Study of biodiesel-assisted ambient aqueous bitumen extraction (BA^{3}BE) for hydrocarbon production from mineable oil sands

by

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Abstract

Surface mining followed by Clark's hot water bitumen extraction (HWBE) process has been employed in the current mineable oil sands industry for massive bitumen production. This method is faced with numerous challenges such as high energy consumption, limited bitumen quality, production from poor-processing ores, and intractable sludge tailings settling.

As a viable alternative to HWBE, a novel biodiesel-assisted ambient aqueous bitumen extraction (BA^{3}BE) was developed in this study, which uses no caustic (NaOH) and features pretreating oil sands with a relatively small amount of biodiesel prior to extraction. By applying BA^{3}BE, bitumen recovery from Athabasca oil sands was substantially improved from ~10% (benchmark) to 70–80% with 20 wt% (with respect to bitumen content) biodiesel addition at ambient temperature (25°C). Such temperature is much lower than the case of the current industry practice (45–50°C), indicating a remarkably reduced energy intensity. In addition, BA^{3}BE allowed faster settling of oil sands extraction tailings and led to more compact sediment as compared to the case using caustic, suggesting a satisfactory tailings treatment.

To further improve bitumen recovery and product quality, BA^{3}BE was modified by incorporating the use of frother and demulsifier. Results indicated that the modified BA^{3}BE achieved an increased bitumen recovery from 82.1% (unmodified BA^{3}BE) to 86.4%, with a solvent dosage merely equivalent to half of the unmodified case. Further examination of bitumen product revealed that modified BA^{3}BE reduced the entrained water impurities by ~1/3 and ~1/2 as compared to the unmodified case and the HWBE baseline, respectively.

As part of the environmental impact evaluation, BA^{3}BE was also investigated in the release of toxic chemicals such as naphthenic acids, to tailings water. Results showed that BA^{3}BE was able to reduce significantly the total intensity of released naphthenic acids by the range of 13.9–60.1%, depending on the type of ores. This suggests the evident effectiveness of BA^3BE in reducing the release of major toxic chemicals to oil sands tailings water.

Preface

This thesis is composed of a series of papers that have either been published or in preparation. The following statement describes the author's contributions made to the papers included in this thesis.

1. **Yeling Zhu**, Ci Yan, Qingxia Liu, Jacob Masliyah, and Zhenghe Xu*, Biodiesel-Assisted Ambient Aqueous Bitumen Extraction (BA^{3}BE) from Athabasca Oil Sands, *Energy & Fuels*, 2018, 32 (6), pp 6565–6576. Zhu performed all the experiments, data analysis and manuscript writing. All other authors were involved in the discussion on experimental design and result interpretation, and manuscript edits.

2. **Yeling Zhu**, Yi Lu, Qingxia Liu, Jacob Masliyah, and Zhenghe Xu*, Synergy of Chemical Additives to Enhance Bitumen Recovery from Athabasca Oil Sands using Biodiesel-Assisted Ambient Aqueous Bitumen Extraction (BA^{3}BE) Process, manuscript completed and planned to be submitted to *Energy & Fuels*. Zhu performed all the experiments (except for interfacial tension analysis), data analysis and manuscript writing. Lu was involved in experimental design and helped with interfacial tension measurement. All other authors were involved in the discussion on experimental design and result interpretation, as well as manuscript edits.

3. **Yeling Zhu**, Qingxia Liu, and Zhenghe Xu*, Reduced Naphthenic Acids Release from Mineable Oil Sands by Using Solvent-Assisted Ambient Aqueous Bitumen Extraction (SA^{3}BE) Process with Readily-Biodegradable Solvent, manuscript completed. Zhu performed all the experiments, data analysis and manuscript writing. All other authors were involved in the discussion on experimental design and result interpretation.

Other papers not included in this thesis are listed here.

- Yi Lu, **Yeling Zhu**, Zhenghe Xu, and Qingxia Liu*, Biosurfactants with Pseudo-Gemini Structure and CO_2 Switchability for Enhanced Oil Recovery (EOR), *Tenside Surfactants Detergents*, **2019**, 56 (5). This study focuses on investigating the effect of 3 pseudo-Gemini surfactants on water-oil interfacial properties for enhanced oil recovery from petroleum-bearing materials, and oil spill treatment. Zhu was involved in the discussion on the experimental design, result interpretation and manuscript writing.
- Yi Lu, **Yeling Zhu**, Qingxia Liu, and Zhenghe Xu*, Enhanced Bitumen Recovery from Athabasca Oil Sands by using CO_2-Responsive Surfactants in Solvent-Assisted Ambient Aqueous Bitumen Extraction (SA^3BE), manuscript drafting. This study focuses on the concept of employing the synergistic effect of Lu's responsive chemicals and Zhu's solvent-assisted aqueous extraction in oil sands processing. Zhu was responsible for the bench-scale oil sands extraction experiments, data analysis, and involved in the discussion and experiment of solvent loss analysis.

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Nomenclature

Symbols

$C_{foaming}$	Foaming capacity
d_a	Size of air bubble
d_b	Size of bitumen droplet
$[DBL]_{ultimate}$	Ultimate degree of bitumen liberation
$\mathrm{EAT50}$	Half maximal effective attachment time
h	Mudline height at time t
H	Initial mudline height
h/H	Normalized mudline height
$[h/H]_{ultimate}$	Ultimate normalized mudline height
P_a	Probability of attachment
P_c	Probability of collision
P_d	Probability of detachment
$R_C(t)$	Bitumen collection rate
S_b	Surface area flux
$t_{stability}$	Existence time of foam
$v_{norm,ini,DBL}$	Normalized initial bitumen liberation rate
$v_{ini,stl}$	Initial settling rate

Abbreviations

BA^{3}BE	Biodiesel-assisted ambient aqueous extraction
CCD	Charge-coupled device
DBL	Degree of bitumen liberation
DLVO	Derjaguin-Landau-Verwey-Overbeek
EC	Ethylcellulose
EO-PO	(Ethylene oxide-co-propylene oxide) polymer
GHGs	Green-house gases

HSPs	Hanson solubility parameters
HWBE/HWEP	Hot water bitumen extraction process
IFT	Interfacial tension
M-BEU	Modified-Batch-Extraction-Unit
MIBC	Methyl isobutyl carbinol
MFTs	Mature fine tailings
PSD	Particle size distribution
SEP	Solvent extraction process
SA^3BE	Solvent-assisted ambient aqueous extraction
SCO	Synthetic crude oil
SQW	Square-weighted
WBEP	Water-based extraction process
W/O	Water-in-oil

Chapter 1 Introduction

1.1 An Overview of Oil Sands in Alberta, Canada

Oil sands, or bituminous sands, are a type of unconventional petroleum deposits. Oil sands are generally mixtures of high-viscosity bitumen, water and host solids. (Larter and Head 2014) Economic incentives of oil sands industry rely on the entrapped bitumen or ultra-heavy oil to be liberated, concentrated, collected and purified from the original ores before being sold directly or upgraded into high-value oil product (2010), i.e., synthetic crude oil (SCO).

Oil sands can be found in several locations around the world, including Canada, Venezuela, the United States and Russia. Alberta's oil sands reserve in Canada is one of the largest in the world. According to Alberta Energy Regulator (AER 2018), the established crude oil reserves reached 164 billion bbl by 2018, which was the third largest in the world, only after Venezuela (302.8 billion bbl) and Saudi Arabia (266.3 billion bbl) (OPEC 2018).

In Canada, bitumen recovery from oil sands is much more complicated and difficult than conventional crude oil (CCO) production due to various factors, especially the complexity and diversity of oil sands composition, high viscosity nature of bitumen and the cold weather of Canada. This may be the most probable explication for the fact that though Alberta oil sands were first discovered in as early as 18th century, no effective industrial approach towards bitumen production from these 'black golds' was invented until early 20th century, when the methodology of hot water treatment with caustic (alkaline) was proposed by Dr. Karl Clark. For a long period of time, oil sands were not regarded as part of world oil reserves, primarily due to high capital investment and operating cost of oil sands industry. Dominating factors encouraging bitumen production from oil sands rely on consecutive boost in crude oil consumption and development of economy-beneficial bitumen recovery technologies.

Alberta oil sands deposits are located at various depths from the earth’s surface. The overlay material above oil sands reserves, usually known as overburden or spoil, ranges from tens of meters to more than one kilometer. Currently, mining-extraction and in-situ extraction are two major approaches utilized in Canada for commercial production of bitumen from oil sands reserves (Czarnecki, Radoev *et al.* 2005):

- Mining-extraction, which targets at oil sands deposits of overburden less than 70 m. The typical stages of processing mineable oil sands involve the removal of overburden, then oil sands are excavated, conditioned, concentrated and purified via complex physical and chemical treatments to achieve bitumen production with high recovery of >90%. Most mining-extraction is currently operated in Athabasca River area.
- In-situ extraction, which focuses on deposits of overburden more than 200 m, such as steam-assisted gravity drainage (SAGD). In-situ oil sands extraction features bitumen recovery from deep oil sands reservoirs via wells. Fluid carriers, such as high-temperature steam, are injected into reservoirs via wells and water/bitumen mixtures are generated in-situ and produced via pumping, followed by proper dewatering. Generally, 20–60% of the total in-situ bitumen is recovered, depending on local geological formation and operation conditions.

According to Alberta Energy Regulator (AER 2018) and Canadian Association of Petroleum Producers (CAPP 2018), the crude bitumen production will be boosted from ~2.7 million bbl/d in 2017 to ~4.2 million bbl/d (estimated) in 2035. It is evident that such considerable increase in production will be mainly contributed by mined and in-situ bitumen.

1.2 Background and Motivations: Industrial Practice for Mineable Oil Sands

Clark's hot water bitumen extraction (HWBE) process is the industrial practice that has been making the tremendous subterranean oil resources available to us (Masliyah, Zhou *et al.* 2004, 2013). As illustrated in Figure 1.1, a general HWBE process covers the following key steps:

- Oil sands are mined, properly crushed (not shown), and mixed with hot process water, which comprises water and processing aids (caustic), to produce oil sands aqueous slurry of 40–55°C.
- Conditioned oil sands slurry is introduced to hydrotransport pipelines or to tumblers, where bitumen detaches from solid and becomes aerated.
- Aerated bitumen is skimmed off as froth (typically, consisting of 60% bitumen, 30% water and 10% solids, in weight) from the slurry in gravity separation apparatuses, i.e., primary separation vessels (PSV), while the rest is rejected as extraction tailings (ET).
- Froth deaerated and diluted with naphtha (naphthenic froth treatment, NFT) or light paraffins (paraffinic froth treatment, PFT), to have most of the water and solids removed from diluted bitumen as froth treatment tailings (FTT).
- Diluted bitumen can be further treated in atmospheric distillation, where bitumen is produced as product and solvents/diluents are reclaimed for continuous operation.
- After the retained solvent is recovered by tailings solvent recovery unit (TSRU), FTT is combined with ET and sent to tailings pond.
- After decantation, most tailings water can be recycled back to the extraction plant, making up ~78% of total water consumed (CAPP 2018).

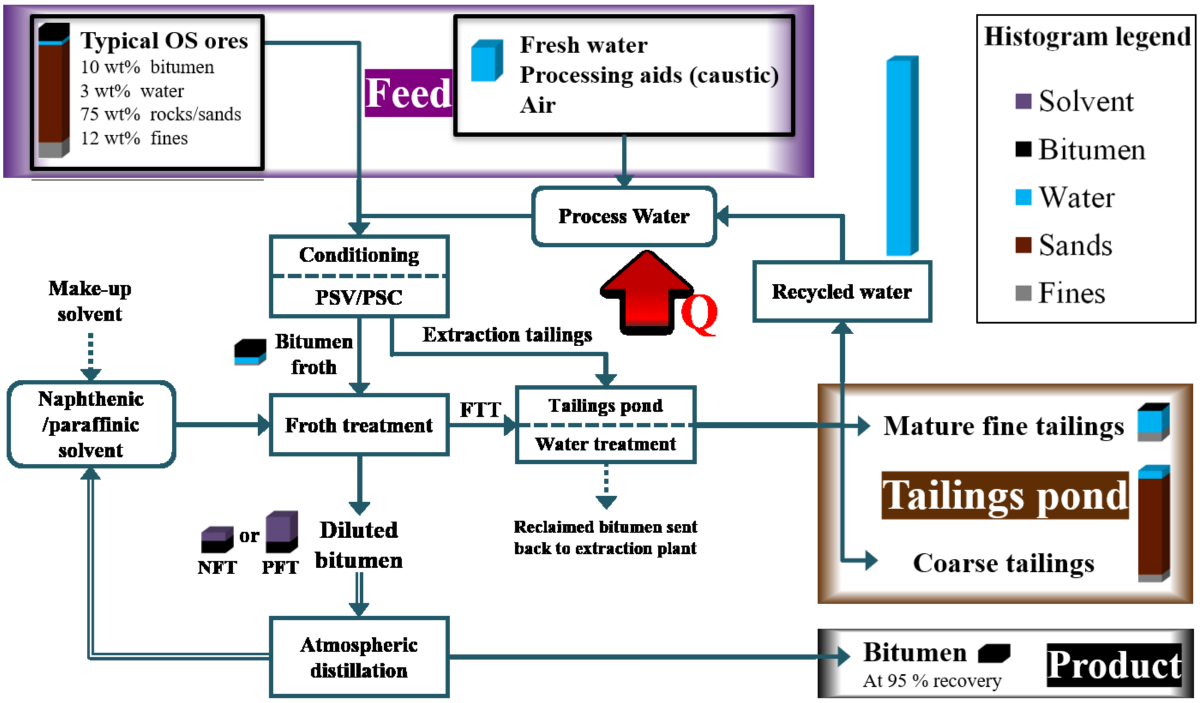


Figure 1.1 Hot water bitumen extraction (HWBE): the industrial practice for mineable oil sands. The height of bars represents relative mass of each stream, with colors referring to different components within a stream.

Ever since Clark's pioneering work of hot water-based bitumen extraction process, the technology of bitumen production from mineable oil sands has succeeded in transferring the 'locked' Alberta's underground black gold into a reliable and profitable energy supply, and made Canada the current 5th largest oil producer in the global oil market (CAPP 2018). Nevertheless, the Clark Hot Water Extraction (CHWE) for mined oil sands presents a series of operational and environmental issues and challenges, as detailed in the following subsections.

1.2.1 Energy intensity and green-house gas emissions

Bitumen production from mineable oil sands has a relatively high energy intensity, which was reported in the magnitude of 0.3-0.4 GJ/bbl bitumen (Gosselin, Hrudey *et al.* 2010). The

EROEI (Energy Returned on Energy Invested) of the mineable oil sands industry was found in the order of 8-14 (comprising bitumen extraction and upgrading) (Gray 2010), indicating that the energy equivalent of 1 bbl of SCO, typically in the form of natural gas, is consumed in order to produce an amount of energy equivalent to 8-14 bbl SCO. It has been widely identified that one major contributor to the high energy intensity of the current HWBE procedure relies on the relatively high operation temperature (40–55°C).

Several government-tracking green-house gases (GHGs) can be produced in Canada oil sands industry, including CO_2, nitrous oxide and methane. Due to the massive production of oil sands bitumen, the high energy intensity has made the oil sands industry the second largest direct CO_2 emissions contributor in Alberta (Gosselin, Hrudey *et al.* 2010). Considering that Canada has made a series of international commitments to reduce GHGs emission, including the government's commitment of '30% GHG cut below 2005's level by 2030'(CBC-News 2015), it is of crucial urgency and significance for commercial operators to reduce the quantity of GHGs directly emitted by oil sands industry and keep pace with the federal and provincial GHGs emission strategy.

1.2.2 Poor processability of poor-quality ores

The processability of oil sands ores is critically dependent on their quality. Good-quality ores containing high bitumen content and low fines allow good bitumen recovery and high froth quality. However, with the depletion of good-quality ore deposits and increasing demand on bitumen production, mining and processing medium-grade ores and even low-grade ores, which contain a large content of fines and may get severely weathered, is becoming a norm. A series of issues exist in the current approach for bitumen extraction from poor mineable oil sands, and many of them become even more difficult to handle during processing ores with high percent fines. Currently, major issues include: 1) reduced bitumen recovery; 2) increased water/solids content in bitumen froth and 3) water (with dissolved salts) contamination in diluted bitumen (Budziak, Vargha-Butler *et al.* 1988, Masliyah, Zhou *et al.* 2004).

1.2.3 Fresh water consumption

Water is utilized as extraction medium in CHWE process. Since water is immiscible with most of the heavy organics in bitumen, large quantities of water with processing aids must be applied in operation, in order to reduce the viscosity of bitumen and facilitate bitumen liberation and aeration for good recovery. In Alberta, the water used in bitumen extraction comes from two sources – the water recycled from clarified tailings ponds and the fresh water intake from local rivers. Typically, 2-3 bbl of fresh water (CAPP 2018) is consumed for 1 bbl of bitumen produced, varying among different operators and mining pits. Though such fresh water only makes up partial (~ 22%) of the total water intake (CAPP 2018), the demand on fresh water is still as high as 182 million m^3/year, due to the high bitumen production in mined oil sands industry. Intensive water withdrawal from river burdens the local river system and has negative impact on the environment. In addition, the monthly flow in local rivers exhibits extremely large season-to-season variation. Especially, the water flow in winter is apparently low in local rivers, which limits the water withdrawal for mineable oil sands (Hooshiar, Uhlik *et al.* 2012).

1.2.4 Tailings pond and water pollution

The huge volume of mineral tailings produced in mineable oil sands industry bring quite a few challenging problems. It is reported (Gosselin, Hrudey *et al.* 2010) that at a 90% bitumen recovery, for 1 bbl SCO production, approximately 3.3 bbl of raw tailings are produced and discharged to tailings containment ponds. Coarse solids together with a portion of fine solids are quickly rejected to form dykes and beaches, while the dewatering of such coarse solids is rapid and convenient to process. However, the majority of fine solids entrapping the remaining water becomes fluid fine tailings, which requires long settling time to further consolidate and gradually form (in average) 2 bbl mature fine tailings (MFTs), which is extremely stable over time if untreated (2010). The MFT contains about 70 wt% water that cannot be economically and efficiently recovered using current technologies (Wang, Harbottle *et al.* 2014). A notable observation is that the accumulation rate of oil sands tailings is in the same magnitude as freshwater intake, implying that the majority of the freshwater intake ends up trapped in the MFT. Data reveals that as a result of continuous expansion of mineable oil sands operations, depletion of high-grade ore deposits and mining of low-grade high-fine ones, the total area of tailings ponds increased rapidly from 176 km^2 in 2015 (Canada 2018) to 220 km^2 in 2017 (Kent 2017). The presence of tailings ponds brings about a series of safety and environmental concerns, for example, tailings leakage due to potential dam/dyke damage (WISE 2015). Attempts to minimize the volume of tailings mainly include composite/consolidated (CT) process, thin lift drying and chemical assisted centrifugation/filtration (Gosselin, Hrudey *et al.* 2010). Several projects that focused on tailings treatment have also been put forward by industrial operators, such as the *TRO*™ by Suncor (Suncor 2015) and the atmospheric fines drying technology by Shell Canada (Website 2010). However, there is still a long way to go before a satisfactory fast and complete dewatering of MFT could be achieved.

Another problem related to tailings treatment is the solvent/diluent loss to tailings and water pollution (Allen 2008, Allen 2008). It has been identified that the solvent/diluent that is used for froth treatment gets partially lost to the froth treatment tailings (FTTs), leading to increased operating expenditure (OPEX) for new diluent purchase and difficulty in fulfilling the government's diluent loss requirement (< 4 bbl diluent/solvent loss per thousand bbl bitumen produced). Furthermore, the lost solvent/diluent, together with the residue bitumen that is not recovered in the extraction process, contributes to the harmful substances in the tailings ponds and deteriorates the water quality. For example, polycyclic aromatic hydrocarbons (PAHs) and naphthenic acids are common hazardous chemicals: PAHs are toxic, mutagenic and carcinogenic (Wilson and Jones 1993, Haritash and Kaushik 2009), while naphthenic acids derived from bitumen are far less biodegradable and more harmful to the environment than commercial naphthenic acids (Scott, Mackinnon *et al.* 2005, Kannel and Gan 2012, Brown and Ulrich 2015). Such harmful substances present in oil sands tailings can migrate via wind, evaporation and seepage and therefore become a severe threat to the environment, especially to the local biodiversity and ecological integrity by affecting air quality, soil and underground water tables (Wang, Harbottle *et al.* 2014). Recent research has been focused on two aspects: reducing organic content in tailings by increasing the recovery of bitumen from oil sands, and developing advanced catalysts for degradation of those pollutants (Lazar, Varghese *et al.* 2012).

1.3 Objectives and Scope of This Thesis

The main objective of this work is to develop a novel technical substitute for the industrial HWBE process, to produce high-quality bitumen from mineable oil sands (especially poor-grade ones) at reduced energy consumption and minimized environmental footprint.

In the first part, biodiesel was for the first time employed as pretreatment diluent to conduct bitumen extraction from mineable oil sands without the use of caustic at ambient temperature, which is named biodiesel-assisted ambient aqueous bitumen extraction (BA^3BE). Fundamental studies on bitumen liberation and aeration revealed the benefit of biodiesel use.

Experimental results of real oil sands agreed well with the hypothesized benefits of biodiesel pretreatment, showing that higher bitumen recovery with faster and more complete tailings settling were obtained using BA^{3}BE, compared to a bench-scale industrial demonstration.

In the second part, model frother (methyl isobutyl carbinol) and polymer demulsifier (ethylene oxide-propylene oxide copolymer) were employed together with BA^{3}BE, to further improve the bitumen extraction performance in mineable oil sands processing to meet industrial expectations. Bitumen recovery was further enhanced using the modified BA^{3}BE at reduced solvent consumption, as well as high-quality diluted bitumen product with a substantial reduction in water entrapment.

In the third part, an insight into the effect of BA^{3}BE on one important environmental concern, i.e., the release of toxic naphthenic acids to tailings water, was provided to give a comprehensive evaluation of this novel mineable oil sands processing technique. The study revealed a remarkable reduction in the release of toxic naphthenic acids by substituting industrial HWBE with BA^{3}BE.

The major contribution of the thesis is the proposal of BA^{3}BE, a novel technical alternative to process mineable oil sands, in a way where more high-quality hydrocarbon is produced, less energy is consumed, and the environmental footprint is minimized. A proof-of-concept of this novel technique was provided by a series of bench-scale demonstrations, which clearly supported the aforementioned advantages of BA^{3}BE over the industrial practice. Last but not the least, the proposed BA^{3}BE technique has big prospect for commercialization because it requires similar facilities and procedures that are already employed in the current industry.

1.4 Structure of This Thesis

This thesis is organized on a paper basis. Chapter 3-5 are research articles, either published in or ready to be submitted to scientific journals. The key content of each chapter is summarized as follows:

Chapter 1 gives the introduction of the thesis, including the background and motivations, objectives and the scope.

Chapter 2 presents a comprehensive literature review on recent technical alternatives for mineable oil sands, especially the solvent-integrated technologies. The reasons why hybrid extraction technique is used and why biodiesel is chosen as the solvent, are also discussed.

Chapter 3 provides the fundamental study of biodiesel-assisted ambient aqueous bitumen extraction (BA^{3}BE) for improved bitumen recovery from model solid surface and its performance in treating real poor-grade Athabasca oil sands. A complete version of this chapter has been published as:

> Yeling Zhu, Ci Yan, Qingxia Liu, Jacob Masliyah, and Zhenghe Xu*, Biodiesel-Assisted Ambient Aqueous Bitumen Extraction (BA^{3}BE) from Athabasca Oil Sands, *Energy & Fuels*, **2018**, 32 (6), pp 6565–6576.

Chapter 4 discusses the synergistic effects of two processing aids (frother and polymer demulsifier) on top of the basic BA^{3}BE to achieve further improved bitumen recovery and higher bitumen quality with less trapped water in product, as well as enhanced tailings settling. A complete version of this chapter is planned to be submitted to *Energy & Fuels*:

> Yeling Zhu, Yi Lu, Qingxia Liu, Jacob Masliyah, and Zhenghe Xu*, Synergy of Chemical Additives to Enhance Bitumen Recovery from Athabasca Oil Sands using Biodiesel-

Assisted Ambient Aqueous Bitumen Extraction (BA^3BE) Process, manuscript completed and planned to be submitted to *Energy & Fuels*.

Chapter 5 investigates the effect of BA^3BE on reduced release of toxic naphthenic acids to extraction tailings, to provide a comprehensive evaluation of BA^3BE. A complete version of this chapter is planned to be submitted:

Yeling Zhu, Qingxia Liu, and Zhenghe Xu*, Reduced Naphthenic Acids Release from Mineable Oil Sands by Using Solvent-Assisted Ambient Aqueous Bitumen Extraction (SA^3BE) Process with Readily-Biodegradable Solvent, manuscript completed.

Chapter 6 summarizes the conclusions of the thesis and recommendations for future research.

All References include all the referenced literature in the thesis, which are cited in the "Author-Date" format.

Appendix I-VI provide additional literature, calculations and figures for each chapter.

Chapter 2 Literature Review

2.1 Solvent-Integrated Techniques for Mineable Oil Sands Processing

To better resolve the challenges faced in current oil sands industry (Section 1.2), a series of emerging technologies for enhanced bitumen recovery and less environmental footprints have been proposed and investigated as viable alternatives to the conventional CHWE. From the solvent usage perspective, these technological alternatives can be roughly classified into two categories: 1) solvent-integrated processes, which are discussed in the following sub-sections; and 2) solvent-free processes, which are not the scope of this thesis and are briefly described in Appendix III. It is notable that in this thesis, solvent refers to nonaqueous liquid (gas, in certain cases) and can be pure substance or mixture of several substances.

2.1.1 Fundamentals of Solvent-Integrated Process

Solvent-integrated processing covers a wide range of oil sands processing methods. Techniques that only incorporate the use of solvent(s) are classified as solvent extraction; techniques that use a small portion of water together with solvent(s) are classified as water-assisted solvent extraction; in addition, certain techniques are essentially derived from CHWE, but few quantities of solvent(s) are consumed to enhance the extraction performance. It is important to clarify that CHWE is not herein classified as solvent-involved extraction even though naphthenic (or paraffinic) solvents are occupied in froth treatment, as the solvents are merely used for product purification, but not for bitumen extraction.

Whatever difference may exist among these designs, it is of great importance to understand what is going on during solvent interaction with oil sands for the development of any solvent-involved extraction. In a general solvent-integrated extraction, solvent is required to have a good compatibility (i.e. solvation, miscibility or swelling (Gray 2010)) with bitumen, to achieve a maximum recovery of bitumen from raw feeds (Hanson and Sherk 1979). When admixed with oil sands (typically in a stirred tank or rotating contactor), solvent solubilizes and dilutes the entrapped target hydrocarbon (bitumen, or certain fractions of bitumen), which substantially reduces its viscosity and makes it readily for liberation/separation from gangue solids. General interactions that occur when a solvent contacts oil sands ores was suggested by Leung et, al. (Leung and Phillips 1985):

- Solvent transfers from fluid environment to the oil sands surface.
- Solvent diffuses into and soaks oil sands matrix.
- Oil sands matrix breaks up from the “softening” and “swelling-up” effects of the solvent.
- Bitumen dissolves in solvent.
- Bitumen gets released from the oil sands surface to the fluid environment.

