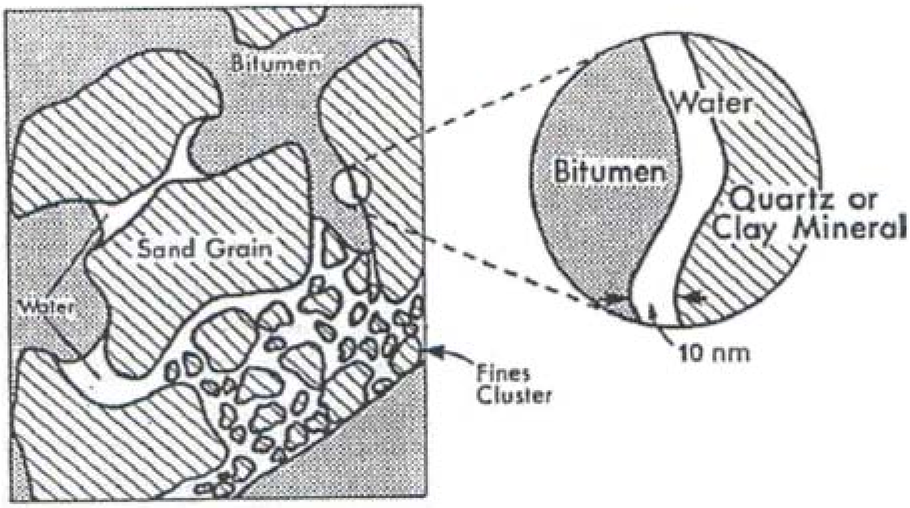


Figure 1.1 The classical model of the microscopic structure of Athabasca oil sands proposed by Takamura (1982)

Oil sand deposits are found throughout the world, with the two largest reserves located in Venezuela and Canada. In Canada, these oil deposits are located in northern Alberta: i) Athabasca, ii) Cold Lake and iii) Peace River. To make full use of this resource, the Canadian Federal and Provincial Governments have invested heavily in oil sands research since the 1920’s.

The “pathway” for bitumen recovery from oil sands was first identified by Dr. Karl Clark (1927), introducing the hot water separation process, now known as the “Clark Hot Water Extraction” (CHWE) process. In its infancy, the oil sands industry recovered bitumen for the construction industry. It wasn’t until the economics and technologies became favourable in the 1950’s that the industry began to focus on production of fuel oil (Blair, 1951). With an ever increasing global energy demand and dwindling conventional oil reserves, oil sands have served as a welcome energy resource since the late 1960’s.

Current industrial practice for bitumen recovery is based on two methods: surface and in situ mining. Surface mining describes an open-pit mine operation where the oil sands are excavated and transported by trucks to an extraction facility. At the extraction facility the oil sands are mixed with hot/warm water to aid bitumen liberation and recovery, which will be discussed further in Section 1.2. For deeper (>75 m) bitumen reserves, in situ recovery methods such as vapour extraction (VAPEX), toe to heal air injection (THAI), cyclic steam stimulation (CSS), and steam-assisted gravity drainage (SAGD) are used to reduce bitumen viscosity and increase its flowability. VAPEX and THAI involve the use of solvents as a viscosity modifier. CSS injects steam into the oil sands formation through a vertical well, recovering through the same well, while SAGD injects steam through a horizontal well to liquefy the bitumen, which subsequently drains into a second horizontal well for recovery. Currently, CSS and SAGD are the two techniques used commercially in the Alberta oil sands industry.

According to the ERCB report (2011), Canadian oil sands deposits hold an estimated 1.7 trillion barrels (initial volume in place) of crude bitumen. From the established reserves, about 20% is accessible by surface mining and 80% is considered recoverable by in situ methods. The Athabasca deposit is the largest crude bitumen reserve in the world and is shallow enough to permit surface mining. As of December 2010, there are 95 active oil sands projects in Alberta. Six of these are surface mining projects and the remaining use in situ methods. About 1.3 million barrels of crude are produced every day from Athabasca oil sands. That number is expected to more than double within the next decade.

1.2 Water-based bitumen extraction process

After mining, bitumen is separated from sand using a hot water extraction process that was patented in 1928 by Dr. Karl Clark. The Great Canadian Oil Sands (GCOS), now Suncor Energy Inc., successfully scaled up the CHWE process for industrial production in 1967. Syncrude Canada Ltd. began their commercial operations in 1978 in the Fort McMurray area. With the depletion of conventional crude oil and a continuously increasing demand on petroleum and its products, more and more global energy companies are commencing operations in the Alberta region. Among them, Shell Canada Ltd. started operations as Albian Sands Energy Inc. in early 2003, and Canadian Natural Resources Limited started commercial production as the Horizon Project in 2008. By the end of 2010, Syncrude (Mildred and Aurora), Suncor, Shell (Muskeg River and Jackpine), and CNRL’s Horizon account for 41, 31, 15, and 13 per cent of total mined bitumen, respectively (ERCB, 2011).

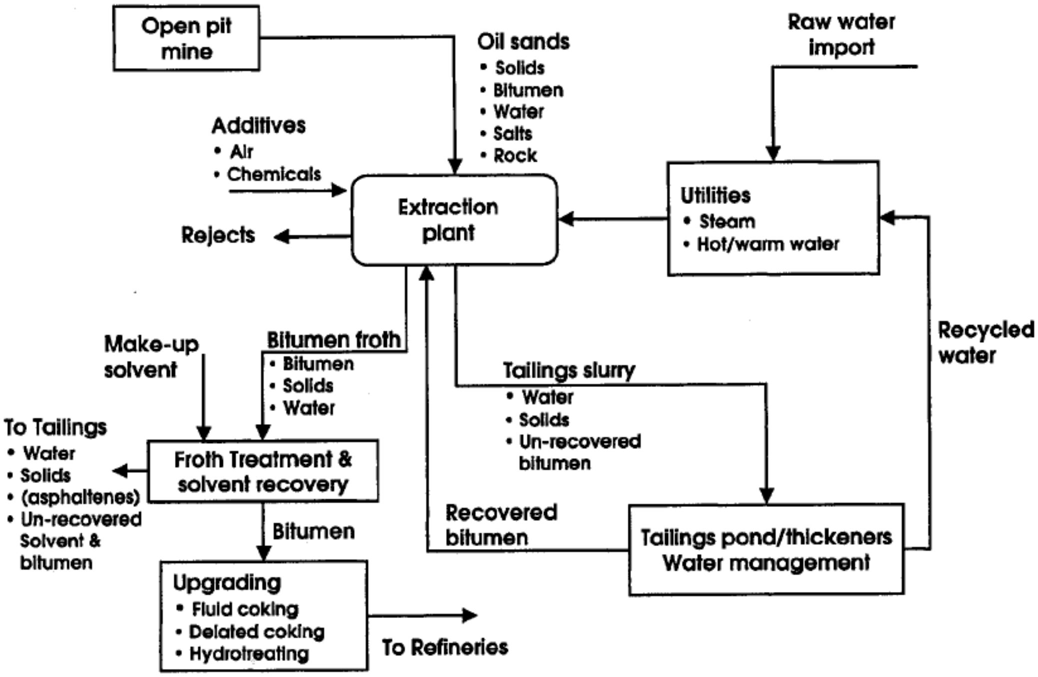


Figure 1.2 Flow chart for the commercial water-based bitumen production process (Masliyah and Gray, 2010)

Figure 1.2 shows a typical bitumen extraction scheme for an open mine operation. In open mining heavy-duty shovels are used to excavate and load oil sands onto trucks for transportation to bitumen extraction facility. At the extraction facility lumps of oil sand ore are crushed and mixed with warm process water containing caustic (usually NaOH), forming an aqueous slurry. The slurry is then conditioned at elevated temperatures to aid bitumen liberation. Traditionally, conditioning drums are used to liberate bitumen at 80 ^{o}C. More recently, lower temperatures (35-50 ºC) have been used to facilitate liberation, with conditioning taking place in a pipeline leading to the primary separation cell (PSC). At a temperature of 35-50 ^{o}C and a slurry pH between 8-8.5, bitumen recedes to form droplets that liberate from sand grains under fluid shear. To assist separation, air is entrained into the slurry to aerate liberated bitumen. Aerated bitumen droplets have an apparent density less than water and hence float to form a froth layer “rich” in bitumen. Typical residence time for separation in a PSC is approximately 20 minutes. The recovered froth usually contains 60 wt% bitumen, 30 wt% water, and 10 wt% solids. Coarse solids settle to form tailings which are removed from the PSC prior to disposal in a tailings dam. Middlings which is a mixture of sand, water and bitumen remains suspended in the PSC and is removed to undergo a secondary flotation to recover bitumen not carried over in the froth. The remaining slurry from the secondary flotation step is then combined with the tailings slurry and pumped to a tailings pond for ultimate disposal.

Solids and water carried over with bitumen froth are removed in the froth treatment process prior to bitumen upgrading. Bitumen upgrading to synthetic crude oil is comparable to conventional crude oil treatment using thermal and catalytic processing steps, such as coking, cracking or hydrotreating. The synthetic crude oil is then piped to a refinery for further physical and chemical processing to produce gasoline, diesel, jet oil and other petrochemical products.

1.3 Objective of study

This study was motivated by the work of Dr. Jan D. Miller at the University of Utah. Miller and co-workers showed that in order to achieve satisfactory separation in the water-based process, bitumen viscosity needs to be lowered to a critical value of 2 Pa·s, regardless of the oil sands origin and characteristics. In addition to the work of Miller and co-workers, effect of bitumen viscosity on Athabasca oil sands processability has received limited attention. The motivation of this research is to explore the role of bitumen viscosity on the processability of Athabasca oil sands.

Currently, open-pit mining operations use warm or hot water to extract bitumen from oil sand ores and further treat the froth with naphtha or paraffinic diluent to remove solids and water carried over from the PSC. A previous study has shown that the energy consumption for a 1^{o}C increase per tonne of oil sand ore is 5 million Joules (Cymerman et al., 2006). The energy intensive process unavoidably emits greenhouse gases which are an environmental concern. Hence, an alternative to the current hot water extraction process is desirable. Solvent-assisted extraction is one possible alternative. Here, thermal energy input at the beginning of the extraction process can be minimized (operated at ambient temperature) through the addition of solvents which act to reduce the viscosity of bitumen. The type of solvent used can either be the same as the one used during froth treatment, or an alternative that would be chosen based on its volatility and commercial value. In the current study, the performance of solvent-assisted extraction will be determined using kerosene and naphtha.

During the literature review process, it was found that the viscosity data of Athabasca bitumen have a large discrepancy between each publication. Variations in the experimental data most likely result from differences in sample preparation technique (Miller et al., 2006). Such discrepancies can be removed by recovering bitumen in the absence of solvent addition.

Based on our current knowledge, the objectives of this study include:

1) Determine the feasibility to isolate bitumen by centrifugation. Centrifuging will be used to recover bitumen directly from oil sand ore, removing error associated with solvent addition.
2) Measure bitumen viscosity at different temperatures and with different solvent additions using a rotational rheometer. Bitumen viscosity along with its solids and water content will be reported. Viscosity data for bitumen isolated from different ores will be compared.
3) Establish a correlation between temperature and solvent addition.
4) Evaluate the role of bitumen viscosity in the extraction process. A series of experimental tests with a Denver flotation cell will be conducted to investigate the impact of bitumen viscosity on Athabasca oil sands processability.
5) Investigate the feasibility to use solvent-assisted extraction at ambient temperature.

1.4 Outline of thesis

Chapter 1 discusses the Athabasca oil sands, its formation, microscopic structures, and the two industrial methods used for bitumen extraction. A review of the water-based bitumen extraction process is given. The objectives of the current research are described

Chapter 2 reviews the literature on bitumen extraction, the methods used for bitumen sample preparation and bitumen viscosity measurement.

Chapter 3 describes the experimental conditions used throughout the study. This chapter reports in detail the instrumentation and the method used to prepare solvent-free bitumen samples, measurement of bitumen viscosity and investigation of bitumen viscosity importance on ore processability.

Chapter 4 discusses experimental data correlating bitumen viscosity with temperature and solvent addition. The rheological data are used to better understand the importance of bitumen viscosity on ore processability.

Chapter 5 draws overall conclusions and presents suggestions for future research.

Chapter 2 Literature Review

2.1 Bitumen flotation from oil sand ore

Flotation has long been considered the single most important method in mining to separate minerals from ores hence; the Canadian oil sands industry has applied such a technique to recover bitumen. With bitumen and water having similar densities, a density difference is required in order to separate liberated bitumen from the slurry. The density difference can be achieved by lowering the apparent bitumen density by aeration. For the water-based process to be successful the following four steps have to take place:

1) Bitumen recession forming droplets
2) Liberation of bitumen from sand grains
3) Attachment of the liberated bitumen to air bubbles (aeration)
4) Flotation of the aerated bitumen

To understand the mechanisms controlling processability it is essential to resolve the challenges encountered in extraction. Systematic studies looking at bitumen recovery from oil sand ores have been ongoing for several decades. Masliyah et al. (2004) stated that in addition to the varying physical and chemical properties of the oil sand ores, the physical (pH, temperature, surface and interfacial properties), chemical (chemical additives) and hydrodynamic (air bubble generation and size control) parameters of the extraction process are equally as important when optimizing the process.

Miller and Misra (1982; 1991) showed that the hot-water extraction process is influenced by many physical and chemical variables. Variables such as bitumen viscosity, sand particle size distribution, temperature, pH, time of digestion, flotation and degree of agitation, all influenced processability. The authors concluded that the best flotation response is measured between pH 7.8 to 9.0, relating to a maximum in the contact angle between an air bubble and bitumen surface.

2.1.1 Process temperature

Schramm et al. (2003a) carried out Batch Extraction Unit (BEU) tests on Athabasca oil sand ores at temperatures between 50 ^{o}C and 80 ºC. Over this temperature range there was no substantial change in primary bitumen recovery. By lowering the processing temperature to 25 ºC, an order of magnitude decrease in primary bitumen recovery was observed. This reduction is believed to relate to changes in bitumen viscosity, interfacial tension and interfacial charge. A further study by Schramm et al. (2003b) showed that a maximum in the rate of recovery can be achieved when the bitumen-water interfacial electric charge is maximized and the interfacial tension minimized.

Long et al. (2005; 2007) studied the temperature effect on bitumen recovery for the water based extraction process. The authors showed that processability is sensitive to a critical temperature. At temperatures exceeding 35 ºC the adhesion force between bitumen droplets and clays reduces. This adhesion force is critical to bitumen recovery since slime coating (clay coating of the bitumen droplets) has an adverse effect on bitumen aeration.

2.1.2 Solids wettability

The overall efficiency (bitumen recovery and bitumen froth quality) is governed by many interactions between all components: bitumen, solids, water and air. Dai and Chung (1996) showed that the hydrophobicity of sand plays an important role in bitumen recession and liberation, with flotation efficiency increasing with decreasing hydrophobicity. Hydrophobic solid particles tend to aerate more easily than hydrophilic particles hence; hydrophobic particles have an adverse effect on froth quality.

Nguyen et al. (2004) confirmed the results of Chung (1996) showing that the interaction between an air bubble and a hydrophilic surface is repulsive, while the interaction between an air bubble and a hydrophobic surface is repulsive at a long distance and attractive at a short distance depending on the particle hydrophobicity.

Hupka et al. (2004) has shown that a more hydrophobic bitumen surface will readily attach to an air bubble and consequently improve flotation quality.

Dang-Vu et al. (2009) studied the wettability of solids recovered from several oil sand ores. The authors applied four techniques: i) contact angle, ii) solids surface tension, iii) particle partition method and iv) water drop penetration time, concluding that water drop penetration time on a compressed disc is most sensitive to characterize wettability of fine solids, while particle partition is most sensitive when characterizing wettability of coarse solids. They further studied the effect of solids wettability on processability of oil sand ores and observed that for both fine and coarse solids, an increase in hydrophobicity results in a reduction in bitumen recovery and bitumen froth quality.

2.1.3 Slime coating phenomena

Bitumen aeration is dependent upon bitumen hydrophobicity and bitumen droplet size. Surface hydrophobicity of bitumen depends on water chemistry and surface interactions with fine mineral solids (clays). Interaction between bitumen droplets and solids is referred to as slime coating. Slime coating not only impedes bitumen aeration by acting as a steric barrier between the bitumen droplet and air bubble, but will significantly deteriorate bitumen froth quality since a greater proportion of fines are carried over in the bitumen froth (Liu et al., 2002a; Liu et al., 2004a; Masliyah et al., 2004).

Liu et al. (2002b; 2004b) were able to relate the interaction potential between bitumen and fines to the zeta potential. Their study validated slime coating of montmorillonite on bitumen droplets in the presence of calcium and magnesium ions. Kaolinite was not observed to slime coat under the experimental conditions.

Ding et al. (2006) observed slime coating at 25 ºC in deionized water but not in plant recycled processing water. The authors proposed that the detrimental effect of illite clay on bitumen recovery was due to its acidity, with the negative effect overcome through the addition of NaOH.

Darcovich et al. (1989) using adhesion surface tension showed that extracted solids with the highest carbon content had the highest level of hydrophobicity.

2.1.4 Surfactants

Clark and Pasternack (1932) systematically studied the water-based bitumen extraction process, identifying surface-active agents as a key component in processability. According to Leja and Bowman (1968) these surface-active agents are predominantly water-soluble salts of naphthenic carboxylate surfactants and smaller amounts of sulfonate compounds. Sanford (1983) concluded that these surfactants are released by the introduction of NaOH. Such surfactants not only promote bitumen liberation and aeration, but they also promote solids flotation. Hence, there is a balance which is to be achieved if the bitumen recovery and froth quality are to remain high.

Schramm et al. (1984a; 1984b; 1985) developed a surface-tension-monitored titration method to measure the anionic surfactants in hot water processing of Athabasca oil sand ores. Studying the interfacial properties of the process, Schramm et al. advocated a theory in which electrostatic forces drive separation of bitumen from the oil sands matrix and, bitumen is aerated by a dispersive rather than an attachment mechanism.

2.1.5 Process aids

Hupka et al. (2004) studied the water-based bitumen recovery process with addition of diluent (kerosene) and sodium tripolyphosphate ($Na_5P_3O_{10}$). Changes in bitumen viscosity, oil sand porosity and bitumen-water interfacial tension were considered in regards to bitumen recovery from Utah oil sands. To achieve satisfactory bitumen recovery, the authors showed that the bitumen-water interfacial tension should be less than 7 mN/m, preferably less than 4 mN/m. This is in agreement with the work of Schramm et al. (2003b) who reported that bitumen separation from oil sands can be facilitated by lowering the bitumen-water interfacial tension to a few mN/m. Bitumen flotation with the addition of $Na_5P_3O_{10}$ and pre-treated at 50-60 °C produced a very high quality bitumen froth. Most importantly, after four successive recycles of the process water, the froth grade and recovery remained unchanged with rapid settling and almost bitumen free tailings water.

Gu et al. (2003) developed a novel induction timer to measure the air bubble-bitumen induction time for different processing conditions (water chemistry and temperature). The use of oily bubbles (kerosene-coated) has been theoretically shown to reduce induction time, and experimentally verified by Gu's induction timer (Su et al., 2006). The experimental observation has been further validated in a microflotation cell for minerals flotation (Liu et al., 2002a; 2002b) and a hydrotransport extraction system for bitumen recovery (Wallwork et al., 2003).

Experiments have also shown that short-chain amines can drastically decrease the induction time and improve bitumen recovery by 50% (Wang et al., 2010).

Kerosene and methyl isobutyl carbinol (MIBC, also known as methyl amyl alcohol) were considered for use as process aids for the development of cold water or Low Energy Extraction (LEE). The amount of kerosene and MIBC varies depending on the grade of the oil sand ore. In his discussions with Schramm, Czarnecki speculated that the role of MIBC may lie in the stabilization of gas bubbles in the process (Schramm et al., 2003a).

2.1.6 Weathering of ore

Ren et al. (2009a; 2009b; 2009c) systematically studied the effect of weathering (also named aging) on processability using a good processing ore, a laboratory weathered ore and a naturally weathered ore. From contact angle, film flotation, XPS analysis and ellipsometry thickness measurements, the authors found that mild bitumen oxidation occurred during ore weathering. The loss of innate water resulted in direct contact between organic matters and mineral solids, having an adverse effect on bitumen recovery, bitumen flotation rate and bitumen froth quality. The study further confirmed that weathering increased adhesion between bitumen and solids, causing difficulties for bitumen liberation hence, poor processability.

2.2 Bitumen viscosity on bitumen recovery

Bitumen liberation is a critical step influencing processability. Under a given chemistry condition, lowering bitumen viscosity would make bitumen layer much easier to recess from sand grains, thus facilitating bitumen liberation.

Hupka et al. (1983; 1993; 2004) studied the importance of bitumen viscosity when processing U.S. oil sands by the addition of kerosene. Their study concluded that the amount of kerosene addition depends on processing temperature, original bitumen viscosity and oil sands grade. The authors showed that there is a good agreement between bitumen recovery and its viscosity. To achieve a bitumen recovery greater than 90%, bitumen viscosity must be reduced to 0.5~2 Pa·s at the temperature of digestion, regardless of oil sands type, grade or origin, shown in Figure 2.1. In fact, if bitumen viscosity was to be controlled below 6 Pa.s, bitumen recovery could keep 80% or higher.

Further experiments were completed with different types of diluents such as; kerosene, hexane, heptane and toluene (Hupka and Miller, 1993; Schramm et al., 1998; Stasiuk and Schramm, 2001; Harjai, 2007). However, most solvents have received limited attention because of their cost or volatility (Yang et al., 1989). For U.S. oil sands the modified process is under a modest temperature (50-55 °C) which has an apparent advantage on energy saving and operation safety. For Athabasca oil sands the operating temperature can be as low as 25 °C (Schramm et al., 2003b).

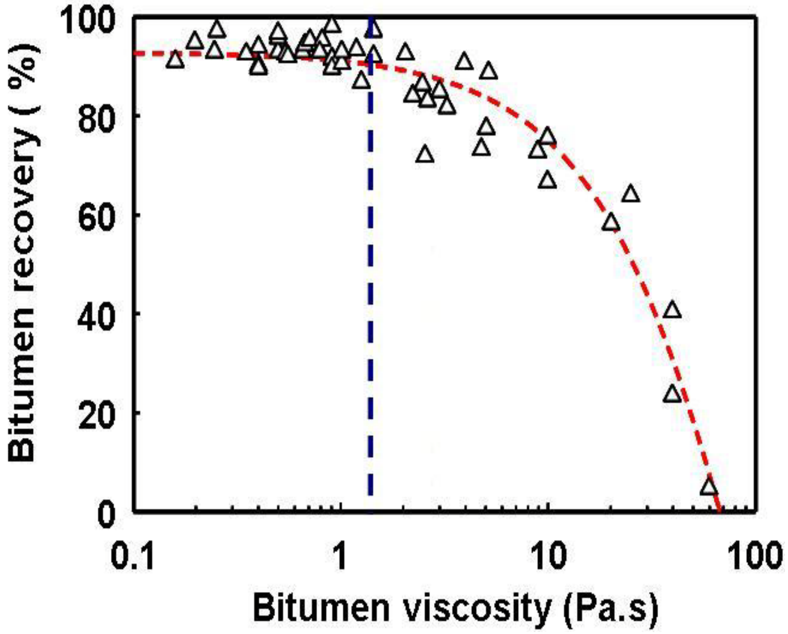


Figure 2.1 Bitumen viscosity importance on bitumen recovery for water-based bitumen extraction process (Reproduced from Hupka et al., 1983; 1993; 2004)

Lelinski et al. (2004) showed that for high bitumen viscosities, recession and liberation from the sand grain is slow, lowering the transfer rate between the sand and air bubble hence, lowering the efficiency of bitumen separation.

Schramm et al. (2003b) have shown that a reduction in viscosity by increasing the processing temperature or through the addition of diluents, enhances bitumen separation for Athabasca oil sand ores. For temperatures above 50 °C changes in separation efficiency are negligible, while for temperatures below 50 °C a clear drop-off is observed. An explanation for such behaviour relates to solvent solubility in the aqueous slurry when the processing temperature is below 50 °C and, a surface tension increase with decreasing processing temperature, which may suggest a reduced ability of the aqueous phase to float bitumen.

For the diluent-assisted bitumen extraction process, separation efficiency depends on penetration time, which is the time required for kerosene to interact with bitumen under processing conditions. The porous structure of oil sands enables kerosene to diffuse via capillary adsorption. For oil sands of the same bitumen viscosity, a higher oil sands grade leads to a longer penetration time. For oil sands of the same bitumen grade, a higher bitumen viscosity leads to a longer penetration time. To emphasize the importance of diluent addition in water-based bitumen recovery, Hupka et al. (1983) classified oil sands into four groups according to their bitumen viscosity. The classification is listed below, Table 2.1.

Table 2.1 Classification of oil sands according to bitumen viscosity

Oil sands type	Bitumen character	Bitumen viscosity (Pa·s)		Recommendations for processing
		50 °C	90 °C	
I	Light	<1.5	<0.1	Diluent unnecessary
II	Moderate	1.5–102	0.1–5	Diluent optional
III	Heavy	102–106	5–103	Diluent necessary
IV	Very heavy	>106	>103	Oil sand not amenable to hot water separation

2.3 Bitumen rheology and viscosity measurement

2.3.1 Newtonian and non-Newtonian fluids

“Rheology” was first formalized by Isaac Newton in the late seventeenth century, observing that some liquids could be made to flow more easily than others and that the flow rate of each material depended on the force to which they were subjected. These observations are now more formally described by stress (σ) and strain (γ). Stress is the force acting on a sample per unit area and strain is the amount of deformation in response to the applied stress. The viscosity (μ) of a liquid can be suitably described by the following shear deformation model, shown in Figure 2.2, where:

σ (stress) = force per unit area, expressed as Pa

γ (shear strain) = relative deformation in shear (no units)

$\dot{\gamma}$ (shear rate) = change of shear strain per unit time, expressed as s^{-1}.

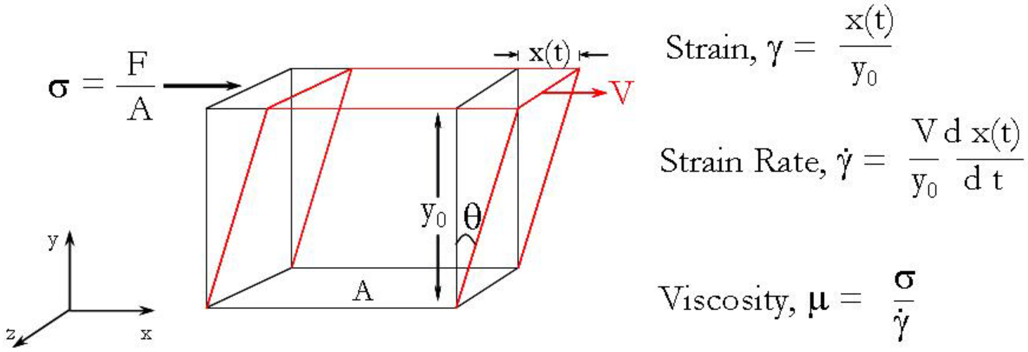


Figure 2.2 Definition diagram for shear deformation

As shown in Figure 2.2, viscosity can be mathematically expressed as the ratio between the shear stress and the shear rate. In general terms, viscosity is a measure of the resistance of a material to deform under either shear stress or extensional stress, i.e. for a fluid it is a measure of the resistance to flow.

From the expression described above, fluids can be classified as either Newtonian or non-Newtonian. A Newtonian fluid is an idealized fluid whose viscosity is constant with shear; i.e., the shear rate is proportional to the shear stress. Many liquids exhibit Newtonian behaviour over a very narrow range of shear rates. At a critical condition the linear relationship between shear stress and shear rate no longer holds. These fluids are known as non-Newtonian fluids and a typical flow curve is shown in Figure 2.3. Non-Newtonian fluids can be further subcategorized:

1) Non-Newtonian time dependent liquids: the viscosity of a fluid is dependent on the shear rate and the time of shearing. Such fluids can be described as a) thixotropic, a decrease in viscosity with time under a constant shear rate or shear

stress followed by a gradual recovery when the force is removed; and b) rheopectic, an increase in viscosity with time under constant shear rate or shear stress followed by a gradual recovery when the force is removed.

2) Non-Newtonian time independent liquids: the viscosity of a fluid is dependent on the shear rate but independent of the time of shearing. These fluids include: a) shear thinning, a decrease in viscosity with increasing shear rate, also referred to as pseudoplasticity; and b) shear thickening, an increase in viscosity with increasing shear rate, also referred to as dilatancy.

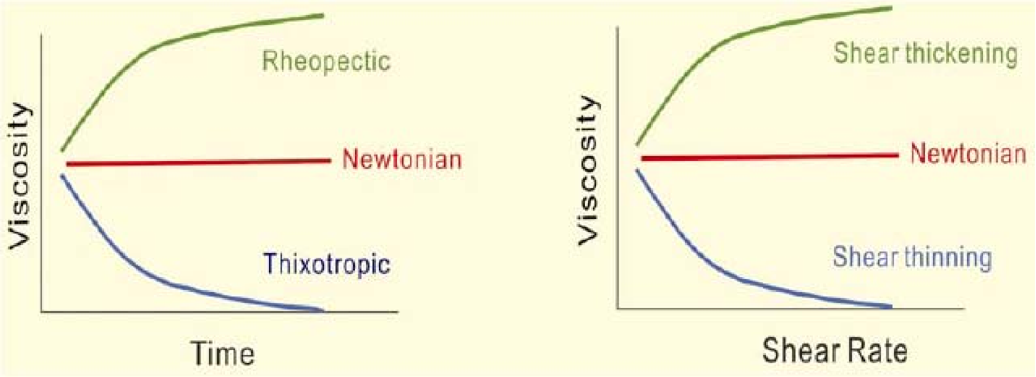


Figure 2.3 Schematic curves of different flow types

The rheological features of a flow curve are better identified if the data are plotted on a logarithmic scale, see Figure 2.4. At low shear rates (zero shear region) Newtonian behaviour is often exhibited. With increasing shear the viscosity reduces and the fluid can be described as non-Newtonian shear thinning. This region takes the form of a power law (straight line on logarithmic axes), with the power-law index used to determine the degree of shear thinning. At extremely high shear rates a second Newtonian region develops and for certain fluids/suspensions, shear thickening may be observed.

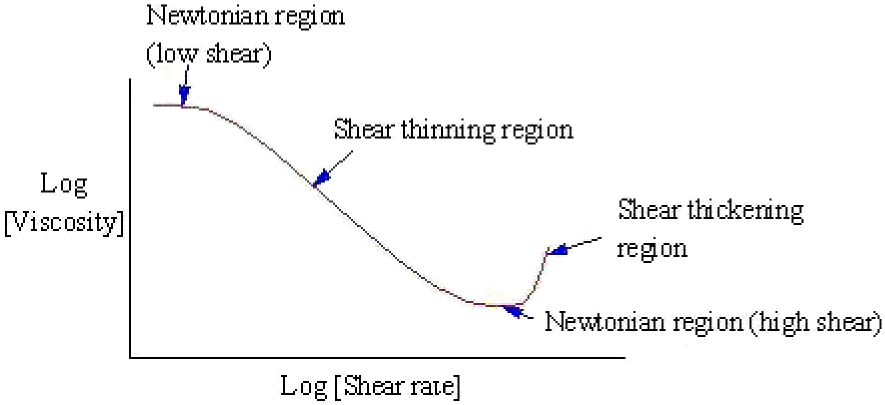


Figure 2.4 Generalized flow curve

2.3.2 Rheological properties of bitumen

Ward and Clark (1950) studied several Athabasca bitumen samples collected from different sites. Using a pressure driven capillary viscometer they observed Newtonian behaviour for bitumen at 29.1 °C.

Dealy (1979) studied bitumen extracted from Athabasca, Cold Lake and Lloydminster. The author concluded that bitumen displayed some degree of non-Newtonian behaviour at 27.5 °C, with the onset of shear-thinning observed at low shear rates 0.1 to 1 s^{-1}. A 10% reduction in viscosity was observed for all the samples. The author further attempted to explain the viscosity variations through asphaltene molecular aggregation and de-aggregation.

Schramm and Kwak (1988) investigated the rheological properties of

Athabasca bitumen, concluding that bitumen treated at 80 ^{o}C (hot water process) behaves as a Newtonian fluid. The rheological properties of bitumen at lower temperatures were not investigated.

Seyer and Gyte (1989) measured the viscosity of bitumen recovered from Athabasca and Cold Lake deposits as a function of temperature and organic solvent addition. They noted that some of the bitumen and bitumen/solvent mixtures exhibited non-Newtonian behaviour.

Ukwuoma and Ademodi (1999) studied Nigerian oil sands bitumen extracted by toluene. The effects of temperature and shear rate were considered. Their data showed non-Newtonian fluid behaviour, with shear thickening at low temperatures (<30 °C). With increasing temperature the bitumen became more Newtonian like.

Moran and Yeung (2004) measured a bitumen viscosity of around 1250 Pa·s at 22.5 °C from Syncrude coker feed bitumen. The viscosity was measured using the drop shape recovery technique which avoided the problem of viscous heating, an issue at high shear rates when using a rotational viscometer.

Hasan et al. (2009) using a rotational rheometer studied the rheological properties of Athabasca bitumen and Maya crude oil obtained by nanofiltration at 200 °C. When measuring the samples at 25 °C Newtonian behaviour was observed. The temperature dependence of rheological behavior is more evident for Athabasca bitumen than for Maya crude oil. Changes to the asphaltene aggregate structure, asphaltene-maltene interaction, and/or asphaltene self-association contribute to the temperature dependence on bitumen viscosity. Their study also showed that maltenes played a crucial role in the rheological behaviour of bitumen and heavy oil, due to the occurrence of solid-liquid transitions for maltenes over a broad temperature range. Studying the same samples, Bazyleva et al. (2010) completed viscosity measurements on the same rheometer, concluding that Athabasca bitumen and Maya crude oil behaved as shear thinning fluids up to 37 °C and 7 °C, respectively. Both are Newtonian at higher temperatures.

2.3.3 Viscosity measurement of Athabasca bitumen

An accurate measurement of bitumen viscosity is extremely important since the viscosity will influence in situ recovery, transportation and extraction performance. There is a vast literature on Athabasca bitumen viscosity, but these samples are often influenced by solvent residue, or mixtures of dissolved gas and solvent. Also, the measurement techniques and procedures are not clearly described and as such, interpretation of the data is often difficult to achieve. For example, some bitumen samples are centrifuged from the ore directly, but their viscosities are not complete without presenting the solids and water content.

Viscosity data collected on Athabasca bitumen samples is shown in Figure 2.5. Clearly, there is a large disparity in viscosity over the temperature range considered. In addition, even for the same sample (Syncrude coker feed) viscosity measured at an equivalent temperature can be different. For example, the studies of Wallace and Henry (1987) and Moran and Yeung (2004) on Syncrude coker feed show a difference in the measured viscosity, most likely a result of different measurement approaches. Wallace and Henry (1987) used a Brookfield cone and plate viscometer, while Moran and Yeung (2004) used a drop shape recovery method.

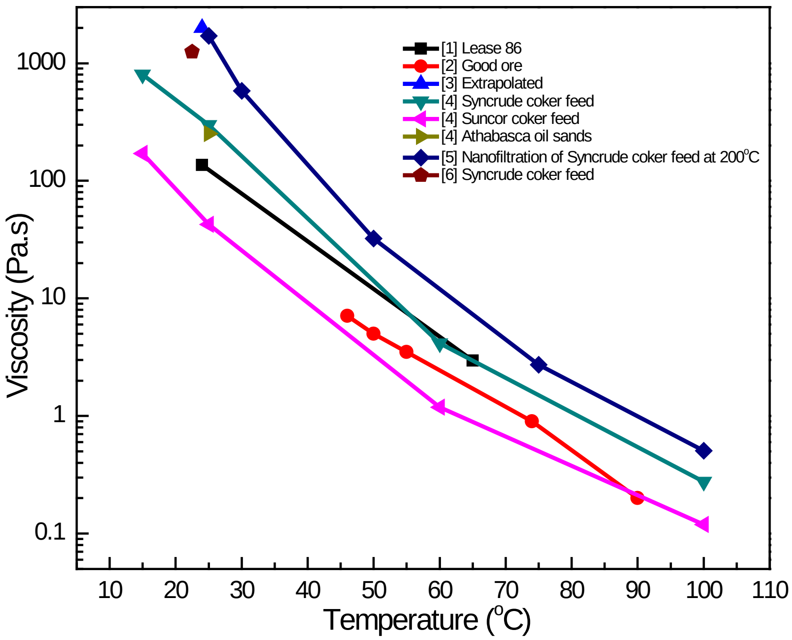


Figure 2.5 Athabasca bitumen viscosity data

[1] Seyer and Gyte (1989) [2] Hupka et al. (1987) [3] Shu, W. R. (2008) [4] Wallace and Henry (1987) [5] Hasan et al. (2009) [6] Moran and Yeung (2004)

Miller et al. (2006) noted that because of the inherently problematic sample preparation methods, viscosity data before the mid-1980s are considered controversial.

Hasan et al. (2009) and Bazyleva et al. (2010) showed that differences in the oil sand ore source, the bitumen extraction and post-extraction processes, rheological instrumentation applied and operating parameters, all affect the measurement of bitumen viscosity, potentially leading to three orders of magnitude variance.

2.3.4 Viscosity correlation of bitumen and solvent mixtures

Based on the first published method by Cragoe (1933), to predict viscosities of liquid mixtures, Shu (1984) proposed a general correlation for calculating the viscosity of heavy crude (heavy oil or bitumen) and light organic solvent mixtures by utilizing empirical viscosity data from literature and in-house measurements. His prediction showed improvements upon the Cragoe model for binary mixtures with high viscosity ratios. Shu commented that the correlation would not apply to mixtures where excessive asphaltene precipitation occurred.

Shu's model involved four equations (2-1~2-4), where μ is the viscosity of the blending heavy oil system consisting of A and B; x_A and x_B are component weighting factors; V_A and V_B are volume fractions; ρ_A and ρ_B are specific gravities; $\Delta\rho=\rho_A-\rho_B$ and α is determined from viscosities and densities.

$$\ln \mu = x_A \ln \mu_A + x_B \ln \mu_B \tag{2-1}$$

$$x_A = \frac{\alpha V_A}{\alpha V_A + V_B} \tag{2-2}$$

$$x_B = 1 - x_A \tag{2-3}$$

and

$$\alpha = \frac{17.04 \Delta\rho^{0.5237} \rho_A{}^{3.2745} \rho_B{}^{1.6316}}{\ln(\frac{\mu_A}{\mu_B})} \tag{2-4}$$

Miadonye et al. (1995; 2000) proposed two more generalized correlations to predict the viscosity of bitumen and diluent binary systems. In their correlations there was no requirement to input the densities of the constituents. The average absolute deviation between the predicted and experimental values was 8.7%, whereas, for binary systems the correlation yielded higher percentage errors up to 20%, due to the viscosity difference between the bitumen and diluent. Improvements were later made to the correlation reducing the overall deviation to approximately 13.5%, better than predictions from Shu's correlation. The mass fraction of the diluent in the binary system could be estimated with an overall deviation of 5.5%.

Wen and Kantzas (2006) developed regression viscosity models for predicting mixture viscosities from NMR spectra data. The authors data were compared to results from Shu's and Cragoe's models, concluding that the predictions from NMR-based model are similar to those from Shu's model and superior to those of Cragoe's model.

For these correlations, one important point needs to be emphasized: without an accurate bitumen viscosity the reliability of the correlation data is questionable.

2.4 Centrifugation method for bitumen sample preparation

Traditionally, bitumen samples are extracted using organic solvents either directly or indirectly. Both methods can potentially lead to solvent residue problems. It has been well documented that bitumen viscosity is extremely sensitive to solvent addition. Also, if solvents are entirely removed, the sample would lose light ends which affects bitumen viscosity. When using solvents there is no separation method that guarantees bitumen free from alteration. However, with a solvent-free advantage, centrifugation appears to provide a solution to many existing sampling concerns.

Wallace et al. (1984) centrifuged bitumen directly from oil sand ore at 1780g, 70 ºC. The authors discussed the pros and cons of the centrifugation method. Pros: bitumen has no contact with a solvent and the loss of light ends will be avoided; cons: the presence of solids and water may limit the application of this technique.

Potoczny (1984a; 1984b) obtained bitumen using both centrifugation and solvent extraction methods, measuring the surface tension of bitumen. The author measured changes in bitumen surface tension which related to the sample preparation method.

Henry and Fuhr (1992) employed two techniques to prepare bitumen samples: solvent extraction and ultracentrifugation. They centrifuged bitumen directly from oil sands at 198000g, 20 ºC. Their study showed that centrifuged bitumen contains some emulsified water and a small amount of solids. However, the amount of solids was found to be equivalent to the amount of solids from solvent-extracted bitumen.

Chapter 3 Materials and Methods

3.1 Bitumen samples preparation

3.1.1 Materials

Four ores were used through the study: i) high bitumen content good processing ore F11A, ii) average bitumen content average processing ore SYN704, iii) artificially weathered F11A ore (namely W-F11A) and iv) high bitumen content poor processing ore or naturally weathered ore SUNOXI. Oil sand ores were supplied by Suncor Energy Inc. and Syncrude Canada Ltd.. W-F11A was prepared by artificially weathering F11A ore in an oven under controlled conditions (0.5 cm thick layer of F11A ore heated in an oven at 50 °C with air ventilation for 5 days).

3.1.2 Characterization of oil sand ore

Dean Stark apparatus was used to characterize each ore to determine bitumen, water and solids content. A detailed procedure of the Dean Stark apparatus is given in Section 3.3. A table summarizing the bitumen, water and solids content including fines content is shown in Table 3.1. Using the industry standard, fines are defined as mineral solids having a diameter less than 44 μm (mesh size 325 U.S.).

Table 3.1 Characterization of oil sand ores

Ore	Description	Composition (wt%)			Fines in solids (-44μm) wt%
		Bitumen	Water	Solids	
F11A	High grade, good	14.3	5.2	80.4	0.1
W-F11A	Artificially weathered	14.6	1.6	83.8	0.8
SYN704	Average	9.6	6	84.4	25.5
SUNOXI	Naturally oxidized, poor	12.8	2.7	84.5	3

3.1.3 Centrifugation of oil sand ore

Centrifugation of each ore was completed using a Rotanta 460R centrifuge (Hettich Centrifuges, UK). The centrifuge is equipped with a heating function enabling experiments to be completed up to 90 °C. Heating the oil sand ore is advantageous since the bitumen viscosity can be lowered to enhance separation from the oil sands. Stainless steel tubes (Beckman Coulter Inc., Canada) each of 120 mL in volume were used throughout the study. After a trial and error study, 50 °C and 18000g were conditions chosen to maximize bitumen recovery. Higher temperatures could not be used due to: i) loss of light end, and ii) the mobility of bitumen would lead to re-soaking of the oil sands after centrifugation. 18000g is the maximum g-force of the centrifuge.

A flowchart illustrating the centrifugation steps used throughout the study is shown in Figure 3.1.

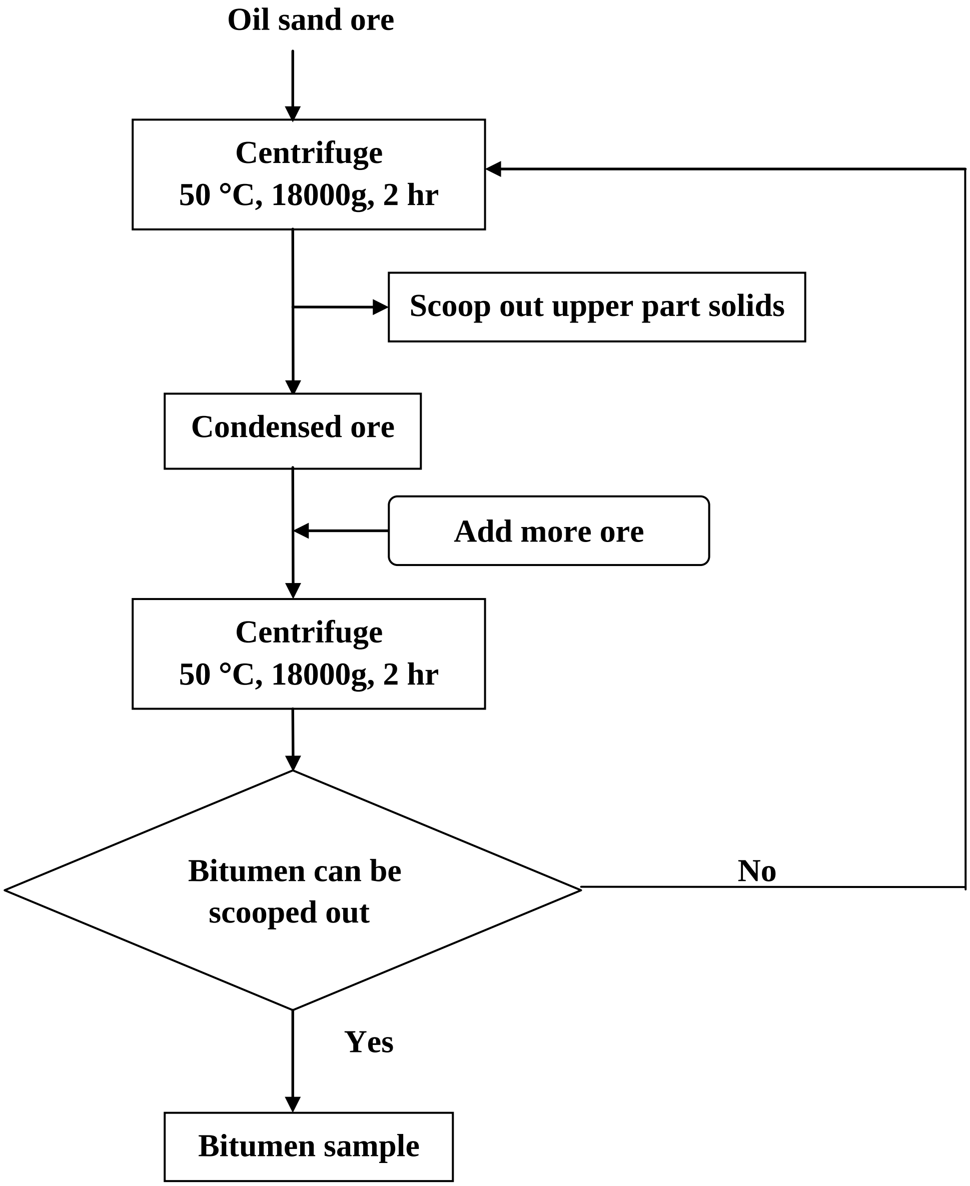


Figure 3.1 Flow chart of bitumen sample preparation from the centrifugation method

First, the oil sands are thawed out which may take up to three hours depending on the ambient temperature. The ore is then transferred into centrifuge tubes, making sure to balance opposing tubes. The centrifuge is operated at 18000g, 50 °C for 2 hours. After each run solids are removed and more ore added until clean bitumen can be observed. Bitumen is then gradually recovered, repeating the centrifugation process until enough bitumen has been recovered.