Several factors strongly affect the kinetics and thermodynamics of the processes mentioned above, including solvent diffusion and mass transfer, solubility between solvent and bitumen, and interaction of solids and connate water in the presence of solvent.

2.1.1.1 Solubility

From the bitumen extraction perspective, the performance of bitumen recovery is governed by solubility, that is, the ability of solvent to dissolve and mobilize bitumen fractions, which in turn shows intense influence on multiple aspects, e.g., bitumen viscosity control, solid/liquid separation and removal of product impurities. For a specified solvent, certain bitumen fractions with good solubility can be soaked and dissolved in such solvent and hence easily recovered, while those with poor solubility are precipitated and left over along with solid stream. For example, in the industrial practice for froth treatment, compared to naphtha that allows maximum recovery of all bitumen fractions along with certain impurities (up to 1 wt% fines and 2 wt% emulsified water) in product, in paraffinic froth treatment partial asphaltene fractions that have poor solubility in paraffinic solvents are precipitated with water and solids, allowing faster settling and resulting in drier and cleaner product.

In as early as 1970s, the Hildebrand solubility parameters were introduced to characterize the ability of bitumen fractions getting dissolved in certain non-polar solvents. The Hildebrand solubility parameters correlate the solubility of non-polar solvents to their heat of vaporization and molar volume, providing a satisfactory estimate of solubility of bitumen in a given solvent. Typically, if a solvent has a set of parameters closer to that of bitumen, such solvent is expected to dissolve more bitumen fractions at the same concentration. For higher accuracy in prediction, more studies on the derivatives of HSPs were carried on in the last few decades, as summarized in Table 2.1.

Table 2.1 Application of Hildebrand solubility parameters and its derivatives in interpreting bitumen solvent interaction

Calculation of Hi-SPs	**Main conclusions**	**Reference**
$\delta = \gamma V_M^{-\frac{1}{3}} = \left(\frac{\Delta H^V - RT}{V_M}\right)^{\frac{1}{2}}$	- Tests are carried out at solvent/bitumen = 40/1, V/V. - Solvent with $\delta < 7.8\ cal^{\frac{1}{2}} mol^{\frac{1}{2}} cm^{-\frac{3}{2}}$ precipitates asphaltene. - Positive correlation exists between the chain length of paraffin (or olefins) and the solubility of bitumen in such solvent.	(Mitchell and Speight 1973)
$\ln \phi_{a,max} = \left(\frac{V_{asp.}}{V_{sol.}} - 1\right) - \left(\frac{V_{asp.}}{V_{sol.}}\right)\left(\frac{1}{z}\right) - \frac{V_{asp.}}{RT[(\delta_a - \delta_s)^2 + 2l_{12}\delta_a\delta_s]}$	- $\phi_{a,max}$characterizes the maximum volume fraction of asphaltene soluble in mixture. - The extended Flory-Huggins (EFH) is more accurate in modeling alkanes.	(Andersen and Speight 1999)
$\delta = \left[\left(\frac{\Delta H^V}{M} - \frac{RT}{rM}\right)\rho\right]^{\frac{1}{2}}$	- The average number of monomers in an asphaltene aggregate was defined as *r* and introduced for calibration. - Solvent with δ: $18.0 - 19.0\ MPa^{\frac{1}{2}}$allows good bitumen recovery greater than 75%.	(Wang, Zhang *et al.* 2014)

Due to the limited application of Hildebrand solubility parameters in non-polar systems where dispersion force is predominant in the intermolecular interactions, it was further developed as Hansen solubility parameter to deal with more complex system. Hansen solubility parameter consists of three elements: energy from dispersion forces (δ_d), energy from dipolar intermolecular forces (δ_p) and the energy from intermolecular hydrogen bonds (δ_h) (Hansen 2007), as given in Equation 2.1.

$$(Ra)^2 = 4(\delta_{dB} - \delta_{dA})^2 + \left(\delta_{pB} - \delta_{pA}\right)^2 + (\delta_{hB} - \delta_{hA})^2 \tag{2.1}$$

For a particular substance A with given interaction radius R_0, the Hansen solubility parameter states that A can dissolve in B, if indicator $RED = \frac{R_0}{R_a} < 1$. Redelius established a fundamental research to determine the three solubility parameter elements of an ideal solvent that dissolve the whole bitumen (Redelius 2000). His study on Venezuelan bitumen found that a solvent, with values of Hansen solubility parameter elements closer to $\delta_d = 17\ MPa^{\frac{1}{2}}, \delta_p = 0, \delta_h = 3\ MPa^{\frac{1}{2}}$, is expected to dissolve all bitumen fractions in the given bitumen.

In addition to the solubility parameter (or solvent type), the bitumen concentration also impacts the solubility of bitumen. Therefore, it is reasonable that solvent to bitumen (S/B) ratio is a generally acknowledged parameter in any solvent-involved extraction. Figure 2.1A shows asphaltene concentration in bitumen after treatment as a function of S/B with common light paraffins at room temperature. Whatever solvent type, it is straightforward that no bitumen fraction was precipitated when the bitumen content dominated in mixing (at low S/B ratio). Elevating the solvent addition increased the asphaltenes precipitation and eventually a steady residual asphaltene concentration in bitumen was achieved at S/B >10. Similar results were reported by other researchers (Mitchell and Speight 1973, Akbarzadeh, Alboudwarej *et al.* 2005). It is reasonable that with increasing addition of light paraffin that owns a much lower solubility parameter compared to asphaltenes, the solubility parameter of the bitumen-paraffin mixture shifts downwards and therefore leads to an increase in asphaltene reject. In addition, from the solvent type perspective, the heavier n-heptane showed a higher threshold S/B for the onset of asphaltene reject than the lighter n-pentane; at the same S/B, n-heptane rejects less asphaltenes than n-pentane and both can be attributed to the closer Hildebrand solubility of n-heptane to that of bitumen (or asphaltene) compared to n-pentane.

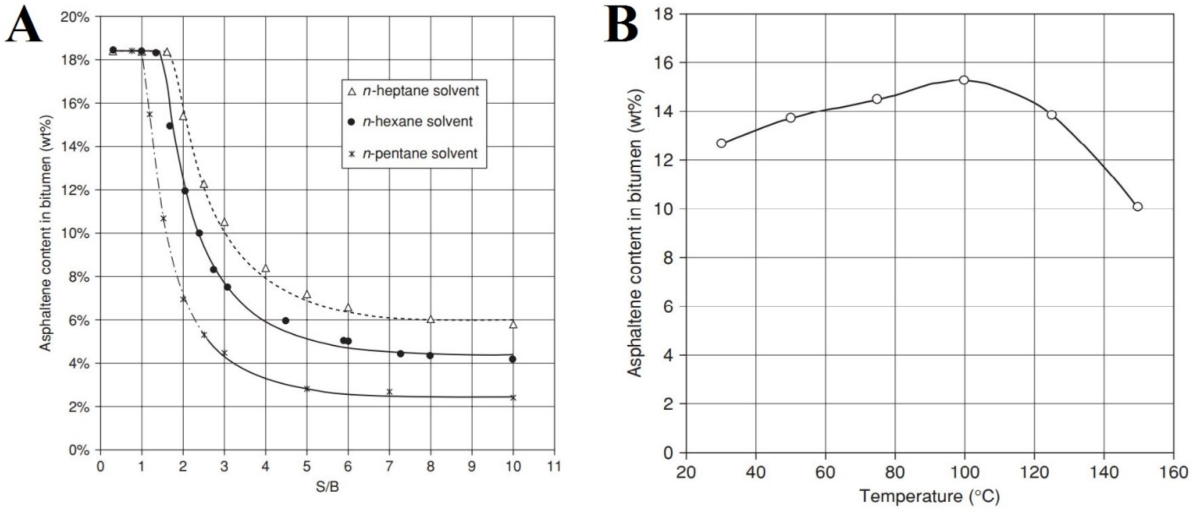


Figure 2.1 Asphaltene content in bitumen after treatment with (A) paraffinic solvents at 25°C, and (B) n-pentane as a function of temperature, at S/B=1.4 and a pressure of 400 psi (Long, Dabros *et al.* 2007) .

Temperature is another factor affecting bitumen solubility in solvent. Figure 2.1B shows asphaltene concentration in bitumen after treatment with n-pentane as a function of temperature. The result reported by Long, *et al.* showed that asphaltene solubility increases with increasing temperature from 30-100°C, after which there is a drop in asphaltene solubility (Long, Dabros *et al.* 2007).

2.1.1.2 Mass Transfer and Solvent Diffusion

A key step in solvent-involved extraction, as mentioned in previous sections, is the diffusion of solvent into oil sand aggregates and the bitumen layer at the surface of oil sand grains. According to (Leung and Phillips 1985), in dilute systems (oil sands to solvent ratio less than 1:6 w/w), the convective diffusion mass transfer process is the dominant mechanism at early stage of extraction (up to 85% bitumen recovery), while solvent diffusion into oil sand aggregates is likely the most important limiting factor at the final stage of bitumen recovery or in dense systems. The efficiency of convective diffusion mass transfer process is mainly dependent on solvent dosage and mechanical aids (such as agitation and ablation), which will not be discussed further in this review.

The procedure of solvent diffusion into bitumen can be characterized by Fick's law of diffusion (Leung and Phillips 1985, Durst 2008), as given in Equation 2.2.

$$J_i = -D \cdot \frac{\partial c}{\partial x_i} \tag{2.2}$$

where the mass diffusion flux (J_i) is directly proportional to the mass diffusion coefficient (D) and the concentration gradient of bitumen in solvent $\left(\frac{\partial c}{\partial x_i}\right)$, which is generally regarded to point from bitumen layer to bulky solvent and perpendicular to the bitumen/solvent interface. The bitumen flux can also be expressed regarding the mass transfer coefficient (k') (Leung and Phillips 1985), as given in Equation 2.3.

$$J = -k' \cdot (c_A - c_B), \text{where } k' = D \cdot \frac{1}{z_A - z_B} \tag{2.3}$$

The mass transfer coefficient (k') is proportional to the mass diffusion coefficient. According to Leung, *et al.*, the time-averaged mass transfer coefficient was found adequate to describe the transport of bitumen from bulky bitumen at the surface of oil sand aggregates to the bulky solvent (Leung and Phillips 1985). In stirred tank-based test, solvent with higher aromaticity and lower boiling point, such as benzene and toluene, exhibited 1.4 times the time-averaged mass transfer coefficient that of *Gulfsol-2329*, *Gulfsol-3139* and kerosene, and therefore allowed faster bitumen extraction compared to the latter solvents.

Cormack's research team analyzed 9 solvents with different aromaticity to give a comprehensive study on the effect of mass transfer properties of solvents on bitumen extraction (Cormack, Kenchington *et al.* 1977). In their study, spherical solids aggregates were used to model oil sands lumps where bitumen dissolution originates. In such model, the overall mass transfer coefficient of solvents was determined with respect to that of kerosene, based on parameters readily measurable in experiments, including concentrations of bitumen in solvent, molar volume of solvents and time-dependent efficiency of extraction. Cormack *et al.* concluded that highly aromatic solvents, such as toluene, allow bitumen dissolution 3-5 times faster than an essentially aliphatic solvent such as kerosene. However, concern on Cormack's work arose from the fact that their model did not take the mass transfer limitation into account, as the actual mass transfer efficiency is also influenced by bitumen solubility in solvent. The mass transfer of aliphatic solvents could be severely restrained by the poor accessibility of these solvents into oil sand aggregates due to asphaltene rejection.

Chakrabarty investigated solvent penetration rate, extraction time and bitumen solubility over a range of solvents, including polar, non-polar aliphatic hydrocarbons, toluene and solvent mixture (Chakrabarty 2010), as shown in Figure 2.2. Results showed that n-pentane, an aliphatic solvent, outcompeted toluene with respect to the penetration rate into oil sands matrix, while the latter performed the best among all the tested solvents in maximizing bitumen production. Acetone was discovered to allow the fastest penetration and production of bitumen, but only extract the least amount of bitumen. It was therefore suggested that a solvent mixture (termed as FASTER in the reference), containing 30 vol% acetone and 70 vol% pentane, was the best choice among all the tested solvents for oil sands extraction, as it reached a satisfactory compromise between reducing production time and increasing the amount of extracted bitumen, which led to the highest average bitumen extraction rate. Chakrabarty's findings are also supported by an earlier study carried out by Fu *et al.* on the diffusivities of various solvents in bitumen (Fu and Phillips 1979). They reported that the diffusivity of solvent in bitumen increases with decreased molecular weight of solvent but does not increase with increased aromatic content. Common paraffinic solvents, such as pentane ($D = 14.5\times10^{8}$ cm^2/s) and hexane ($D = 10.7\times10^{8}$ cm^2/s), appeared to possess higher diffusivity than common aromatic solvents, such as toluene ($D = 7.78\times10^{8}$ cm^2/s) and benzene ($D = 8.19\times10^{8}$ cm^2/s). However, it was reported that low aromaticity may not be the only explanation for higher diffusivity of solvent, as further study also supported the possible influence of viscosity reduction on the diffusivity when using light hydrocarbons (Wen, Bryan *et al.* 2003).

The main conclusion from the mass transfer and solvent diffusion is that bitumen can transfer faster into the solvents that are essentially aliphatic, polar, and low in molecular weight compared to aromatic solvents, though in lower quantities due to restrained solubility.

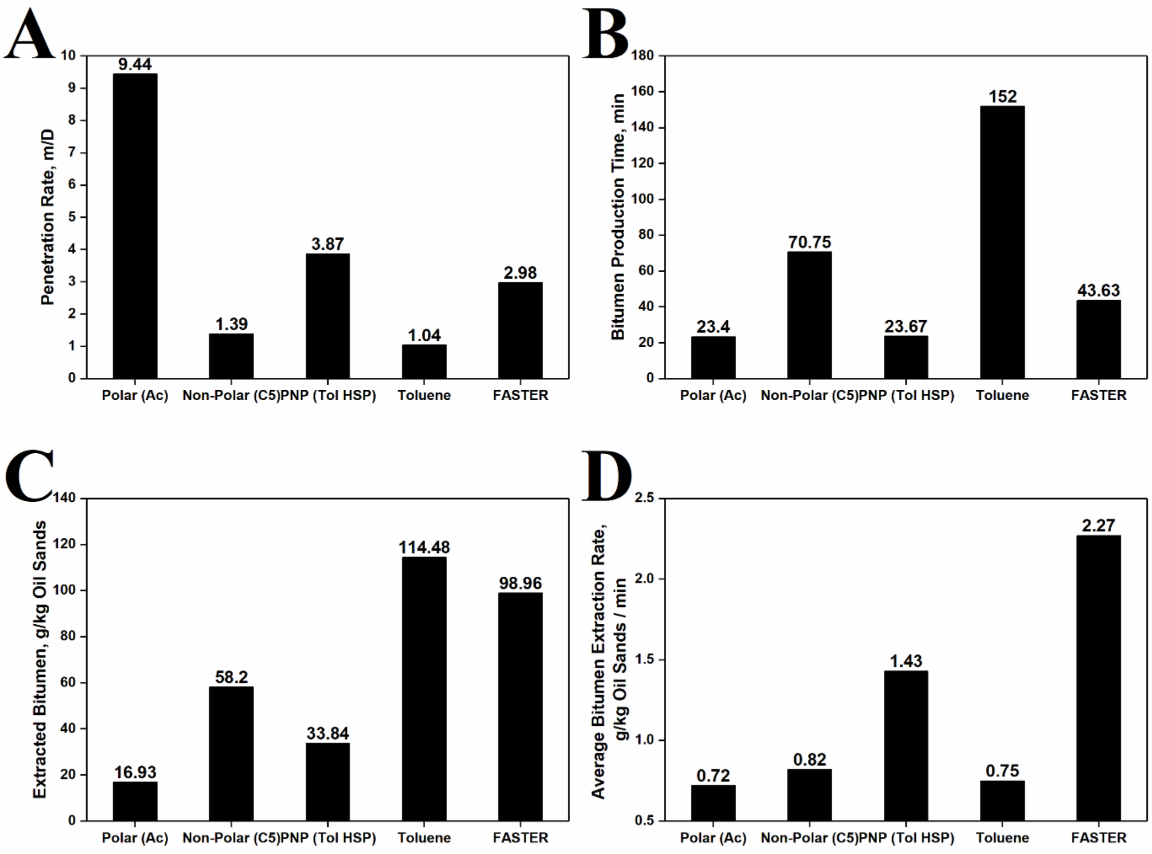


Figure 2.2 Different solvents investigated for (A) average penetration rate into oil sands matrix; (B) bitumen extraction time; (C) total extracted bitumen; and (D) average bitumen extraction rate. Data from Chakrabarty's study (Chakrabarty 2010).

2.1.1.3 Roles of Fine Solids and Water

The role of fine solids and water in solvent-integrated extraction process is not as well understood as in the froth treatment of HWEP, where the use of solvents impacts the concentration of such impurities in diluted bitumen product (2010). Paraffinic solvents facilitate precipitation of partial asphaltenes that agglomerate with fine solids and water to allow easy removal, leading to producing cleaner product (Rao and Liu 2013). On the other hand, naphthenic solvents can solubilize all SARA (saturates, aromatics, resins and asphaltenes) components in bitumen and hence retain more impurities.

Hooshiar *et al.*, used toluene/heptane mixture for bitumen recovery from two types of oil sands ores (Hooshiar, Uhlik *et al.* 2012). The assay of extracted bitumen indicated that the quantities of solids and water could show a difference of over one order of magnitude when the mass ratio of toluene/heptane varied from 70/30 to 0/100. The increase in the relative abundancy of heptane in the solvent mixture resulted in higher solids content and reduced water quantity except for an anomaly for a 10/90 toluene/heptane mixture for both ores. The mechanism of such trend of solids content in extracted bitumen was not well explained as it was contradictory to the well-known knowledge of naphthenic and paraffinic froth treatment. A further study by the same researcher on the type of clays in collected supernatant showed an enrichment of kaolinite compared to the ore (Hooshiar, Uhlik *et al.* 2012). It was also found that clay-bitumen aggregates, rarely found in the investigated high-grade ore, appeared to massively exist in the medium-grade poor-processing ore. Aggregates with similar morphology were also detected in the produced tailings, implying that such composites were relatively stable during the extraction process.

2.1.2 Solvent Extraction (SE) Process

2.1.2.1 Process Description

The initial concept of using solvent in bitumen recovery form oil sands has been proposed over 60 years ago (Bauer and Matthews 1948, George 1954, Gordon 1958, Fisch and Lowman Jr. 1959). Essentially, solvent extraction (SE) process refers to the method that only nonaqueous solvent is used as the extraction medium to achieve bitumen recovery directly from mineable oil sands (Wu and Dabros 2012). Due to the compatibility between bitumen and selected solvent/s and no/little use of water, the problematic processing of the formed three-phase system (bitumen, water and solid) in the water-based extraction (such as CHWE) is converted into a two-phase system (diluted bitumen and solid) by the use of nonaqueous solvent/s, where the connate water in oil sands typically exists together with gangue solid due to solid's hydrophilicity nature. A brief summary of researches and trials on SE techniques is given in *Appendix A*. As illustrated in Figure 2.3, a typical SE process primarily comprises the following steps.

- **Slurry preparation**. Nonaqueous solvent is added to crushed oil sands for slurry preparation. Solvent types that have been investigated so far include pure solvents and mixtures, petroleum distillates and products, and natural extracts and derivatives.
- **Slurry conditioning and extraction**. To achieve an acceptable bitumen recovery, a certain time is required for conditioning, called contact time, which is a function of ore grade/type, ore lump size, solvent type, S/O ratio, agitation rate, operating temperature, etc (Hooshiar, Uhlik *et al.* 2012). Extraction is a diffusion-controlled process and can be controlled by various operational factors, including temperature, lump size (Blaine and Geneva 1977), agitation (Kelly and Poettmann 1968, Porritt, Johanson *et al.* 1978), and integration of sonication/ultrasonication/microwave energy (Baswick 1976, Hart, Schmidt-Collerus *et al.* 1977, Balint, Pinter *et al.* 1983, Abramov, Abramov *et al.* 2009).
- **Solid-liquid separation**. Gravitational settling is most commonly employed for separation of solvent from tailing sludge (Angevine, Carroll *et al.* 1984, Eppig, Paspek *et al.* 1989, Chakrabarty 2010). After bitumen transfers from oil sand solid matrix to the solvent phase, coarse sands with entrapped clay minerals and fines tend to quickly settle down to the bottom and form a separate phase, which can be conveniently removed. The removal of the remaining clay minerals and fines is more difficult and consumes more energy. Common approaches for this step include thermal stripping (Kift, Joshi *et al.* 2015), cyclone (Graham, Helstrom *et al.* 1987,

Duyvesteyn, Joshi *et al.* 2014), centrifugation (Kift, Joshi *et al.* 2012), filtration (Peuker 2014) or a combined use of these. Novel methods for enhanced fine solid removal include displacement by a second solvent (Duyvesteyn and Kift 2012), electrostatic filtration (Cullinane and Minhas 2017) and use of cationic surfactant (in the presence of water) (Alquist and Ammerman 1980).

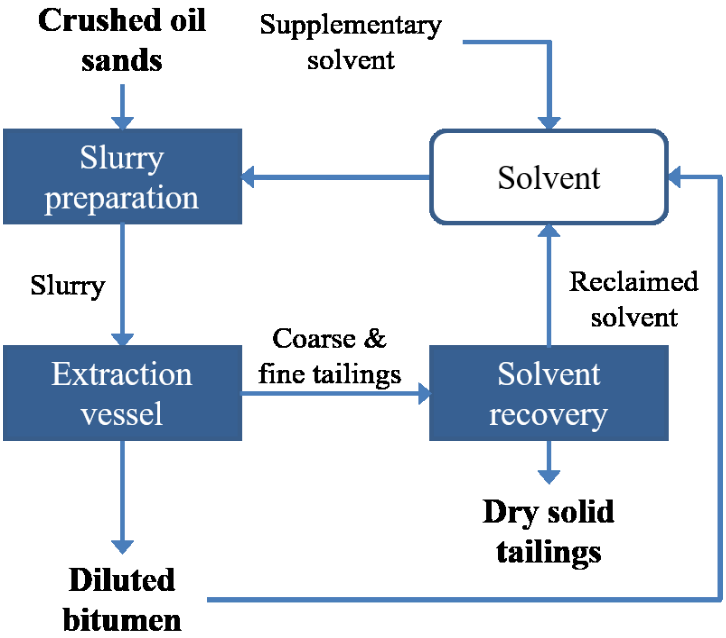


Figure 2.3 The schematic of a typical SE process. (Modified from Funk's work (Funk, May *et al.* 1982))

- **Solvent recovery from diluted bitumen and solid stream**. The solvent in diluted bitumen is usually recovered via distillation by bitumen upgraders and then piped back to the extraction site for continuous operation. Both the solvent reclaimed from diluted bitumen and tailings will be sent back to the extraction step. The dry solids rejected from tailings solvent recovery may contain the precipitated asphaltenes fractions.

It is notable that though SE process promotes recovery from poor processing ore compared to HWBE, it failed to provide equivalent performance when processing high-grade ores, or the commonly-believed 'good-processing' ores (Hooshiar, Uhlik *et al.* 2012). One probable reason for such intriguing phenomenon is that bitumen recovery from solvent sludge could be substantially affected by the stacking of gangue solid. Low-fine ores comprise solids that are essentially large in size and contains small quantities of clays/fines, making diluted bitumen readily entrained in the vacancy formed between solids within the gangue layer. For high-fine ores, such vacancy may be preferably occupied by solids of smaller size, such as fines, indicating a more compact gangue solid stacking and less diluted bitumen entrainments.

2.1.2.2 Challenges of Solvent Extraction Process

Although featuring advantageous extraction efficiency and having been piloted for multiple times during the last 60 years, SE processes still face numerous challenges and concerns that put an obstacle for its commercialization. In general, the major challenge for SE processes rely on the lack of technique for economic and complete separation of organic phase (diluted bitumen) and gangue materials (solids and the entrained water); while, other concerns such as solvent-induced hazards also remain to be cleared and resolved.

Separation of organic phase and gangue materials includes two parts: 1) reclamation of entrapped solvent from solid tailings, and 2) removal of solid from diluted bitumen. A number of publications (Benson 1969, Funk, Prikle *et al.* 1984, Hooshiar, Uhlik *et al.* 2012) revealed that the costly reclamation of solvent from tailings may be the dominating factor limiting the application of SE processes, especially when dealing with low grade ores that contain high content of clays and fine solids. The lost solvent in tailings could introduce various environmental hazards, and recovery of such solvent definitely increases the operating cost (Kenchington and Phillips 1981).

The solid size distribution and solid surface chemistry are two important factors affecting the behavior of tailings condensation. Similar to CHWE, it is widely identified that coarse sands may not introduce severe problems. Coarse sands with hydrophilic surface show weaker adhesive interaction with bitumen. Therefore, it is relatively convenient to recover most of the solvent entrained in coarse tailings, resulting in dry solid that is ready to be sent back to the deposit for land reclamation. However, the clays/fines are believed to be the trouble-makers, even though their roles in fine separation of SE processes are not fully understood so far (Nikakhtari, Wolf *et al.* 2014). One of the reasons for the difficulty in operating fine solid separation is the relatively low settling velocity of clays and fines in diluted bitumen, which is attributed to the small size of such particles. Moreover, such phenomenon becomes more severe when the concentration of clays/fines in diluted bitumen reaches a certain degree and leads to the "hindered settling" that retards any further settling/densification of fine solid suspension. Process additives such as water (Meadus, Sparks *et al.* 1977, Sparks and Meadus 1981, Sparks, Meadus *et al.* 1988) or cationic surfactant (Alquist and Ammerman 1980) have been investigated as binder or flocculant to trap clays and other siliceous solids and form larger particles or flocs that allows easy removal, however the results did not meet expectations.

The other important factor is the solid surface chemistry, which plays a significant role in solid-liquid interaction. For example, the surface of a portion of fines/clays can be partially contaminated by bitumen and become more hydrophobic (Kotlyar, Sparks *et al.* 1998, Sparks, Kotlyar *et al.* 2003). Such fines/clays are called "*oil-wet*" and can be largely formed when the fines/clays are severely coated by asphaltenes, especially in the case aliphatic hydrocarbons are used as nonaqueous solvent (Adams 2014), or when weathered or aged oil sand ores are employed as feedstock. A recent research (Zeng 2015) based on atomic force microscopy provided direct evidence that when cyclohexane was used as solvent, clay particles in oil sands can be covered with asphaltenes within several minutes. As a result, such clay minerals gain a more hydrophobic surface, making them stably dispersed in organic phase and therefore making it much harder to separate clays from diluted bitumen and to recover solvent from fine tailings.