3.1.4 Determination of the solids, water and asphaltene content

To determine the solids content the following procedure was used:

1) Weigh out a small sample of bitumen W_b.
2) Dissolve bitumen in toluene. Shake for 2 hours.
3) Weigh filter paper, 0.1 μm pore size W_p.
4) Filter the toluene solution using a Buchner funnel.
5) Dry the filtration cake and measure the combined weight of the filter paper and filtration cake W_s.
6) W_s - W_p
7) Calculate the solids content (wt%) using:

$$\text{Solids content} = \frac{W_s - W_p}{W_b} \times 100\% \qquad (3\text{-}1)$$

To determine the water content the following procedure was applied:

1) Steps 1 and 2 are consistent with determining the solids content.
2) Measure the water content in toluene using Karl Fisher Titrator W_0.
3) Measure the water content in the bitumen and toluene solution W_1.
4) W_1 - W_0
5) Calculate the water content (wt%) using the following expression:

$$\text{Water content} = \frac{W_1 - W_0}{W_b} \times 100\% \qquad (3\text{-}2)$$

To determine the asphaltene content the following procedure was applied:

1) Weigh small amount of bitumen W_b.
2) Dissolve bitumen in heptanes (bitumen:heptane volume ratio=1:40, shake for 2 hours.
3) Filtrate solution through 0.1 μm filter paper using a Buchner funnel.
4) Wait till the filtration cake is dry enough, weigh filter paper and Buchner funnel and filtration cake W_{p1}.
5) Use toluene to wash the filtration cake until the filtrate is colorless.
6) Wait till the filtration cake is dry enough, weigh the filter paper and Buchner funnel and filtration cake W_{p2}.
7) Get the difference between W_{p1} and W_{p2}.
8) Calculate wt% asphaltene in the bitumen sample:

$$\text{Asphaltene content} = \frac{W_{p1} - W_{p2}}{W_b} \times 100\% \qquad (3\text{-}3)$$

3.2 Bitumen viscosity measurement

3.2.1 Materials

It should be mentioned that the notation used to describe the oil sand will also be used to describe the associated centrifuged bitumen.

Bitumen solvent mixtures were prepared using kerosene (Fisher Scientific, Canada) and naphtha (Syncrude Ltd., Canada). The purpose of using kerosene and naphtha relates to their volatility and commercial value. These mixtures are shaken for 24 hours to ensure homogeneity prior to each viscosity measurement.

3.2.2 AR-G2 rheometer

An AR-G2 rheometer (TA Instruments, USA) was used throughout the study to measure sample viscosities, the instrument setup is shown in Figure 3.2. The body of the rheometer is a single piece aluminum casting consisting of a base and a column. The head of the rheometer which contains a drag cup motor, magnetic and air bearings and, an optical encoder is attached on a ball slide that is mounted within the instrument. A draw rod connected to the motor goes through the unit forming a rotating spindle. Various geometries can be attached to the spindle. A standard Peltier plate temperature control system is mounted on the base of the casing. Using the Peltier thermoelectric effect the plate temperature is controlled. The internal resolution is within ±0.01 ºC. Water is used to adjust Peltier plate temperature (constantly pumped through the plate from an external tank).

The repeatability of the system is at least ±5% and is routinely calibrated using standard mineral oil (Cannon Instrument Company Inc., USA).

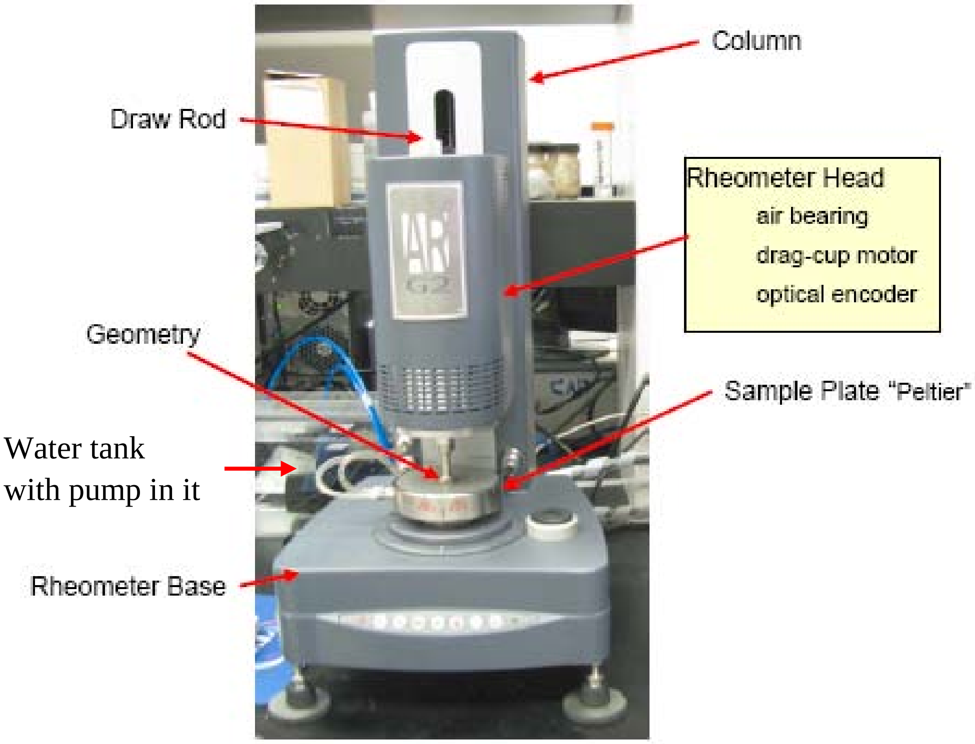


Figure 3.2 Setup of AR-G2 rheometer

3.2.3 Procedure

Based on the particulate size in the recovered bitumen, a 20-mm-diameter parallel plate with a gap setting of 500 μm was used. Sample volume is approximately 0.16 mL. A sample cover was used to minimize weathering effects and reduce errors caused through evaporation.

Bitumen viscosities were measured at 25, 35, 50 and 80 ºC. For the viscosity of bitumen and solvent mixtures, thoroughly mixed samples were tested at 25 ºC with different kerosene or naphtha additions. The decision for running these experiments at 25 ºC will be explained Section 3.3.2.1.

A continuous ramp experiment was used to apply an increasing shear stress on the sample with data collected under equilibrium conditions. Prior to each test, the sample temperature was adjusted using the Peltier plate.

Sample loading is critical for obtaining accurate measurements. Overfilling and underfilling will result in non-representative viscosity values. To accurately load the sample consistently three steps were followed:

1) Sample is initially overloaded on the center of the Peltier plate using a spatula.
2) The parallel plate geometry is lowered onto the sample to the preset gap.
3) Any overloaded sample is trimmed to the rim of the plate to obtain the correct filling volume. To evenly distribute the sample the geometry is rotated at 1 rad/s.

An equilibrium time of 5 minutes is set to eliminate any structure effects and temperature gradients within the loaded sample.

3.3 Influence of bitumen viscosity on processability

3.3.1 Materials

Three of the four oil sands were tested for processability performance except F11A. Process water was obtained from Syncrude Aurora site. The ionic concentrations in the water are shown in Table 3.2. Since pH of the process water was different from pail to pail, water pH was adjusted to 8.5 using 1M NaOH solution prior to each test.

Table 3.2 Ionic concentration in Aurora process water measured by atomic absorption spectroscopy at pH=7.8

Description	Ion concentration (ppm)						
	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	NO_3^-	SO_4^{2-}
Syncrude Aurora plant water	32.2	18.1	22.9	527.4	334.9	33.1	320.4

Toluene (Fisher Scientific, Canada) was used as received for bitumen froth treatment and instrument cleaning. Kerosene and naphtha were used as the solvent to lower bitumen viscosity. Kerosene was studied since the solvent had been considered previously and naphtha was studied due to its economic implications, since naphtha is already used in the extraction process when treating recovered froth from the PSC.

3.3.2 Procedures

A Denver flotation cell (Figure 3.3) was used to obtain bitumen froth samples and, Dean Stark distillation (Figure 3.4) was used to evaluate froth composition and quality.

The Denver flotation cell has long been used as a batch extraction unit to test processability of oil sand ores (Kasongo et al., 2000; Liu et al., 2004a; 2004b; Zhou et al., 2004; Ding et al., 2006). Its configuration allows convenient parameter studies to be completed with accurate control of slurry temperature and pH, mechanical agitation speed, air injection rate, conditioning and flotation times. The Dean Stark distillation technique is used in combination with a reflux condenser and a batch reactor for the continuous separation of water, solids and bitumen. The technique was first developed to determine the water content in petroleum (Dean and Stark, 1920). Chemists from Syncrude Canada Ltd. further developed the method for bitumen froths (Bulmmer and Starr, 1979).

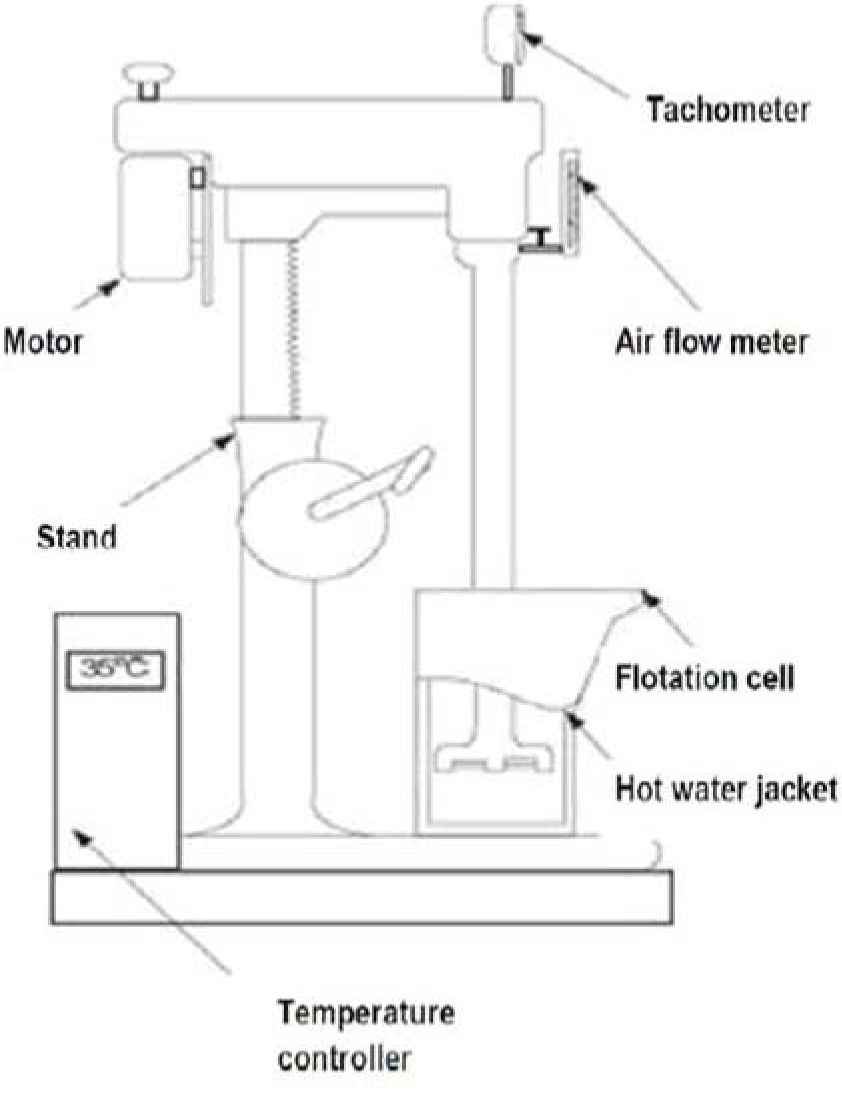


Figure 3.3 Laboratory setup for Denver flotation cell

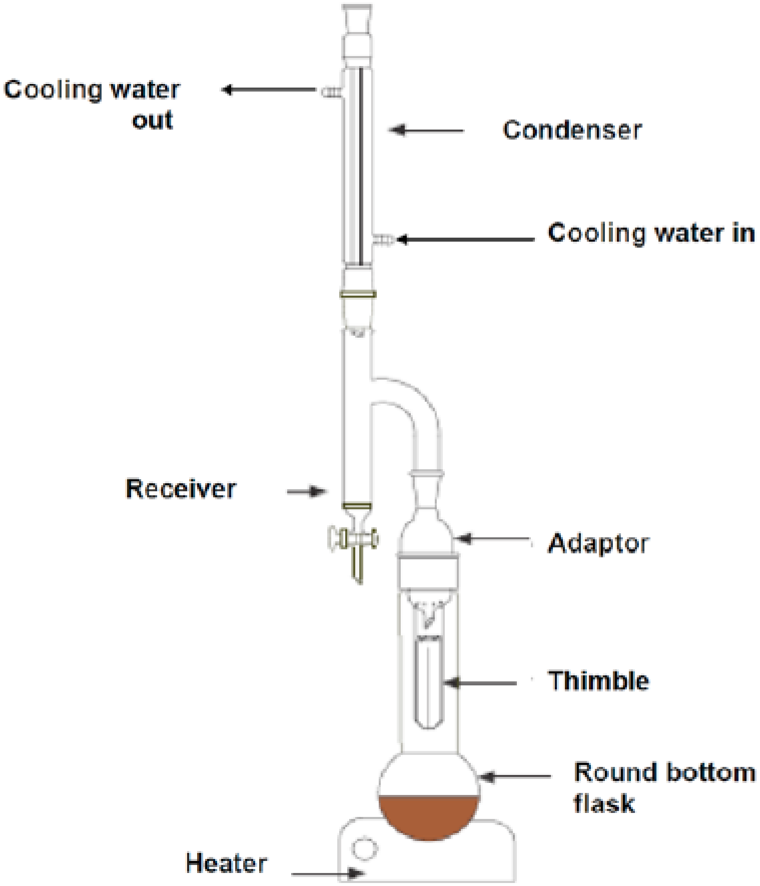


Figure 3.4 Laboratory setup for Dean Stark analysis

3.3.2.1 Denver cell flotation procedure

To standardize the bitumen flotation experiments, operating conditions were fixed to values previously discussed in Harjai (2007) and Qiu (2010). The experimental conditions were: process water pH = 8.5, mechanical agitation speed = 1500 rpm, conditioning time = 5 minutes, air injection rate = 150 mL/min, air injection time = 20 minutes, and flotation time = 20 minutes.

Flotation tests in the absence of solvent addition were completed at different temperatures, 25, 35, 45, and 50 °C. Above 50 °C stable temperature control was difficult to achieve hence; 50 °C was the upper limit for flotation. To evaluate the role of bitumen viscosity in the water-based extraction process, experiments with different solvent additions at 25 °C were completed. 25 °C was chosen since we consider it to be ambient temperature. In addition to the effect of bitumen viscosity on ore processability, we also want to study the feasibility of a solvent-assisted extraction process. As previously discussed, it would be desirable if the extraction process could perform to a high standard without addition of thermal energy.

The procedure below was followed to collect bitumen froth samples:

1) Thaw out 300 g of oil sand ore. For solvent addition cases, kerosene or naphtha was distributed evenly onto the thawed out ore using a plastic pipette. A spatula was used to mix the solvent and ore thoroughly and then left to rest with a cover for 10 minutes.

2) One litre of process water was prepared and pH adjusted to 8.5. Water was then heated to the test temperature and poured into the flotation cell. The water bath of the flotation cell is adjusted to the test temperature as well.

3) The test ore was then transferred into the flotation cell and conditioned for 5 minutes.

4) After conditioning air was injected at a flow rate of 150 mL/min. The flotation test was conducted for 20 minutes. Secondary containers were used to collect the froth samples, with samples collected over the first 2 minutes, next 3 minutes, next 5 minutes and during the last 10 minutes.

5) Weigh thimbles for four samples. Transfer the froth samples to four thimbles respectively, weigh loaded thimbles. Froth samples thus collected will be further analyzed using Dean Stark apparatus. Weight of the collected froth for each sample was the difference between the loaded and unloaded thimbles. Total weight of the froth can be calculated by adding the weight of the four froth samples together.

3.3.2.2 Dean Stark procedure

Bitumen, solids and water content in all recovered froth samples are determined using the Dean Stark apparatus. The following procedure was used to complete bitumen froth analysis:

1) Approximately 220 mL of toluene was added to each of the four distillation flasks. Thimbles containing recovered froth were secured in distillation flasks before attaching the trap and condenser. The trap stopcock should be closed while the cooling water was running.

2) During distillation, water floated by the Denver cell was occasionally collected by the trap. The distillation process was complete once the dripping toluene ran

colourless. At this stage the heating mantle was turned off. To cool the apparatus faster the condenser water was left running for several minutes.

3) Each thimble was removed from the column to a glass jar and placed in a vacuum oven overnight at 60°C.

4) The distillation liquid was transferred into a 250 mL volumetric flask and additional toluene was added to bring the volume to 250 mL. The flask was then shaken and left undisturbed overnight.

5) Condensed water was collected for four samples and weighed. Water content of the froth was determined by adding the four weights together.

6) Weigh fresh filter paper. Pipette 5 mL from the 250 mL stock solution onto the filter paper placed on a watch glass. Use a side to side motion to evenly saturate the filter paper. After 60 minutes of drying weigh the filter paper. The filter paper weight difference is multiplied by 50 for each of the four samples which are then added to determine the bitumen content in the froth.

7) Weigh the dried thimble. Difference between the dried and unloaded thimble was the weight of the solids in each froth sample. Total weight of solids is determined from the addition of the four collected samples.

3.3.3 Calculation of bitumen recovery and evaluation of froth quality

Based on the characterization data and extraction results, bitumen recovery and froth quality (bitumen: solids mass ratio) are calculated using the following equations:

$$\text{Bitumen recovery} = \frac{\text{Weight of bitumen in froth}}{\text{Weight of bitumen in ore}} \times 100\% \qquad (3\text{-}4)$$

$$\text{Bitumen to solids ratio} = \frac{\text{Weight of bitumen in froth}}{\text{Weight of solids in froth}} \qquad (3\text{-}5)$$

Chapter 4 Results and Discussion

4.1 Bitumen characterization

Using methods previously described in Section 3.1.4, the solids, water and asphaltene content for each bitumen sample was determined, see Table 4.1. For all samples, solids and water contents were less than 2 wt% and 1 wt%, respectively. The asphaltene content was more varied with 2.6 wt% and 11.6 wt% measured for SYN704 and SUNOXI, respectively. Asphaltene content in F11A and W-F11A samples was not measured.

Table 4.1 Characterization of bitumen isolated by centrifugation

Bitumen type	F11A	W-F11A	SYN704	SUNOXI
Solids content wt%*	0.7	1	0.68	1.7
Water content wt%	0.28	0.18	0.23	0.9
Asphaltene (C7) wt%	-	-	2.6	11.6

*Solids content is the solids plus organic matter filtrated by 0.1 μm filter paper

Equation 4-1 is the Einstein equation relating the viscosity of a dispersion (μ) to the viscosity of the dispersed medium (μ_0) and the solids volume fraction (φ) (Mardles, 1940).

$$\mu = \mu_0(1+2.5\varphi) \qquad (4\text{-}1)$$

Taking the highest solids content from Table 4.1, we determine that the solids contribution to bitumen viscosity is less than 2%. Hence, the solids effect on bitumen viscosity is considered negligible.

4.2 Bitumen viscosity measurements

Bitumen viscosity measurements were conducted using AR-G2 rheometer at different temperatures and with different kerosene and naphtha additions for the four types of bitumen F11A, W-F11A, SYN704 and SUNOXI.

4.2.1 Rheological property of bitumen at 25 ºC

It is widely accepted that bitumen behaves as a Newtonian fluid at temperatures greater than 25 ºC (Wallace, 1988; Hasan et al., 2009; Masliyah and Gray, 2010). However, its rheological properties at 25 ºC are still debated.

Figure 4.1 shows the flow curves for each bitumen sample measured at 25 ºC.

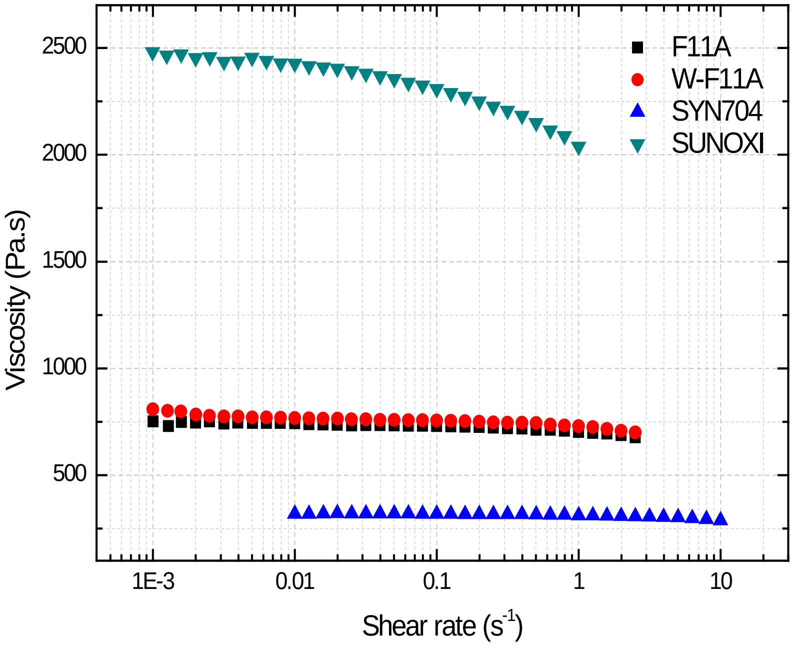


Figure 4.1 Rheological properties at 25 ºC for the bitumen collected by centrifugation method with no solvent added

As shown in Figure 4.1, there are large differences in the measured bitumen viscosities at 25 ºC. The bitumen viscosity at 25 ^{o}C increases in the order of SYN704 < F11A and W-F11A < SUNOXI. These differences are most likely associated with the asphaltene content in the bitumen samples. Although without information on F11A and W-F11A we can only speculate. With similar bitumen viscosities (F11A and W-F11A) it appears that artificial weathering has little effect on the rheological properties.

At low shear rates the bitumen viscosities are shown to be independent of shear hence; bitumen behaves as a Newtonian fluid. With increasing shear all samples exhibit a viscosity dependency on shear. The measured reduction in viscosity with increasing shear is most likely influenced by viscous heating which is in agreement with previous research (Ward and Clark, 1950; Wallace, 1988; Hasan et al., 2009; Masliyah and Gray, 2010). The data also show that the transition to non-Newtonian fluid behaviour is related to bitumen viscosity, i.e. higher the viscosity, lower the transitional shear rate.

4.2.2 Temperature effect on bitumen viscosity

Figure 4.2 shows the effect of temperature on bitumen viscosity. Figures A2.1-A2.4 in Appendix 2 shows the corresponding shear rates for Figure 4.2. Like previously published data, at an equivalent temperature bitumen viscosity appears to be sample specific. The behaviour becomes less important as sample temperature is increased. In comparison to previous studies, bitumen samples in this research have been recovered by centrifugation and avoid any solvent residue or light end loss errors. The differences in bitumen viscosity are believed to relate to the asphaltene or other organic matter contents.

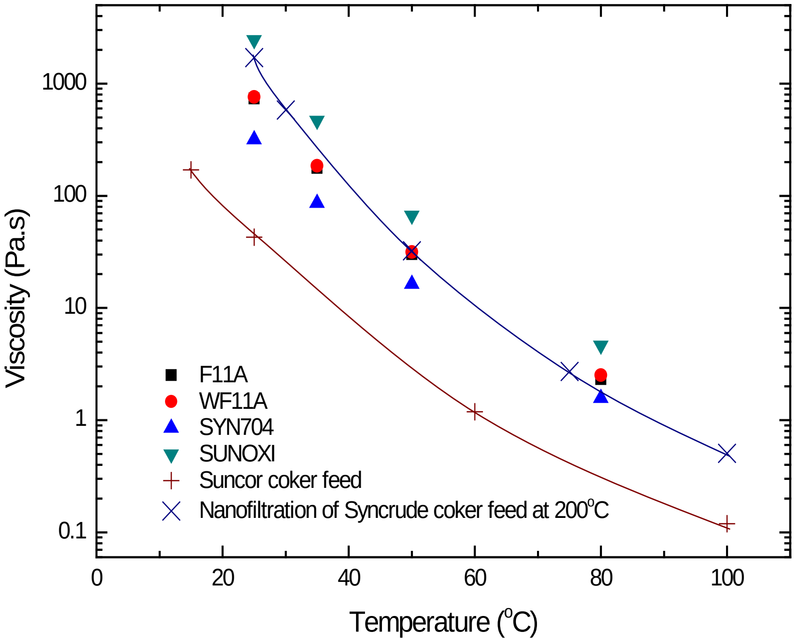


Figure 4.2 Viscosity as a function of temperature with no solvent addition

Bitumen centrifuged from SUNOXI and SYN704 have the highest and lowest viscosities, respectively. Figure 4.2 considers experimental data in this research against two data sets that represent the highest and lowest viscosities previously shown in Figure 2.5. At low temperatures three of the four samples are within the range, while at high temperature (>80 ^{o}C) three of the four samples are outside of this range.

4.2.3 Effect of kerosene and naphtha addition on bitumen viscosity

After shaking the bitumen-solvent mixtures for 24 hours, viscosity measurements were conducted at 25 ºC. The viscosity data are shown in Figure 4.3.

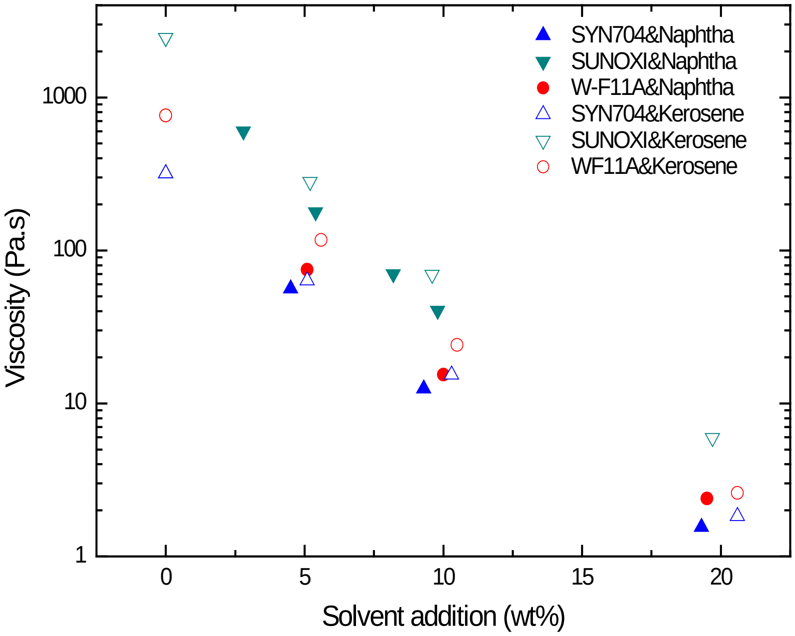


Figure 4.3 Bitumen viscosity with different kerosene and naphtha addition at 25 ºC

Figure 4.3 shows that in both cases, an increase in solvent addition reduces bitumen viscosity. Figures A2.5-A2.12 in Appendix 2 shows the corresponding shear rates for Figure 4.3. The addition of 10 wt% solvent (kerosene or naphtha) reduces the viscosity to below 100 Pa·s, equivalent to the bitumen viscosity at 50 ºC without solvent addition (Figure 4.2). At equivalent solvent concentrations naphtha is more effective in reducing bitumen viscosity, which is in agreement with the findings of Seyer and Gyte (1989), who showed that lower molecular weight solvents have a greater effect on viscosity reduction.

4.3 Correlation of temperature and solvent addition

Two correlation methods were used in this study: graphical and numerical. The two methods gave same results. Graphical method was shown in Appendix. For numerical method, the correlation models discussed in Chapter 2 were considered, but due to limited information (lack of bitumen density), agreements between experimental data and the correlations were poor. However, the following exponential regression model was used to fit the experimental data:

$$\mu = e^{ax^2+bx+c} \qquad (4\text{-}2)$$

where, μ is bitumen (centrifuged bitumen or centrifuged bitumen and solvent binary mixture) viscosity in Pa·s, x is temperature in degree Celsius or solvent addition in weight percentage, and a, b, and c are constants relating to the bitumen type.

Empirical fits using the above correlation are shown in Figures 4.4-4.6 for each bitumen sample. Table 4.2 lists the values for constants a, b, and c and, the coefficient of determination R^2.

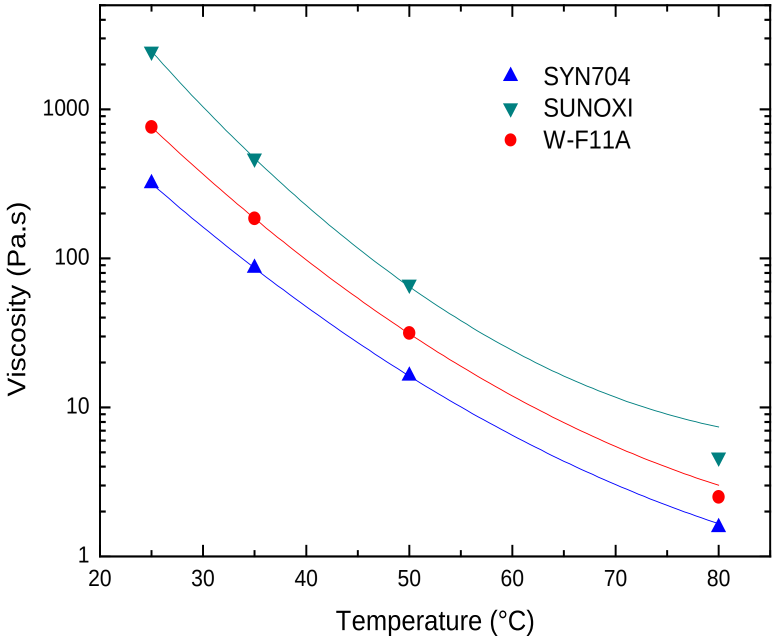


Figure 4.4 Measured viscosities with fitted viscosities by exponential regression model for bitumen at different temperatures with no solvent addition

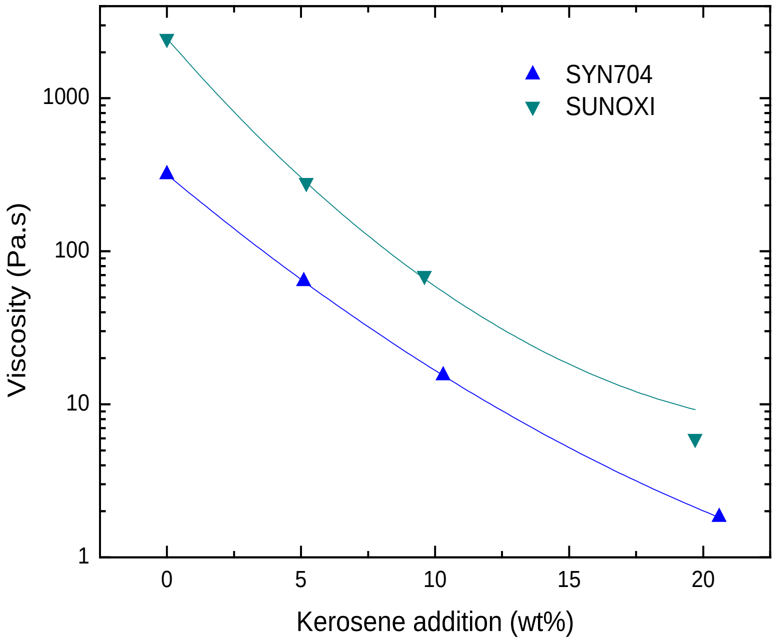


Figure 4.5 Measured viscosities with fitted viscosities by exponential regression model for bitumen with different kerosene addition at 25 °C

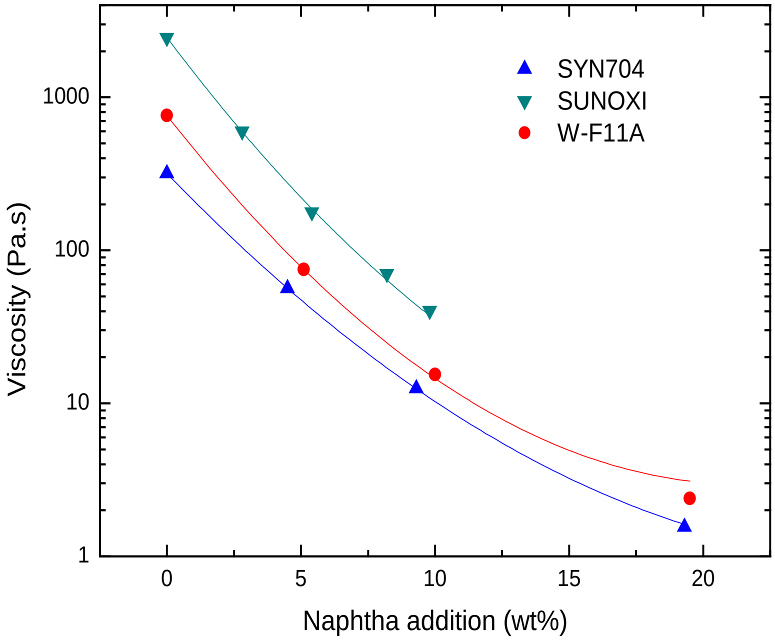


Figure 4.6 Measured viscosities with fitted viscosities by exponential regression model for bitumen with different naphtha addition at 25 °C

Table 4.2 Parameters for bitumen viscosity fitting at different conditions for SYN704, SUNOXI and W-F11A bitumen

Bitumen	Conditions	a	b	c	R^2
SYN704	Temperature	7.81E-04	-0.1775	9.7119	1
	Kerosene addition	0.00411	-0.3364	5.7620	1
	Naphtha addition	0.00639	-0.4082	5.7597	0.99935
SUNOXI	Temperature	0.00133	-0.2451	13.1030	0.99999
	Kerosene addition	0.00778	-0.4562	7.8058	0.99997
	Naphtha addition	0.0112	-0.5372	7.8059	0.99993
W-F11A	Temperature	9.02E-04	-0.1953	10.9541	1
	Naphtha addition	0.0119	-0.5150	6.6346	0.99999

Using the fitting equation, bitumen viscosity can be calculated for any temperature and for any solvent addition. Correlations between solvent addition and temperature based on bitumen viscosity were established via the Goal Seeker tool in Microsoft Excel. We are then able to determine the required solvent addition which equates to the viscosity at a particular temperature.

From ore characterization we previously determined bitumen weight percent of each ore. The bitumen content in each ore is then used to determine the necessary ore solvent dilution that equates to a bitumen viscosity at 25, 35, 45 and 50 ^{o}C. The assumption in this research is that the added solvent only interacts with the bitumen in the oil sand ore.

Bitumen viscosities at the temperatures of interest (25, 35, 45, and 50 °C), and the associated solvent additions (kerosene and naphtha) are listed in Table 4.3. When comparing the solvents more kerosene should be added to match the bitumen viscosity by naphtha addition. This is in agreement with Seyer and Gyte

(1989). Ores with higher bitumen content require more solvent dilution to achieve a desired bitumen viscosity reduction.

Table 4.3 Correlation of temperature and solvent addition and determination of solvent addition for bitumen extraction at 25 °C

Oil sands	Temperature (°C)	Bitumen viscosity (Pa·s)	Kerosene addition		Naphtha addition	
			On bitumen basis (wt%)	On ore basis $\frac{\text{mg kerosene}}{\text{g ore}}$	On bitumen basis (wt%)	On ore basis $\frac{\text{mg naphtha}}{\text{g ore}}$
SYN704	25	318	0	0	0	0
	35	86	4.09	4	3.37	3
	45	27	8.11	9	6.72	7
	50	16	10.08	11	8.38	9
SUNOXI	25	2456	0	0	0	0
	35	470	3.88	5	3.31	4
	45	117	7.67	10	6.56	8
	50	65	9.51	13	8.16	11
W-F11A	25	761	-	-	0	0
	35	185	-	-	2.94	4
	45	54	-	-	5.96	9
	50	31	-	-	7.50	12

For future applications it is important to establish these solvent addition-temperature correlations, such that the feasibility of a low temperature operation can be assessed.

Kerosene-temperature and naphtha-temperature correlations are shown in Figures 4.7 and 4.8, respectively.

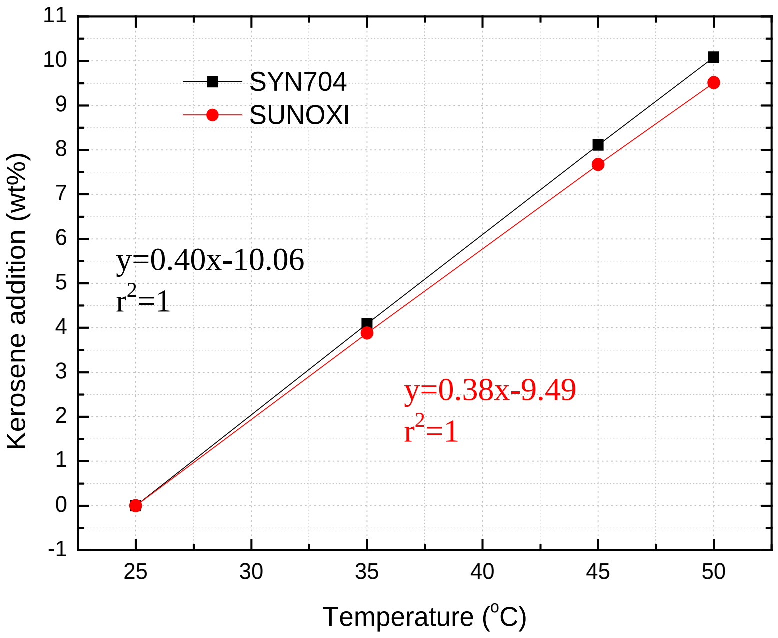


Figure 4.7 Correlation of temperature and kerosene addition for SYN704 and SUNOXI

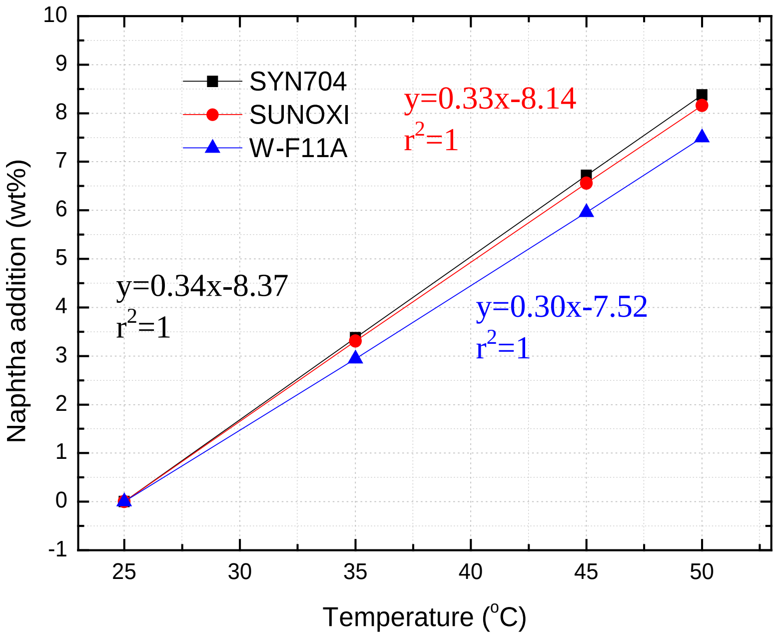


Figure 4.8 Correlation of temperature and naphtha addition for SYN704, SUNOXI and W-F11A

4.4 Influence of bitumen viscosity on oil sand ores processability

Based on these correlations a series of bitumen recovery tests were conducted using a Denver flotation cell. Bitumen recovery and froth quality were measured for oil sand ores SYN704, SUNOXI and W-F11A.

4.4.1 Influence of bitumen viscosity on processability of SYN704

The viscosity effect on bitumen recovery for SYN704 (average ore) is shown in Figure 4.9. It should be noted that the units on the x-axis have been reversed to show increasing recovery with decreasing viscosity. This trend of increasing recovery with decreasing viscosity highlights the importance of viscosity in the extraction process, and underlines the importance of achieving an accurate viscosity measurement such that recoveries can be better predicted.

Figure 4.9 shows that to achieve a recovery greater than 80% bitumen viscosities are to be within the range of 20-45 Pa·s, which is higher than the critical viscosity range (0.5-6 Pa·s) indentified by Hupka et al. (2004). With viscosity greater than 25 Pa·s, it is shown that kerosene addition and temperature increase achieve similar bitumen recoveries. Lower than 25 Pa·s temperature increase is superior to kerosene addition. Over the viscosity range kerosene addition and temperature increase offer significantly enhanced bitumen recoveries over naphtha addition.

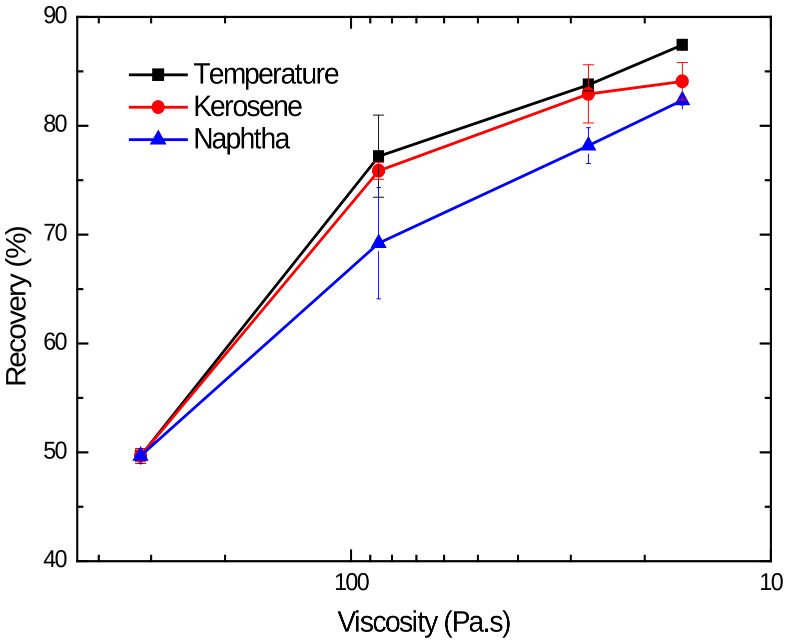


Figure 4.9 Bitumen recovery as a function of bitumen viscosity for average ore SYN704

Bitumen froth quality (bitumen:solids mass ratio) as a function of the measured bitumen viscosity is shown in Figure 4.10. The large standard deviation for the "control" case (25 ºC, no solvent addition) most likely results from ore heterogeneity.

Figure 4.10 shows that the "control" condition produces the best froth quality, indicating that bitumen viscosity reduction through temperature or solvent addition recovers more fines in the froth. In the case of solvent addition, the unwanted effect on froth quality is much greater, which may correspond to changes in solids wettability. Solvent addition may modify the hydrophobicity of the fines and increase the degree of slime coating. Over the viscosity range considered, temperature adjustments result in the highest froth quality.