Therefore, extremely energy-intensive operations, such as thermal stripping (Godin 2014) or vacuum evaporation (Wu and Dabros 2012), are generally required to recover solvent from such homogeneous sludge to the extent required by government (average of <4 bbl of overall solvent loss per thousand bitumen production (Kift, Joshi *et al.* 2015)). To reduce the energy intensity of thermal stripping, it is expected that volatile solvents with low boiling point (T_b) and low latent heat may be competent processing solvent. However, it is notable that the thermal energy demand for tailings solvent recovery is not simply determined by T_b, but the effect of capillary pressure should also be highlighted, as it plays an important role in the vaporization of solvent from fine solid/nonaqueous sludge. The reason is that, during thermal stripping of nonaqueous sludge, solvent film with concave meniscus residing in holes/channels formed by fine solids can be largely generated due to solvent-solids interaction, especially for the "*oil-wet*" clays. According to the Young-Laplace equation, these solvent films vaporize at a temperature apparently higher than the solvent's normal T_b, suggesting the demand of extra thermal energy for complete removal of solvent. In addition, the remaining bitumen in tailings could also trap certain solvent, making solvent recovery more difficult.

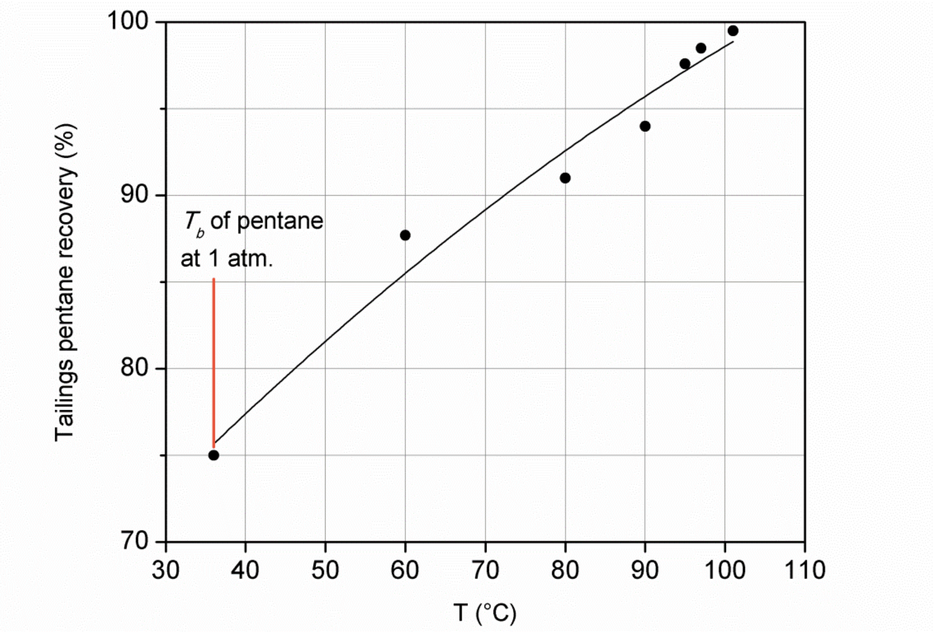


Figure 2.4 Relationship between recovery of tailings pentane and operation temperature (Funk, May *et al.* 1982).

Direct coking (Phillip 1978) and oxidation-extraction process (Duyvesteyn and Morley 2010) have been studied as alternatives for dealing with sludge containing high content of hydrocarbons that are of commercial value but hard to be reclaimed. In the direct coking approach (Phillip 1978), solvent-soaked slurry was directly used as feed for coker to produce organic vapor and high-solid coke. In the oxidation-extraction process (Duyvesteyn and Morley 2010), the large hydrocarbon molecules in nonaqueous slurry were broken down by strong oxidizers into small fragments that are ready to be reclaimed. However, both of them have not been proven fully successful towards commercialization. For the aqueous phase (water and dissolved salts) in diluted bitumen, the majority of the aqueous phase that originates from oil sands is expected to undergo co-precipitation with coarse sands or get attached to fines, though the remaining aqueous mostly exists in the form of water-in-oil (W/O) emulsions and is believed hard to be removed by conventional methods (Nikakhtari, Wolf *et al.* 2014).

Apart from the poor separation between diluted bitumen and gangue materials, concerns about solvent-induced hazards also hinder the application of SE processes. Though the flowsheet of typical SE processes (Figure 2.3) seems less complicated compared to that of HWEP (Figure 1.1), it does not suggest that SE allows comparatively reduced cost and less complexity in operation. As discussed above, to reduce energy intensity of distillation-based solvent recovery, volatile solvent with low boiling point and low latent heat are preferred for SE processes. It is therefore imperative to employ the use of costly airtight facilities in the entire process, to minimize solvent loss, guarantee operation safety and suppress air pollution (Ryu 2012). Moreover, transportation, storage and recovery of volatile solvents that may be flammable and toxic could become a remarkable challenge toward operation safety, which leads to increased CAPEX and OPEX.

Another concern is to select an appropriate solvent that could support satisfactory extraction performance and minimized environmental footprints at the same time. To date, limited data is available regarding the assessment or estimation of the environmental impacts of using SE process in mineable oil sands industry. However, an estimation could be provided by analyzing the toxicity and extraction performance of different solvents.

High-aromaticity solvents (such as toluene) typically allow a higher recovery than low-aromaticity solvents, due to better solubility. Unfortunately, aromatic solvents also tend to exhibit greater negative impacts on the environment, as it shows greater toxicity and stronger resistance to biodegradation. In addition, fine solids were reported to be more difficult to be removed from diluted bitumen when high-aromaticity solvent was used (Zahabi, Gray *et al.* 2010). In comparison, solvents with low aromaticity (such as light paraffinic solvents) are less toxic and easier to undergo biodegradation, while the extraction performance of this type of solvents is not as good as that of aromatic solvents. The reason is that a portion of bitumen (such as asphaltenes) is poorly soluble in such solvents, making them co-rejected along with solids. Many studies proposed to use a secondary solvent to extract and recover the first solvent, which raises the risk of making the chemical composition of tailings slurry even more complex to be treated. In some designs where no secondary solvent is used, the asphaltenes fraction is intended to be left in the gangue for disposal, which definitely leads to an incomplete recovery of bitumen and higher extent of organic pollutant in tailings stream (Duncan, Freitas *et al.* 1969).

2.1.3 Hybrid Extraction (HE) Process

2.1.3.1 Process Description

Aqueous-nonaqueous hybrid extraction process, or hybrid extraction (HE), refers to the processes in which both nonaqueous solvents and water are incorporated for bitumen recovery from oil sands. It needs to be clarified that in our study, though in certain processes water may be used along with solvent, they are still classified as SE processes (Nikakhtari, Wolf *et al.* 2014). The reason is that, in HE processes, water is used as the predominant extraction medium for bitumen liberation and recovery; however, in certain SE processes, water or other aqueous liquid is exclusively employed as the binding agent (also named as bridging or agglomerating agent) at low dosage to facilitate coagulation of fines, while only nonaqueous solvents is employed as extraction medium.

Commercial operators in oil sands industry have long attempted to develop HE process for enhanced oil sands processing, in which solvents are mostly regarded as processing aids. A brief summary of researches and trials on HE techniques is given in Appendix B. Based on the step where solvent is introduced to the extraction, HE processes can be generally classified into two types:

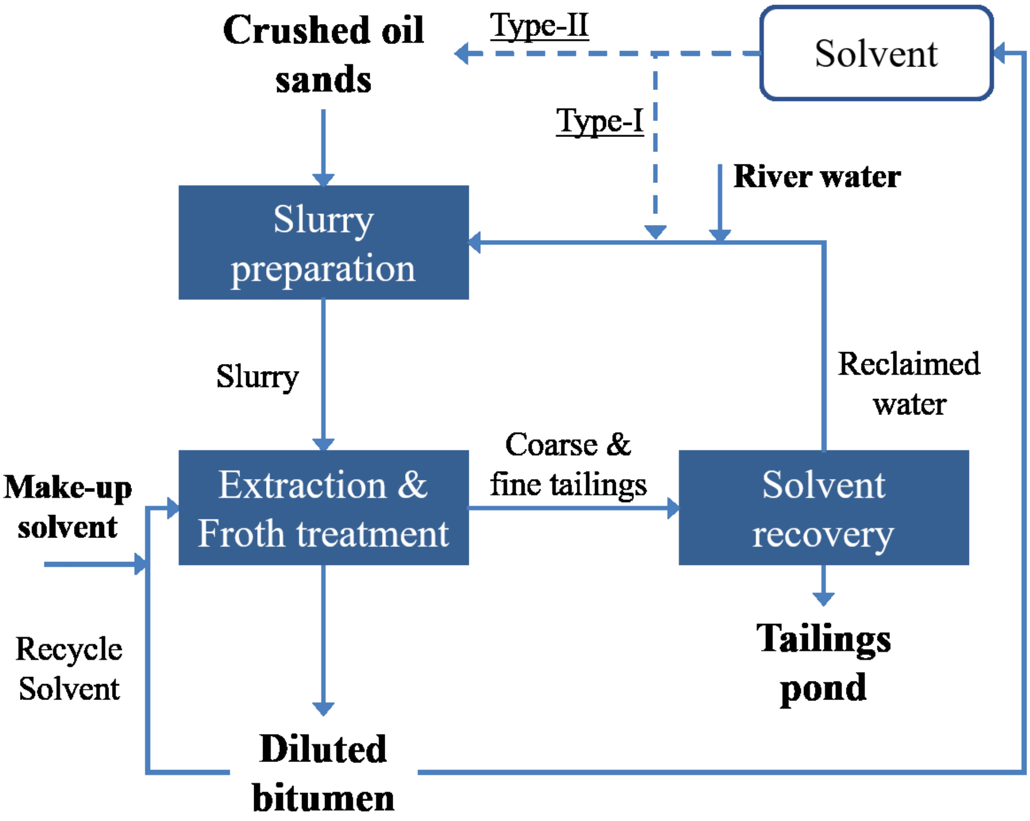


Figure 2.5 Schematic of general HE processes, with dashed lines specifying the different stages of solvent addition between two subtypes (Modified from Yeling's work (Zhu, Yan *et al.* 2018)).

- **Type-I: solvent added to oil sands slurry (that is, after mixing with water).** Solvent is added as a processing aid during oil sands slurry conditioning, followed by a general water extraction process, to achieve bitumen recovery from gangue minerals, as illustrated in Figure 2.5. Typical examples of this type of HE processes include the Other Six Leases Operation's (OSLO) hot water extraction (OHWE) process, OSLO's low-energy extraction (LEE) process (Harjai, Flury *et al.* 2012), and US Oil Sands' (USO's) Grande Pairie Pilot project (Godin 2014).
- **Type-II: solvent added to oil sand ore prior to mixing with water.** More recent research has been conducted to develop this type of aqueous-nonaqueous hybrid

processing of mineable oil sands (Harjai, Flury *et al.* 2012, Lin, He *et al.* 2015, Russell 2017, Zhu, Yan *et al.* 2018). In this alternative, a small amount of solvent (typically <2 wt% of ore) is directly employed in the pretreatment of oil sands, followed by a general water extraction process, as illustrated in Figure 2.5.

Both types of HE processes feature low solvent use. Similar to SE processes, the viscosity of bitumen locked in the solid matrix is reduced by solvent addition in HE processes. However, the solvent dosage in HE case is typically below 2 wt% of oil sands (or 20 wt% of bitumen equivalent), which is 1-2 magnitudes lower than the required amount in most SE processes (Harjai, Flury *et al.* 2012, Godin 2014). Such significant difference in the solvent dosage is attributed to the difference in their processing mechanisms. Distinguished from SE processes where solvent acts as both bitumen viscosity conditioner and carrier for the extraction, HE processes employ solvent exclusively as bitumen viscosity conditioner. Extensive studies have revealed that with solvent addition up to 20 wt% of bitumen, the viscosity of bitumen can be substantially reduced by 2-3 magnitudes to 1-10 Pa·s. Such viscosity is generally regarded as sufficient to allow a satisfactory bitumen extraction from gangue materials, regardless of the ore types, solvent types or temperature (Schramm, Stasiuk *et al.* 2003, Long, Drelich *et al.* 2007).

As for the industrial CHWE, caustic (i.e., sodium hydroxide) is typically used for conditioning oil sands slurry. Masliyah has explained the effect of caustic as follows: the elevated pH increases the wettability of gangue solid surfaces, which facilitates the migration and release of natural surfactant from bitumen to the bitumen-water interface, and leads to improved bitumen recovery (Masliyah, Zhou *et al.* 2004). In contrast, as the pretreatment solvent acts as a partial or complete substitution of caustic in facilitating bitumen liberation for recovery, HE demonstrates the prospect of processing oil sands in a slightly alkaline or even neutral environment. To-date, studies on pilot demonstrations of Type-I HE and preliminary bench-scale trials of Type-II HE have reported satisfactory bitumen recovery at low or no caustic addition, though still depended on ore characteristics (Harjai, Flury *et al.* 2012, Godin 2014, Russell 2017). For example, in OSLO's LEE project, bitumen recovery was found to be in the range of 80-90% from high/medium-grade oil sand ores, which dropped to 50-80% in the case of low-grade ones (Godin 2014). Such recoveries were higher than those operated via caustic-incorporated processing at the same operation temperature (5-35°C).

HE provides a viable solution to alleviate the problem of tailings handling and formation of ultra-stable intractable fine sludge (MFTs) in the current industry. It is well understood that the use of caustic in CHWE deteriorates the tailings settling: the tailings solids, especially clays, become anionized at surface and get dispersed due to particle-particle electrostatic repulsion (2010). In comparison, HE allows oil sands processing at lower pH, suggesting that the extent of clay dispersion could be substantially restrained. As a result, a more rapid and complete tailings settling could be expected, which is significant to resolve the abovementioned challenges in water recycling and land reclamation (Section 1.2.3 and 1.2.4). Currently, investigations on the effect of HE on settling performance of oil sands tailings mainly focuses on Type-II HE (Zhu, Yan *et al.* 2018).

Last but not the least, HE features its commercial competitiveness in terms of capital expenditure. By comparing HE (Figure 2.5) with the industrial CHWE (Figure 1.1), it is straightforward that they share certain similarities in procedures of ore processing and gangue handling. Such finding is noticeable, as it suggests that most of the current production facilities can be retained and made full use of in the novel technique; also, capital investment is mainly required for setup of solvent reallocation system, especially when air-tight processing is not necessary, due to the use of low-volatility solvent. Therefore, the cost for the technological upgrade of production facilities is anticipated to be minimized, which is crucial for HE's industrialization.

2.1.3.2 Challenges of Hybrid Extraction Process

Due to the low dosage of solvent addition and massive water use, many solvent-induced concerns raised in most SE processes may be substantially alleviated in HE processes. One example is the storage and handling of flammable and volatile solvent, which may not become a challenge for operation safety and air quality control as serious as they are in SE (Ryu 2012).

However, several solvent-induced problems still remain for HE processes, as solvent is applied at an early stage of the extraction process. One problem with HE processes could be the poor solvent reclamation from tailings, though the content of tailings solvent is not as high as that of SE tailings. As illustrated in Figure 2.5, a series of units, including hydrotransport and extraction facilities (such as PSV), involve the addition, transportation or recovery of solvent. It is therefore likely that a portion of solvent might get entrained in extraction tailings (ET) and end up in tailings pond. Since ET makes up the majority of tailings, recovery of solvent from such tailings could be intractable. It is notable that the solvent dispersed and entrapped in tailings water might not be a concern, because it could be reclaimed along with water for continuous extraction operation. However, the solvent entrapped in clays and fines remains to be determined and minimized. In addition, the selection of a proper solvent that makes a balance between satisfactory extraction performance and minimized environmental footprints is still of concern, which is similar to SE processes (Section 2.1.2.2).

There is also a huge knowledge gap regarding the water-induced problems of HE processes. Common drawbacks in CHWE, such as formation of undesirable W/O emulsions in diluted bitumen and the generation of massive sludge tailings, remain to be cleared and determined in the case of HE.

2.1.4 Summary

To make a clear comparison between solvent and hybrid extraction processing for mineable oil sands, a summary of selected important operation parameters and Pros/Cons is given in Table 2.2. Comparison of other oil sands processing techniques is given in Table A.1.

Table 2.2 Summary of selected operation parameters in solvent and hybrid extraction for mineable oil sands processing.

Technique	Solvent dosage*	Processing Temperature	PROS	CONS
Solvent extraction (SE)	Commonly 1-2	Room temperature or above	• Water-induced problems addressed	• Intensive solvent use • Solvent recovery from tailings • Serious solvent-induced hazards • Difficulty in choosing proper solvent
Hybrid extraction (HE)	Commonly < 0.02	Room temperature or above	• Ease of application • Relatively enhanced operation safety	• Solvent recovery from tailings • Solvent-induced hazards

* Parts of solvent (in weight) required for processing a unit part of oil sands ore.

2.2 Biodiesel-Based Hybrid Extraction Process

As discussed above, aqueous-nonaqueous hybrid extraction (HE) processes feature great advantages and competitiveness as a novel alternative for bitumen extraction from mineable oil sands industry, while a number of knowledge gaps remain to be clarified, including solvent selection, processing parameters, and tailings settling behaviors. In my study, biodiesel is selected as the candidate solvent used in a HE method for processing mineable oil sands, for improved bitumen recovery at reduced energy input and less environmental footprint.

2.2.1 Fundamentals of Biodiesel

Biodiesel is a renewable biomass-based liquid fuel, consisting of monoalkyl esters (Demirbas 2008). Biodiesel refers to a variety of esterification product of long-chain fatty acids, which can be massively produced from plant oils (such as canola, hemp and palm oils), animal fats (beef tallow, pork lard and poultry fat), waste cooking oil (tap grease) and algae (Demirbas 2008, NRC 2018). Biodiesel belongs to a type of biofuels, which have a long research history as it is believed to be one of the first tested diesel engine fuels in late 1890s (Community 2017). However, it has not raised wide attention until recently when its fuel performance was improved, and its renewability and environmental friendliness were highlighted. Currently, biodiesel is identified as one of the best candidates of diesel substitutes. Biodiesel is miscible with petroleum diesel (referred to as "diesel" in the following discussion, unless mentioned otherwise). Blends of biodiesel and diesel are the most common form that biodiesel is consumed in retail. Many companies use the "*B*" factor to state the amount of biodiesel in any blends. For instance, *B100* refers to pure biodiesel, while *B20* refers to a blend consisting of 20 vol% of biodiesels. It is notable that blends containing 20 vol% biodiesel or less can be used in conventional diesel engines with few modifications (NRC 2018).

Biodiesel is studied as a promising solvent in solvent-assisted ambient aqueous bitumen extraction (SA^3BE) for bitumen production from mineable oil sands. A list of anticipated benefits of using biodiesel is discussed in the following sub-sections.

2.2.1.1 Product quality

It is anticipated that the use of biodiesel in hydrocarbon production should not introduce an evident decline in the quality of retail hydrocarbons. There may be concerns that the integration of biodiesel into mineable oil sands extraction could lead to the presence of biodiesel in diluted bitumen, which may be detrimental to the bitumen quality. Considering its high vaporization temperature, if used as solvent in oil sands extraction and stays in diluted bitumen, not all of such monoalkyl esters in biodiesel can be reclaimed from diluted bitumen by solvent recovery unit. It is reasonable that a considerable portion of biodiesel probably gets retained in the produced bitumen. However, it might not bring about big problems, because the majority of residual biodiesel molecules can undergo hydrogen-deoxygenation (HDO) via hydrotreating by bitumen upgraders (Gray 2010).

The higher heating value (HHV), also known as gross energy, is a parameter commonly used to evaluate the amount of energy released by a specified quantity of fuel (initially at room temperature) once it is combusted and all the products have returned to room temperature (Basu 2010). Report has shown that biodiesel has a HHV value in the range of 39-41 MJ/kg, only slightly lower than that of petrodiesel (43 MJ/kg) and higher than coal (32-37 MJ/kg) (Demirbas 2008). Therefore, the final product, if used as fuel, may not see an evident decline in product quality, even though the contained biodiesel is not completely deoxygenated and hence exists in the final product. Actually, according to the *Renewable Fuels Regulations* enacted by the Canadian federal government, retail diesel product is mandated to carry 2% of renewable fuel (biodiesel) by volume, at which level the blend does not reduce horsepower, torque when serves in engine compared to pure petroleum diesel (Natural Resources Canada 2017, Wolinetz, Hein *et al.* 2019).

2.2.1.2 Operation safety

Biodiesel appears to be the preferred solvent regarding volatility and flammability. Biodiesel has a high flash point (150°C) and a high vaporization temperature, indicating that it is a safer choice than most of the nonaqueous solvents that have been investigated as solvent for mineable oil sands processing, such as diesel (flash point: 64°C) (Demirbas 2008).

2.2.1.3 Environmental impacts

As mentioned above in section 1.2.4, the high solvent loss to the tailings and the toxicity of solvent are the major obstacles suppressing the application of solvent-incorporated bitumen extraction processes. Fortunately, the use of biodiesel may provide a good solution for this problem, as biodiesel may bring much less or negligible environmental impacts. Peterson *et al.* conducted preliminary study on the environmental impacts of biodiesel, showing that the toxicity of biodiesel is much lower than the case of diesel (Peterson and Möller 2004). In their tests, no mortalities and few toxic effects were observed on rats and rabbits with up to 5,000 mg/kg of biodiesel injection. The biodegradation test also revealed that the tested biodiesel degraded at twice the rate of diesel in soil. Moreover, the degradation of diesel was found to generate poorly degradable intermediates, which were marginally observed in biodiesel. A more interesting phenomenon was that the presence of biodiesel seemed to facilitate the biodegradation of diesel, possibly via co-metabolism (Peterson and Möller 2004).

2.2.2 Market Availability of Biodiesel in Canada

Canada has seen a robust increase in biodiesel production in the last decade. Major feedstocks for Canadian biodiesel include yellow grease (used cooking oil), animal fats and canola oil. According to a report released by FAS/USDA (Foreign Agricultural Service, U.S.

Department of Agriculture) in 2018, the nameplate annual production of biodiesel in Canada showed a steady growth from ~230 million liters in 2012, to 641 million liters (estimated) in 2018 (STATISTA 2017), as shown in Figure 2.6. A similar trend is found in the actual production of biodiesel across Canada, which increased sharply from 100 million liters in 2012, to 550 million liters (estimated) in 2018 (STATISTA 2017). It is interesting that such boost in domestic biodiesel production helps Canada become a net biodiesel exporter in the global biofuel market since 2016, as indicated by the imports and exports statistics (Danielson 2018). In summary, the large market-availability of biodiesel across Canada is supported not only by the boost in domestic biodiesel production, but also by the continuous investment on new biodiesel production plants.

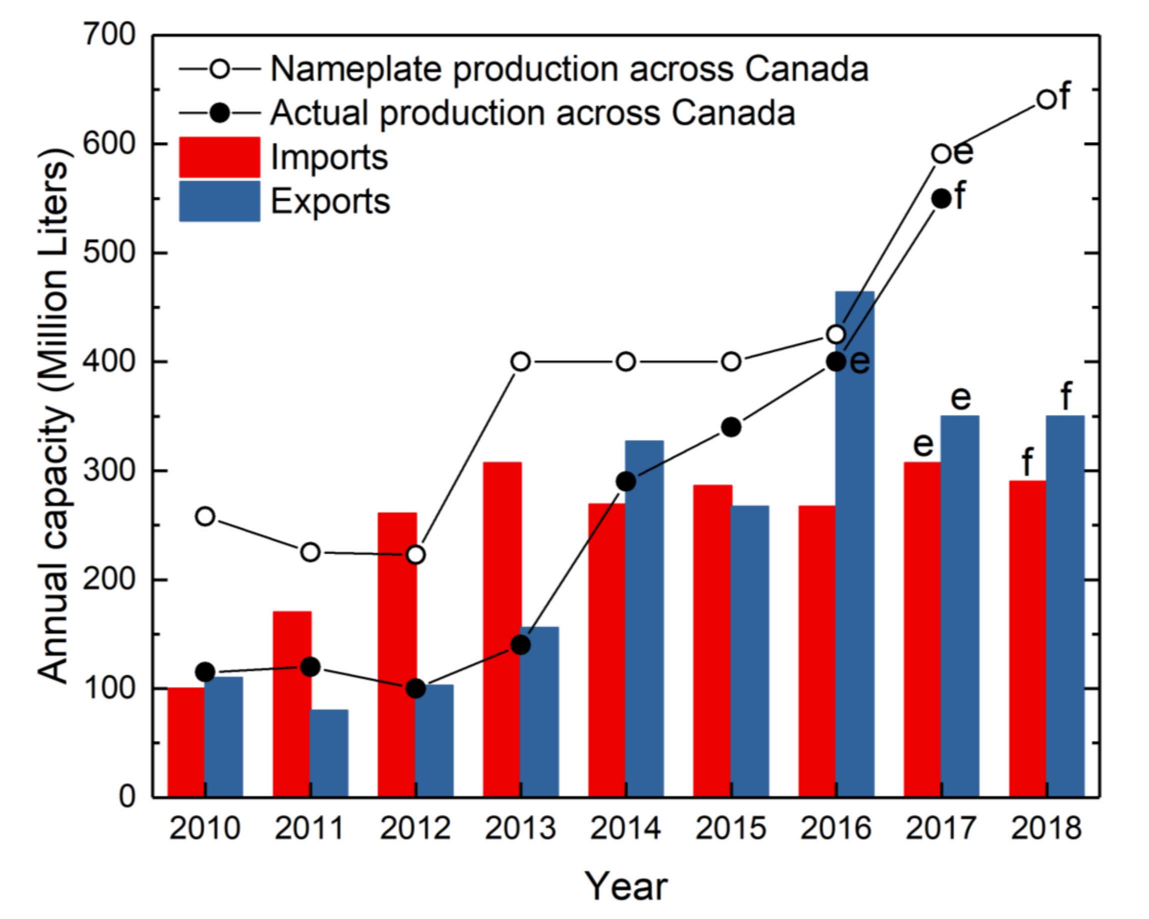


Figure 2.6 Statistics of biodiesel production and biodiesel imports/exports across Canada (Year 2010-2018). Data labelled “e” and “f” indicate estimated and forecasted values, respectively. (Data from (STATISTA 2017, Danielson 2018))

Chapter 3 Biodiesel-Assisted Ambient Aqueous Extraction (BA^{3}BE) for Bitumen Production from Mineable Oil Sands

This chapter is part of the following article published on *Energy & Fuels*.

Yeling Zhu, Ci (David) Yan, Qingxia Liu, Jacob Masliyah, and Zhenghe Xu*, Biodiesel-Assisted Ambient Aqueous Bitumen Extraction (BA^{3}BE) from Athabasca Oil Sands, *Energy & Fuels*, 2018, 32 (6), pp 6565–6576.

3.1 Abstract

The water-based extraction process has been almost exclusively used in the current industry for Athabasca oil sands extraction to produce bitumen and heavy oil. However, the current method is facing various challenges, primarily including high energy intensity, poor processability with poor-quality ores, large consumption of fresh water, and concerns on considerable volume of tailings. Although the technology of using nonaqueous solvent as extraction medium has numerous advantages, problems such as solvent loss to tailings and high capital/operating costs are difficult to address. A biodiesel-assisted ambient aqueous bitumen extraction (BA^{3}BE) process has been herein proposed as an alternative to water-based and solvent-based extraction processes. The results showed a significant improvement in both froth quality and bitumen recovery (increased from ∼10% to ∼80% with biodiesel addition) for processing poor-quality ores at ambient temperature (25°C), which is much lower than the temperatures used in the current industrial practice (40–55°C). The aqueous tailings generated in the BA^{3}BE process were found to feature faster settling and enhanced densification, which is favorable for recovering processing water and improving land

reclamation. Furthermore, the innovative BA^{3}BE extraction process requires similar facilities and procedures as the current industrial processes, which can be considered as an advantage for commercialization.