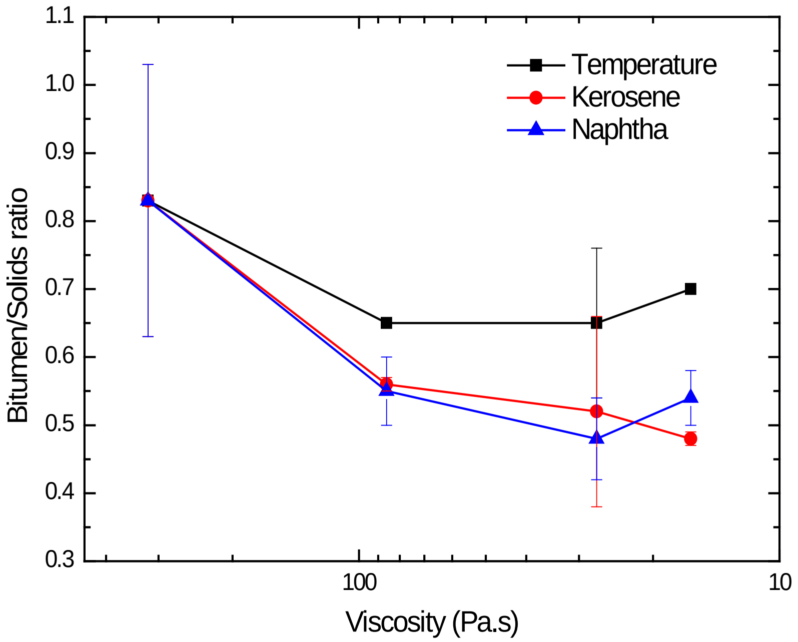


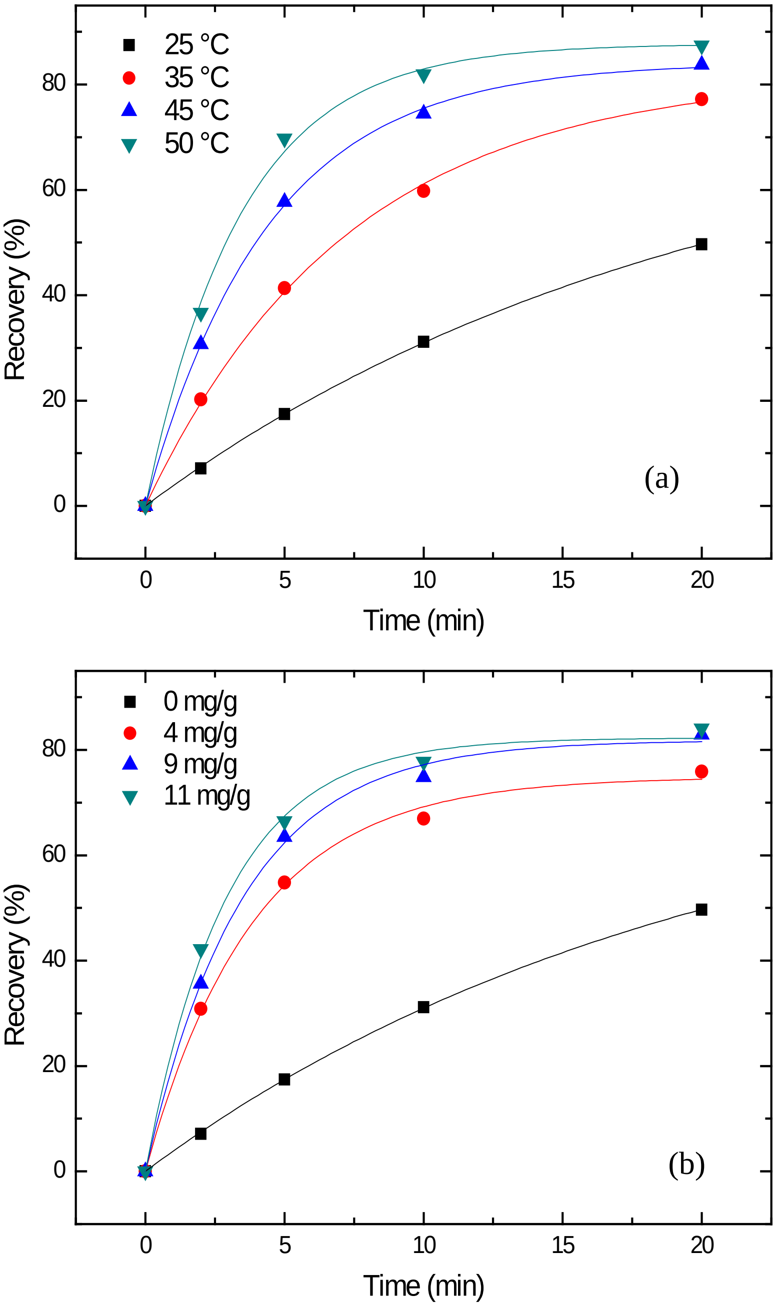
Figure 4.10 Bitumen to solids ratio as a function of bitumen viscosity for average ore SYN704

Figures 4.11 (a), (b) and (c) show bitumen recoveries as a function of flotation time for SYN704 at different temperatures, kerosene and naphtha additions. It is clearly shown that bitumen recoveries are slightly different depending upon the ore treatment method, yet the trends of improved bitumen recovery with reducing bitumen viscosity are very similar.

To quantitatively evaluate the kinetic behaviour of each ore, a commonly used first order kinetic model was chosen (Zhou et al., 2004; Liu et al., 2005):

$$R_t = R_\infty (1 - e^{-kt}) \tag{4-3}$$

where R_t and R_∞ represent the bitumen recovery at time t and t_∞ (ultimate recovery), respectively and, *k* is the flotation rate constant.


■ 25 °C
● 35 °C
▲ 45 °C
▼ 50 °C
Recovery (%)
0
20
40
60
80
Time (min)
0
5
10
15
20
(a)
■ 0 mg/g
● 4 mg/g
▲ 9 mg/g
▼ 11 mg/g
Recovery (%)
0
20
40
60
80
Time (min)
0
5
10
15
20
(b)

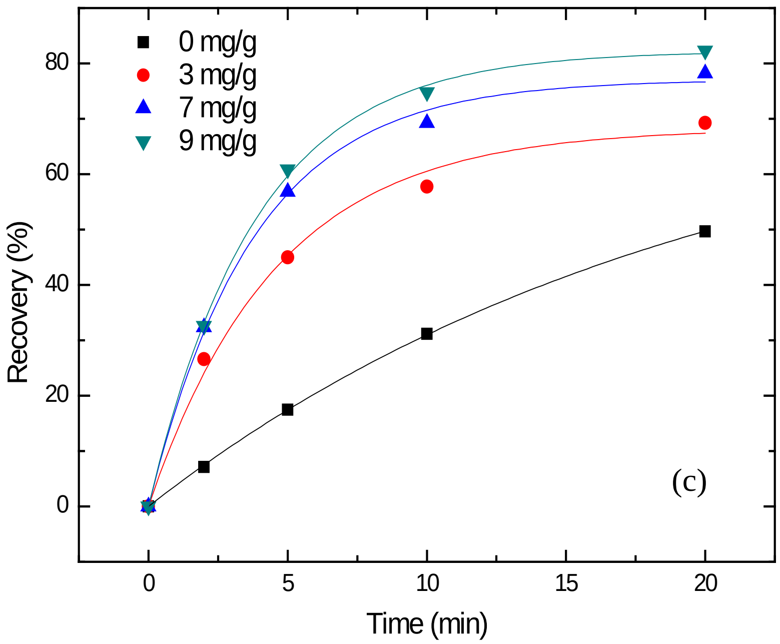


Figure 4.11 Bitumen recovery vs flotation time at different conditions for average ore SYN704 (a) at different temperatures (b) with different kerosene additions at 25 ^{o}C (c) with different naphtha additions at 25 ^{o}C, both (b) and (c) are on mg solvent/g ore basis

Equation 4-3 proved a good fit to the overall bitumen recovery data, see Figures 4.11 a, b and c. The curve fitting parameters for k and R_∞ are summarized in Table 4.4.

Table 4.4 Flotation rate constant (k) and ultimate recovery (R_∞) for SYN704

Bitumen viscosity (Pa·s)	Temperature adjustment with no solvent addition (^{o}C)			Solvent addition at 25 ^{o}C (mg solvent/g ore)					
	Temperature	k (min^{-1})	R_∞ (%)	Kerosene	k (min^{-1})	R_∞ (%)	Naphtha	k (min^{-1})	R_∞ (%)
318	25	0.05	78.4	0	0.05	78.4	0	0.05	78.4
86	35	0.14	82	4	0.26	74.9	3	0.22	68.3
27	45	0.23	84.1	9	0.29	81.8	7	0.26	77.1
16	50	0.29	87.7	11	0.34	82.3	9	0.26	82.2

Table 4.4 shows that the solvent addition flotation rate constants exceed the temperature rate constant in the viscosity range 318 to 86 Pa·s. At the same time the ultimate recovery by temperature increase is greater than that by solvent addition. With a further decrease in bitumen viscosity (86 to 27 Pa·s), the flotation rate constant for temperature increases significantly by 64%, while the solvent addition rate constants show a much smaller increase of 11% and 18% for kerosene and naphtha addition, respectively. Over this viscosity range, ultimate recoveries with solvent addition continue to increase significantly, while for temperature the increase is much smaller. Over the final viscosity decrease from 27 to 16 Pa·s, the temperature flotation rate constant increased by 26% and for kerosene addition by 17%, while the rate constant for naphtha remained unchanged. Independent of the technique to modify viscosity, ultimate recoveries of greater than 80% could be achieved as the viscosity is reduced to 16 Pa·s. Over the viscosity range it was observed that the temperature effect on ultimate recovery was consistently higher than the ultimate recoveries from solvent additions. These general findings are in agreement with Lelinski et al. (2004) who showed that the rates of recession and liberation of bitumen are low when viscosity is high, hence, lowering the efficiency of bitumen separation.

4.4.2 Influence of bitumen viscosity on processability of SUNOXI

As discussed in Section 2.1.2, weathered ores are considered poor processing ores due to the loss of innate water. Several studies have considered the mechanisms involved when processing weathered ores (Dang-Vu et al., 2009; Ren et al., 2009a; 2009b; 2009c; Wang et al., 2010). However, research on bitumen viscosity effect on weathered ore processability has not yet been reported. This section and the section after will focus on this topic.

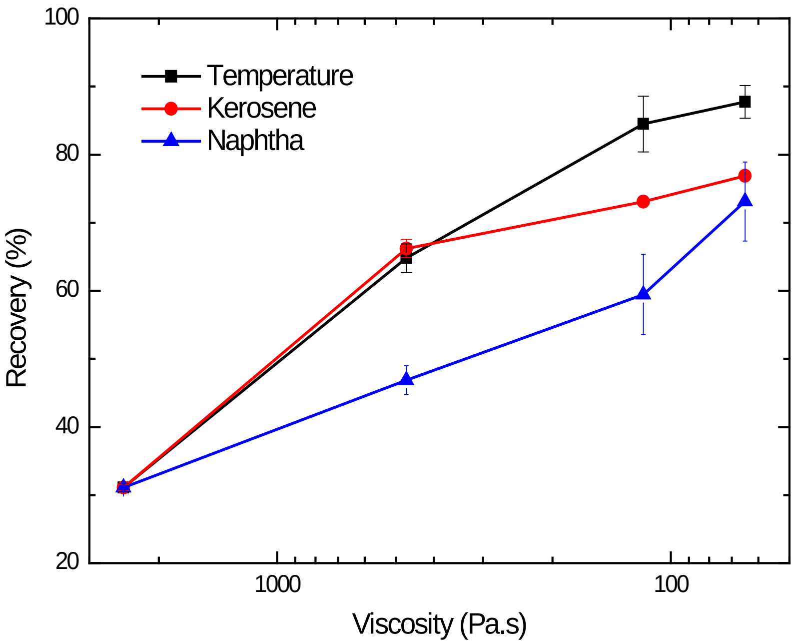


Figure 4.12 Bitumen recovery as a function of bitumen viscosity for naturally weathered ore SUNOXI

SUNOXI which is a naturally weathered ore is regarded as a poor processing ore due to its low recovery. Figure 4.12 shows the effect of bitumen viscosity (modified by temperature and solvent addition) on recovery. All cases show an increase in recovery with a decrease in viscosity. Overall, recoveries by temperature increase exceed those associated with solvent addition, which is in agreement with the study of Schramm et al. (2003a), who measured better recoveries from temperature increase compared to the addition of kerosene. Recovery from naphtha addition can be considered poor over the viscosity range, which most likely relates to the low solvent solubility in the aqueous slurry at low processing temperatures (Schramm et al., 2003b). To obtain a recovery greater than 80%, bitumen viscosities should be less than 170 Pa·s, a value much higher than the critical viscosity range published by Hupka et al. (2004).

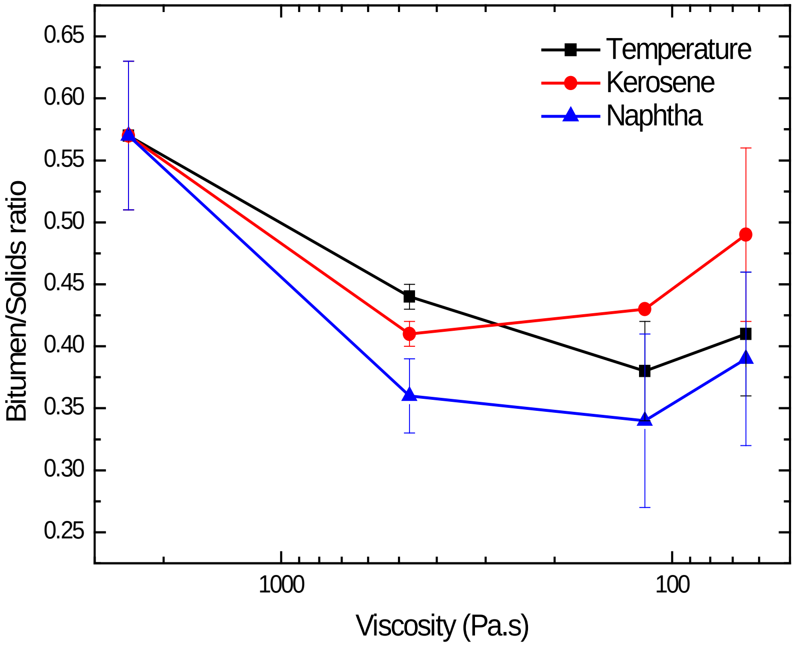
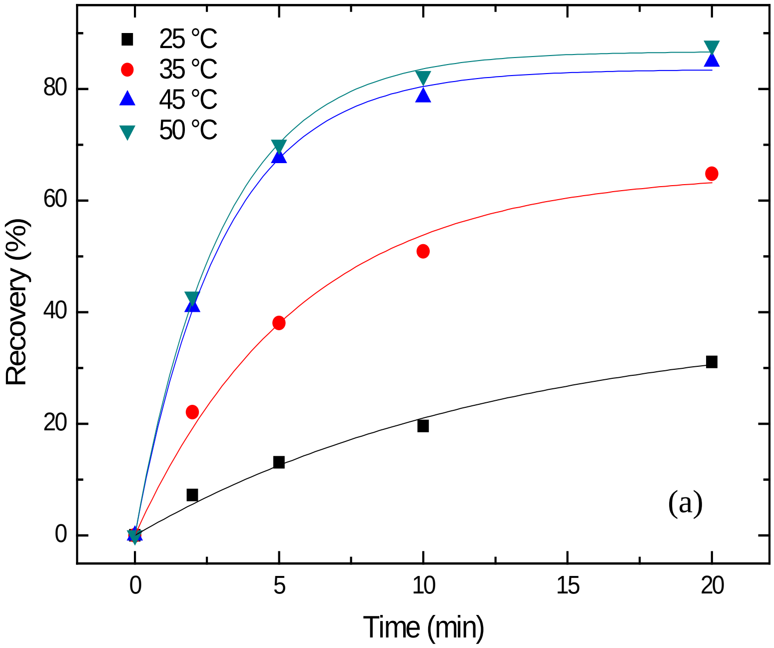


Figure 4.13 Bitumen to solids ratio as a function of bitumen viscosity for naturally weathered ore SUNOXI

The effect of viscosity on bitumen froth quality (bitumen/solids) is shown in Figure 4.13. At viscosities greater than 500 Pa·s, froth qualities from kerosene addition and temperature increase are reasonably similar (temperature provides a slightly better froth quality), which is in agreement with the recovery data. At much lower viscosities a transition point is measured where kerosene addition begins to greatly improve froth quality, and hence, improves against temperature increase. This transition may relate to changes in the solids hydrophobicity at high temperatures, where the solids become more hydrophilic thus improving bitumen liberation. While at the same time bitumen releases more natural surfactants that promote increased recovery of water and solids in the froth (Sanford, 1983). Froth quality from naphtha addition is consistently poor corresponding to its poor recovery.



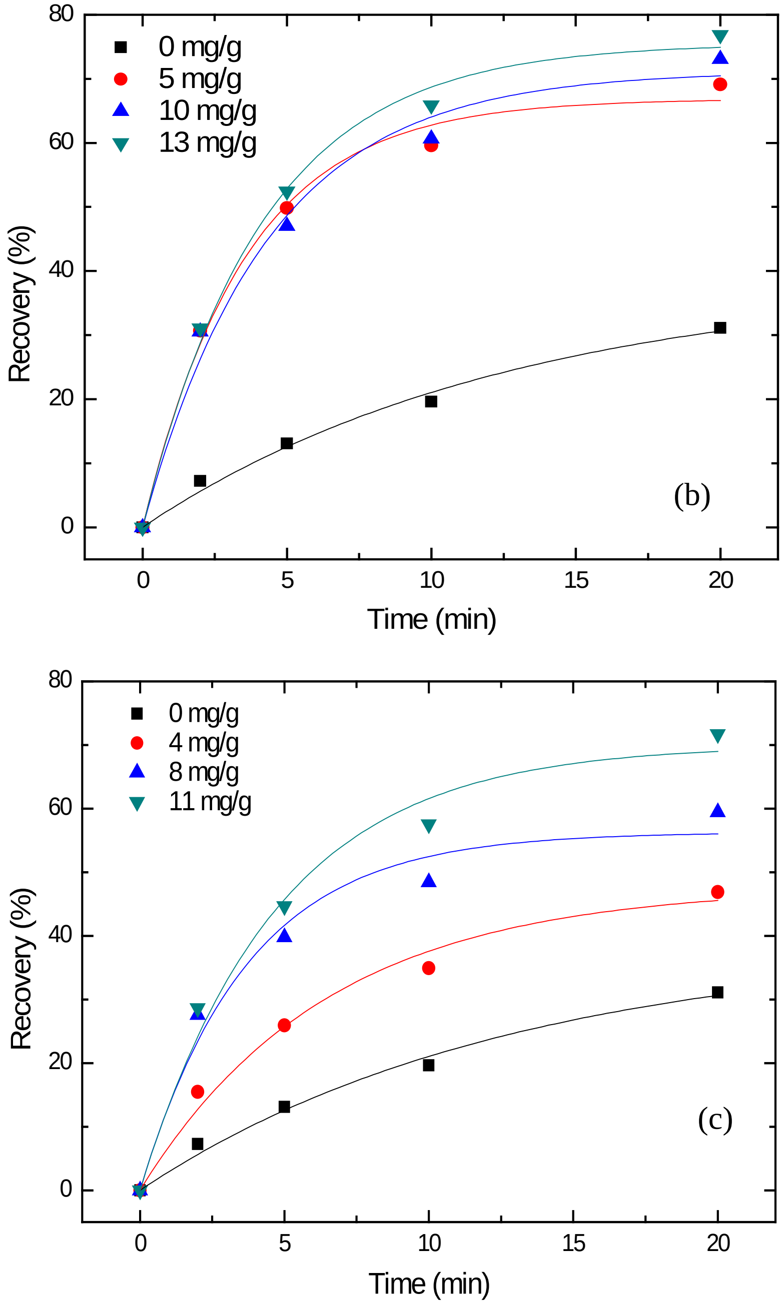


Figure 4.14 Bitumen recovery vs flotation time at different conditions for naturally weathered ore SUNOXI (a) at different temperatures (b) with different kerosene additions at 25 ºC (c) with different naphtha additions at 25 ºC, both (b) and (c) are on mg solvent/g ore basis

Figures 4.14 (a), (b) and (c) show bitumen recoveries as a function of flotation time for the naturally weathered ore SUNOXI, at different temperatures, kerosene and naphtha additions. To evaluate flotation performance, Equation 4-3 was used to calculate flotation rate constants k and ultimate flotation recoveries R_∞. These results are shown in Table 4.5.

Table 4.5 Flotation rate constant (k) and ultimate recovery (R_∞) for SUNOXI

Bitumen viscosity (Pa·s)	Temperature adjustment with no solvent addition (°C)			Solvent addition at 25 °C (mg solvent/g ore)					
	Temperature	k (min^{-1})	R_∞ (%)	Kerosene	k (min^{-1})	R_∞ (%)	Naphtha	k (min^{-1})	R_∞ (%)
2456	25	0.08	38.7	0	0.08	38.7	0	0.08	38.7
470	35	0.17	65.2	5	0.28	66.9	4	0.15	47.7
117	45	0.33	83.5	10	0.23	71.2	8	0.27	56.3
65	50	0.33	86.7	13	0.24	75.5	11	0.21	70

Table 4.5 shows that temperature increase has a greater impact on R_∞. For solvent additions, flotation rate constants show a maximum at 0.28 min^{-1} and 0.27 min^{-1} for kerosene and naphtha, respectively, whereas R_∞ continues to increase with decreasing bitumen viscosities. Within the bitumen viscosity range, kerosene addition enhances R_∞ more than naphtha which is most likely due to their solubilities in the oil sand ore.

4.4.3 Influence of bitumen viscosity on processability of W-F11A

Figure 4.15 shows bitumen recoveries as a function of bitumen viscosity for temperature increase and naphtha addition. At the lowest bitumen viscosity, recovery through temperature increase (50 ºC) is greater than 90%, while for naphtha (12 mg naphtha/ g ore) it is much lower at only 47%, compared to an initial recovery of 26% for the “control” case (25 ºC, no naphtha addition). This shows that naphtha has very limited effect on improving bitumen recovery for this laboratory weathered ore compared with temperature increase approach. If we are to consider Hupka's criteria for good recovery (>80%), a bitumen viscosity lower than 70 Pa.s would be required, again this value considerably exceeds the 0.5-6 Pa.s region specified by Hupka et al. (2004).

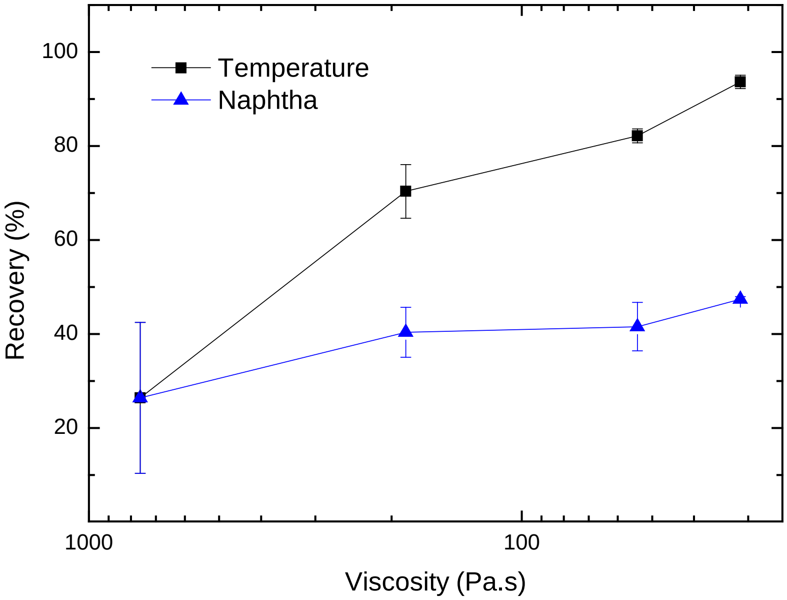


Figure 4.15 Bitumen Recovery as a function of bitumen viscosity for laboratory weathered ore W-F11A

It is widely reported that weathering/aging leads to evaporation of the connate water and volatile hydrocarbons and, oxidation changes the chemical and surface properties of the bitumen and mineral solids. These aging processes can increase the solids hydrophobicity (Liu et al., 2005; Ren et al., 2009a; 2009b; 2009c; Masliyah and Gray, 2010). Table 3.1 shows that the artificially weathered ore (W-F11A) has a low innate water content of 1.6 wt%, which can lead to greater interactions between bitumen and solids, and hence, increase the energy required for liberation. Ultimately, these changes have a negative effect on bitumen recovery.

From Figure 4.15, temperature increases can lead to good recoveries from the weathered ore, while naphtha has little effect. An explanation for the poor performance when naphtha is added to the oil sand ore is not known and further studies should be completed to gain a better understanding.

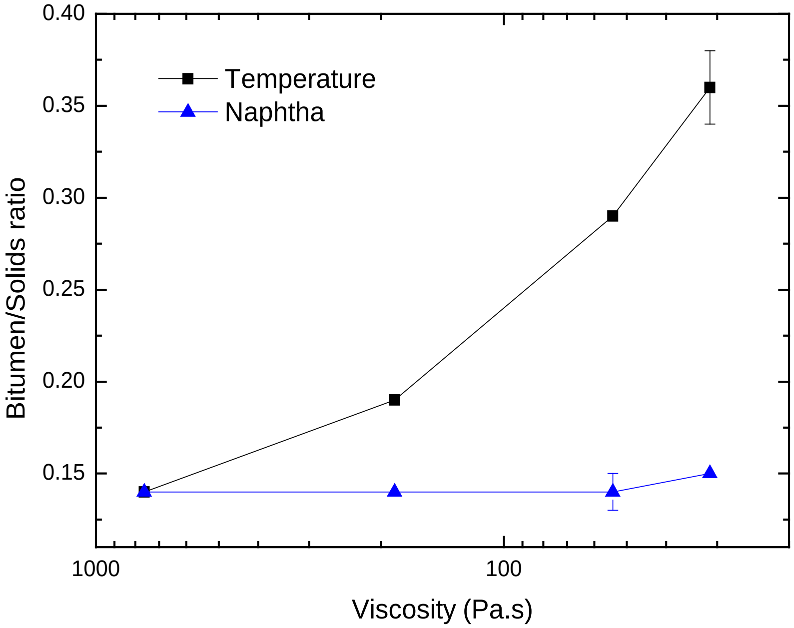


Figure 4.16 Bitumen to solids ratio as a function of bitumen viscosity for laboratory weathered ore W-F11A

The effect of bitumen viscosity on froth quality for W-F11A is shown in Figure 4.16. Unlike previous ores SYN704 and SUNOXI, froth quality is the poorest in the “control” case (25 ºC, no naphtha addition), improving with increasing temperature, but remaining independent of naphtha addition. The trend with temperature is dissimilar to the previous ores. For the weathered ore (W-F11A) a higher temperature is desirable to produce a better froth quality. This behaviour is consistent with the research of Ren et al. (2009b) who showed an improvement in bitumen froth quality at higher processing temperatures for an artificially weathered ore.

Figures 4.17 (a) and (b) show bitumen recoveries as a function of flotation time for the artificially weathered ore W-F11A at different temperatures and naphtha additions. Equation 4-3 was used to calculate the flotation rate constants k and ultimate flotation recoveries R_∞, with results listed in Table 4.6.

Table 4.6 Flotation rate constant (k) and ultimate recovery (R_∞) for W-F11A

Bitumen viscosity (Pa·s)	Temperature adjustment with no solvent addition (°C)			Naphtha addition at 25 °C (mg naphtha/g ore)		
	Temperature	k (min^{-1})	R_∞ (%)	Naphtha	k (min^{-1})	R_∞ (%)
761	25	0.07	45.1	0	0.07	45.1
185	35	0.19	69.3	4	0.31	36.7
54	45	0.18	98.9	9	0.25	39.4
31	50	0.19	95.8	12	0.24	45.3

In Table 4.6, over the viscosity range 761 to 3150 Pa·s, the flotation rate constant is higher for naphtha addition compared with temperature increase. While the ultimate recovery by temperature increase is significantly higher than that achieved through naphtha addition.

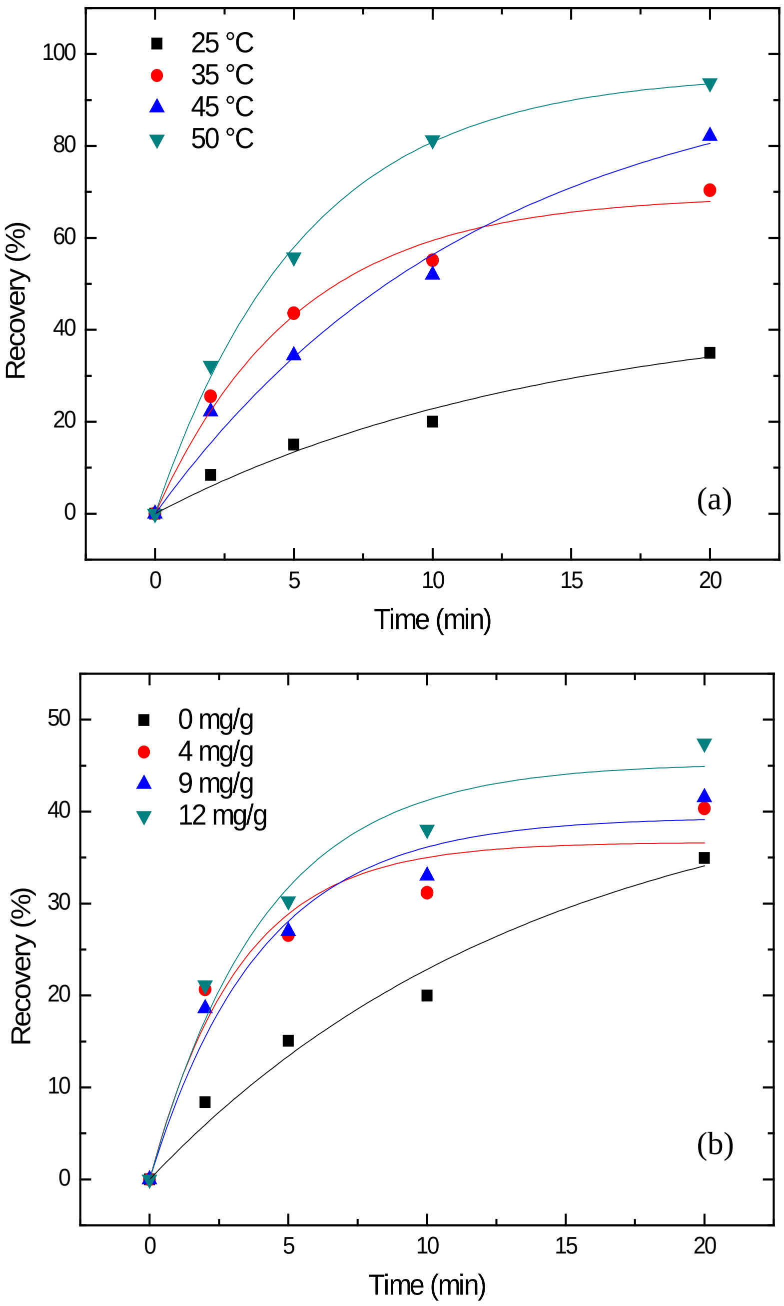


Figure 4.17 Bitumen recovery vs flotation time at different conditions for laboratory weathered ore W-F11A (a) at different temperatures (b) with different naphtha additions based on mg naphtha to g ore at 25 ºC

4.4.4 Comparison of viscosity effect on bitumen recovery for SUNOXI, SYN704 and W-F11A

Figure 4.18 provides a direct comparison of bitumen recoveries for three ores (SUNOXI, SYN704 and W-F11A), as well as the three types of viscosity modifier used throughout the study: i) temperature increase, ii) kerosene and iii) naphtha addition. Clearly, the case of W-F11A stands out as being particularly insensitive to naphtha addition, since the recovery remains low over the viscosity range. As previously discussed, such behaviour is not understood and should be studied further. There doesn't appear to be any clear trends, but we can say that temperature increase and kerosene addition lead to good recoveries as the viscosity is lowered.

If we are to compare the "control" cases, one would expect a lower bitumen viscosity to produce a higher recovery. This is certainly the case when comparing SUNOXI and SYN704. However, W-F11A which exhibits some "strange" behaviour, again fails to follow such a trend. With a viscosity in between SUNOXI and SYN704 it produces a recovery as low as 25%, 7% below the SUNOXI ore.

To achieve a recovery greater than 80%, a minimum viscosity range of 20~170 Pa·s is desirable (Figure 4.18, orange double dash lines). This wide range is clearly due to the critical condition being specific to the type of ore and the method of viscosity adjustment. Based on the data, it is clear that viscosity is not the only parameter that should be considered when analyzing recovery data. Previous researchers have shown that a multitude of parameters are equally important in bitumen recovery as discussed in Chapter 2 (Hupka et al., 2004; Masliyah et al., 2004).

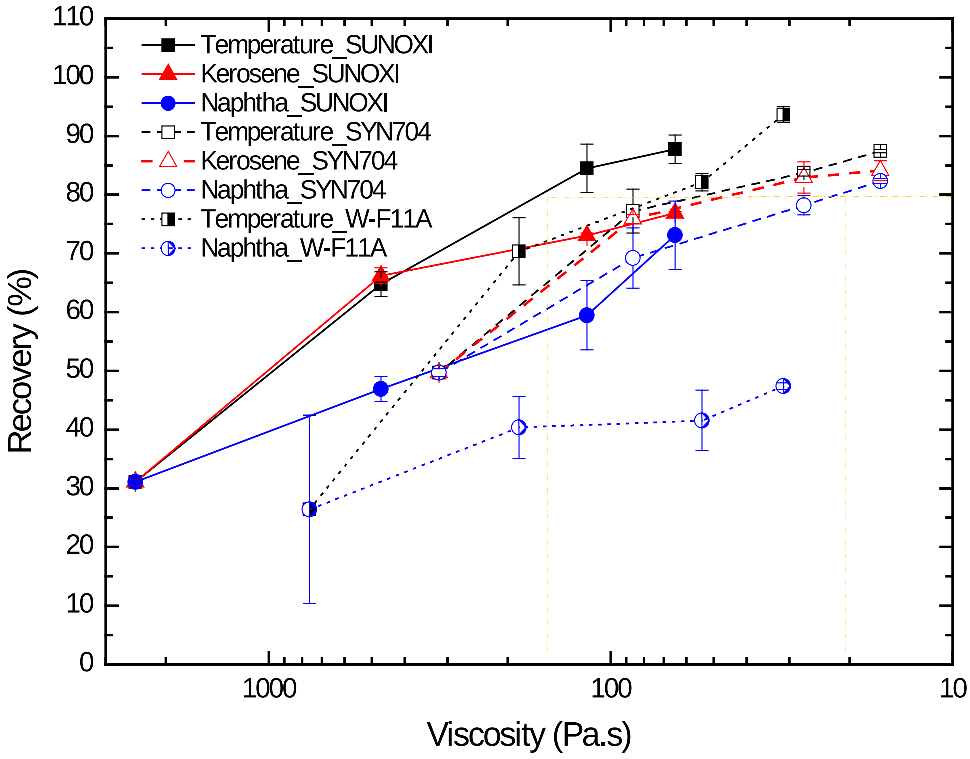
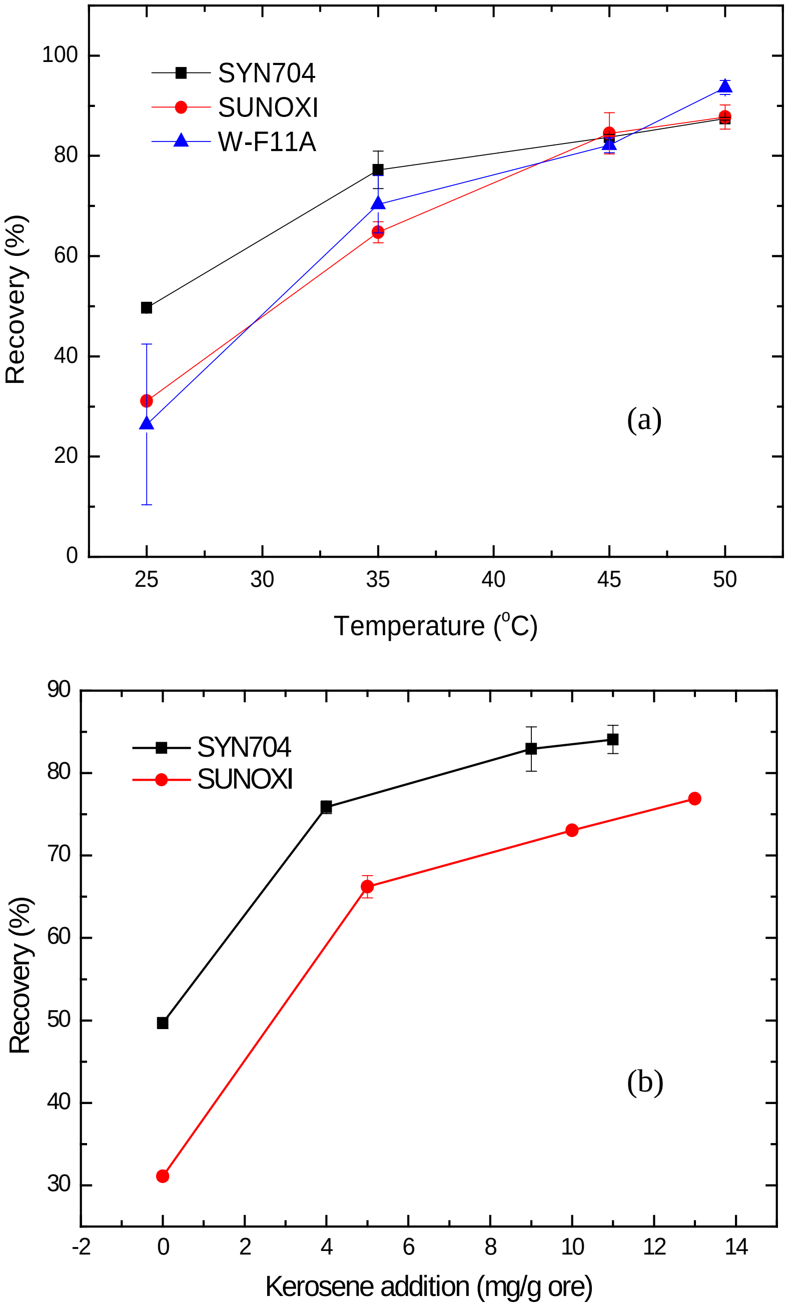


Figure 4.18 Bitumen recovery as a function of bitumen viscosity for naturally weathered ore SUNOXI, average ore SYN704, and laboratory weathered ore W-F11A

For ease of comparison, the effect of each viscosity adjustment method (temperature increase, kerosene and naphtha addition) on bitumen recovery is shown in Figures 4.19 (a), (b) and (c) for SUNOXI, SYN704 and W-F11A ores.



SYN704
SUNOXI
W-F11A
(a)
Recovery (%)
0
20
40
60
80
100
25
30
35
40
45
50
Temperature (°C)
SYN704
SUNOXI
(b)
Recovery (%)
30
40
50
60
70
80
90
-2
0
2
4
6
8
10
12
14
Kerosene addition (mg/g ore)

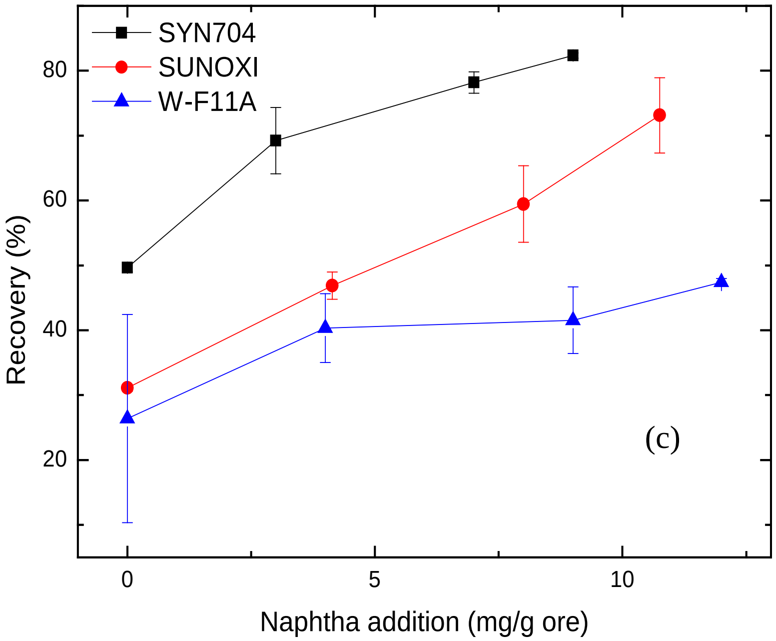


Figure 4.19 Temperature and solvent addition effect on bitumen recovery for naturally weathered ore SUNOXI, average ore SYN704, and laboratory weathered ore W-F11A (a) temperature effect (b) kerosene effect at 25 °C (c) naphtha effect at 25 °C

Figure 4.19 (a) shows the effect of temperature increase on bitumen recovery from 25 to 35 °C bitumen recovery doubles in the case of the two weathered ores (SUNOXI and W-F11A). Since the “control” case (25 °C, no solvent addition) starts high for average ore SYN704, bitumen recovery increases substantially for this ore but not doubles. It can be concluded that temperature increase is an effective means to improve bitumen recovery. Performance enhancements are significant and appear to be independent of ore type.

Figure 4.19 (b) shows the effect of kerosene addition on bitumen recovery for SYN704 and SUNOXI ores. At approximately 10 mg/g ore kerosene addition, bitumen recovery levels off and appears to become independent of solvent addition. Further tests at higher kerosene additions are needed to confirm this behaviour.

Figure 4.19 (c) shows the effect of naphtha addition on bitumen recovery. As we have shown throughout this section naphtha addition has a lesser effect on bitumen recovery when compared with kerosene. For naphtha we do not observe a plateau in recovery especially for SUNOXI and W-F11A, which is most likely a result of the lower recoveries measured over the viscosity range.

4.4.5 Comparison of viscosity effect on bitumen froth quality for SUNOXI, SYN704 and W-F11A

Froth quality as a function of bitumen viscosity is shown in Figure 4.20 for three ores. Clearly, there are a range of froth qualities which appear dependent on the type of ore. The froth quality (bitumen: solids) for each ore is: 0.5~0.8 (SYN704), 0.35~0.55 (SUNOXI), and 0.15~0.35 (W-F11A). Even though SYN704 has the most fines, it still produces high quality froths in comparison with SUNOXI and W-F11A. The experiments have shown that there is no specific relationship between bitumen viscosity and bitumen froth quality. It seems that the intrinsic physical and/or chemical properties of the oil sand ore govern the quality of froth produced.

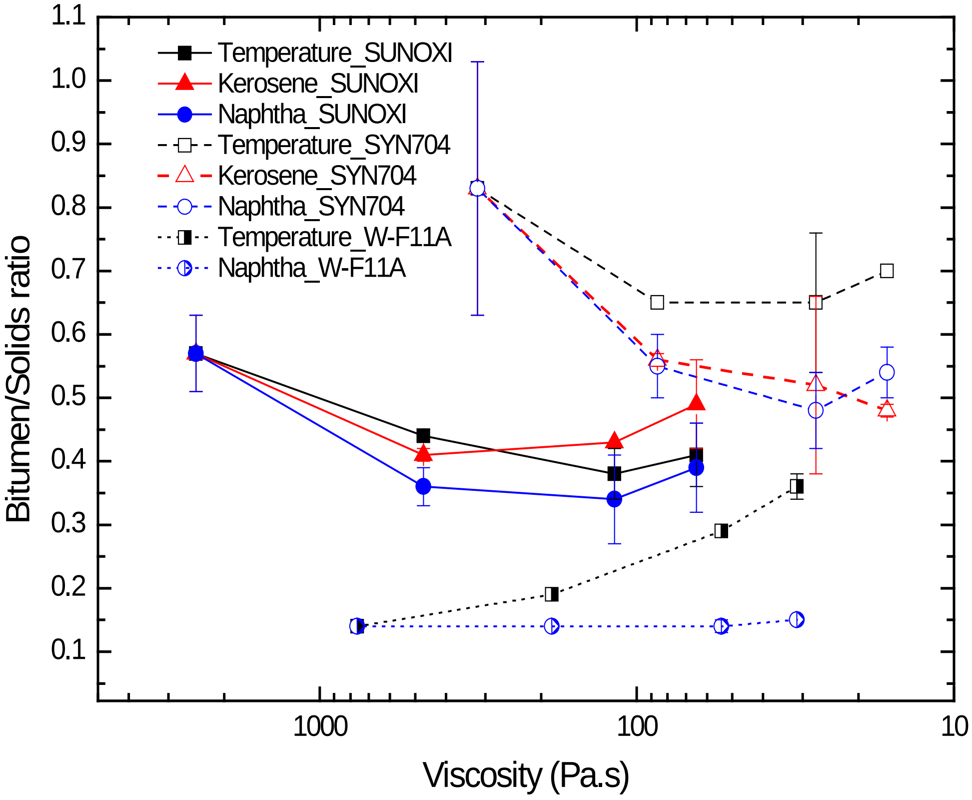
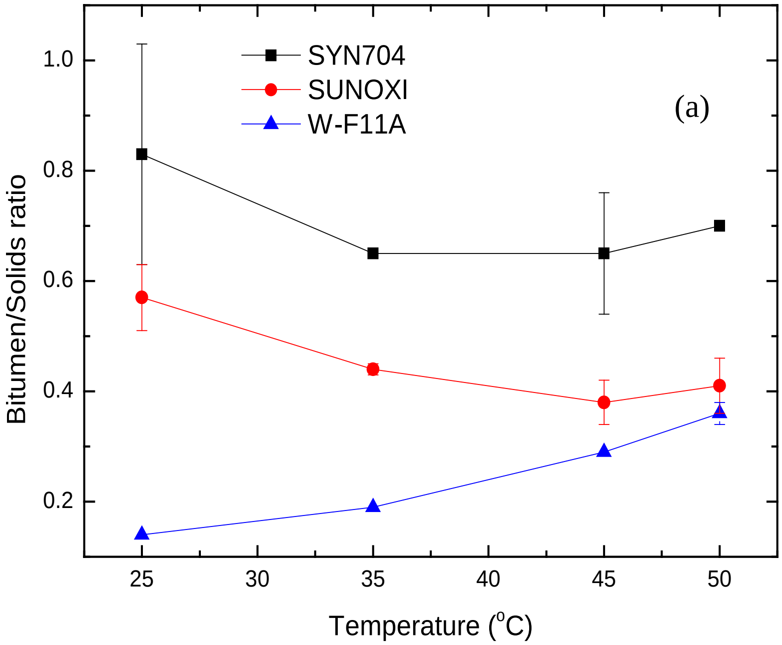


Figure 4.20 Bitumen to solids ratio as a function of bitumen viscosity for naturally weathered ore SUNOXI, average ore SYN704, and laboratory weathered ore W-F11A

Figures 21 (a), (b) and (c) compare froth qualities of each ore against the bitumen viscosity modified either by temperature increase or solvent addition. Figure 4.21 (a) shows temperature having little effect on froth quality. For SYN704 and SUNOXI ores, froth quality reduces from the control case with increasing temperature (25 ºC to 35 ºC). As the temperature exceeds 45 ^{o}C the froth quality is observed to slightly improve. Such improvements with temperature are in agreement with Long et al. (2005; 2007) who showed that the adhesion force between bitumen and clay reduces at temperatures greater than 35 ºC, hence improving froth quality. W-F11A ore shows a gradual improvement in froth quality with increasing temperature.

Figure 4.21 (b) shows the effect of kerosene addition on froth quality. Clearly, kerosene has a detrimental effect on froth quality for both SYN704 and SUNOXI froths reducing in quality with increasing dilution. Froth quality for SUNOXI decreases from 0 to 5 mg/g ore kerosene addition before slightly increases at higher kerosene concentrations. Froth quality for SYN704 keeps decreasing over the investigated kerosene addition range.