3.2 Introduction

Athabasca oil sands are one of the most important unconventional petroleum resources and have become a reliable fossil fuel supply to the world over the last decades. The Clark hot water process (Clark 1929, Clark 1944) has been the major method to extract bitumen from mineable oil sands, which made the tremendous subterranean resources commercially available. Nevertheless, the hot water extraction process (HWEP) faces numerous challenges in the current industry. With the depletion of easy-processing ores and increasing demand on bitumen production (AER 2018), mining and processing of poor-quality ores, which contain a significant amount of fine solids or could be heavily weathered, are becoming a norm. Processing this type of oil sands ore in HWEP requires more energy and produces more waste, making the bitumen production inefficient and less profitable. In the current industry, 2–3 bbl of intractable mature fine tailings (MFTs) consisting of fine solids, water, and unrecovered bitumen are generated to produce 1 bbl of bitumen, resulting in two vital problems. On the one hand, this huge amount of MFT sludge needs to be stored in engineered tailings ponds, since no effective practical technology is found for their consolidation. It raises a series of safety and environmental concerns (WISE 2015), such as tailings leakage and groundwater pollution. On the other hand, a large volume of fresh water is consumed and entrapped in MFTs. Furthermore, only 8.5–14 units of energy are produced at the expense of 1 unit of energy consumed in the production process, which is much lower than energy production from other sources (Table 1). Such high energy intensity is mainly attributed to the high operating temperature (40–55°C) of current bitumen extraction process (Harjai, Flury *et al.* 2012). Therefore, there is a great incentive to develop an ambient temperature process for Athabasca oil sands. However, due to the inherent poor processability of oil sands, directly reducing the operating temperature below the current practice would substantially decrease bitumen recovery. It is thus challenging to further reduce energy intensity and corresponding GHG emission in the current operation mode (Gosselin, Hrudey *et al.* 2010).

Table 3.1 EROEI (Energy Return on Energy Invested) of Different Energy Resources (Gray 2010)

Source	EROEI
Hydro-electricity [a]	11 – 267
Conventional oil [a]	19 – 100
Wind	18 (in average)
Athabasca mineable oil sands	8.5-14
In-situ oil sands (SAGD [b])	5.5

[a] The high scattering of EROEI in hydro-electricity and conventional oil is attributed to variability of the resource reserve and local geography.

[b] SAGD: steam-assisted gravity drainage.

To deal with the challenges faced by the current oil sands industry, numerous technologies for optimized bitumen production have been proposed as possible alternatives to the HWEP. Among them, the solvent extraction process (SEP) has been considered to become the most promising as it features several benefits, including enhanced bitumen recovery (typically >90%) due to an effective reduction of viscosity with the use of solvent. In SEP, nonaqueous solvents such as hydrocarbons (Duncan, Freitas *et al.* 1969, Funk 1979, Angevine, Carroll *et al.* 1984), petroleum distillates (Chung and Dickert 1985, Paspek, Hauser *et al.* 1993, Ledbetter, Bishop *et al.* 2009, Garner, Wiwchar *et al.* 2010, Fan, Shafie *et* *al.* 2015), and natural extracts (Fan and Shafie 2012, Bohnert and Verhulst 2013, Fan, Shafie *et al.* 2015) are used to solubilize bitumen, separate diluted bitumen from gangue by solid–liquid separation, and recycle the solvent by distillation. For example, Sparks and Meadus (Sparks and Meadus 1981, Meadus, Bassaw *et al.* 1982, Meadus, Chevrier *et al.* 1982) of the National Research Council of Canada developed solvent extraction-spherical agglomeration (SESA) technology, in which a high bitumen recovery of >90% was achieved from low-grade high-fine ores at an oil sands-to-solvent mass ratio (O/S) of 1:0.66. A two-solvent process was developed by Shell Ltd (Duyvesteyn 2014, Kift, Joshi *et al.* 2015). In this two-solvent SEP, an aromatic solvent (e.g., toluene) is used first to completely extract bitumen from oil sands, followed by a second, preferably a volatile polar solvent (e.g., methanol) to elute the first solvent from resultant tailings for more effective low-energy solvent recovery (Duyvesteyn 2014, Kift, Joshi *et al.* 2015).

Although piloted several times (Meadus, Bassaw *et al.* 1982, Meadus, Chevrier *et al.* 1982), SEP has so far never been commercialized at any large scale operations. The main reason for this lack of commercialization is the requirement of a relatively large amount of solvent (O/S ratio commonly in the range of 1:0.5–1:2 w/w) for an acceptable bitumen recovery. Due to the volatile, flammable, and toxic nature of most organic solvents, purchase, transportation, storage, and recovery of a large amount of solvent can induce extra capital/operating costs, severely threaten operating safety (Ryu 2012), and greatly increase complexity of the process. Another drawback of SEP is the difficulty in reclamation of solvent from the solvent-soaked tailings, especially those in the form of sludge containing an abundant amount of fines (Wu and Dabros 2012). Although volatile solvents are preferentially used to allow a relatively low operating temperature for solvent recovery, the energy intensity of evaporation-based solvent recovery is still too high to make SEP commercially competitive. In the SESA technology for example, the capital and operating expenditure is estimated to be 4 times and 2 times higher than that in the HWEP (Godin 2014), respectively.

With increasingly stringent environmental and economic pressures as discussed above, the pursuit for greater economic benefits and less environmental footprints has been promoting the development of new oil sands extraction technologies. The aqueous-solvent hybrid bitumen extraction (ASHBE) process, a technology recently proven to be practical in a lab scale by Xu *et al.* (Harjai, Flury *et al.* 2012), provides an attractive compromise for optimized processing of oil sands, making use of solvent addition to provide a viable solution to its drawbacks. It is a particularly viable solution to the current challenge of HWEP, as the solvent is already used in the downstream oil–water separation process of the current HWEP. In the ASHBE process, oil sand ores are pretreated directly with a relatively small amount of solvent (typically <2 wt% of the ore) for conditioning before conventional water-based extraction process. On the basis of an early theory of SEP proposed by Leung and Phillips (Leung and Phillips 1985), the promises of the ASHBE process can be postulated as follows: (1) A given portion of solvent (also known as diluent in froth treatment of oil sands industry) is transferred from a solvent tank to the surface of oil sand ores. (2) Diluent diffuses into the ore lump and bitumen to reduce the viscosity of bitumen. (3) Solvent-pretreated oil sand ores are mixed with water in slurry preparation, followed by a conventional water-based extraction process, including slurry hydrotransport and bitumen separation, which has been well-elaborated by Masliyah (Masliyah, Zhou *et al.* 2004).

Studies on different types of oil sands samples demonstrated satisfactory bitumen recovery from poor processing ores using ASHBE process at ambient temperature (Harjai, Flury *et al.* 2012). Moreover, the performance of bitumen recovery in ASHBE process exhibits little dependence on the characteristics of ores, indicating a robust process to deal with complex variability of oil sand ores. Since the dosage of solvent addition in the ASHBE process is much lower than most SEP, and more importantly water is used as the major extraction medium in the HWEP, the solvent loss to the tailings is significantly reduced (Harjai, Flury *et al.* 2012). In summary, the novel ASHBE process provides a promising prospect of processing Athabasca oil sands as an energy-saving, commercially competitive, and environmentally friendly approach.

3.3 Biodiesel-Assisted Hybrid Extraction Process

For an ideal ASHBE process, it is of critical importance to select a specific solvent that shows good compatibility with bitumen to achieve adequate dilution of bitumen at low dosage. Biodiesel, a biomass-based green solvent, refers to a variety of esterification products (typically with methanol) of long-chain fatty acids that are derived from vegetable oils, animal fats, and algae (Demirbas 2008). Biodiesel is selected in this study as a candidate solvent in the oil sands processing for its unique properties, including good bitumen compatibility with bitumen at ambient temperature, certain molecular polarity for enhanced penetration into bitumen, reduced use of processing aids (specifically, caustic), low toxicity, and good biodegradability, which will be discussed in the following paragraphs.

The biodiesel-assisted ambient aqueous bitumen extraction (BA^3BE) process is illustrated in, with the water-based extraction process being included for comparison. Hanson solubility parameters (HSPs) is an important parameter to evaluate the compatibility of a solvent with bitumen. On the basis of tests with different solvents on Venezuelan bitumen, Redelius predicted that a solvent should have "optimum HSPs" around $\delta_d = 17\ \text{MPa}^{1/2}$, $\delta_p = 0\ \text{MPa}^{1/2}$ and $\delta_h = 3\ \text{MPa}^{1/2}$ to dissolve all bitumen in oil sands (Redelius 2000). A recent patent by Chakrabarty revealed the benefits of using polar solvent for oil sands processing (Chakrabarty 2013). Although some polar solvents such as acetone were shown to extract only a small portion of bitumen, a superb penetration efficiency in bitumen of at least 6 folds higher than the commonly used good solvents such as pentane and toluene has been found (Chakrabarty 2013).

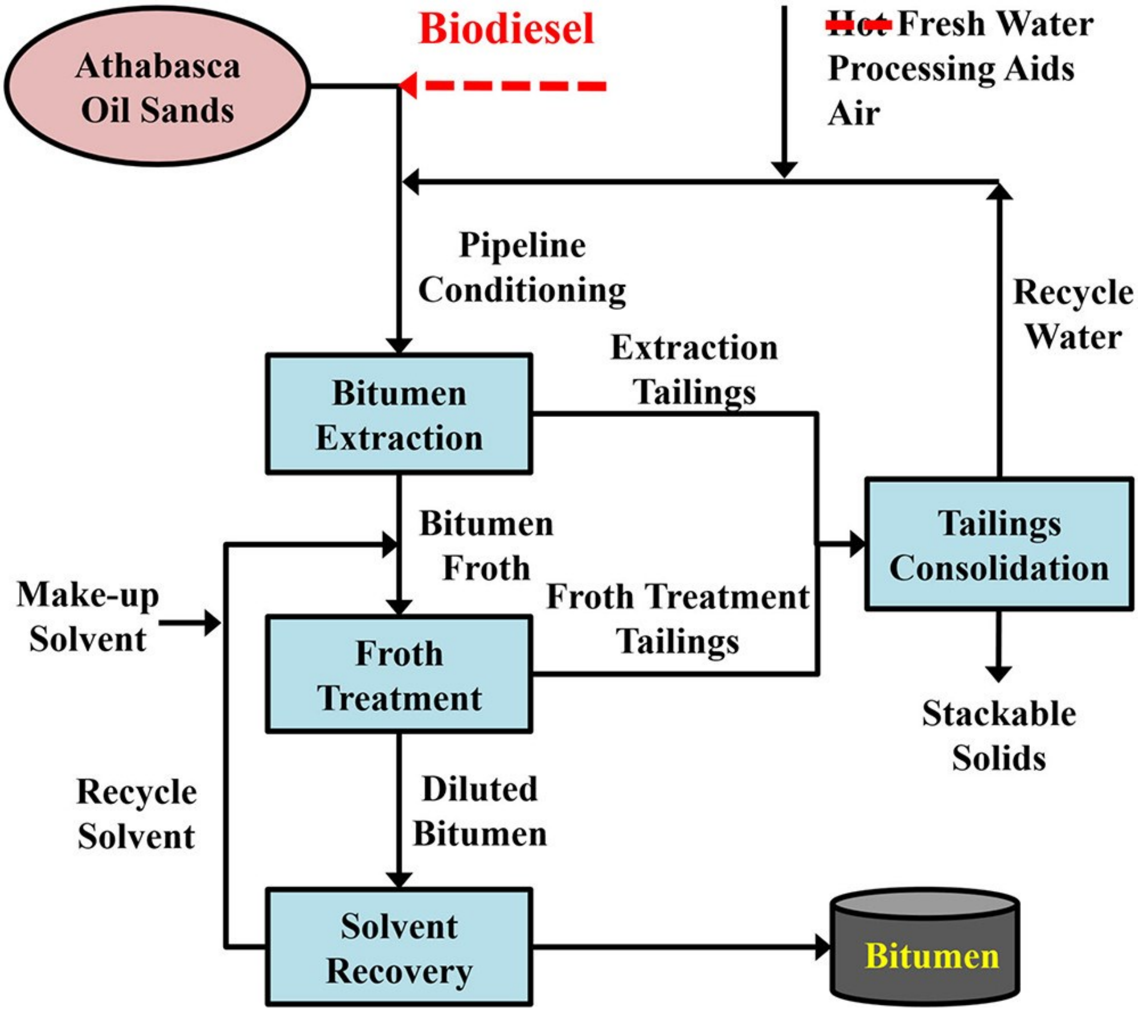


Figure 3.1 Schematic of the current water-based extraction process (solid lines) and the innovative biodiesel-assisted hybrid bitumen extraction process (dashed lines). A small amount of biodiesel is added as the process aids upfront for oil sands pre-treatment to reduce bitumen viscosity and operating temperature.

It is therefore desirable to search for a proper solvent with certain polarity that allows rapid diffusion and homogenization in bitumen to effectively and rapidly reduce the viscosity of bitumen in oil sands. As reported by Krähenbühl (Batista, Guirardello *et al.* 2013), the common HSPs of biodiesel are in the range of $\delta_d = 15.0 - 16.1\ \mathrm{MPa}^{1/2}$, $\delta_p = 3.7 - 6.7\ \mathrm{MPa}^{1/2}$ and $\delta_h = 6.6 - 9.3\ \mathrm{MPa}^{1/2}$. These values are close to the "optimum HSPs" for mutual dissolution and hence a good compatibility of biodiesel with bitumen. This hypothesis was confirmed by a preliminary test that showed no phase separation nor was visible asphaltene precipitation observed when bitumen was blended with biodiesel up to 30 wt%. On the other hand, the higher molecular polarity and hydrogen-bonding contributions in the HSPs of biodiesel make it a good solvent for penetration into bitumen and hence rapid bitumen recovery.

Looking back into the current industrial HWEP, the use of caustic may facilitate the release of excessive natural surfactant such as naphthenic acids to enhance bitumen liberation while hydrolyzing solid surfaces to make them more negatively charged. As a result, fine solids become highly stabilized, leading to production of intractable fine sludge (Masliyah, Zhou *et al.* 2004). In comparison, the BA^{3}BE process allows processing of oil sands at little or no caustic addition. In this manner, difficulties in dealing with problems of tailings settling and consolidation can be greatly alleviated (Sury and Stone 1995). Furthermore, due to reduced use of caustics, the solvent loss to tailings in BA^{3}BE process is anticipated to be reduced greatly as compared with the solvent loss in the SEP.

In addition, biodiesel is a preferable choice to common solvents in perspective of alleviating negative environmental impacts, such as low carbon solvent, low toxicity, and good biodegradability (Peterson and Möller 2004, Peterson and Möller 2005). As derived from biomass, each carbon atom in biodiesel is originated essentially from free carbon dioxide via photosynthesis, indicating that biodiesel consumption makes a negligible contribution to GHG emission. The toxicity of biodiesel, as reported by Peterson and Möller (Peterson and Möller 2004, Peterson and Möller 2005), is much lower than common solvents such as petroleum diesel (referred to as "diesel" in the following). In their research, no mortalities and few toxic effects are observed with rats and rabbits up to 5000 mg/kg of biodiesel injection. In addition, biodegradation tests show that biodiesel degrades twice the rate of diesel in soil. The degradation of diesel generates poorly degradable intermediates, especially intractable polyaromatic hydrocarbons (PAHs), which are hardly present in biodiesel's case. Therefore, BA^{3}BE process is likely to provide a practical approach toward the solution of both solvent loss and solvent toxicity, which are the major obstacles limiting applications of any solvent-involved bitumen extraction processes.

The objective of this research is to develop an innovative biodiesel-assisted ambient aqueous bitumen extraction (BA^{3}BE) process for Athabasca oil sands by bench scale laboratory tests. The effect of biodiesel addition on various aspects including bitumen recovery, tailings consolidation, and bitumen liberation/aeration kinetics is evaluated. Common solvents including diesel and kerosene are also investigated for comparison. To examine the feasibility of the BA^{3}BE process, bitumen recovery tests are carried out on different types of Athabasca oil sands. To determine if the current oil sand processing temperature (40–55°C) could be further reduced, all extraction experiments are conducted at ambient temperature (25°C). The role of solvent addition in bitumen liberation and bitumen aeration is investigated by in situ bitumen liberation visualization cell and induction timer, respectively. The effect of solvent addition on tailings properties, especially on settling and consolidation of fine/sludge tailings, and the extent of solvent loss to tailings is also evaluated. The innovative BA^{3}BE process does not only reduce the energy intensity and GHG emissions but also allow improved tailings consolidation, optimized tailings solvent recovery, and reduced environmental footprints.

3.4 Experimental

3.4.1 Materials

Oil Sand Ores: two different Athabasca oil sands ores used in this study (noted as Ore P and Ore M) were obtained from Syncrude Canada. As shown in Table 3.2, Ore P contained a significant content of fine solids (>35 wt%) and was considered to be poor processing ore in the current industrial HWEP. Ore samples were kept in a freezer to minimize ore weathering, including dehydration, loss of light hydrocarbon, and oxidation of bitumen. Prior to their use, samples were homogenized at room temperature to ensure consistency in composition.

Table 3.2 Composition of Oil Sand Samples Used in This Study

Source	**Composition (wt%)**			
	Bitumen	**Water**	**Solids**	**Fines** [a]
Ore P	9,2	2.6	88.2	35.6
Ore M	11.4	2.3	86.3	8.2

[a] Fraction of fines (defined as mineral solids with sizes less than 44 μm) in total solids.

Process Water: process water was directly collected from Syncrude industrial stream and used as the aqueous medium without any modification. The surface tension of the process water was obtained to be $\gamma = 71.22 \pm 0.05$ mN/m using a process tensiometer (KRUSS K-12). The pH of the process water was 7.5. The electrolyte concentration of process water was determined by an ion chromatography (DIONEX ICS-3000, for all the ions except for CO_3^{2-}/HCO_3^-) and a Total Organic Carbon Analyzer (SHIMADZU TOC-L) in inorganic carbon measurement mode for CO_3^{2-}/HCO_3^-) to be 20.6 ppm K^+, 690.8 ppm of Na^+, 19.4 ppm Mg^{2+}, 83.0 ppm of Ca^{2+}, 444.0 ppm of Cl^-, 10.3 ppm F^-, 478.6 ppm of SO_4^{2-}, 71.0 ppm of NO_3^-, and 527.7 ppm of CO_3^{2-}/HCO_3^-.

3.4.2 Solvent

Three types of solvents were used for the oil sands pre-treatment. Biodiesel was obtained from Alberta Innovates–Technology Futures and was found to primarily consist of methyl myristate ($CH_3(CH_2)_{12}COOCH_3$) and methyl palmitate ($CH_3(CH_2)_{14}COOCH_3$) as determined by gas chromatography/mass spectroscopy (Varian CP-388/Saturn 2200). The petroleum diesel was purchased from Shell Ltd. The kerosene was purchased from RICCA Chemical Company. The Fourier transform infrared (FTIR) spectra of these three solvents, obtained by NICOLET iS50 spectroscopy (Thermo Scientific), are shown in Table 3.2. For biodiesel, the peak at ~1745 cm^{-1} corresponds to the C=O stretch in esters. It is interesting to note a similar peak presented in the spectrum of commercial diesel but at notably weak absorbance. This could be explained by the presence of a small amount of biodiesel (2 wt%) in the retail diesel fuel, as mandated by the Government of Alberta in 2014 (Natural Resources Canada 2017).

Previous work demonstrated that the interfacial tension between bitumen, water, and solids played an important role in the bitumen extraction (Drelich and Miller 1994). In this study, the interfacial tension between solvents and process water was determined using the same tensiometer and the results are shown in Table 3.3. Much lower interfacial tension of biodiesel suggests that the biodiesel contained more surface-active compounds than the other two solvents, as desired for bitumen extraction. The viscosity of the solvents was also measured using a rheometer (model AR-G2, TA Instruments) with the results being given also in Table 3.3. Although the viscosity of biodiesel is slightly higher than the viscosity of the other two solvents, it remains 6 orders of magnitude lower than the viscosity of bitumen. It is therefore anticipated that the addition of biodiesel to the bitumen would greatly reduce the viscosity of bitumen and hence enhance bitumen extraction as desired.

Table 3.3 Partial Characteristics of the Solvents Used in This Research at 20°C

Solvent	Density [a] (g/mL)	Viscosity (mPa s)	Interfacial tension [b] (mN/m)
Biodiesel	0.8746	5.34	6.33 ± 0.02
Diesel	0.8410	2.39	18.01 ± 0.04
Kerosene	0.8089	1.91	42.40 ± 0.02

[a] Density data was provided by manufacturers.

[b] Interfacial tension was referred to the solvent–process water interface, and the data were collected after an equilibrium time of 15 min.

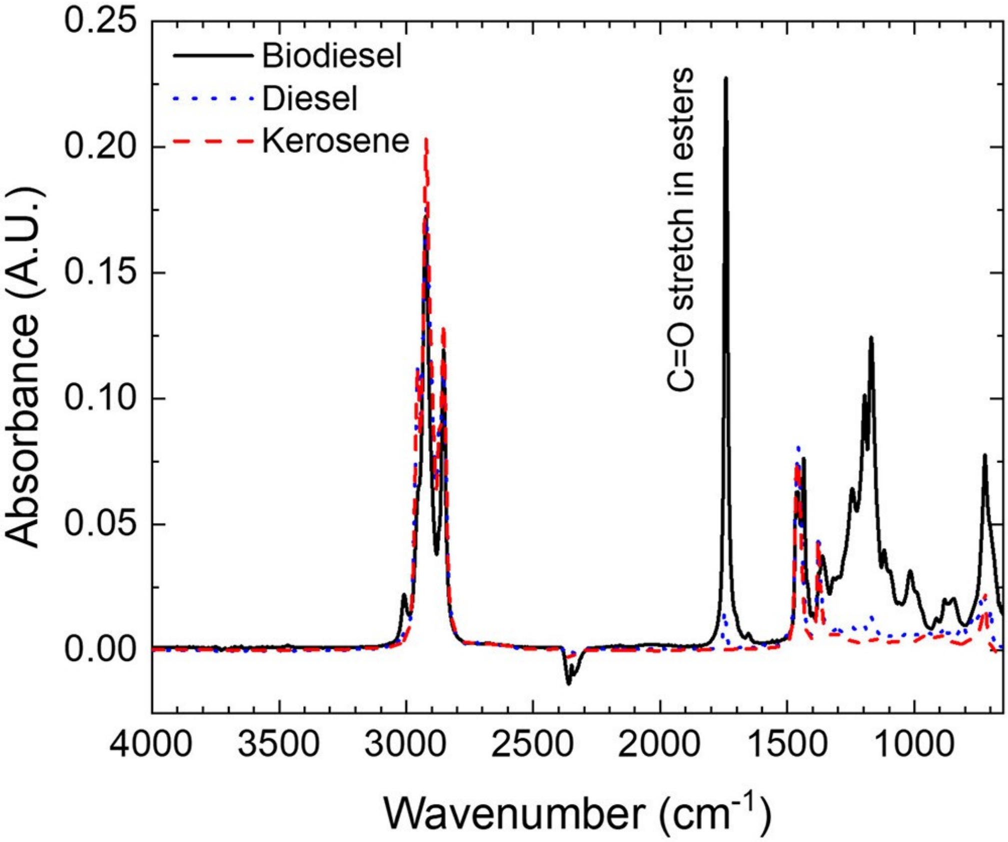


Figure 3.2 FTIR-ATR spectra of the solvents used in this study.

3.4.3 Effect of Solvent Soaking on Bitumen Viscosity

The effect of solvent conditioning on bitumen viscosity was investigated. Samples of solvent pretreated bitumen were prepared by adding a designated amount of solvent into a small glass bottle filled with approximately 5 g of Athabasca oil sand bitumen. All the samples were stored at 50°C for 1 week to guarantee good homogenization. The concentration of solvent was determined by

$$C(solvent) = \frac{m(after\ homogenization) - m(bottle\ with\ bitumen)}{m(after\ homogenization) - m(empty\ bottle)} \times 100\% \qquad (3.1)$$

The viscosity of solvent-soaked bitumen was determined using the above-mentioned rheometer. For high viscosity regime (>50 Pa s), a plate geometry of 20 mm in diameter and 500.0 μm in gap (TA Instruments) was used over a shear rate range from 0.1 to 1 s^{-1}, while for low viscosity regime, a cylinder-cup geometry of 28 mm in bob diameter and 30 mm in cup diameter (TA Instruments) was used over a shear rate range from 10 to 100 s^{-1}.

3.4.4 Bitumen Recovery from Solvent-Soaked Oil Sands

A thin layer of weighed oil sands sample (500.0 ± 0.1 g) was placed on a large glass pan, followed by the addition of a designated amount of biodiesel, diesel, or kerosene. To achieve satisfactory mixing, a simple commercial atomizer (100 mL polypropylene spray bottle by QUO) was used to quantitatively and evenly distribute the solvent over the entire ore sample. The sample was then sealed with aluminum foil and left still for 20 min soaking (Harjai, Flury *et al.* 2012), which is considered sufficient to achieve good homogeneity of solvent in bitumen (see corresponding discussion in Appendix IV). During the oil sands pre-treatment, the change in the total weight of oil sands ore and solvent was found negligible (below the detection limit of 0.1 g).

Bitumen recovery tests on the solvent-soaked oil sands were carried out using a costume-modified Batch-Extraction-Unit (M-BEU) at 25.0 ± 0.1°C in a three-stage process: slurry conditioning, primary flotation, and air-induced secondary flotation. The slurry conditioning was conducted by mixing 250 mL process water with the pretreated ore and agitating the mixture at 800 rpm with the air being added into the system at a rate of 150 mL/min for 10 min. The air pump was then stopped, and additional 800 mL process water was added to the dense slurry. The slurry was agitated at 600 rpm for 10 min during which primary froth was continuously collected into a pre-weighed thimble. The air was pumped in again at 150 mL/min, while the slurry was agitated at 800 rpm for 15 min during which the secondary froth was collected into a separate thimble. It is important to note that both the primary and secondary froth was collected immediately without a substantial drainage process that helps the rejection of water/solid entrainment. Such a method of collecting the froth would lead to a lower bitumen content in froth (mostly <40%) as compared with the bitumen froth from commercial operations (~60%). After a total of 20 min flotation, there was little bitumen froth generated. The identical procedure was applied to the untreated oil sands as the control (baseline) tests for comparison.