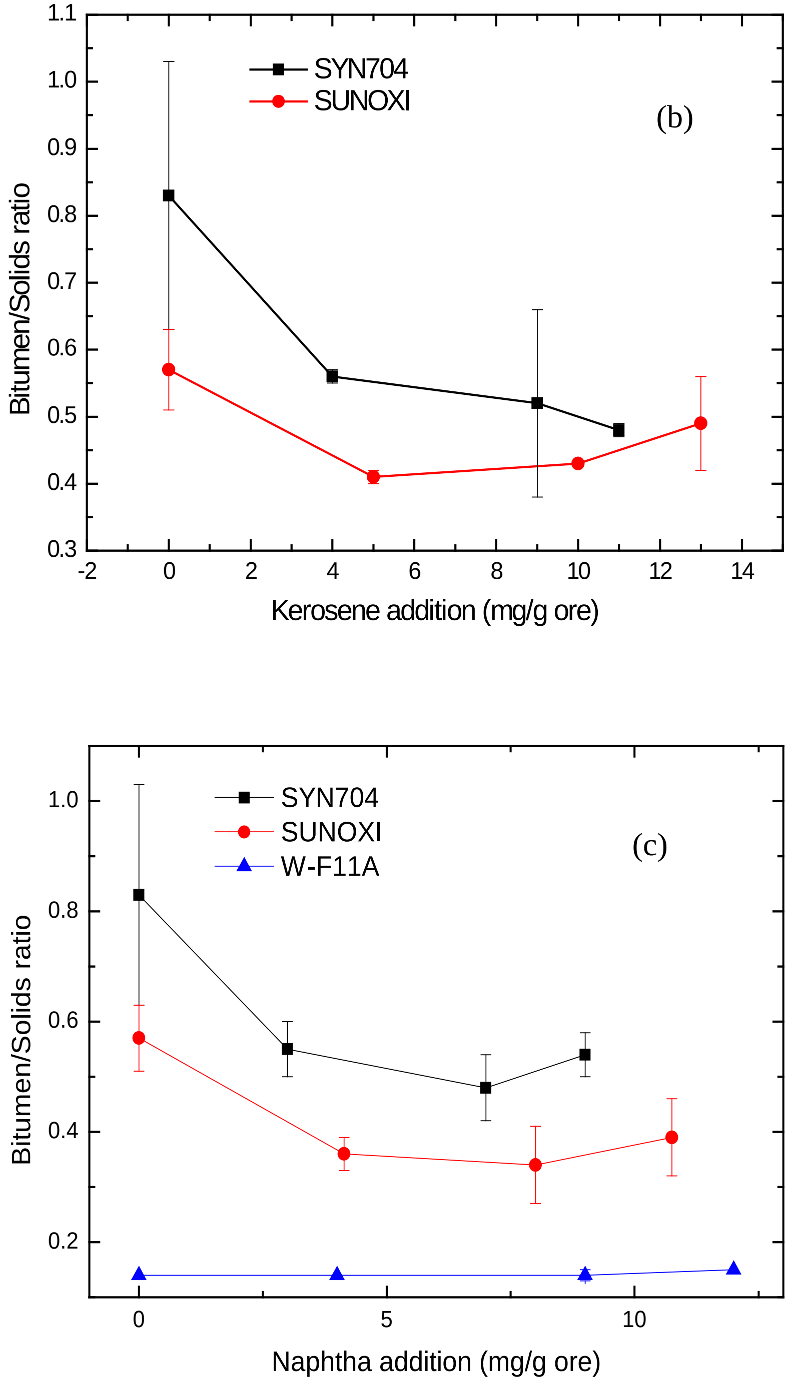


Figure 4.21 Temperature and solvent addition effect on bitumen froth quality for naturally weathered ore SUNOXI, average ore SYN704, and laboratory weathered ore W-F11A (a) temperature effect (b) kerosene effect at 25 °C (c) naphtha effect at 25 °C

As shown in Figure 4.21 (c), for both SYN704 and SUNOXI the cases with naphtha addition have a worse froth quality than the “control” case (25 ºC, no naphtha addition). The influence of naphtha addition on the froth quality of W-F11A is negligible.

Chapter 5 Conclusions and Suggestions for Future Research

Among the many factors influencing bitumen extraction from oil sand ores, the role of bitumen viscosity was investigated in this study. The experimental work included: i) isolate bitumen from oil sand ore using centrifugation, ii) measure the viscosity for the isolated bitumen using a rotational rheometer, with experimental variables including temperatures and solvent type and addition, and iii) evaluate the role of bitumen viscosity in the water-based bitumen extraction process.

5.1 Conclusions

1) Bitumen viscosity at same temperature appears ore specific; artificial weathering has slightly effect on bitumen viscosity; bitumen viscosity for naturally weathered ore is the highest among the four types of ores.
2) Processability of oil sand ores vary significantly among the examined ores at same bitumen viscosity reduction level. To achieve a satisfactory bitumen recovery of 80% or greater, bitumen viscosity needs to be controlled within the range of 20~170 Pa·s.
3) Bitumen froth quality in terms of bitumen to solids ratio is dominated by ore type, independent of processing conditions.

4) At the same viscosity reduction, kerosene is superior to naphtha in terms of bitumen recovery and bitumen froth quality.
5) Among all the investigated conditions, temperature increase produces an overall better processability than solvent addition cases.
6) Among all the examined ores, the overall processability of the average ore is the best, whereas the overall processability of the artificially weathered ore is the worst at all conditions.
7) Solvent addition could be an alternative to thermal energy adjustment for the water-based bitumen extraction process however it is not the case for artificially weathered ore tested in this study.

5.2 Suggestions for future work

Though thermal adjustment brings better overall performance for the water-based bitumen extraction process, the cost and environmental issues are becoming increasingly more important for today's oil sand industries. Fuel cost and the greenhouse gas emissions make low temperature solvent-water hybrid process a promising alternative. Some research even goes further to investigate the feasibility of non-aqueous extraction (Mani, 2010).

In this research, the role of bitumen viscosity is highlighted. However, for a complex system such as the solvent-assisted water-based bitumen extraction process, the roles of many other factors especially the interfacial properties between or among the components in the system need to be identified in order to gain a better understanding of the extraction mechanism, thus improving bitumen recovery from oil sand ores.

The following recommendations are made for future research into solvent-water hybrid bitumen extraction process:

1) Differentiate the function of kerosene and naphtha addition on ore processability. Study the interfacial properties between bitumen and clay, bitumen and air bubble, clay and air bubble in the solvent-assisted bitumen extraction process.
2) Investigate solvent distribution in both bitumen froth and tailings. Investigate any possible solvent loss in the whole process and find solutions to minimize the loss.
3) Investigate the feasibility to reduce the intake of water in the solvent-assisted process. Find out the minimum operable water intake for such a process.
4) Find other process aids favourable both bitumen liberation and aeration and depressing solids flotation. Meanwhile, the economy of the selected process aids should be considered.

References

Bazyleva, A. B.; Hasan, A.; Fulem, M.; Becerra, M.; Shaw, J. M., *Journal of Chemical and Engineering Data* **2010** 55(3): 1389-1397.

Blair, S. M., *Report on the Alberta Bituminous Sands*. **1951**.

Bulmmer, J. T.; Starr, J., *Syncrude Analytical Methods for Oil Sand and Bitumen Processing* **1979**: 58-68.

Clark, K. A.; Blair, S. M., *The Bituminous Sands of Alberta Part ⅠⅡⅢ.* **1927** Edmonton.

Clark, K. A.; Pasternack, D. S., *Industrial and Engineering Chemistry* **1932** 24: 1410-1416.

Cragoe, C. S., *World Petroleum Congress Proc.* **1933** Ⅱ: 529.

Cymerman, G. J., Ng, S., Siy, R., and Spence, J., Paper 2191, CIM Mining Conference & Exhibition--Vancouver, BC, Canada (2006).

Dai, Q.; Chung, K. H., *Fuel* **1996** 75(2): 220-226.

Dang-Vu, T.; Jha, R.; Wu, S. Y.; Tannant, D. D.; Masliyah, J.; Xu, Z. H., *Colloids and Surfaces a-Physicochemical and Engineering Aspects* **2009** 337(1-3): 80-90.

Darcovich, K.; Kotlyar, L. S.; Tse, W. C.; Ripmeester, J. A.; Capes, C. E.; Sparks, B. D., *Energy & Fuels* **1989** 3(3): 386-391.

Dealy, J. M., *Canadian Journal of Chemical Engineering* **1979** 57(6): 677-683.

Dean, E. W.; Stark, D. D., *Journal of Industrial and Engineering Chemistry-Us* **1920** 12: 486-490.

Ding, X. L.; Repka, C.; Xu, Z. H.; Masliyah, J., *Canadian Journal of Chemical Engineering* **2006** 84(6): 643-650.

ERCB, *Energy Resources Conservation Board ST98:Alberta's Energy Reserves 2010 and Supply/Demand Outlook 2011-2020* **2011**: 1-18.

Gu, G. X.; Xu, Z. H.; Nandakumar, K.; Masliyah, J., *International Journal of Mineral Processing* **2003** 69(1-4): 235-250.

Harjai, S. K., *M.Sc. Thesis, University of Alberta (Canada)* **2007**.

Hasan, M. A.; Fulem, M.; Bazyleva, A.; Shaw, J. M., *Energy and Fuels* **2009** 23(10): 5012-5021.

Henry, D.; Fuhr, B., *Fuel* **1992** 71(12): 1515-1518.

Hupka, J.; Cortez, A.; Miller, J. D., *Min. Eng. (Littleton, Colo.) ; Vol/Issue: 35:12* **1983**: Pages: 1635-1640.

Hupka, J.; Miller, J. D., *Minerals and Metallurgical Processing* **1993** 10(3): 139-144.

Hupka, J.; Miller, J. D.; Drelich, J., *Canadian Journal of Chemical Engineering* **2004** 82(5): 978-985.

Hupka, J.; Oblad, A. G.; Miller, J. D., *AOSTRA J.* **1987** 3: 95-102.

Kasongo, T.; Zhou, Z.; Xu, Z. H.; Masliyah, J., *Canadian Journal of Chemical Engineering* **2000** 78(4): 674-681.

Leja, J.; Bowman, C. W., *Canadian Journal of Chemical Engineering* **1968** 46(6): 479-&.

Lelinski, D.; Drelich, J.; Miller, J. D.; Hupka, J., *Canadian Journal of Chemical Engineering* **2004** 82(4): 794-800.

Liu, J.; Mak, T.; Zhou, Z.; Xu, Z., *Minerals Engineering* **2002a** 15(9): 667-676.

Liu, J.; Zhou, Z.; Xu, Z.; Masliyah, J., *Journal of Colloid and Interface Science* **2002b** 252(2): 409-418.

Liu, J. J.; Xu, Z. H.; Masliyah, J., *Canadian Journal of Chemical Engineering* **2004a** 82(4): 655-666.

Liu, J. J.; Xu, Z. H.; Masliyah, J., *AIChE Journal* **2004b** 50(8): 1917-1927.

Liu, J. J.; Xu, Z. H.; Masliyah, J., *Energy & Fuels* **2005** 19(5): 2056-2063.

Long, J.; Drelich, J.; Xu, Z. H.; Masliyah, J. H., *Canadian Journal of Chemical Engineering* **2007** 85(5): 726-738.

Long, J.; Xu, Z.; Masliyah, J. H., *Energy and Fuels* **2005** 19(4): 1440-1446.

Mani, F., *M.Sc. Thesis, University of Alberta (Canada)* **2010**.

Mardles, E. W. J., *Nature* **1940** 145: 970-970.

Masliyah, J.; Zhou, Z.; Xu, Z.; Czarnecki, J.; Hamza, H., *Canadian Journal of Chemical Engineering* **2004** 82(4): 628-654.

Masliyah, J. H.; Gray, M. R., *Oil Sands Extraction & Upgrading-Intensive Short Course Notes*. **2010** Calgary.

Miadonye, A.; Latour, N.; Puttagunta, V. R., *Petroleum Science and Technology* **2000** 18(1): 1-14.

Miadonye, A.; Singh, B.; Puttagunta, V. R., *Fuel Science & Technology International* **1995** 13(6): 681-698.

Miller, J. D.; Misra, M., *International Journal of Mineral Processing* **1982** 9(3): 269-287.

Miller, K. A.; Nelson, L. A.; Almond, R. M., *Journal of Canadian Petroleum Technology* **2006** 45(4): 42-48.

Misra, M.; Miller, J. D., *Fuel Processing Technology* **1991** 27(1): 3-20.

Moran, K.; Yeung, A., *Canadian Journal of Chemical Engineering* **2004** 82(4): 813-820.

Nguyen, A. V.; Evans, G. M.; Nalaskowski, J.; Miller, J. D., *Experimental Thermal and Fluid Science* **2004** 28(5): 387-394.

Potoczny, Z. M., Vargha-Butler, E.I., Zubovits, T.K. and Neumann, A.W., *AOSTRA J. Research* **1984a** 1(2): 107-115.

Potoczny, Z. M., Vargha-Butler, E.I., Zubovits, T.K. and Neumann, A.W., *AOSTRA Journal of Research* **1984b** 1(2): 117-120.

Qiu, L., *M.Sc. Thesis, University of Alberta (Canada)* **2010**.

Ren, S.; Dang-Vu, T.; Zhao, H.; Long, J.; Xu, Z.; Masliyah, J., *Energy & Fuels* **2009a** 23(1): 334-341.

Ren, S. L.; Zhao, H. Y.; Dang-Vu, T.; Xu, Z. H.; Masliyah, J. H., *Canadian Journal of Chemical Engineering* **2009b** 87(6): 879-886.

Ren, S. L.; Zhao, H. Y.; Long, J.; Xu, Z. H.; Masliyah, J., *AIChE Journal* **2009c** 55(12): 3277-3285.

Sanford, E. C., *Canadian Journal of Chemical Engineering* **1983** 61(4): 554-567.

Schramm, L. L.; Kwak, J. C. T., *Journal of Canadian Petroleum Technology* **1988** 27(1): 26-35.

Schramm, L. L.; Morrison, C.; Stasiuk, E. N., *Fuel Processing Technology* **1998** 56(3): 243-261.

Schramm, L. L.; Smith, R. G., *Colloids and Surfaces* **1985** 14(1): 67-85.

Schramm, L. L.; Smith, R. G.; Stone, J. A., *American Chemical Society* **1984** 187(APR): 73-PETR.

Schramm, L. L.; Smith, R. G.; Stone, J. A., *Colloids and Surfaces* **1984** 11(3-4): 247-263.

Schramm, L. L.; Stasiuk, E. N.; Yarranton, H.; Maini, B. B.; Shelfantook, B., *Journal of Canadian Petroleum Technology* **2003a** 42(8): 55-61.

Schramm, L. L.; Stasuik, E. N.; Turner, D., *Fuel Processing Technology* **2003b** 80(2): 101-118.

Seyer, F. A.; Gyte, C. W., *AOSTRA Technical Handbook on Oilsands, Bitumens and Heavy Oils* **1989** 6: 153-184.

Shu, W. R., *SPE Journal* **1984** 24(3): 277-282.

Stasiuk, E. N.; Schramm, L. L., *Fuel Processing Technology* **2001** 73(2): 95-110.

Su, L.; Xu, Z.; Masliyah, J., *Minerals Engineering* **2006** 19(6-8): 641-650.

Takamura, K., *Canadian Journal of Chemical Engineering* **1982** 60(4): 538-545.

Ukwuoma, O.; Ademodi, B., *Fuel Processing Technology* **1999** 60(2): 95-101.

Wallace, D., Ed. A Review of Analytical Methods for Bitumens and Heavy Oils. **1988** AOSTRA Technical Publication Series. Edmonton.

Wallace, D.; Henry D., *AOSTRA J.* **1987** 3: 239-248.

Wallace, D.; Polikar, M.; Ferracuti, F., *Fuel* **1984** 63(6): 862-864.

Wallwork, V.; Xu, Z.; Masliyah, J., *Canadian Journal of Chemical Engineering* **2003** 81(5): 993-997.

Wang, L. X.; Dang-Vu, T.; Xu, Z. H.; Masliyah, J. H., *Energy & Fuels* **2010** 24: 3581-3588.

Ward, S. H.; Clark, K. A., *Report 57, Research Council of Alberta* **1950**.

Wen, Y.; Kantzas, A., *Journal of Canadian Petroleum Technology* **2006** 45(4): 56-61.

Yang Y. J., K. B., and J. D. Miller, *Engery Processing/Canada* **1989**: 14-21.

Zhou, Z.; Kasongo, T.; Xu, Z.; Masliyah, J., *Canadian Journal of Chemical Engineering* **2004** 82(4): 696-703.

Appendix 1

This appendix shows the graphical method for correlation of solvent addition and temperature through bitumen viscosity. The two lines with arrows in each figure demonstrate how to determine the amount of solvent addition at 25 ºC by equalizing bitumen viscosity at 35 ºC with no solvent addition.