The bitumen froth collected was analyzed for bitumen, solids, and water content using a well-established Dean–Stark procedure with toluene as the refluxing solvent (Starr and Bulmer 1979). Preliminary tests on refluxing of any solvent used in this study for pre-treating the oil sands showed that the majority of the solvent added, similar to bitumen, was retained in the refluxing solvent with the solvent loss less than 0.2%. The bitumen recovery was thus calculated on the basis of total hydrocarbon (bitumen + pre-treating solvent) in each ore sample, as shown in Equation 3.2.

$$Recovery = \frac{m(collected\ oil\ phase)}{m(bitumen\ in\ ore)+m(pretreatment\ solvent)} \times 100\% \qquad (3.2)$$

3.4.5 Bitumen Liberation Analysis

In situ bitumen liberation visualization cell has been proven to be a powerful tool to determine bitumen liberation in real time (Srinivasa, Flury *et al.* 2012). In this study, the bitumen liberation tests were conducted using the same cell at ambient temperature. Detailed experimental procedures have been reported in the literature (Harjai, Flury *et al.* 2012, Srinivasa, Flury *et al.* 2012). In brief, the process of bitumen liberation from oil sands sample in an aqueous medium was recorded under a stereo-optical microscopy. By analyzing the recorded high-resolution images, the rate of bitumen liberation was obtained. Under the microscopy, the region of oil sands sample occupied by bitumen was conveniently distinguished as dark areas. As shown in , when a stream of process water was allowed to flow on top of the oil sands sample, the bitumen (the dark region at T = 10s) was continuously liberated from the sand grains that became brighter on the image (T = 600s), from which the degree of bitumen liberation (DBL) was conveniently calculated as a function of time to assess the effect of any process variables, such as solvent addition on bitumen liberation. In accordance with a previous study (Harjai, Flury *et al.* 2012), adding a small amount (up to 20 wt%) of the given solvents to an oil sands ore was found to exhibit an unmeasurable effect on the darkness of bitumen, making the DBL results highly accurate and reproducible.

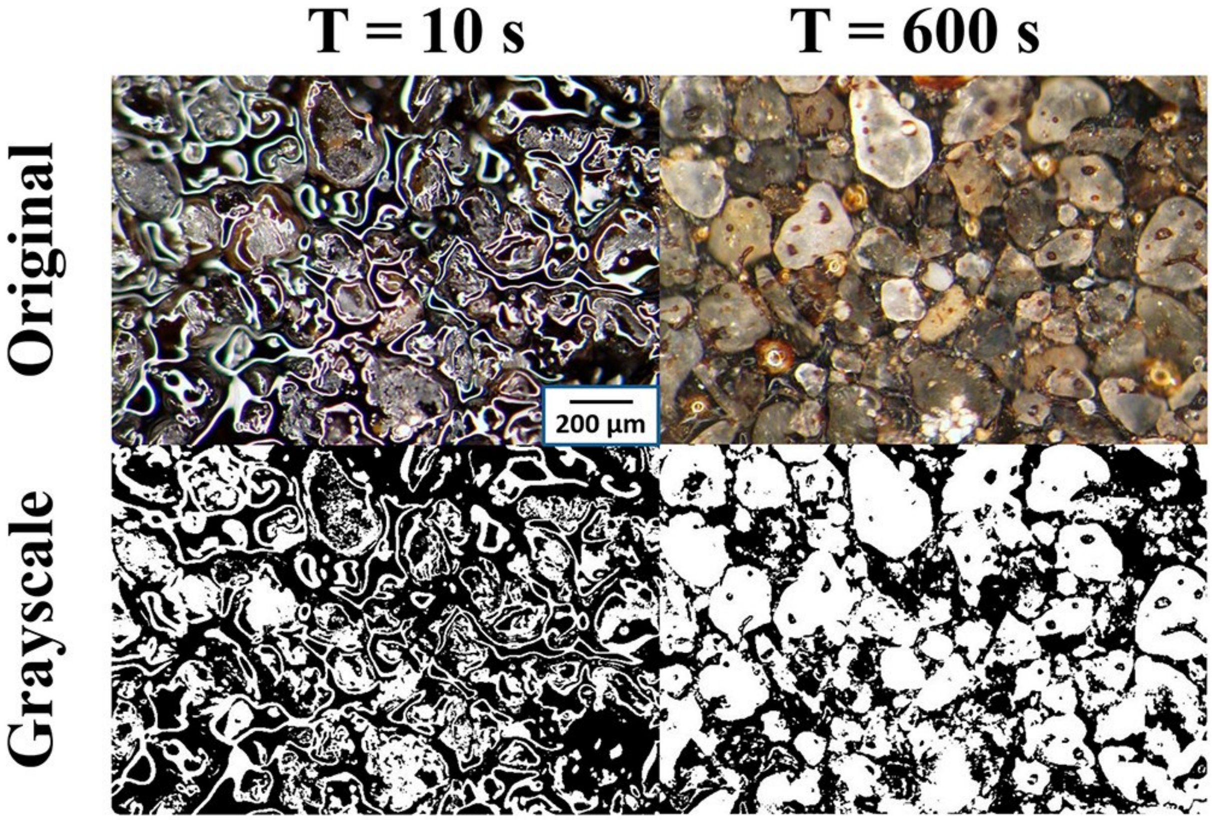


Figure 3.3 Bitumen liberation from sand grains to the aqueous phase is precisely reflected by variation in the gray scale of oil sands surfaces in the process water under an optical microscope. The photos show the transition of color to grayscale and hence black/white images for quantitative analysis of bitumen liberation.

3.4.6 Induction Time Measurement

Induction time refers to the minimum contact time required for successful attachment of bitumen to an air bubble. It is usually used to study the bitumen aeration properties. A short induction time represents a fast attachment, corresponding to a good bitumen aeration and hence favored bitumen flotation. In this study, the bitumen isolated from oil sands sample by centrifugation was used to study the effect of solvent addition on bitumen aeration. Specifically, the bitumen sample isolated from oil sands sample was soaked with a given amount of solvent for 1 week in a sealed container. In a typical induction time measurement, the solvent-soaked bitumen sample was placed in a sample holder and the sample holder was then immersed in a desired process water. An air bubble of given size was generated in process water on the tip of a glass capillary with the other end of the glass capillary attached to the diaphragm of a speaker. The speaker through the diaphragm drives the air bubble to contact with the bitumen surface for a pre-set period of time, while the attachment state was assessed after retraction of the bubble from the bitumen surface. The process for each contact time was repeated 50 times. The time of contact leading to 50% successful attachment was defined as induction time and recorded for comparisons. All the induction time experiments were conducted at 25.0 ± 1.0°C throughout this study. The detailed procedures and parameters used in the induction time measurements were given elsewhere (Harjai, Flury *et al.* 2012).

3.4.7 Tailings Analysis

There are two major problems in handling tailings of any solvent-involved oil sands processes (i.e., the difficulty of tailings consolidation and the problems of solvent loss to the tailings). To study the tailings consolidation behavior, the extraction tailings from each bitumen recovery test was collected in a glass jar. The settling of solids was evaluated from the descending of the mudline (i.e., the interface between the supernatant liquid and solid-rich suspension/sediment layer), measured visually over time with the help of the scales on the cylinder. To investigate the settling of fine solids, the turbidity of the supernatant was measured over time with Micro 100 Turbid meter (HF Scientific, Inc.). The net solvent loss to the extraction tailings was determined in a jar-based extraction test. In detail, 50 g of oil sands was placed in a glass jar and pretreated with 10 wt% (calculated on the basis of bitumen) biodiesel for 20 min. After adding 100 mL processing water, the jar was sealed and homogenized at ambient temperature by a mechanical shaker (model 6000, Eberbach

Scientific Instruments & Apparatus) set at “high” for 3 h. The froth collected right after was referred to as the 1st froth, while the froth collected after another 1 h homogenization at an elevated temperature of 70°C was referred to as the 2nd froth, with the remaining as the final tailings. A light hydrocarbon (cyclo-pentane) was used as the froth treatment agent to reject solid and water from the two froths and final tailings. The solvent (cyclo-pentane) was then removed from the organic phase at its boiling point (49°C). The concentrated extract, consisting mainly of bitumen and biodiesel, was then diluted with a designated amount of toluene before the biodiesel content was determined quantitatively using FTIR at the characteristic peak 1745 cm^{-1} of biodiesel. A liquid sample holder of two parallel KBr windows at a fixed spacing of 0.1 mm was used in this quantitative FTIR analysis. Toluene solutions of biodiesel in a concentration range of 0–5 wt% with and without bitumen were analyzed to construct a standard calibration curve. Results showed that the integrated area of FTIR patterns at the characteristic peak of biodiesel is hardly affected by the presence of 5 wt% bitumen as shown in Figure A.5 (in Appendix IV), but features strong linear correlation to the concentration of biodiesel, as presented in Figure A.6.

3.5 Results and Discussion

3.5.1 Effect of Solvent on Viscosity

It has long been recognized that bitumen recovery from oil sands is closely correlated with bitumen viscosity (Hupka, Miller *et al.* 1983, Hupka and Miller 1991, Schramm, Stasiuk *et al.* 2003, Drelich 2008). Tests on Athabasca oil sands showed that to achieve a satisfactory bitumen recovery, the viscosity of bitumen must be reduced to the level of 1–10 Pa s (Schramm, Stasiuk *et al.* 2003, Long, Drelich *et al.* 2007), regardless of the ore types or extraction process. In this study, it was observed that the bitumen viscosity was consistently and substantially reduced with increasing concentration of biodiesel, diesel, and kerosene in bitumen. As shown in Figure 3.4, the bitumen viscosity (scattered dots) was found to drop over 3 orders of magnitude (from 2.22 × 103 Pa s down to below 10 Pa s) with 19.6 wt% of the solvents added to the bitumen. It is interesting to note a slightly higher viscosity of bitumen with the same amount of solvent addition for biodiesel than for the other two solvents. Such a difference was reasonable because the viscosity of biodiesel was higher than the viscosity of the other two solvents (Table 3.3). The viscosity of bitumen with solvent addition was estimated using the Shu model (Shu 1984), and the results plotted in Figure 3.4 show a good agreement between the results from the model prediction and experimental measurement.

It is clear that the bitumen viscosity can be effectively reduced with the addition of the three solvents. With ~20 wt% of solvent addition, the bitumen viscosity was reduced sufficiently to below 10 Pa s, which could facilitate an acceptable bitumen recovery at ambient temperature. Whereas in water-based extraction, an equivalent bitumen viscosity reduction could only be achieved with a notably higher operating temperature at 50–60°C (Seyer and Gyte 1989).

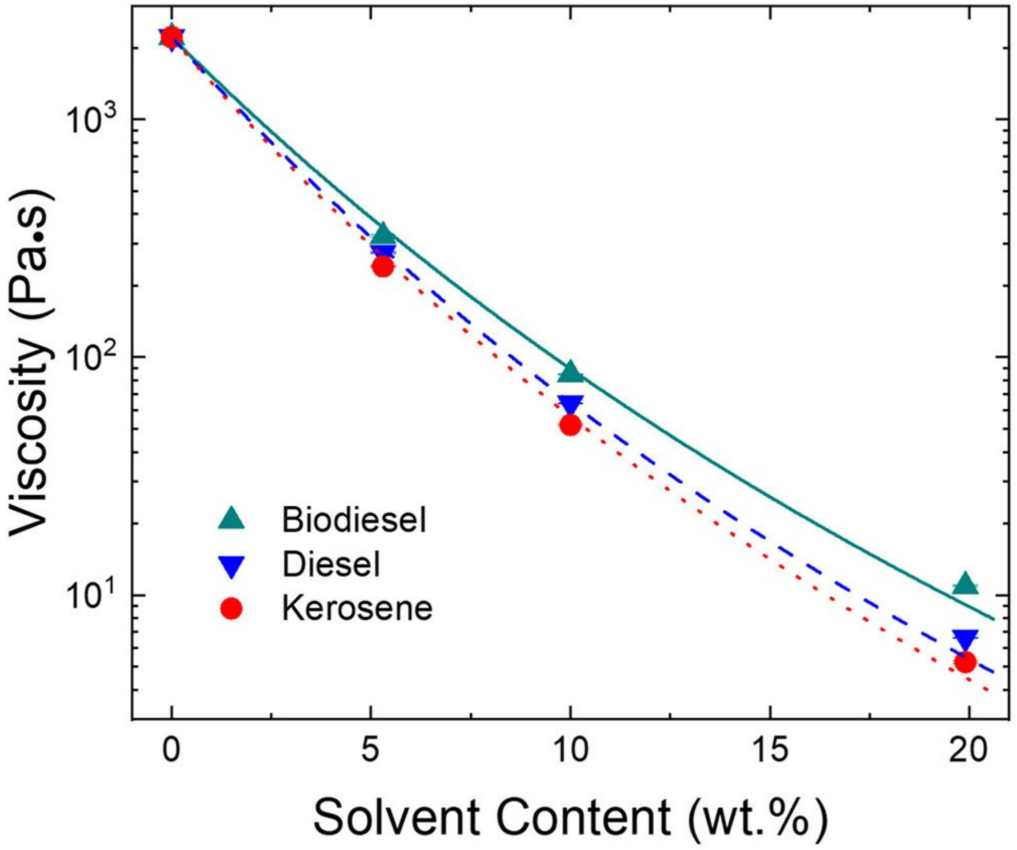


Figure 3.4 Effect of solvent addition on viscosity of bitumen at 25.00 ± 0.05°C: symbols measured experimentally and lines prediction from Shu model.

3.5.2 Effect of Biodiesel Addition on Bitumen Liberation

To achieve an in-depth understanding of the role of biodiesel in the bitumen recovery enhancement, it is of great importance and interest to study the two dominant processes of bitumen recovery: bitumen liberation and bitumen aeration. The influence of biodiesel addition on bitumen liberation was investigated using Ore P with and without biodiesel addition in the process water as a comparison to SEP and water-based extraction process (WBEP) at ambient temperatures, respectively. Bitumen liberation kinetics was investigated using an in situ bitumen liberation visualization cell (Srinivasa, Flury *et al.* 2012), and the results of degree of bitumen liberation (DBL) are summarized in Figure 3.5. To achieve quantitative analysis, a hyperbola-type empirical expression, shown as Equation 3.3, was used to evaluate the bitumen liberation performance.

$$DBL(\%) = \frac{mt}{n+t} \tag{3.3}$$

In Equation 3.3, the degree of bitumen liberation equals 0 at t = 0, referring to the initial state with no bitumen liberation. At $t \rightarrow \infty$, the expression approaches the limit of $[DBL]_{ultimate} = \left(\frac{mt}{n+t}\right)_{t\rightarrow\infty} = m$, in agreement with the previous works (Harjai, Flury *et al.* 2012, Srinivasa, Flury *et al.* 2012). The value of m therefore could be considered the limit of overall bitumen liberation for a given ore at a particular set of operating conditions. For better comparison, the initial rate of bitumen liberation is normalized in this study by the ultimate DBL, m, as relative initial bitumen liberation rate, $v_{norm,\ DBL}$, i.e.,

$$v_{norm,\ DBL} = \left[\frac{d(DBL)}{dt}\right]_{t=0} \Big/ m = \frac{1}{n} \tag{3-4}$$

$v_{norm,\ DBL}$ is a measure in the rate of bitumen liberation from a solid surface to the bulk aqueous phase. A higher $v_{norm,\ DBL}$ represents a faster bitumen liberation process, and thus an enhanced bitumen recovery from oil sands. The fitting parameters and corresponding $v_{norm,\ DBL}$ of all bitumen liberation tests are summarized in Table 3.4.

The interfacial properties between bitumen and water play an important role in bitumen extraction (Drelich and Miller 1994). For the WBEP system, both the normalized initial bitumen liberation rate and ultimate DBL were higher than the baseline case but much lower than the case with solvent addition as shown in Figure 3.5 and Table 3.4. The migration of natural surfactants was greatly restricted by the high viscosity of bitumen at operating temperature of 25°C as in the baseline case. The addition of caustic enhanced liberation of natural surfactants from bitumen to the bitumen–water interface and/or further to water phase.

As shown in Figure 3.5A, a significant boost in the ultimate liberation ratio from ~30% (the blank group) to >85% was achieved with 20 wt% biodiesel addition to the ore, indicating a significant enhancement in bitumen liberation with increasing biodiesel addition. Similarly, the normalized initial rate of bitumen liberation ($v_{norm,\ DBL}$) also increased significantly from 0.0401 to 0.1406 and 0.2652 s^{-1} with 10 and 20 wt% biodiesel addition, as illustrated in Table 3.4. Biodiesel addition to the ore is therefore clearly shown to benefit the rate of bitumen releasing from sands surfaces.

Table 3.4 Fitting parameters of hyperbola function for bitumen liberation kinetics, and ultimate DBL and normalized initial bitumen liberation rate $v_{norm,\ DBL}$ for Ore P at 25°C.

Test Groups		**Fitting Parameters**			**Results**	
		$\boldsymbol{m}$	$\boldsymbol{n}$	**R^2**	$[DBL]_{ultimate}$ **(%)**	$v_{norm,\ DBL}$ **(s^{-1})**
No solvent	Blank	11	25	0.966	11	0.040
	0.05 wt.% NaOH [a]	29	15	0.990	29	0.065
Solvent [b]	10 wt.% Biodiesel	67	7.1	0.971	67	0.14
	20 wt.% Biodiesel	85	3.8	0.998	85	0.27
	10 wt.% Diesel	70	5.4	0.978	70	0.19
	10 wt.% Kerosene	68	4.3	0.985	68	0.23

[a] Dosage of caustic is in reference to original ore.

[b] Dosage of solvent is in reference to bitumen content in the original ore.

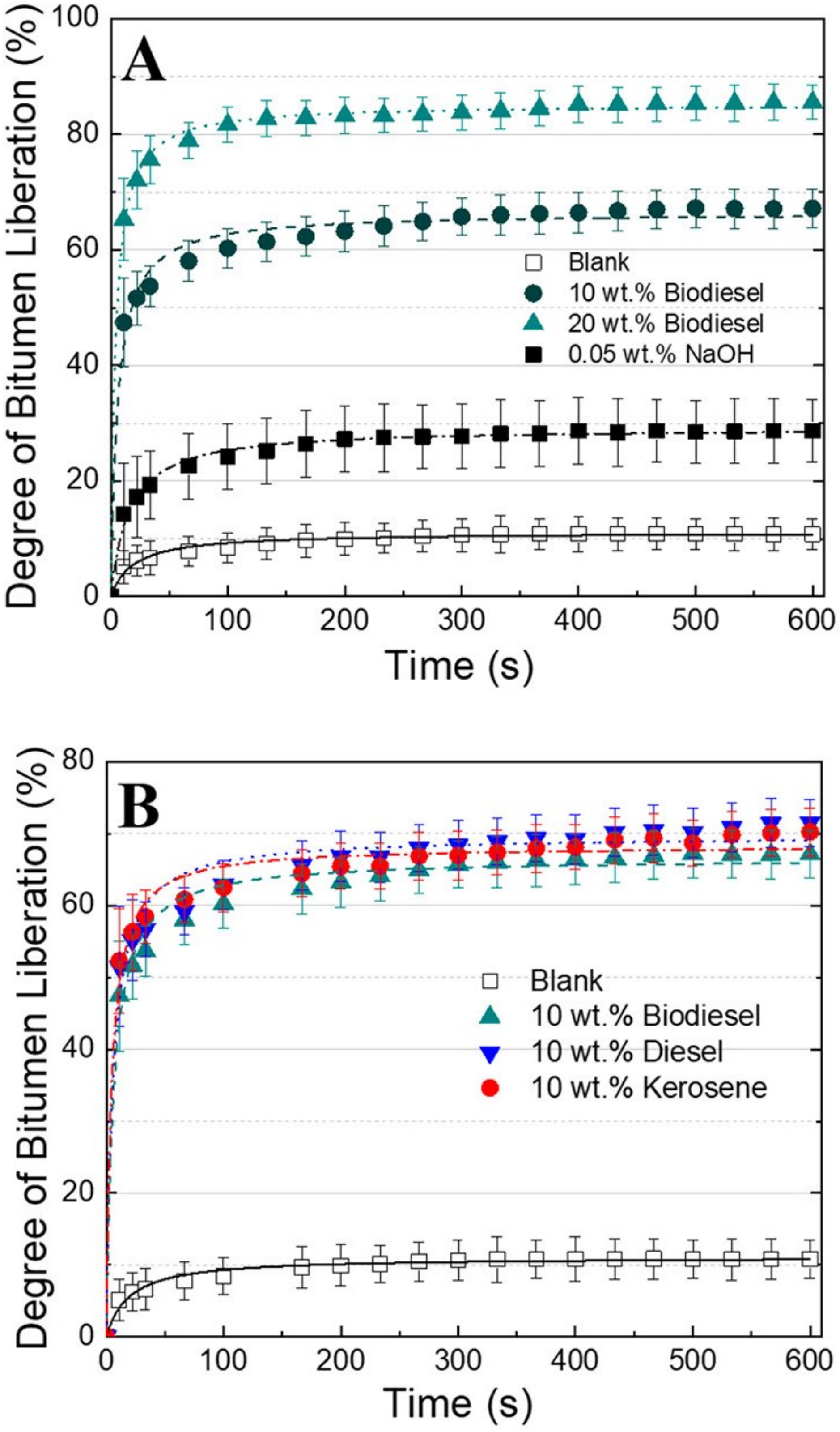


Figure 3.5 Effect of (A) biodiesel addition at different dosage, and (B) addition of biodiesel, diesel or kerosene, on bitumen liberation kinetics of Ore P at 25°C and pH of 7.52, with the

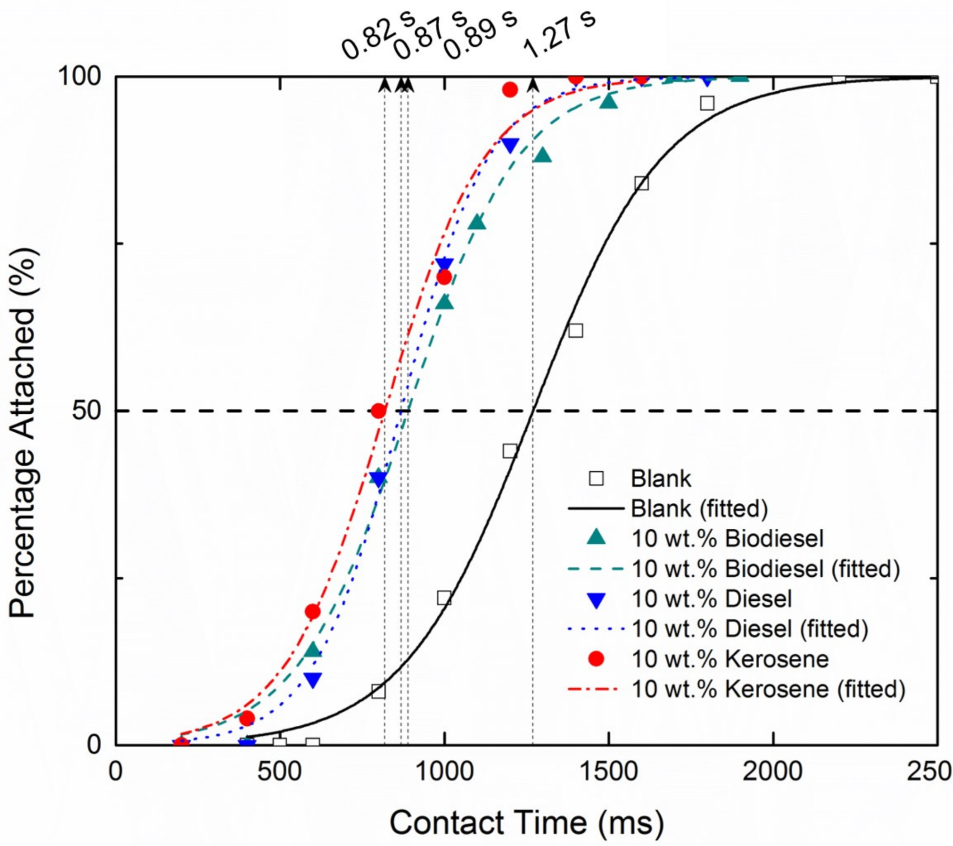
curves as the corresponding hyperbola fitting of Equation 3.3. Bitumen liberation was also analyzed without biodiesel but with 0.05 wt% NaOH (on ore basis) as a simulation to WBEP.

Although the observed desirable effect of biodiesel addition on bitumen liberation could certainly be attributed to the solvent-induced reduction in bitumen viscosity (Zhang 2012) that improved diffusion of natural surfactants from bulk bitumen to the bitumen–water interface, the presence of interfacial active components in biodiesel may also contribute to some degree to the desirable interfacial properties that enhance bitumen liberation. Biodiesel is known to contain an abundant amount of methyl ester groups, which makes biodiesel have a stronger affinity with water than common organic solvents (e.g., toluene), as shown by lower interfacial tension between biodiesel and water (as listed in Table 3.3) than between Athabasca bitumen and water (in the range of 10–15 mN/m (Moran, Yeung *et al.* 2000)). In the BA^{3}BE process, the surfactant in biodiesel dissolved in bitumen to reduce the viscosity of bitumen further reduces the bitumen–water interfacial tension. The reduction in bitumen–water interfacial tension leads to a lower contact angle (measured through aqueous phase) of bitumen on sand surface and hence enhanced bitumen liberation from the sand surfaces. The results in Figure 3.5B show that the initial bitumen liberation could be increased by using the solvent of lower viscosity. However, for all the solvents tested, bitumen liberation was observed to finish at 300 s after the start of the experiment. More discussions about bitumen liberation kinetics can be found in the Appendix IV.

3.5.3 Effect of Biodiesel Addition on Bitumen Aeration

Bitumen aeration is an important criterion to evaluate the performance of bitumen flotation. The results of induction time (EAT50) measurements are shown in Figure 3.6. A significant reduction of the induction time from 1269.9ms to 527.5ms was obtained as the content of biodiesel added to bitumen increased from 0 to 20 wt%, as shown in Figure 3.6A, suggesting enhanced bitumen-air bubble attachment. The enhanced bitumen aeration was obtained with continuously increasing the content of biodiesel. Comparable improvement in the bitumen aeration was observed when studying the effect of diesel and kerosene addition. It was predicted by Masliyah (2010) that the mobility of surfactants at the bitumen–water interface was inversely correlated with the viscosity of bitumen. When a bitumen droplet contacted with an air bubble, bitumen with lower viscosity due to solvent treatment would allow for a more rapid removal of surfactants from the contact area, facilitating the drainage of intervening aqueous film to accomplish a rapid attachment (2010).

Nevertheless, as shown in Figure 3.6B, all the solvent-treated bitumen featured a much shorter induction time than the blank group (labelled as ☐). A similar phenomenon was observed by Harjai *et al.* (Harjai, Flury *et al.* 2012) The increased mobility of bitumen–water interface after solvent addition was considered to benefit the depletion of intervening water between the air bubble and bitumen, leading to a considerable reduction in induction time. As discussed in previous sections, such reduction in induction time would greatly improve bitumen attachment to air bubbles in flotation and therefore increase bitumen recovery. As shown in Figure 3.6B, the solvent-treated bitumen samples featured little difference in induction time regardless of solvent type, indicating a weak dependence of bitumen aeration on the type of solvent used in this study.


0.82 s
0.87 s
0.89 s
1.27 s
100
50
0
0
500
1000
1500
2000
2500
Percentage Attached (%)
Contact Time (ms)
Blank
Blank (fitted)
10 wt.% Biodiesel
10 wt.% Biodiesel (fitted)
10 wt.% Diesel
10 wt.% Diesel (fitted)
10 wt.% Kerosene
10 wt.% Kerosene (fitted)

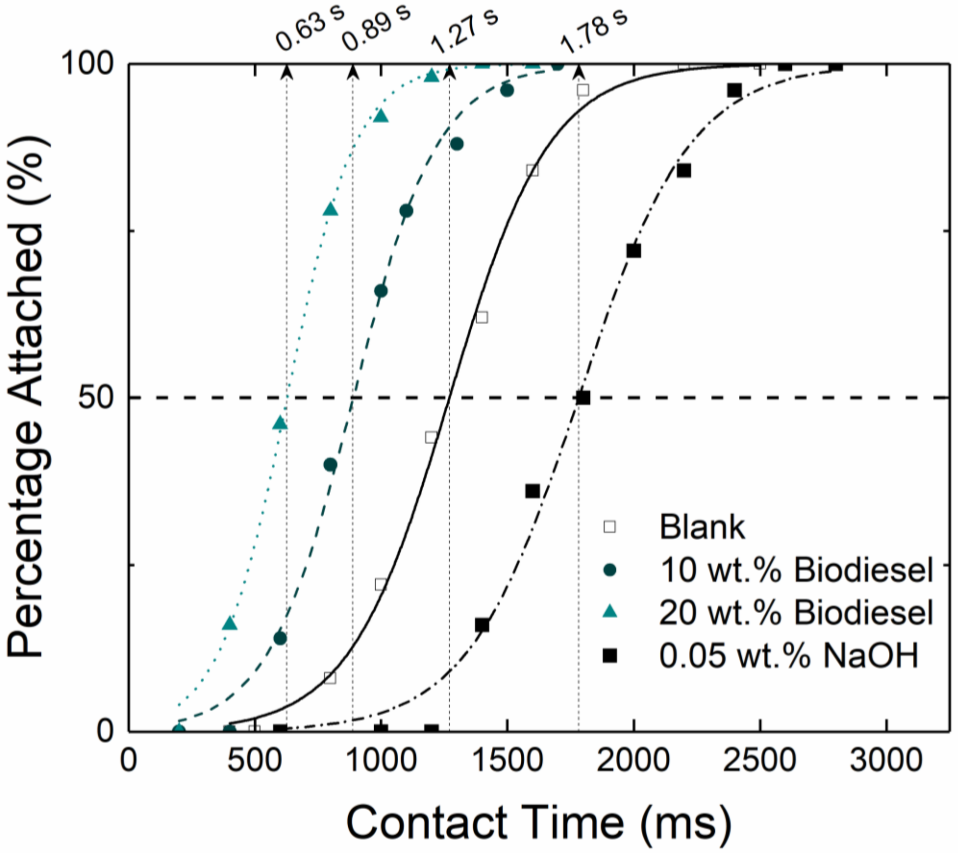

0.63 s
0.89 s
1.27 s
1.78 s
100
50
0
0
500
1000
1500
2000
2500
3000
Percentage Attached (%)
Contact Time (ms)
Blank
10 wt.% Biodiesel
20 wt.% Biodiesel
0.05 wt.% NaOH

Figure 3.6 Effect of (A) biodiesel addition at different dosages and (B) addition of biodiesel, diesel, or kerosene on bitumen-air bubble attachment in process water, at 25°C and pH of 7.52. A dose–response relationship (Wilson, Si *et al.* 2006), $PA(\%) = \frac{100}{1+10^{(EAT50-t)p}}$, was used to fit the experimental data of percentage attachment and hence to determine EAT50.

3.5.4 Bitumen Extraction from Oil Sands

Bitumen extraction tests were conducted from two different oil sands ores (P and M). In this study, bitumen extraction performance was evaluated based on bitumen recovery and froth quality. To develop a low-temperature oil sands extraction process with reduced caustic usage, all the extraction tests were conducted at 25°C and, unless otherwise specified, with Syncrude process water (pH = 7.52) being used as extraction medium. As shown in Figure 3.7, a relatively low bitumen recovery of 8.6% and 52.7% (data points at zero solvent dosage) was obtained without any solvent or caustic addition from Ore P and M, respectively, indicating a poor processability of these two ores. For comparison, the extraction using water-base extraction process (WBEP) was also conducted under the same conditions, with caustic (NaOH) at 0.05 wt% of the original ore being added as a processing aid. The results of these WBEP extraction tests showed a certain increase in the bitumen recovery from 8.6% to 32.2% and from 52.7% to 68.5%, for Ore P and Ore M, respectively. Such an improvement was in accordance with the observation in the common industrial practices (Sanford and Seyer 1979, 2010) that an enhanced bitumen recovery from oil sands could be achieved over the pH range of 8.5–9.

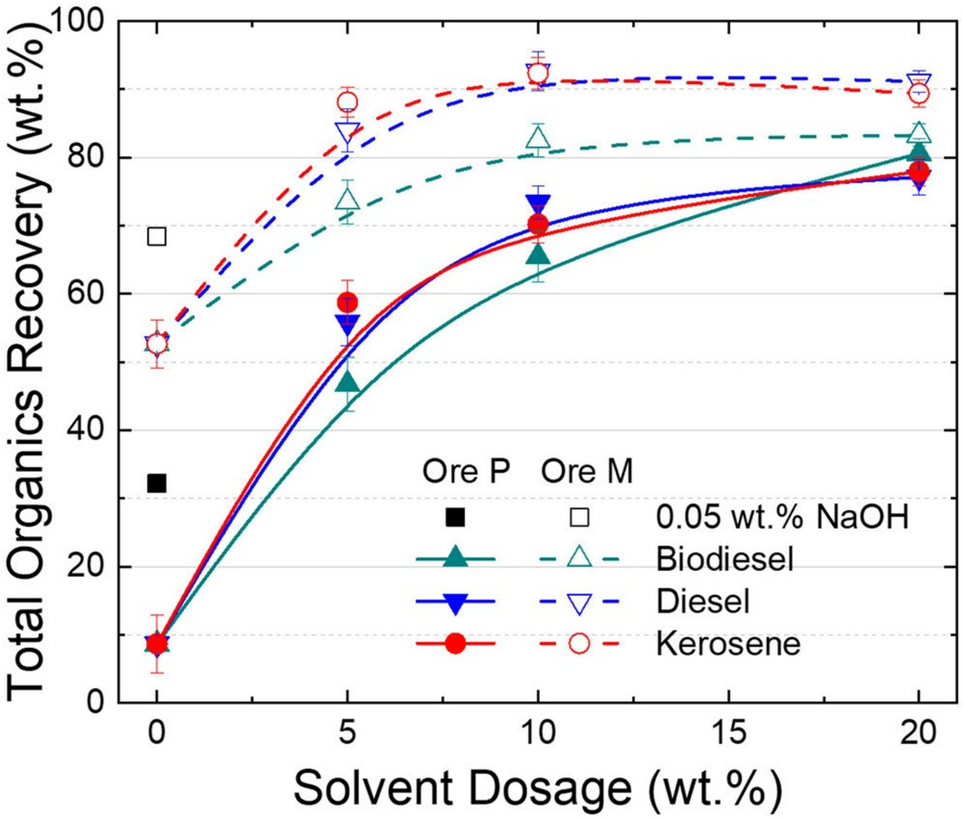


Figure 3.7 Effect of solvent addition/pre-treatment on bitumen recovery from Ore P (solid dots) and Ore M (hallow dots) at 25°C and pH 7.52 without caustic addition. The amount of solvent added is shown in terms of bitumen content initially in the ore.

In addition to the improvement in bitumen recovery, caustic addition in WBEP tests also led to a slight increase in bitumen content of the froth from 10.3 wt% to 13.3 wt% for ore P (black bars in Figure 3.8A). Accompanying this increase is the increase in the solids content from 18.4 wt% to 23.6 wt% (brown bars in Figure 3.8A) in the froth from WBEP extraction tests. Such an increase is attributed to the increased bitumen recovery with caustic addition, possibly due to the entrapment of fine solids in water carried over to the froth and/or entrapment of fine solids between bitumen droplets attached to bubbles.(27) It is interesting to note little variation in bitumen to solid ratio (B/S) of 0.560 (blank) and 0.564 (WBEP) tests. A similar trend was obtained for Ore M but to a lesser extent in variation as compared with the case for Ore P, as shown in Figure 3.8B.

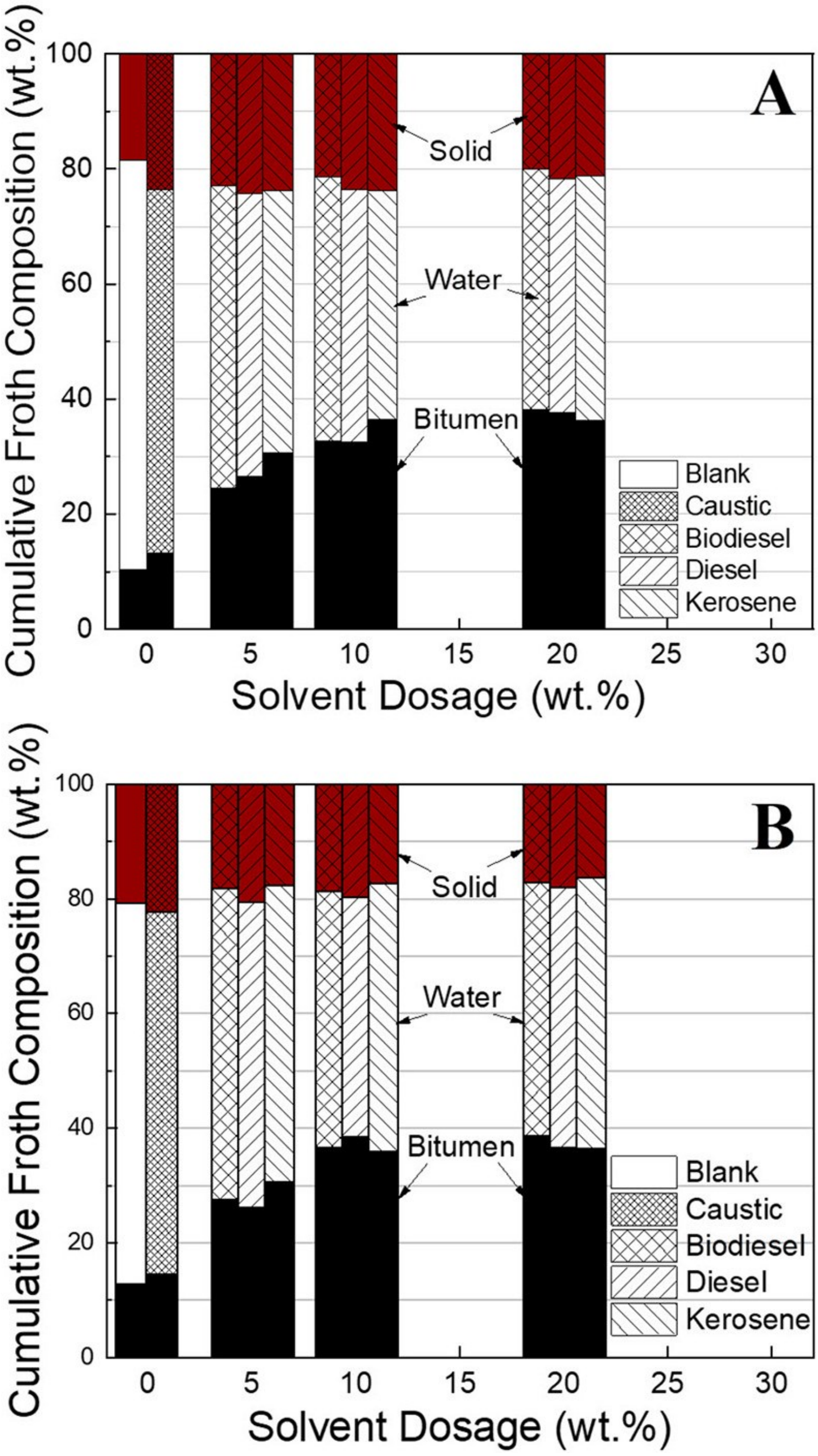


Figure 3.8 Effect of solvent addition/pre-treatment on bitumen froth quality from (A) Ore P and (B) Ore M at 25°C and pH of 7.52 (except for the group marked with caustic, which was obtained with 0.05 wt% NaOH addition of original ore), showing a general increase in

bitumen content and a slight increase in solids content with solvent addition from 0 to 20 wt% of bitumen content in the ore.

To demonstrate the feasibility of biodiesel-assisted hybrid extraction process, bitumen extraction tests were conducted at different biodiesel dosages. Texts with petroleum diesel and kerosene were also conducted for comparison. In the following discussion, the amount of solvent addition was defined on the basis of bitumen content in the original oil sands ore. For Ore P, an initial 5 wt% solvent addition in ore pre-treatment was found to improve the bitumen recovery remarkably from 8.7% to 46.8%, 55.8%, and 58.7%, with the addition of biodiesel, diesel, and kerosene, respectively. The improvement in bitumen recovery achieved at a solvent dosage as low as 5 wt% in solvent-assisted extraction tests at room temperature was more significant than that obtained with caustic addition in WBEP for both Ore P and Ore M, as shown in Figure 3.7. Further increase in solvent addition to 20 wt% boosted the bitumen recovery to ~80%. A similar solvent-induced enhancement of bitumen recovery was obtained for Ore M, as also shown in Figure 3.7. Interestingly, the maximum bitumen recovery was achieved at a solvent dosage of 10 wt% for the case of Ore M. Such a variation in the optimal solvent dosage with the type of ores was also reported in the literature (Harjai, Flury *et al.* 2012), suggesting that the optimal solvent dosage for good processing ore was lower than that for poor processing ores.

For froth quality analysis in Figure 3.8, the solvent addition in general resulted in a significant increase in bitumen content of the froth from 10 to 36 wt% for both ores. In addition, the froth quality did not appear to be sensitive to the solvent type, suggesting that the improved bitumen content is predominantly linked to the reduction of bitumen viscosity by solvent addition. In summary, the hybrid extraction tests at ambient temperature revealed a notable improvement in both bitumen recovery and froth quality with the addition of three solvents at dosages less than 15 wt% of bitumen in the ore. Such improvement once again acknowledged the benefits of hybrid extraction in reducing the solvent usage and energy intensity in oil sands processing, as a comparable bitumen recovery could only be achieved at a much higher solvent dosage in the SEP (Duncan, Freitas *et al.* 1969, Funk 1979, Angevine, Carroll *et al.* 1984, Chung and Dickert 1985, Paspek, Hauser *et al.* 1993, Ledbetter, Bishop *et al.* 2009, Garner, Wiwchar *et al.* 2010, Fan and Shafie 2012, Bohnert and Verhulst 2013, Fan, Shafie *et al.* 2015).

3.5.5 Tailings Consolidation

A major concern with HWEP is the production and storage of large quantities of intractable fluid fine tailings. It is therefore important to investigate the effect of solvent addition on tailings consolidation. For comparison, the consolidation of tailings from water-based extraction with caustic addition was also investigated. The whole tailings from each bitumen extraction test were collected and stored in glass jars for solid sedimentation. The results of tailings settling are shown in Figure 3.9, and the results on turbidity measurement of the corresponding supernatant are shown in Figure 3.10. A hyperbola model given in the Equation 3.5, as proposed by Yaromko (Yaromko 1977), was found to be adequate to describe the mudline descending in this study.

$$h/H = \frac{\alpha t}{\beta + t} + 1 \tag{3.5}$$

where [h/H] is the normalized mudline height defined as the ratio of height of the mud layer to that of total sludge tailings, as shown in the inset of Figure 3.9; α and β are two empirical parameters of the hyperbola correlation. At $t = 0$, h/H equals 1, referring to the initial state. When$t \to \infty$, $[h/H]$ approaches a limit $[h/H]_{untimate}$ of $\alpha + 1$, which can be considered as the consolidation limit under natural gravity (2010). The initial settling rate $v_{ini,\ stl}$ characterized by α/β is a useful parameter to evaluate the settling characteristics of sludge tailings. As shown in Figure 3.9, settling of all the tailings investigated follows Equation 3.5 and the fitting parameters are summarized in Table 3.5. Ideally, a large $v_{ini,\ stl}$ and a small $[h/H]_{untimate}$ values are desirable in the tailings processing, as they imply rapid settling and good consolidation with maximum release of water for recycle, respectively.

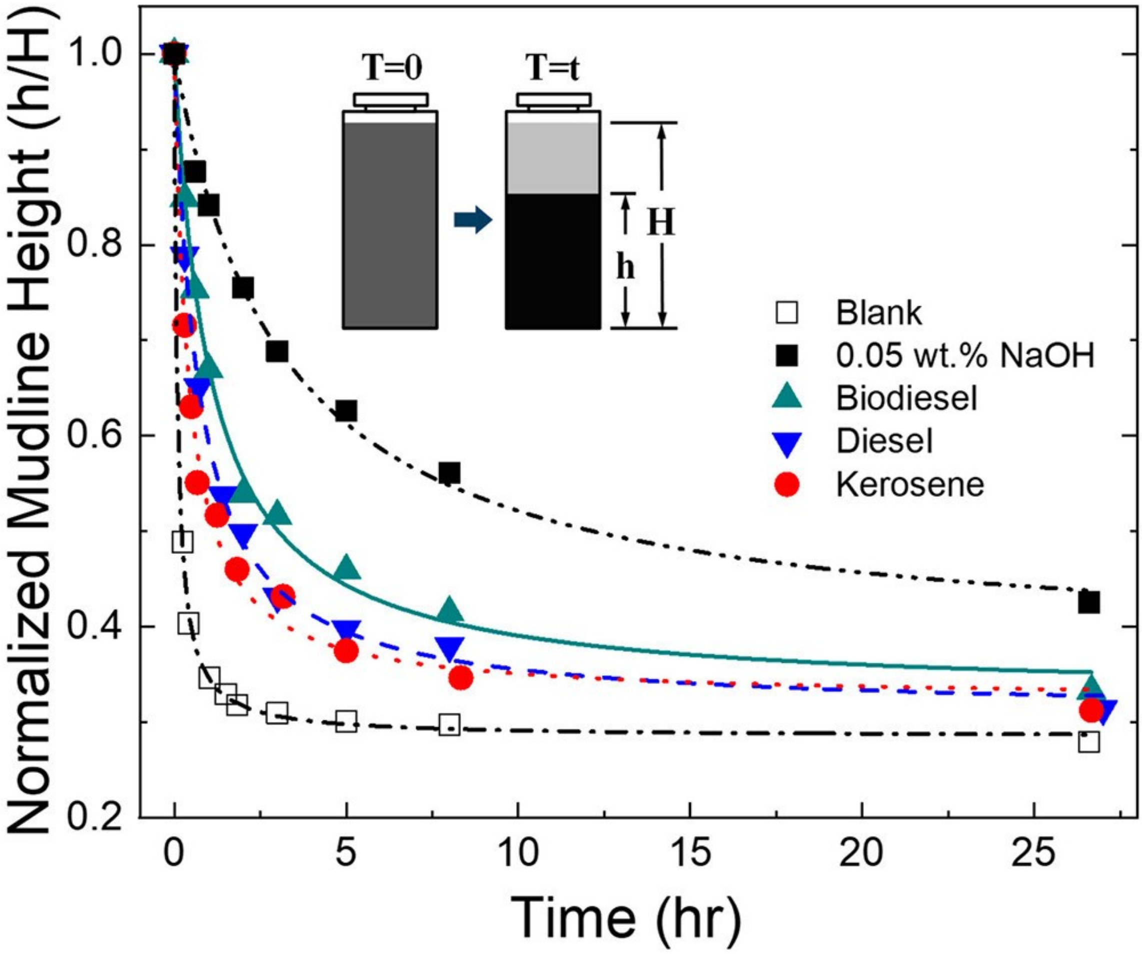


Figure 3.9 Effect of solvent addition on tailings settling/consolidation with the lines being the fit of settling curve to hyperbola correlation (Equation 3.5). Tailings from the solvent-assisted hybrid extraction process at 25°C from Ore P were obtained at the solvent dosage of 20 wt% of bitumen in the ore.

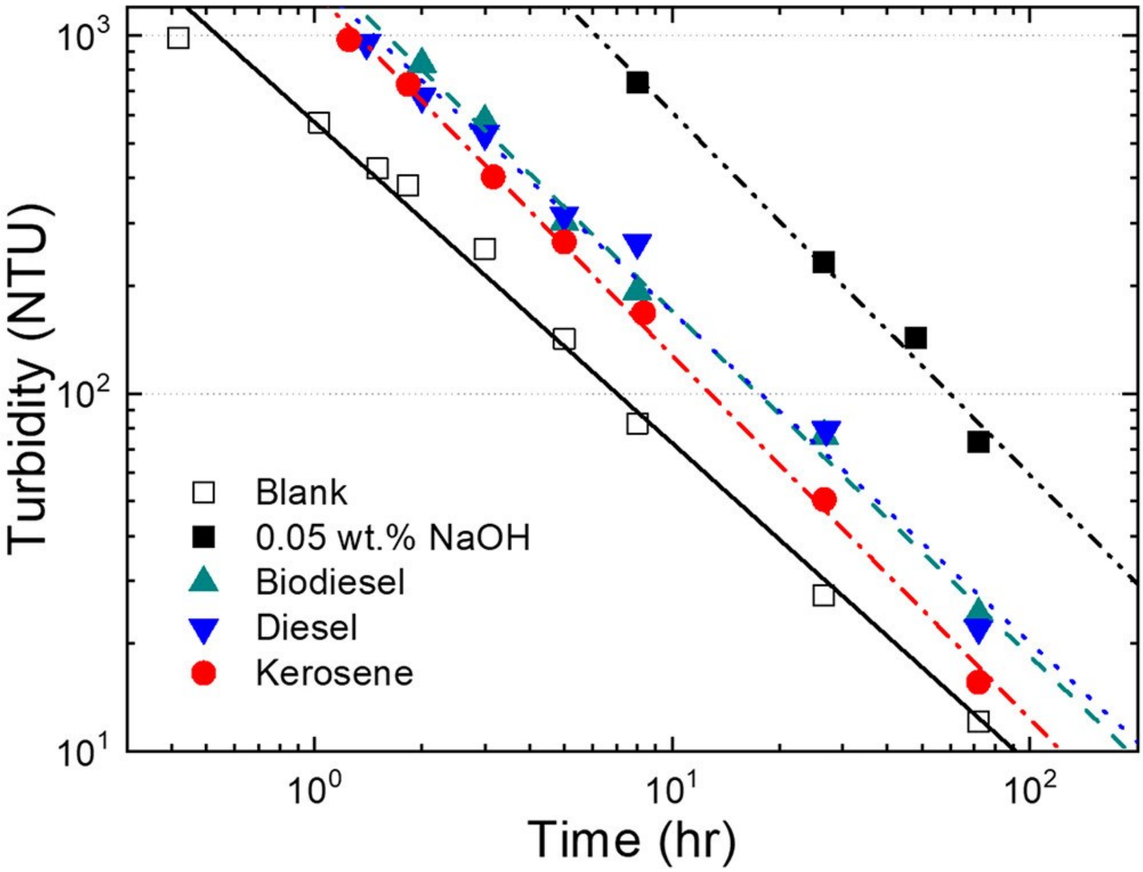


Figure 3.10 Effect of solvent addition on the turbidity of supernatant from the settled tailings obtained from solvent-assisted hybrid extraction process of Ore P at 25°C. The solvent dosage is kept at 20 wt% of bitumen in the ore.

The blank group appeared to allow the highest settling rate ($v_{ini,\ stl} = 7.592\ \mathrm{hr}^{-1}$) and the most compact sediment ($[h/H]_{ultimate} = 0.2848$), which was probably due to insufficient digestion of oil sands that led to low bitumen recovery as shown in Figure 3.7. The insufficient digestion resulted in an apparent reduction in the amount of dispersed solids as shown in Figure 3.10 and hence a rapid settling of tailings solids. With caustic addition at 0.05 wt.% of ore as practiced in current WBEP, the $v_{ini,stl}$ value was found to be significantly reduced, accompanied with a notable increase in $[\mathrm{h/H}]_{\mathrm{ultimate}}$. This dramatic change is attributed to the increased liberation of bitumen and dispersion of fine solids as a result of a significant increase in pH of slurry with caustic addition (Masliyah, Zhou *et al.* 2004).

Table 3.5 Hyperbola Fitting Parameters for Tailings Settling/Consolidation and Estimated Initial Settling Rate and Ultimate Sediment Height. [a]

Test Groups		**Fitting Parameters**			**Results**	
		$\boldsymbol{\alpha}$	$\boldsymbol{\beta}$	**R^2**	$v_{ini,stl}$ **(hr^{-1})**	$[h/H]_{ultimate}$
No solvent	Blank	-0.72	0.094	0.999	7.6	0.29
	0.05 wt.% NaOH [b]	-0.63	3.1	0.999	0.20	0.37
Solvent [c]	10 wt.% Biodiesel	-0.67	1.1	0.996	0.64	0.33
	20 wt.% Biodiesel	-0.69	0.70	0.998	0.99	0.31
	10 wt.% Diesel	-0.68	0.42	0.991	1.6	0.32
	10 wt.% Kerosene	-0.72	0.094	0.999	7.6	0.29

[a] Dosage of caustic is in reference to original ore.

[b] Dosage of solvent is in reference to bitumen content in the original ore.

It has been found in this study that solvent addition greatly influences the tailings settling as shown in Figure 3.9 and Figure 3.10. The initial settling rate of tailings increased in the order of kerosene > diesel > biodiesel ≫ WBEP. This order appears to correlate with increased content of polar components in the solvents as kerosene < diesel < biodiesel. The polar components appear to enhance dispersion of fine solids by enhanced removal of bitumen from solid surfaces as revealed in an enhanced order of bitumen liberation. In addition, unrecovered bitumen/solvent trapped in the tailings although small in amount could contribute to the increased viscosity of slurry in the order of kerosene < diesel < biodiesel, which led to a reduced settling rate of fine solids in the same order. On the other hand, the ultimate sediment height appeared to show no obvious variation for the tailings treated with different solvents (0.327, 0.311, and 0.324, for biodiesel, diesel, and kerosene treated groups, respectively), indicating little dependence of the compactness of aged sediment on solvent type.

The observations of tailings consolidation agreed well with the results given in Table 3.6 of zeta potential measurement on tailings supernatants. For all the processes at the highest solvent addition dosage, the zeta potentials of tailings supernatant were all found to be lower than −20 mV, which were much lower than the WBEP baseline group (−28.6 ± 0.4 mV), indicating a stronger repulsion between solids and more stabilized suspension with caustic addition. Compared with the case of WBEP with caustic addition, the tailings produced from solvent-assisted hybrid bitumen extraction process featured clearly the improved tailings consolidation kinetics and enhanced compactness of the final sediment, especially the rapid settling of fine solids.

Table 3.6 Zeta Potential Data of the Tailings Supernatant Samples (Raw Supernatant: 10 mM KCl Aqueous = 1:10 v/v) after 30 Min Equilibrium Time, at 25°C*

	Biodiesel	Diesel	Kerosene	0.05 wt.% Caustic
Tailings supernatant zeta potential (mV)	-18.4 ± 0.3	-17.8 ± 0.2	-17.4 ± 0.2	-28.6 ± 0.4

* The dosage of solvents was 20 wt% with respect to the initial bitumen content.