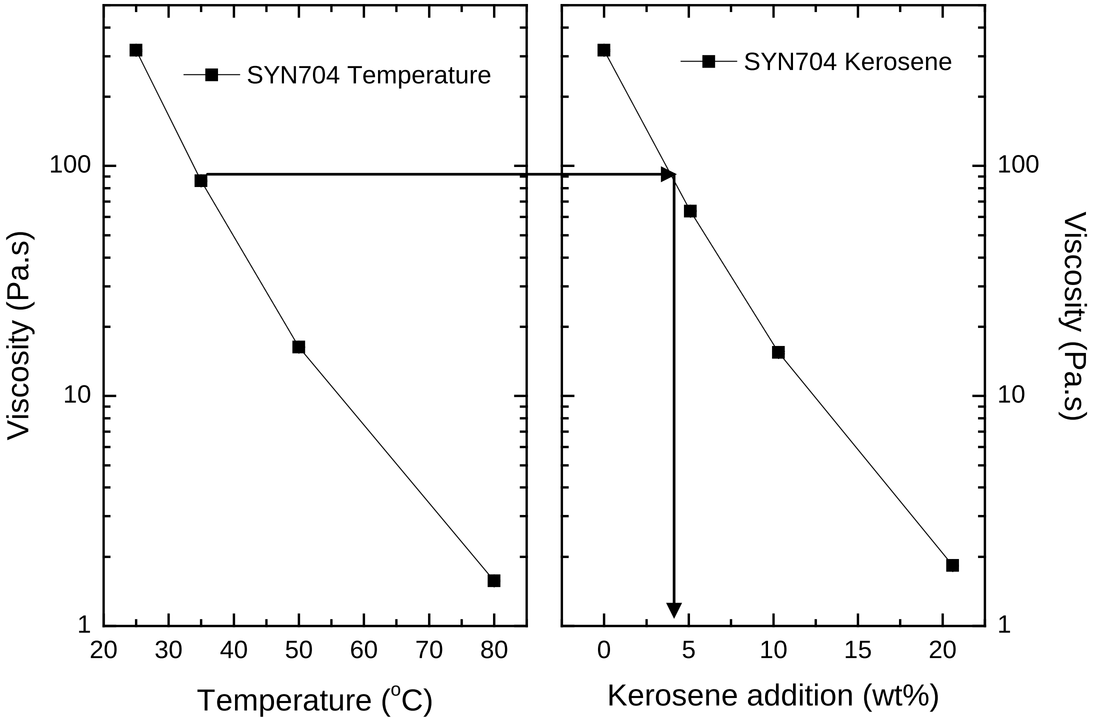


Figure A1.1 Determination of kerosene addition at 25 ºC for SYN704

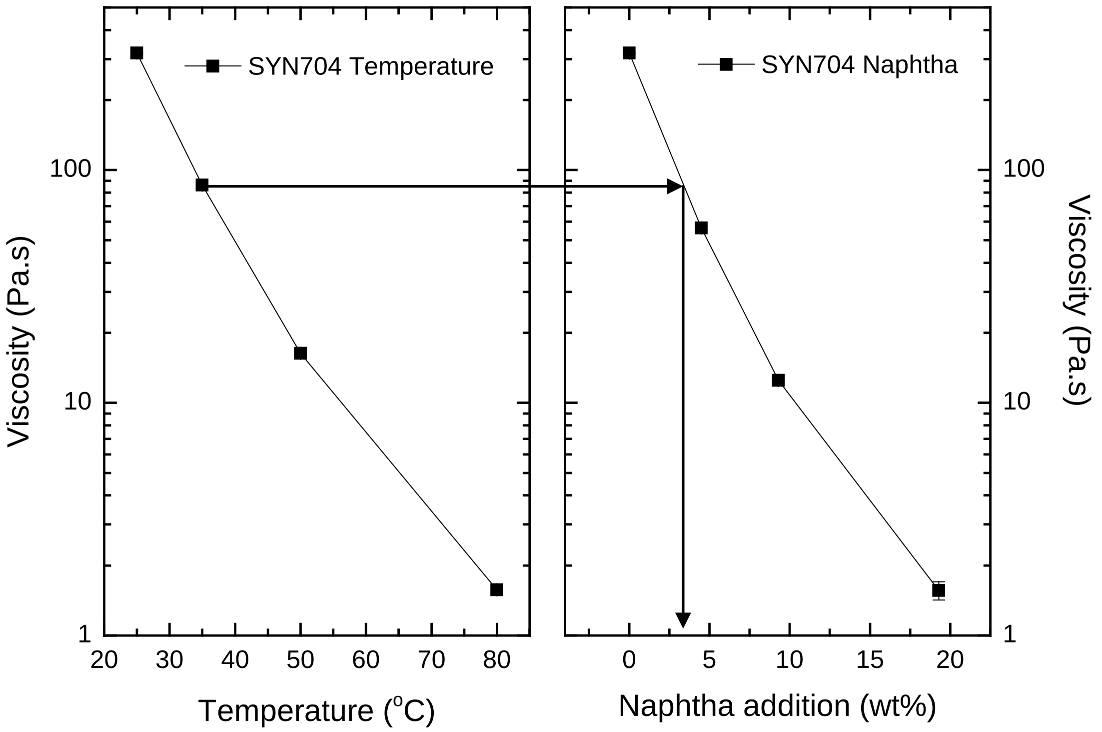


Figure A1.2 Determination of naphtha addition at 25 ºC for SYN704

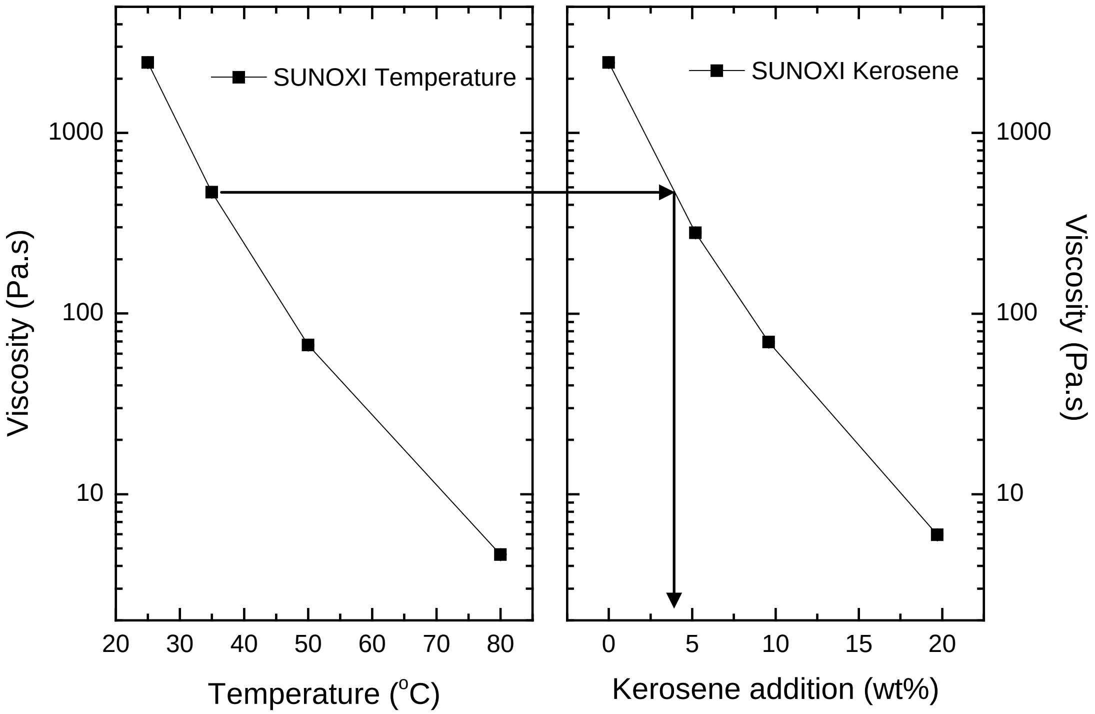


Figure A1.3 Determination of kerosene addition at 25 ºC for SUNOXI

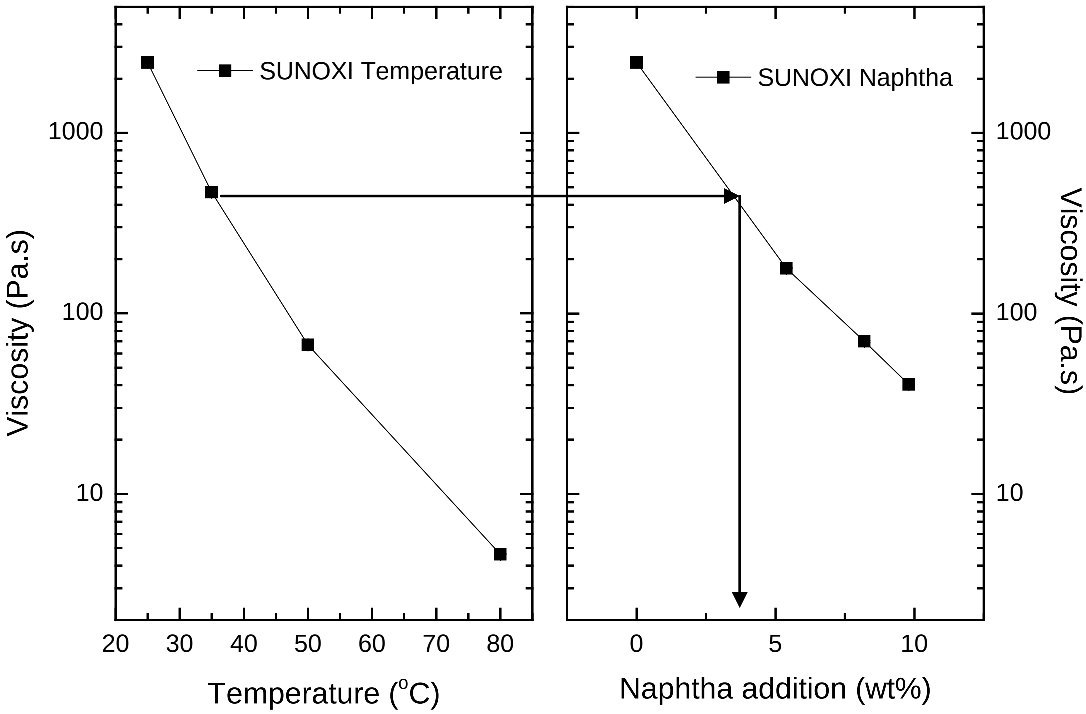


Figure A1.4 Determination of naphtha addition at 25 ºC for SUNOXI

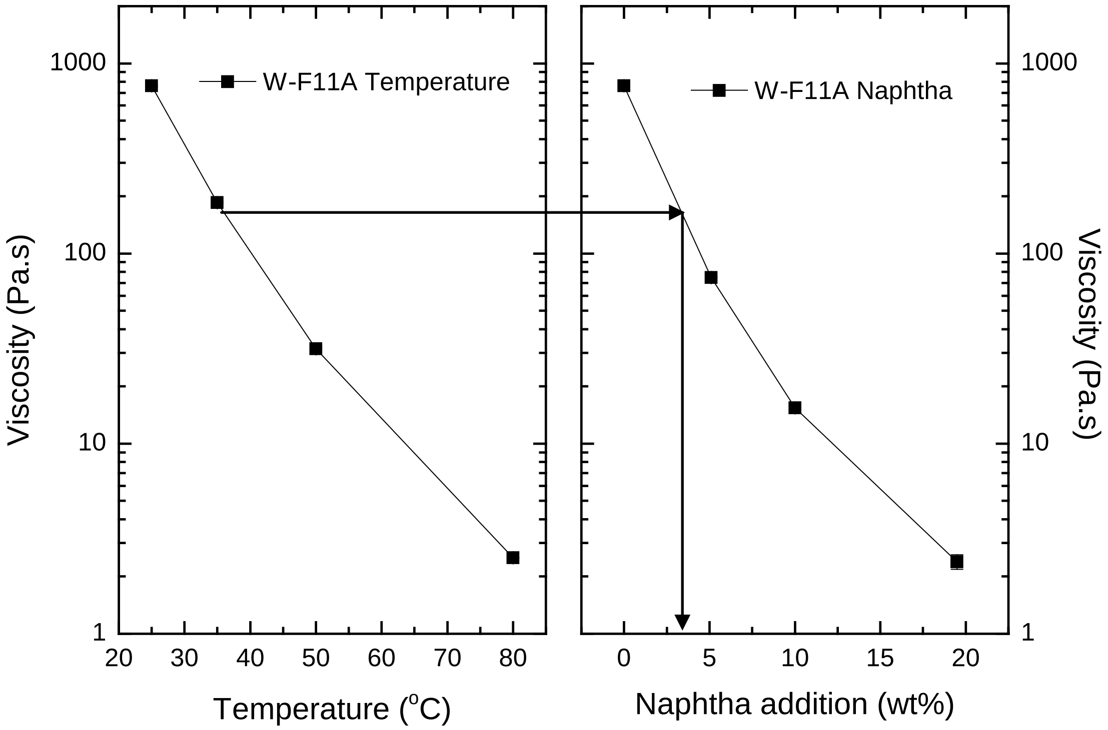


Figure A1.5 Determination of naphtha addition at 25 ºC for W-F11A

Appendix 2

This appendix shows the viscosity-vs-shear rate figures at different temperatures without solvent addition for four types of bitumen (F11A, SYN704, SUNOXI and WF11A) and with different solvent additions (kerosene and naphtha) at 25 °C for three types of bitumen (SYN704, SUNOXI and WF11A).

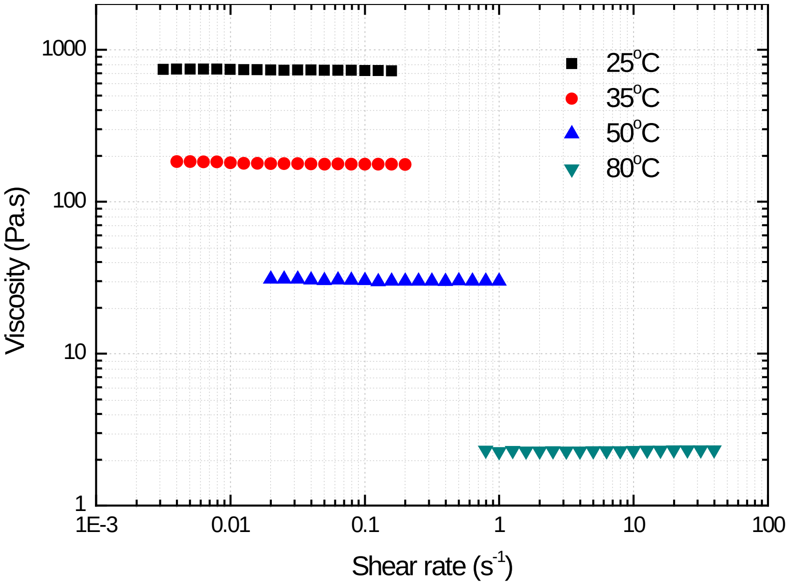


Figure A2.1 Viscosity vs shear rate for F11A bitumen at different temperatures without solvent addition

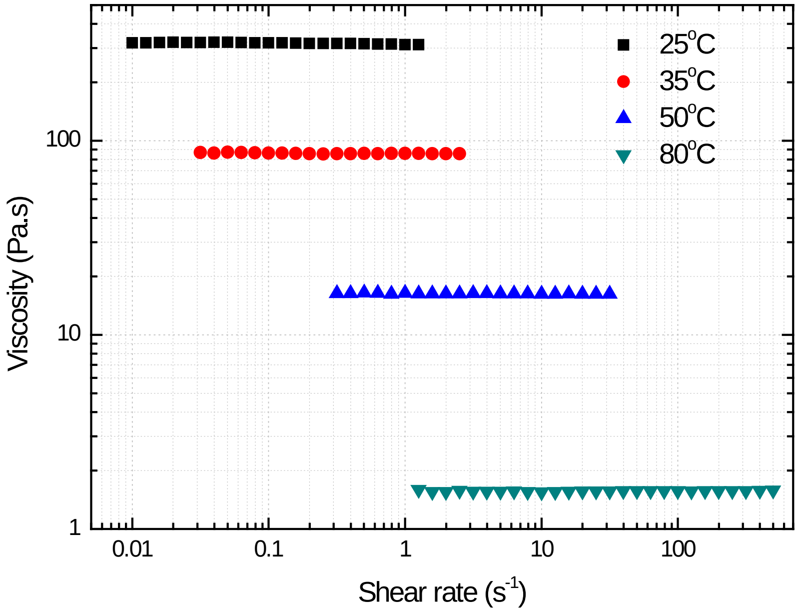


Figure A2.2 Viscosity vs shear rate for SYN704 bitumen at different temperatures without solvent addition

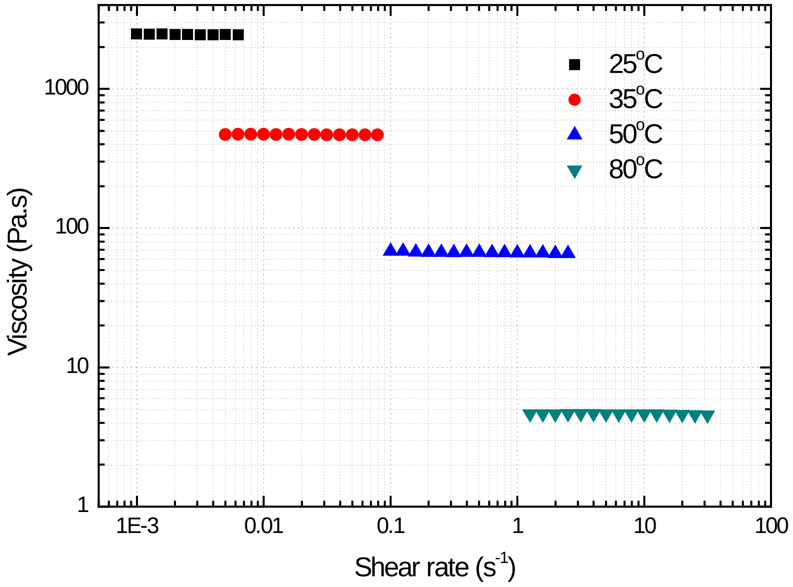


Figure A2.3 Viscosity vs shear rate for SUNOXI bitumen at different temperatures without solvent addition

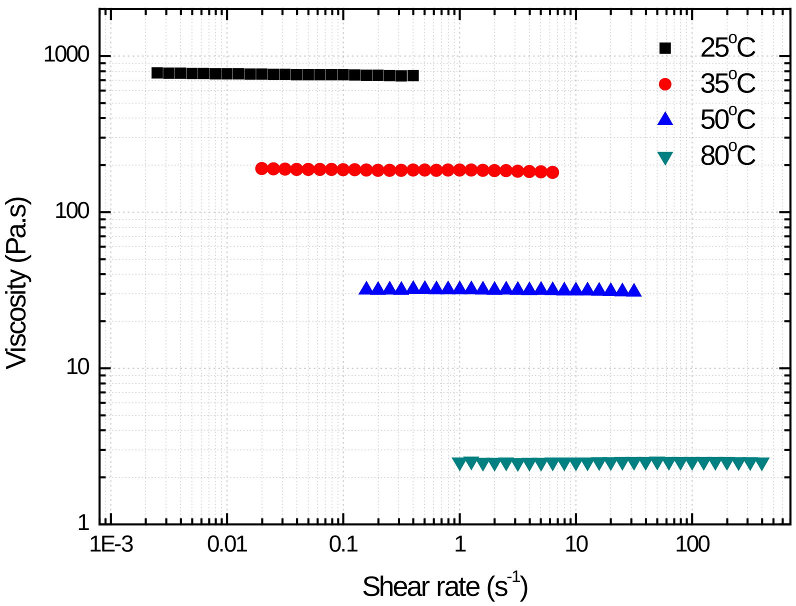


Figure A2.4 Viscosity vs shear rate for W-F11A bitumen at different temperatures without solvent addition

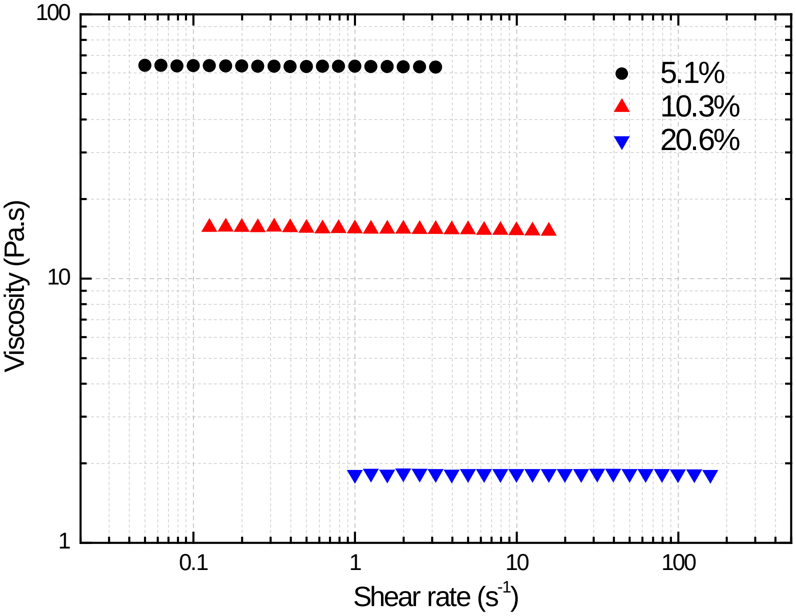


Figure A2.5 Viscosity vs shear rate for SYN704 bitumen with different kerosene additions at 25 °C

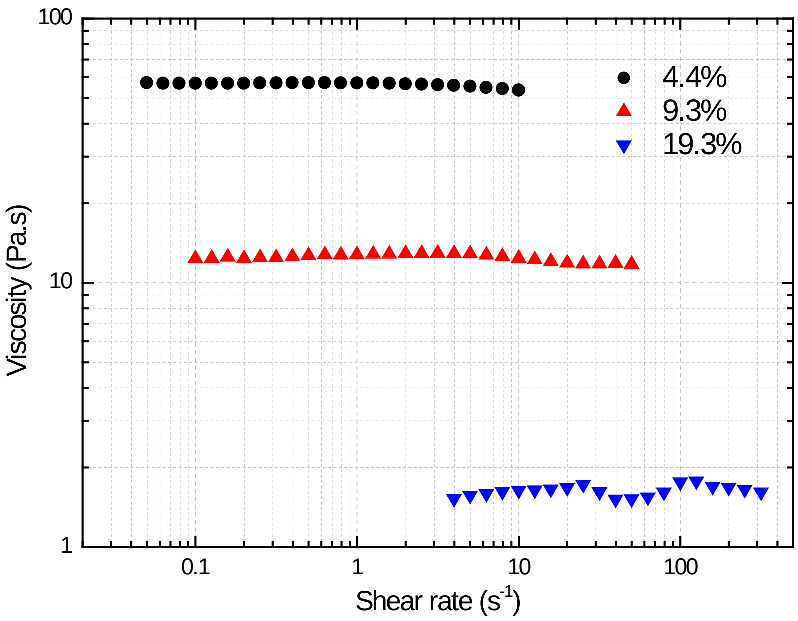


Figure A2.6 Viscosity vs shear rate for SYN704 bitumen with different naphtha additions at 25 ^{o}C

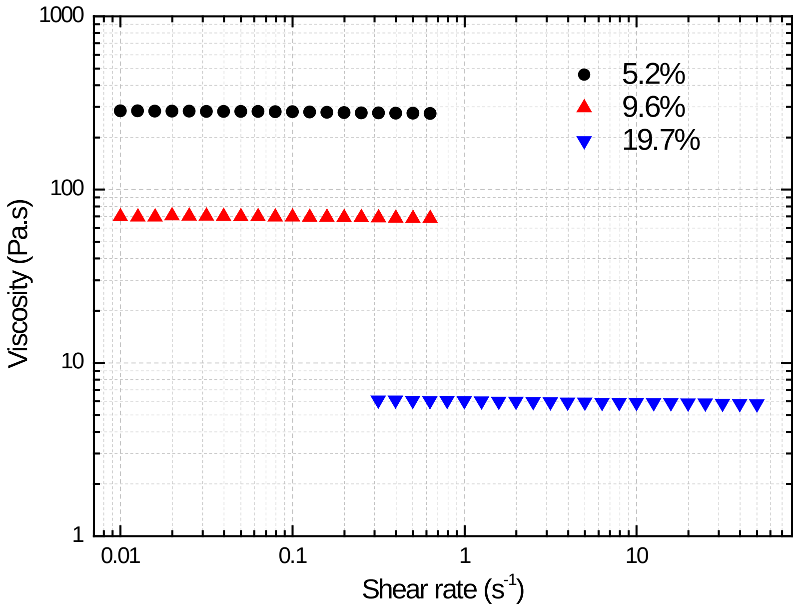


Figure A2.7 Viscosity vs shear rate for SUNOXI bitumen with different kerosene additions at 25 ^{o}C

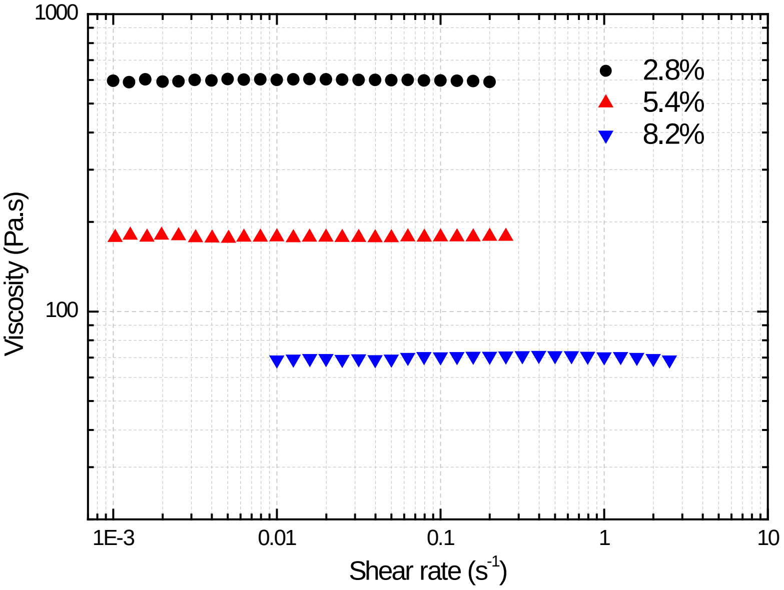


Figure A2.8 Viscosity vs shear rate for SUNOXI bitumen with different naphtha additions at 25 °C

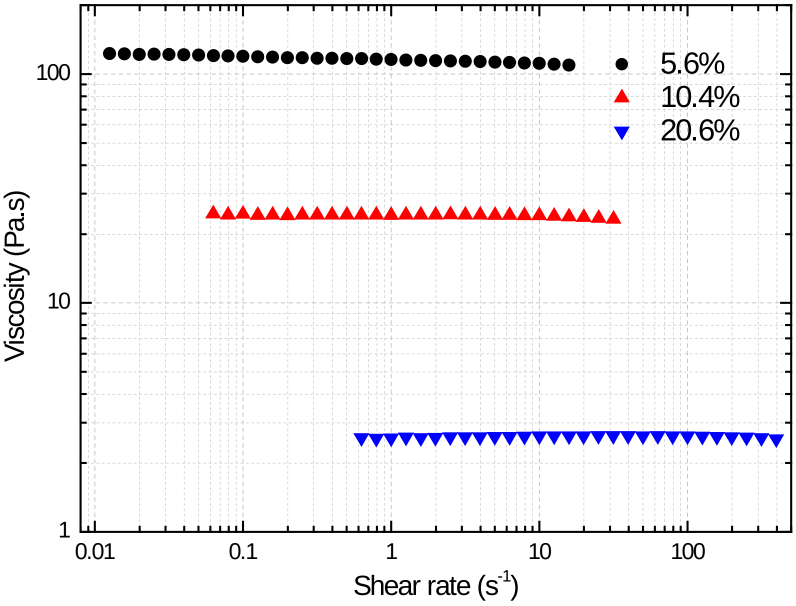


Figure A2.9 Viscosity vs shear rate for W-F11A bitumen with different kerosene additions at 25 °C

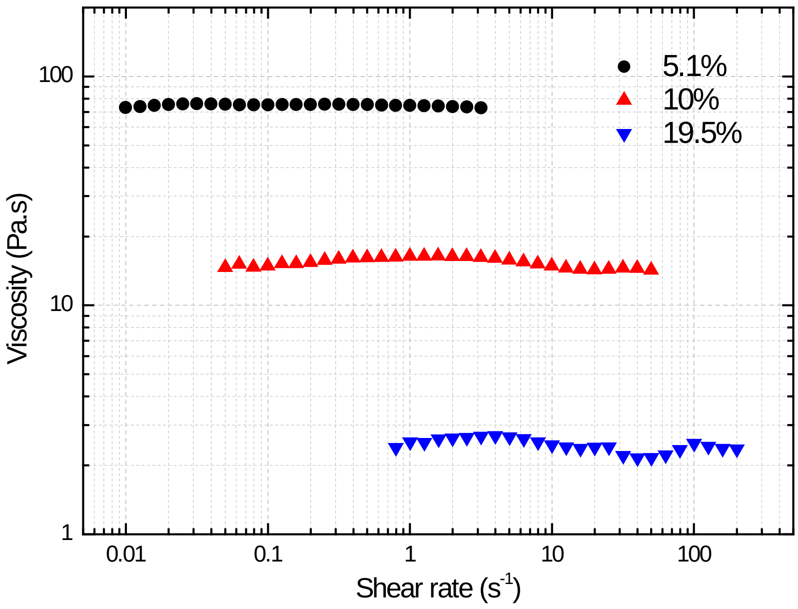


Figure A2.10 Viscosity vs shear rate for W-F11A bitumen with different naphtha additions at 25 ^{o}C