3.5.6 Solvent Loss to Tailings

It is always desirable to minimize the biodiesel loss to tailings due to the high retail value of biodiesel. The solvent dispersed in tailings water can be reclaimed and recycled to the extraction process along with the recovery water. Therefore, the net solvent loss is attributed only to the trapped solvent in solid tailings, which can be estimated from the extent of solvent trapped in solid tailings. Due to the difficulty in sampling from a large quantity of inhomogeneous tailings in MBEU-based extraction, the biodiesel content in froth stream was tested in a jar-based demo extraction and quantified by FTIR.

The results of biodiesel partition in each froth stream and final tailings of the jar-based demo extraction are shown in Table 3.7. The biodiesel/bitumen ratio was found to reduce from 10.5% to 9.4% in the firth and second froth and reach the lowest value of 7.5% in the bitumen trapped in final tailings. The amount of biodiesel trapped in the tailings was found to be 7.91 × 10^{-5} g/g of tailings. Although there was still a certain amount of biodiesel lost to tailings, such observation directly supports that the added biodiesel preferentially stayed with bitumen rather than with solids or water in either processing slurry or tailings. As a result, it is of vital importance to further improve the recovery of bitumen from tailings, in order to minimize the solvent loss to tailings.

Table 3.7 Summary of Biodiesel Distribution in the Jar-Based Extraction Procedure

	Bitumen (g)	Biodiesel (g/g Bitumen)	Calculated Biodiesel (g)
Initial State	5.7 (/50 g Ore M)	0.1	0.570
1st Froth (25 C)	3.33	0.105	0.350
2nd Froth (70 C)	2.21	0.094	0.208
Final Tailings	0.153	0.075	~0.011
Mass Balance	~99.9%		~99.9%

In summary, BA^3BE process has been demonstrated in this study for its good performance in bitumen extraction at ambient temperatures and tailings consolidation. However, further study is required, especially investigating the means to improve the recovery of unrecovered bitumen and biodiesel from tailings, in order to make BA^3BE process a practical alternative to the current HWEP for the mineable oil sands industry. In the present work, the extent of biodiesel hydrolysis is negligible under the given conditions of BA^3BE process (Jakeria, Fazal *et al.* 2014). As we know, aliphatic acid and methanol can be generated via biodiesel hydrolysis under desired conditions (Leung, Koo *et al.* 2006, Demirbas 2008). Since the number of carbon atoms of the biodiesel molecules is typically in the range of 16–20 (Demirbas 2008), which partially overlaps with that of the natural surfactants (e.g., naphthenic carboxylic acids) in bitumen, the aliphatic acids can be considered to be chemically related to the natural surfactants in bitumen. Therefore, biodiesel can potentially become a substitute for naphthenic acids under certain conditions that facilitates bitumen liberation for higher bitumen recovery. To enhance surface activity of biodiesel, one interesting idea could be taking the advantage of biodiesel hydrolysis in the future study. Since the dosage of solvent addition in the ASHBE process is about one magnitude lower than that in most SEP and more importantly less volatile solvent such as biodiesel could be used in ASHBE, the solvent loss to the tailings is significantly reduced and solvent-induced safety concerns are expected to be alleviated (Harjai, Flury *et al.* 2012). As mineable oil sands industry has already gained great experiences on handling such solvents as naphtha and C5–C7 paraffinic solvents used in the froth treatment of current processes, it would also be valuable to explore the use of widely available by-product of bitumen upgrading such as petroleum diesel as the solvent as such an approach would alleviate the need to purchase/ship large volume of solvent (biodiesel) while taking advantage of chemical additives and blends of solvents to enhance ASHBE without compromising the safety and solvent cost/availability.

3.6 Conclusions

This research demonstrated the feasibility of implementing an innovative biodiesel-assisted ambient aqueous bitumen extraction (BA^{3}BE) process for Athabasca oil sands using an environmentally friendly solvent. Biodiesel represents a renewable, biodegradable, noninflammable, and low toxic alternative to the common solvents such as petroleum diesel or kerosene. In perspective of extraction performance, the biodiesel-based hybrid extraction process, similar to petroleum diesel and kerosene, proved to allow oil sands processing at ambient temperature (25°C) to reduce energy intensity, while maintaining desirable bitumen recovery and froth quality. For the Athabasca oil sands samples studied, the biodiesel addition was found to greatly promote both subprocesses of bitumen recovery: bitumen liberation and bitumen aeration. An optimum biodiesel dosage appeared to be around 20 wt% of the bitumen in the ore. Biodiesel addition to oil sands facilitated a rapid bitumen liberation rate, an enhanced ultimate degree of bitumen liberation, and an apparent reduction in the induction time of bitumen-air bubble attachment. The innovative BA^3BE process not only enhanced the tailings consolidation kinetics but also showed a trend of reduced solvent loss to solid tailings compared to SEP, making it an ideal alternative for the mineable Athabasca oil sands processing with less negative environmental impacts and lower energy costs.

Chapter 4 Synergy of Chemical Additives in Biodiesel-Assisted Ambient Aqueous Bitumen Extraction (BA^3BE) for Enhance Bitumen Production from Mineable Oil Sands

This chapter is part of the following article submitted to *Energy & Fuels*.

Yeling Zhu, Yi Lu, Qingxia Liu, Jacob Masliyah, and Zhenghe Xu*, Synergy of Chemical Additives to Enhance Bitumen Recovery from Athabasca Oil Sands using Biodiesel-Assisted Ambient Aqueous Bitumen Extraction (BA^3BE) Process

4.1 Abstract

The massive unconventional petroleum resources in Athabasca oil sands in Alberta, Canada are currently being excavated and processed using the hot water bitumen extraction (HWBE) process. A major challenge associated with HWBE process is high energy intensity for maintaining an operation temperature at 40-55°C. Solvent-assisted ambient aqueous bitumen extraction (SA^3BE) processes, in which a portion of solvent is directly used for oil sands pretreatment prior to extraction process, have been reported capable of substantially reducing the energy intensity via ambient temperature operation. However, there is still a gap between the current SA^3BE process and industrial expectations. This study focuses on optimization of biodiesel-assisted ambient aqueous bitumen extraction (BA^3BE), an example of SA^3BE, by incorporating the use of methyl isobutyl carbinol (MIBC) and ethylene oxide-propylene oxide (EO-PO) copolymer in oil sands pretreatment. The idea is to take advantage of chemicals and/or demulsifiers used downstream of bitumen extraction process by their addition upfront as in the case of biodiesel-assisted hybrid extraction process. With the addition of chemicals in the improved BA^3BE process, both bitumen liberation and bitumen

flotation efficiency were improved significantly by 10 wt% (of bitumen) solvent. The results from bench-scale experiments revealed a higher bitumen recovery and high-quality bitumen froth by the improved BA^{3}BE at ambient temperature as compared with the basic BA^{3}BE and HWBE process.

4.2 Introduction

Oil sands in Northern Alberta, Canada, are one of the largest crude reservoirs in the world, with an estimated commercially recoverable bitumen reserve of about 165 billion bbl (AER 2018). The current industrial practice for shallow oil sands deposits is exclusively open-pit mining followed by hot water bitumen extraction (HWBE) process. Although it accounts for a massive production of 1.3 million bbl/day of raw bitumen in Alberta, HWBE process still faces numerous challenges (Masliyah, Zhou *et al.* 2004, 2010). With the depletion of easy-processing oil sand ores, mining and handling of poor-processing ores is becoming a norm. Poor-processing ores commonly contain large quantities of fine solids and are therefore unfavored in HWEB process, due to great demand for energy, lower bitumen recovery and more intensive wastes generation. As a result, the production of bitumen from oil sands by HWEB process becomes less profitable. Due to the inherent poor processability of oil sands, the processing slurry is required to be heated and operated at an elevated temperature of 40-55°C to achieve a satisfactory bitumen production, which substantially raises the energy/emission intensity. Since there exists no efficient practical technology for consolidation of fluid tailings in industry, the oil sands tailings is currently impounded in engineered tailings ponds, which was reported to cover a total area of 220 km^2 in 2017 and is believed to keep expanding (Kent 2017). Such treatment of processing waste (tailings) not only raises numerous safety and environmental concerns (WISE 2015), but also makes the entrapped water unavailable for continuous production (Wang, Feng *et al.* 2010). Moreover, in a froth cleaning process based on naphthenic solvent, the diluted bitumen produced typically contains 1.0-2.5 wt% water and 0.3-0.8 wt% solids that are in the form of intractable solid-stabilized water-in-oil (W/O) emulsions, causing severe problems in the downstream operations (Wang 2011). There is hence an urgent need to develop more advanced oil recovery technologies that can reduce the intensity of energy consumption and water utilization, minimize the carbon footprint and facilitate a clean bitumen production in dealing with poor-processing oil sands.

Many progresses have been made in studying solvent-assisted ambient aqueous bitumen extraction (SA^{3}BE) process (Harjai, Flury *et al.* 2012, Russell 2017), which takes advantage of solvent addition while developing a viable solution to overcome its drawbacks. An improved bitumen recovery was achieved using SA^{3}BE process with the addition of several types of solvents, including kerosene and petroleum diesel (Harjai, Flury *et al.* 2012, Russell 2017). Moreover, SA^{3}BE process exhibited a desired robustness in handling complex variability of oil sand ores, as bitumen recovery was found to be merely marginally dependent on the characteristics of ores using SA^{3}BE process as compared with conventional CHWE process. A more rapid consolidation and increased compactness of extraction tailings were also observed in SA^{3}BE process because of restrained dispersion of clays at no/reduced use of caustics. However, there are still a few knowledge gaps to be addressed before SA^{3}BE could move on to a large-scale demonstration test. Addition of 10 wt% kerosene (with respect to bitumen content initially in the ore) for conditioning was found to improve the bitumen recovery from poor-processing ores by 40–60% (Harjai, Flury *et al.* 2012). However there is still a significant loss of 10–20% bitumen in the tailings stream. Recovery of such remaining bitumen appears to be difficult by merely addition of excessive solvent in oil sand pretreatment (Harjai, Flury *et al.* 2012). Although SA^{3}BE process introduces a higher bitumen content in froth at ambient temperature, the negligible reduction of solid impurities (primarily clays) in bitumen froth suggests the need to consume a comparable amount of diluent for froth treatment as in the HWBE process (Harjai, Flury *et al.* 2012). More importantly, there has been no report so far on the effect of SA^{3}BE on formation of unwanted water emulsions in diluted bitumen, which calls for further study in this area.

Methyl isobutyl carbinol (MIBC), a frother widely used in mineral processing industry(Farrokhpay 2011), is commonly known for its effect in reducing the surface tension of liquid water (Long, Xu *et al.* 2005). Schramm *et al.* reported the use of MIBC together with kerosene as the process aid in water-based extraction process at 25°C and showed a good bitumen recovery from certain oil sands that was comparable to that achieved using caustic chemical alone at an elevated temperature of 80°C (Schramm, Stasiuk *et al.* 2003). MIBC is therefore shown to be a promising processing aid in oil sands extraction. It is therefore natural to investigate whether MIBC could be used to further enhance bitumen extraction by SA^{3}BE process. Polymeric demulsifiers are amphiphilic polymers capable of flocculating emulsion droplets to facilitate inter-droplet coalescence, making them readily separated from the bulky fluid. A number of fundamental investigations have been conducted on certain polymeric demulsifiers, including cellulose derivatives (Feng, Xu *et al.* 2008, Feng, Mussone *et al.* 2009, Feng, Wang *et al.* 2011, Wang, Segin *et al.* 2011), polyoxyalkylates (Czarnecki, Moran *et al.* 2007), and ethylene oxide-propylene oxide (EO-PO) demulsifiers (Pensini, Harbottle *et al.* 2014), to assess their demulsification behaviors in removing the intractable W/O emulsions encountered in petroleum industry. For example, ethylcellulose (EC) was found to allow transformation of rigid interface of W/O emulsions into fragments (Feng, Wang *et al.* 2011), which provides favorable areas on the emulsions to enhance their coalescence. In the bench-scale demo tests of the same study, the addition of ethyl-cellulose polymer at a dosage of 130 ppm was found adequate to allow the removal of up to 90% of water emulsions from diluted bitumen (Feng, Xu *et al.* 2008). Pensini *et al.* conducted a fundamental study on the effect of EO-PO block copolymers on the interfacial mobility and morphology of asphaltene-stabilized W/O emulsions (Pensini, Harbottle *et al.* 2014). In their study, the reduction in the stiffness of interfacial asphaltene films was found to be positively correlated to the addition of EO-PO copolymers due to their gradual penetration into asphaltene films.

The objective of this study is to further optimize the biodiesel-assisted ambient aqueous bitumen extraction (BA^{3}BE), an example of SA^{3}BE process, for mineable oil sands processing. Specifically, we focused on the feasibility study of applying frother and polymeric demulsifier to further increase bitumen recovery and produce high-quality bitumen froth of reduced impurities at ambient temperature. Biodiesel was used as the pretreatment solvent in oil sands processing due to its desirable properties, including good compatibility with bitumen at ambient temperature, reduced use of caustics and less environmental footprint (Zhu, Yan *et al.* 2018). For proof-of-concept purpose, MIBC and EO-PO demulsifier (abbreviated as "EO-PO" in the following) were chosen as the frother and demulsifier, respectively. To gain fundamental understanding on how MIBC and EO-PO improve BA^{3}BE process, their effects on bitumen viscosity and bitumen-water interfacial properties were studied. Bench-scale laboratory extraction tests were conducted to correlate the influence of MIBC and EO-PO on bitumen liberation and bitumen aeration with the performance of actual oil sands extraction. The effect of MIBC and EO-PO on tailings properties was also studied from settling and consolidation tests of the produced fine/sludge tailings.

4.3 Experimental

4.3.1 Materials

A stream of bitumen collected from vacuum distillation feed (VDF) was used for viscosity, interfacial property and bitumen droplet size measurement. Methyl isobutyl carbinol (MIBC) purchased from Sigma Aldrich (Canada) was used as received. EO-PO was provided by Baker Hughes, Inc. The EO content (i.e., the number of EO groups divided by the number of EO and PO groups) was 35% and the molecular weight was ~12000 g/mol. Biodiesel was provided by Alberta Innovates – Technology Futures and consisted primarily of methyl myristate and methyl palmitate, as determined by Varian CP-388 / Saturn 2200 gas chromatography-mass spectroscopy (GC-MS) (Zhu, Yan *et al.* 2018). The Fourier-transform infrared spectroscopy (FTIR) spectra of MIBC and biodiesel are shown in Figure A.7. Industrial-grade naphtha was obtained from Syncrude Canada Ltd. Poor-grade Athabasca oil sands ore used in this study was also from Syncrude Canada Ltd. As described in

Table A.2, this ore contained a significant amount of fines and was generally regarded as poor processing ore in the current HWBE process. Ore samples were kept in a freezer to minimize ore weathering, including dehydration, loss of light hydrocarbons and oxidation of bitumen. Prior to each test, samples were de-frozen at room temperature for 4 hours, followed by thorough homogenization to ensure consistency in composition. Process water used in this study was supplied by Syncrude, Canada. Characteristics of process water was given in a previous publication (Zhu, Yan *et al.* 2018).

4.3.2 Bitumen Recovery from Oil Sands

The procedures of bench-scale of bitumen extraction tests are shown schematically in Figure 4.1. A thin layer of weighed oil sands sample (300.0 ± 0.1 g) was placed on a large glass pan, followed by the addition of a designated amount of biodiesel using a commercial atomizer (100 ml polypropylene spray bottle, QUO), to achieve a uniform distribution of biodiesel in the sample. For experiments involving the use of MIBC and EO-PO, both chemicals were dissolved at given dosage in biodiesel prior to its spreading on oil sands sample. The ore sample was then sealed with an aluminum foil and left still for 20 min soaking (Harjai, Flury *et al.* 2012), followed by being used as the feed for bitumen extraction test using a modified Batch-Extraction-Unit (M-BEU). Both primary froth (without induced air; mimicking the froth collected from industrial primary separation cell, PSC) and secondary froth (mimicking the froth collected from industrial induced-air flotation) were collected from the extraction test to evaluate bitumen recovery and froth quality. The temperature was maintained at 25°C throughout the extraction operation. For comparison, a HWBE demonstration test was conducted in parallel at 40°C with the slurry being conditioned at pH 9.0, adjusted using NaOH. Detailed procedures on bitumen extraction tests can be found in a previous report (Zhu, Yan *et al.* 2018).

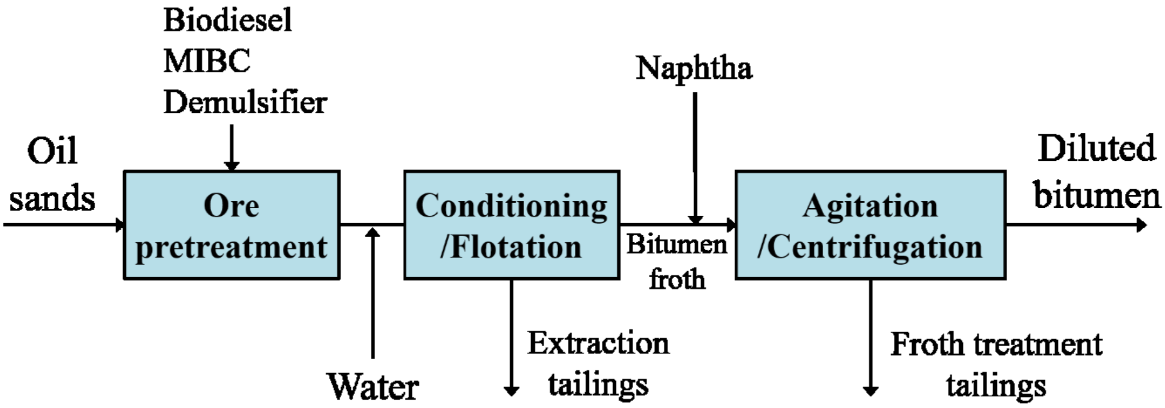


Figure 4.1 Schematic of the optimized SA^{3}BE process studied in this research.

To achieve good analysis of bitumen froth, two characterization methods of the collected bitumen froth were used. In one case, both primary and secondary froths were analyzed for bitumen, solids and water composition using a well-established Dean-Stark procedure with toluene as refluxing solvent (Starr and Bulmer 1979). In the other case, naphthenic froth treatment (NFT) was applied to the two bitumen froth streams. In this case, the froth was mixed with naphtha at the naphtha : bitumen mass ratio of 0.65 : 1. After aging at 25°C for 2 hours, the water content in the phase-separated diluted bitumen (top phase) was quantified by Karl-Fischer coulometric titration.

4.3.3 Viscosity and Interfacial Tension

VDF bitumen blended with biodiesel (case of basic BA^3BE) was prepared by adding a designated amount of biodiesel into a small glass bottle filled with approximately 5 g of pure bitumen sample. All the samples were stored at 60°C for 1 week to ensure complete mixing and good consistency in composition prior to use. For MIBC or EO-PO treated bitumen (case of improved BA^3BE), these chemical additives were dissolved in biodiesel at given concentration before mixing with bitumen using the above-mentioned procedures to achieve satisfactory blending homogeneity. Viscosity of prepared bitumen samples was measured using a commercial rheometer (AR-G2, TA Instruments, US). Plate geometry was used at shear rates of 0.1 to 1 s^{-1} for samples of high viscosity (> 50 Pa·s), while cylinder-cup geometry was used at shear rates of 10 to 100 s^{-1} for bitumen sample of lower viscosity.

Interfacial properties between bitumen and process water are important to bitumen recovery and highly dependent on chemicals added to bitumen (He, Lin *et al.* 2014). As a prerequisite for bitumen-water interfacial tension (IFT) measurement, the densities of solvent-soaked bitumen samples were determined using a density meter (DDM 2910, Rudolph Research Analytical, US) and the results are given in Table A.3. With known density of bitumen samples, the IFT were then determined by the pendant drop method using T200 Theta Optical

Tensiometer (Biolin Scientific). Briefly speaking, a solvent diluted bitumen droplet (around 7 μL) was generated carefully at the end of a needle with flat tip in a cuvette filled with process water (3 mL). After the bitumen droplet was held in the process water for 20 minutes to ensure a complete relaxation of drop shape, images of the droplet were captured by a high-speed CCD camera at 1 frame/second (FPS) for 30 minutes. The IFT values were obtained by analyzing the images using One-Attension software (Biolin Scientific). The numerical average of the last 50 values was reported as the IFT in this study. Each set of measurements was done in triplets.

4.3.4 Bitumen Liberation

As well documented in an early publication (Masliyah, Zhou *et al.* 2004), bitumen liberation and aeration are two major sub-processes in extracting bitumen from mineable oil sands. In this study, bitumen liberation was measured using a well-designed in-situ liberation visualization cell at ambient temperature. The oil sands ore with or without chemical additives was used in this test of measurements. Details on experimental procedures were reported in previous publications (Harjai, Flury *et al.* 2012, Srinivasa, Flury *et al.* 2012, Zhu, Yan *et al.* 2018). In brief, by analyzing the high-resolution images of ore/process water interface recorded by a camera (Olympus, SZX10) mounted on a stereo-optical microscopy, the percentage of bitumen that successfully released from sand grain surfaces in an aqueous medium was conveniently obtained. The degree of bitumen liberation (DBL), a function of exposure time of the ore to the process water, was calculated from the percentage of released bitumen, based on the same equation used in a previous publication (Zhu, Yan *et al.* 2018). Liberation tests under each condition were repeated three times to ensure reproducible results.

4.3.5 Foaming of Process Water

To gain a sound understanding of bitumen flotation efficiency, the effect of chemical additives on foaming behavior of process water was studied using a graduated glass column. The demo solution was prepared by adding VDF bitumen with or without chemical additives to process water at a concentration of 0.5 wt%. Proper ultrasonication described in a previous paper was applied to better disperse bitumen in solution (Chen, Peng *et al.* 2015). After the glass column was filled with a fixed amount of the prepared demo solution, air was purged at a constant flow rate (200 mL/min) via a glass frit (bubble atomizer) from the bottom of the column to form a stable foam above the bubbly process water. The foaming characteristics was quantified in two perspectives: 1) foaming capacity, $C_{foaming}$, measured as the height from the bottom of process water to the top of stable foam divided by the ultimate height of the process water after turning off the air purge; and 2) foaming stability, $t_{stability}$, measured as the time required for the foam to collapse after air purge was turned off. Each foaming test was done in triplets.

4.3.6 Size Distribution of Bitumen Droplets

The size of bitumen droplets in the process water was determined using a focused-beam reflectance measurement (FBRM) (Mettler-Toledo Lasentec, Model S400A). The principle and operating parameters of FBRM were reported in another study (Chen, Peng *et al.* 2015). The VDF bitumen (at a concentration of 0.5 wt%) treated with a designated amount of biodiesel and chemical aids was first dispersed in the process water by sufficient ultrasonication (Chen, Peng *et al.* 2015). To minimize the interference of solid particles in process water, particles larger than 0.2 μm in the original process water were removed by filtration prior to its use. The bitumen droplet size distribution was measured as chord length

(CL) by FBRM after bitumen was emulsified for 20 min (Chen, Peng *et al.* 2015). The results from FBRM are presented as the cumulative particle size distribution (C-PSD). The CL_{50}, or the median size, was defined as the chord length that corresponded to 50% of C-PSD.

4.3.7 Bitumen Aeration

Bitumen aeration characteristics was evaluated by determining the induction time (Gu, Xu *et al.* 2003), which refers to the minimum contact time required for successful attachment of bitumen to an air bubble of particular dimensions. A short induction time indicates a rapid attachment, corresponding to a desirable bitumen aeration and hence bitumen flotation. In this study, VDF bitumen was treated with a designated amount of biodiesel with or without MIBC or EO-PO addition. The prepared bitumen sample was placed on a Teflon sample holder for a sufficient period of time to form a smooth bitumen surface, which was later placed as a whole into the process water for the induction time measurement using a well-developed induction timer. Details on this measurement were given elsewhere (Harjai, Flury *et al.* 2012).

4.3.8 Tailings Analysis

In industrial practice, there are two streams of tailings, i.e., the extraction tailings and froth treatment tailings (FTT). The FTT stream is generally treated by a set of tailings solvent recovery units (TSRU), as it is profitable to recover solvent from such tailings stream that is in a relatively small volume and contains high concentration of solvent (Masliyah, Zhou *et al.* 2004, 2013). Therefore, this study focused mainly on the extraction tailings stream, which is in a huge volume and contains a low concentration of unrecovered bitumen, making it difficult to treat. In this study, sludge tailings from oil sands extraction test was collected in a graduated jar with the descending of the mudline being continuously recorded.

To investigate the extent of solvent loss to tailings, the organics in the real oil sands tailings were collected by the Dean-Stark apparatus operation at a reduced temperature of 150°C. Following a well-developed method (Zhu, Yan *et al.* 2018), the content of biodiesel in toluene solution was determined quantitatively using FTIR at its characteristic IR absorption peak of 1740 cm^{-1} (Figure A.9). Toluene solutions of biodiesel in a concentration range of 0-5 wt% were analyzed by FTIR to provide a standard calibration curve (Figure A.10) for biodiesel loss determination. Results showed a negligible influence of this biodiesel characteristic IR peak by the presence of 5 wt% bitumen and/or MIBC (Figure A.9). The loss of MIBC in tailings water was found to be difficult to quantify due to its evaporation from diluted bitumen during flotation, as indicated by a solvent loss test (Figure A.11).

4.4 Results

Bench-scale bitumen extraction from real oil sands was conducted in this study to examine the performance of total hydrocarbon recovery using the modified BA^3BE where MIBC and EO-PO are incorporated. To reduce the solvent consumption, 10 wt% (of bitumen) solvent addition was used in this this study, which was half the dosage used in our previous study (Zhu, Yan *et al.* 2018).

4.4.1 Impact on Bitumen Recovery

As shown in Figure 4.2, both primary and secondary recoveries were found to increase substantially with the use of solvent. Specifically, the total recovery was found to increase from ~20% for the case without solvent addition to 58.8-75.3% for the case with solvent addition. The latter case was comparable to or higher than the total recovery from the HWBE baseline test (62.3%) conducted at a higher temperature (40°C), confirming the enhanced recovery of SA^{3}BE process (Harjai, Flury *et al.* 2012, Zhu, Yan *et al.* 2018). More importantly, increasing MIBC dosage in solvent was found to further improve both primary and secondary recovery, contributing to a further increase in total recovery up to ~25%. On the other hand, compared with the recovery without EO-PO (white bars), an evident improvement in both primary and secondary recovery was observed in their corresponding cases with 1,500 ppm (of bitumen) EO-PO addition (adjacent grey bars). In summary, using both MIBC and EO-PO in the modified BA^{3}BE with a total solvent addition of 10 wt% increased substantially the total hydrocarbon recovery, even being compared with the basic BA^{3}BE case of a higher total solvent addition (20 wt%), as shown in Figure A.8.

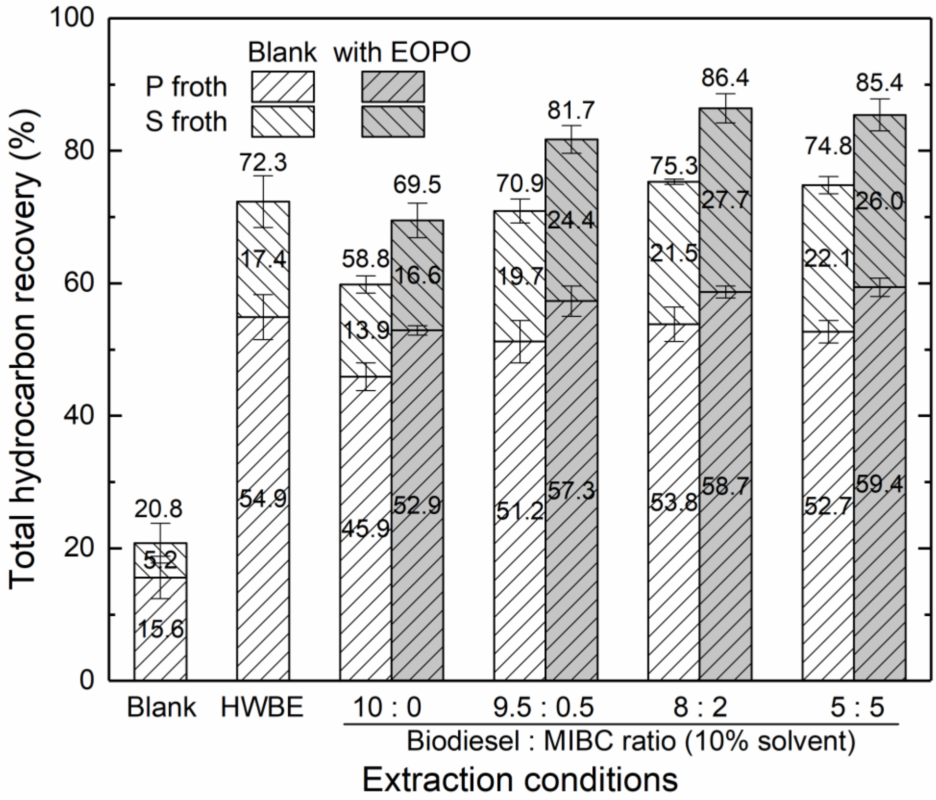


Figure 4.2 (A) Total hydrocarbon recovery from P (primary) froth and S (secondary) froth in bench-scale mineable oil sands processing, at 25°C, except for the HWBE baseline (at 40°C), and (B) comparison of total hydrocarbon recovery between HWBE, four 10 wt% solvent addition groups and 20 wt% biodiesel addition group. Labels specify bitumen recovery from each stream (center of bars) or combined recovery (top of bars). Oil sands were pretreated with 10 wt% (of bitumen) biodiesel-MIBC mixtures at specified mass ratio, with or without 1,500 ppm EO-PO.

4.4.2 Impact on Froth Quality

The quality of froths collected (Figure 4.1) was analyzed to determine the solid, water and bitumen content (2010, Harjai, Flury *et al.* 2012). In general, a decrease in solid and water content in froths is always desirable for more efficient and less energy intensive downstream froth treatment (Harjai, Flury *et al.* 2012). As shown in Figure 4.3, , solvent addition were found to improve froth quality, indicated by a higher bitumen content and lower solid content as compared with the case without solvent addition (the “Blank” test). In fact, the quality of the froth with solvent addition matched almost to the case of HWBE baseline. Such finding suggests that the modified BA^{3}BE operated under a much milder condition (neutral pH and ambient temperature) allows an equivalent froth quality to that of the industrial HWBE operated at a higher pH of 9.0 and a higher temperature of 40°C. In addition, examining the groups with variable biodiesel-MIBC ratios revealed that the change of MIBC dosage appears to have little effect on the quality of primary froths. However, the solid content of the secondary froths was found to increase with increasing MIBC addition, accompanied by a decrease in bitumen content (Figure 4.3). The optimum biodiesel : MIBC mass ratio of solvent mixture appeared to be 8:2, as it achieved a satisfactory hydrocarbon recovery (Figure 4.2) without a noticeable reduction in froth quality (Figure 4.3). In the cases with 1,500 ppm

EO-PO addition, froth quality appears to be subtly dependent on MIBC addition for both primary and secondary froths. Overall, the biodiesel : MIBC mass ratio of 8:2 was found to be the optimum solvent composition for ore pretreatment, among all tests.

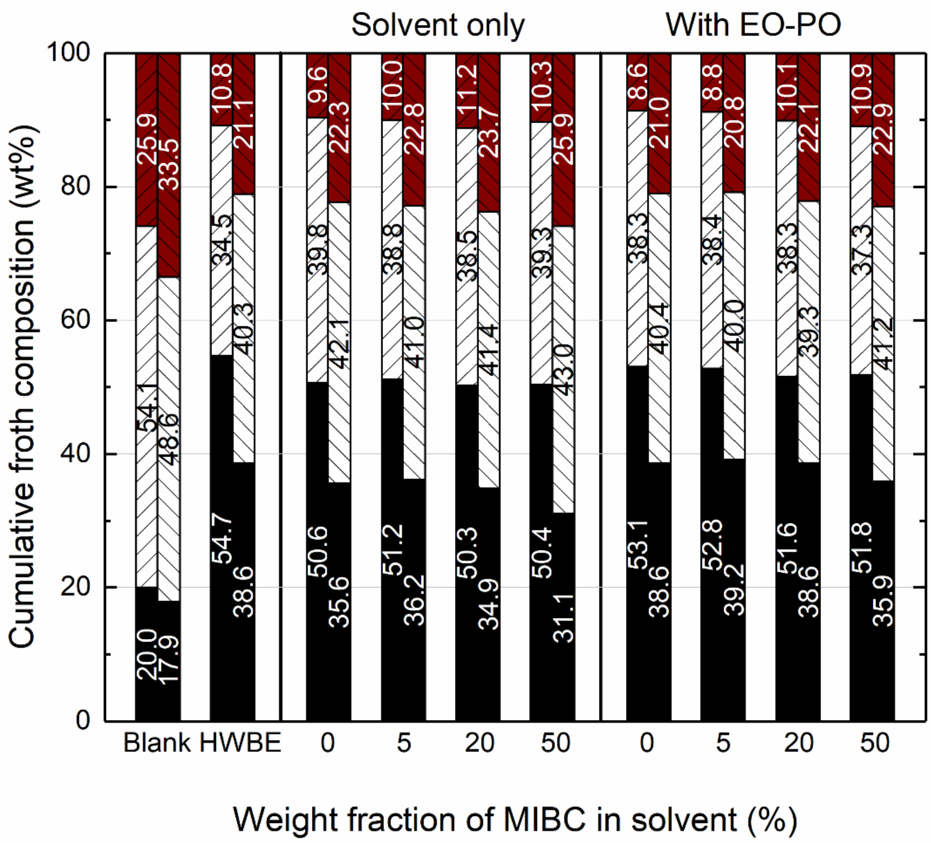


Figure 4.3 Composition of P (primary) froth (slashed) and S (secondary) froth (counter-slashed) collected from bench-scale extraction tests at 25°C, except for the HWBE baseline (at 40°C). Labels specify weight fraction of bitumen (black bars), water (white bars) and solids (brown bars) in each stream. Oil sands were pretreated with 10 wt% (of bitumen) biodiesel-MIBC mixture of variable mass ratios, with or without 1,500 ppm EO-PO, except for the solvent-free “Blank” group and the HWBE baseline.

4.4.3 Impact on Froth Treatment

As mentioned above, the presence of W/O emulsions is a major problem in petroleum industry, as it could cause various issues to the oil upgrading and refining operations, including reduced pipelining capacity, upgrader corrosion and catalyst fouling (Masliyah, Zhou *et al.* 2004). Froth treatment therefore becomes an integrated part of oil production from oil sands, as it reduces entrained water and solids in bitumen froth by first diluting the bitumen froth with a solvent, typically either naphtha or paraffin liquids. As discussed above, EO-PO copolymer has been studied as demulsifier for heavy oil industry to improve the removal of water and solids from diluted bitumen or heavy oil. It is one of our objectives to minimize the formation of stable W/O emulsions in bitumen froth by using EO-PO copolymer in our hybrid extraction process.

To evaluate such hypothesis, bitumen froth was diluted using naphtha to mimic an industrial practice of naphthenic froth treatment. The water content in the aged diluted bitumen, mostly in the form of W/O emulsions, was determined by Karl-Fischer coulometric titration. The water content present in both primary and secondary froths in the basic BA^{3}BE was found to be reduced by roughly 1/3 as compared with the HWBE baseline (Figure 4.4). Such a reduction in water content was reasonable, as fine solids and asphaltene in the case of HWBE became more hydrophilic at a higher pH, which facilitated the generation and stabilization of W/O Pickering emulsions and led to a higher water content in diluted bitumen. Varying the MIBC dosage in solvent appeared to exhibit negligible influence on the entrained water content (Figure 4.4). However, at highest MIBC dosage (50% of solvent), the secondary froth was found to contain slightly higher water content, possibly due to the relatively more vigorous flotation and hence formation of more W/O emulsions in bitumen froth at high MIBC dosage. The use of 1,500 ppm EO-PO was found to further reduce water content by 0.3-0.5 wt% (grey bars in Figure 4.4) on the top of solvent treatment, in support of the demulsification effect of EO-PO copolymer in BA^{3}BE process. Overall, the content of water in EO-PO treated diluted bitumen was found to be equivalent to ~2/3 of the solvent-only case, or around half of the HWBE case, indicating that the modified BA^{3}BE provides a viable solution to remarkedly alleviate the W/O-induced issues.

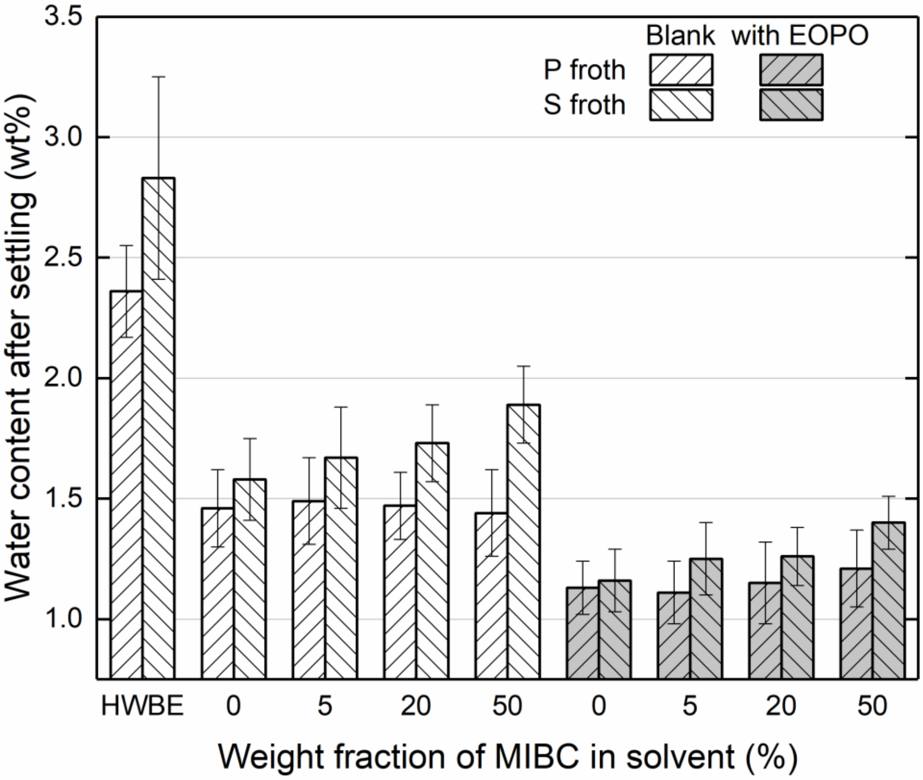


Figure 4.4 Water content of P (primary) froth and S (secondary) froth collected from bench-scale extraction tests at 25°C, except for the HWBE baseline (40°C). Oil sands were pretreated with 10 wt% (of bitumen) biodiesel-MIBC mixture of variable mass ratios, with or without 1,500 ppm EO-PO, except for the HWBE baseline.

4.5 Discussion

As supported by real oil sands extraction (Figure 4.2, 3.3 and 3.4), enhanced bitumen recovery and improved froth quality were achieved using the modified BA^{3}BE, where MIBC and EO-PO copolymer were incorporated with BA3BE. However, the mechanism of how MIBC and EO-PO contributed to such improvement in bitumen extraction and product quality remained unclear. Therefore, it is important to understand the fundamentals whether and how they made a difference on each key step of the extraction operation, such as bitumen liberation and air-induced flotation. The effects of MIBC and EO-PO on the characteristics of extraction tailings were also examined for a comprehensive evaluation.

4.5.1 Effect of Chemical Aids on Bitumen Viscosity

The kinetics of bitumen extraction from oil sands is dramatically influenced by the viscosity of bitumen (Hupka, Miller *et al.* 1983, Hupka and Miller 1991, Drelich 2008). According to previous studies, a viscosity of 10 Pa·s is typically considered as the maximum allowed to obtain a sufficient bitumen fluidity for a satisfactory recovery (Schramm, Stasiuk *et al.* 2003, Long, Drelich *et al.* 2007). As shown in Figure 4.5, the viscosity of bitumen was found to gradually drop over two magnitudes to ~10 Pa·s with 20 wt% of the biodiesel added to the VDF bitumen. This result agrees well with the viscosity of diluted bitumen predicted by Shu's model (Shu 1984), and explicates the higher bitumen recovery of the extraction test with 20 wt% biodiesel addition, than the case with 10 wt% biodiesel use (Figure 4.2B) and the case of "Blank" (Figure 4.2A). In comparison, an equivalent viscosity reduction to ~10 Pa·s is achieved by increasing the operation temperature to 50°C, in the industrial HWBE process (Seyer and Gyte 1989).

The dependence of bitumen viscosity on the addition of given chemical aids was studied as shown in Figure 4.5. With the replacement of up to 50 wt% of the added biodiesel with MIBC and/or addition of up to 1,500 ppm EO-PO emulsifier, the viscosity of bitumen was found to exhibit no statistical difference to that of the bitumen blended with an identical amount of biodiesel (i.e., the case of basic BA^{3}BE). According to the blending theory (Shu 1984), the addition of a viscous EO-PO copolymer would be detrimental to viscosity reduction of bitumen. However, such effect appeared to be insignificant in this study as shown in Figure 4.5, possibly due to the notably low dosage of such polymeric emulsifier. Thus, the mixing ratio of biodiesel and MIBC, and the addition of EO-PO within the test range appear to make a negligible difference to the viscosity of diluted bitumen.

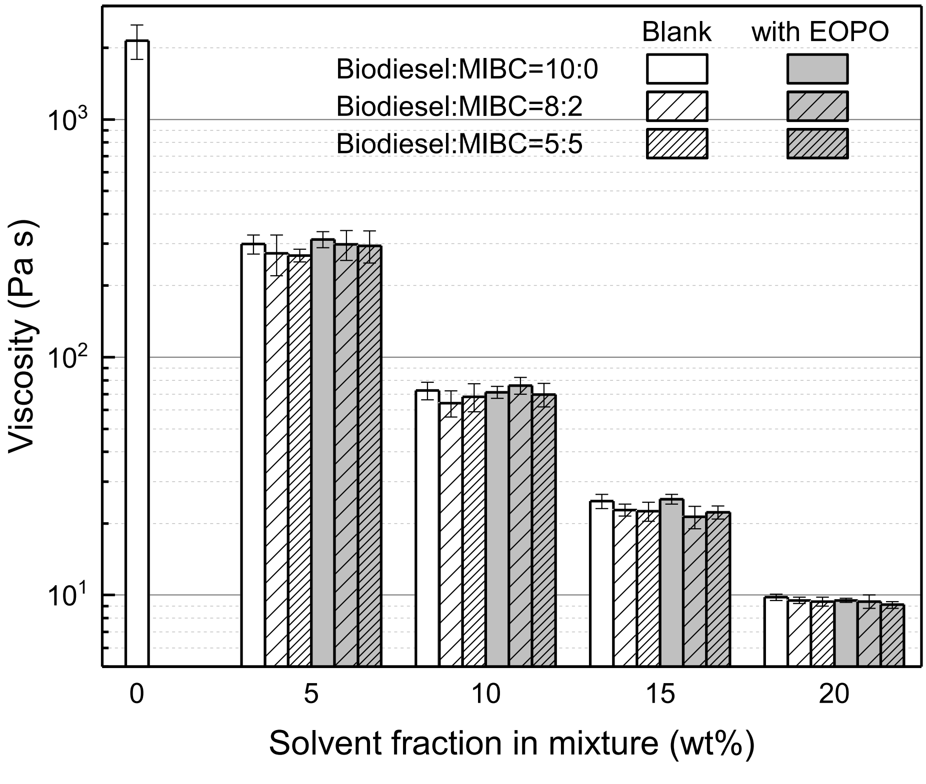


Figure 4.5 Effect of solvent mixture of biodiesel and MIBC (w/w), with/without EO-PO, on bitumen viscosity at 25.00 ±0.05°C. EO-PO concentration was 1,500 ppm in terms of the mass of bitumen.

Overall, bitumen viscosity was reduced by 10 wt% (of bitumen) solvent addition. However, such extent of bitumen viscosity reduction appears to be not sufficient for a satisfactory bitumen recovery (~10 Pa·s), indicating that there must be other effects that also contributed to the enhanced bitumen recovery in the modified BA3BE with 10 wt% solvent dosage (Figure 4.2).

4.5.2 Effect of Chemical Aids on Bitumen-Water Interfacial Tension and Bitumen Liberation

As well elaborated by Masliyah *et al.* (Masliyah, Zhou *et al.* 2004), interfacial properties play a critical role in bitumen recovery from oil sands. For a complete removal of bitumen from sand surfaces, a small contact angle of water in bitumen-sand-water system is favored, which could be achieved by reducing the bitumen-water IFT ($\gamma_{B/W}$) (2010). Previous studies revealed that in HWBE process, $\gamma_{B/W}$ could be reduced from 15-20 mN/m to 7-10 mN/m by adjusting the slurry conditioning pH from near neutral (pH = 7) to an industrial processing pH (pH = 8.5-9) with NaOH addition (Drelich and Miller 1994, 2010). In this study, a similar decrease in $\gamma_{B/W}$ was obtained by treating bitumen with a certain amount of solvent, as shown in Figure 4.6 and also by He *et al.* (He, Lin *et al.* 2014). In specific, $\gamma_{B/W}$ was found to be around 13 mN/m with 10 wt% (of bitumen) solvent addition, which was exactly the case of basic BA^{3}BE. The $\gamma_{B/W}$ was found to reduce continuously to lower than 7 mN/m with increasing MIBC dosage to 50 wt%. The addition of 1,500 ppm EO-PO (with reference to bitumen) was found to contribute to an additional 1-2 mN/m reduction in $\gamma_{B/W}$. The effect of EO-PO agrees well with the results from an earlier study that showed a similar reduction in $\gamma_{B/W}$ with polymeric demulsifier addition (Feng, Mussone *et al.* 2009).

To obtain a direct view of the effect of chemical aids on bitumen liberation, real-time bitumen recession and release from oil sands was investigated using a well-established in-situ visualization technique (Srinivasa, Flury *et al.* 2012). Bitumen liberation kinetics was quantitatively analyzed based on a hyperbola-type fitting expression developed previously, as shown in Equation A.1 (in Appendix V). The relative initial bitumen liberation rate ($v_{norm,\ DBL}$) and ultimate DBL ($[DBL]_{ultimate}$), two important indicators to assess bitumen liberation, can then be calculated from these two fitting parameters by Equation A.2 and Equation A.3, with results presented in Table A.4. A higher $v_{norm,\ DBL}$ indicates a faster bitumen liberation process, while a higher $[DBL]_{ultimate}$ represents a more complete bitumen removal from solid surfaces. The results of DBL kinetics are presented in Figure 4.7, with corresponding $v_{norm,\ DBL}$ and $[DBL]_{ultimate}$ values being summarized in Table 4.1.

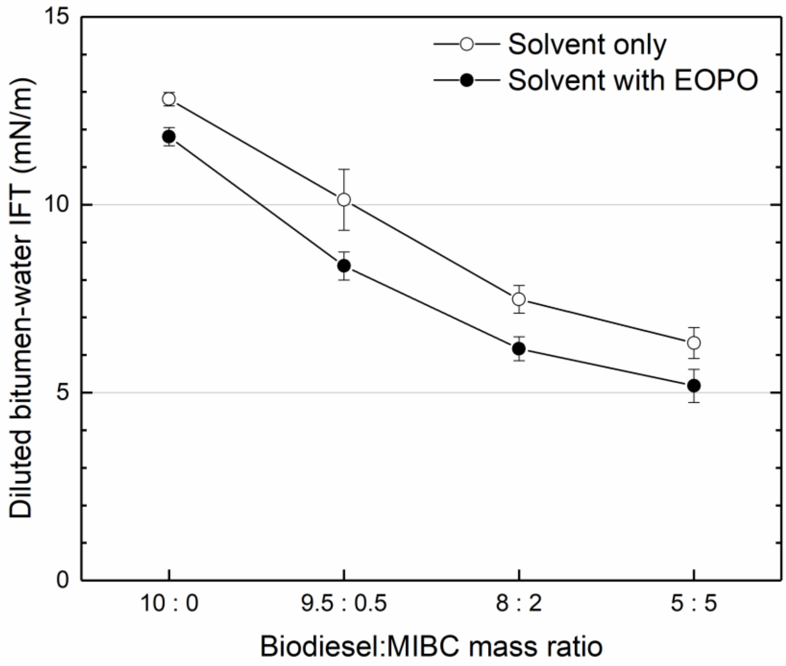


Figure 4.6 Interfacial tension ($\gamma_{B/W}$) between water and bitumen soaked with 10 wt% solvent of biodiesel containing variable amount of MIBC with or without 1,500 ppm EO-PO demulsifier of bitumen at 25°C.

Table 4.1 $[DBL]_{ultimate}$ and $v_{norm,\ DBL}$ calculated from the fitting parameters of hyperbola function for bitumen liberation, at 25°C. Standard deviation is calculated based on 95% confidence interval.

Biodiesel : MIBC mass ratio*	**EO-PO**	**Results**	
		$v_{norm,\ DBL}$ (×0.1 s^{-1})	**$[DBL]_{ultimate}$ (%)**
No solvent	Blank	0.23±0.02	24.8±2.7
10:0	Blank**	1.3±0.1	70.8±1.5
	1500 ppm***	2.2±0.2	70.7±1.2
9.5:0.5	Blank	2.3±0.2	69.8±1.2
	1500 ppm	3.3±0.3	70.4±0.7
8:2	Blank	3.1±0.3	70.8±1.0
	1500 ppm	3.8±0.3	72.1±0.7

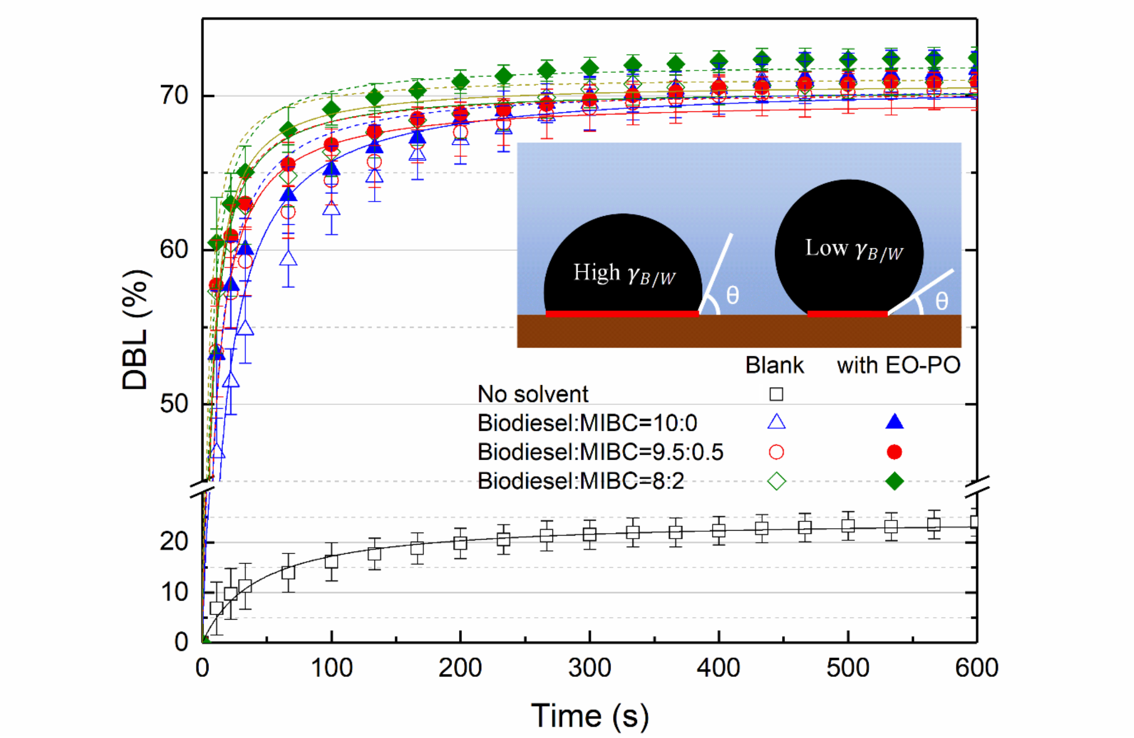


Figure 4.7 Bitumen liberation kinetics of oil sands ore pretreated with 10 wt% biodiesel-MIBC mixture of variable mass ratio with or without 1,500 ppm EO-PO, at 25°C. Curves represented the best fitted lines of Equation A.1 with solid curves for the case without EO-PO and dashed curves for the case with EO-PO. Inset shows the dependence of contact area and

contact angle between bitumen and solid on $\gamma_{B/W}$ of the same bitumen droplet at equilibrium stage.

Solvent addition were found to increase $v_{norm,\ DBL}$ by one magnitude as compared to the case without solvent treatment (Table 4.1), indicating a faster bitumen removal from oil sands by pretreating oil sands with 10 wt% solvent. Such improvement in bitumen release was reasonable as the use of solvent not only contributed to a remarkable reduction in bitumen viscosity (Figure 4.5), but also led to a reduced $\gamma_{B/W}$ (Figure 4.6). It was also observed that the initial bitumen liberation could be accelerated with increasing the amount of MIBC added over the range tested (Figure 4.7). Such correlation could be attributed to the change of solid surfaces during bitumen detachment. Since the bitumen recession on solid surface was relatively fast at low bitumen viscosity, the variation of DBL in this study was dominated by the detachment of bitumen from solid surfaces. Masliyah *et al.* (2010) showed that the energy change (ΔG) during bitumen detachment, where a bitumen-solid interface ($\gamma_{B/S}$) with area of ΔA is replaced by a bitumen-water interface ($\gamma_{B/W}$) and a water-solid interface ($\gamma_{W/S}$), is given by

$$\Delta G = \Delta A \cdot (\gamma_{B/W} + \gamma_{W/S} - \gamma_{B/S}) \tag{4.1}$$

ΔG can also be expressed as

$$\Delta G = \Delta A \cdot \gamma_{B/W}(1 - \cos\theta) \tag{4.2}$$

by replacing unmeasurable interfacial tensions with Young's equation in Equation 4.1. Equation 4.2 shows that the energy change associated with detachment of bitumen from solid surfaces in water was always positive, indicating that such detachment is a thermodynamically unfavorable process. It is therefore necessary to provide additional energy by mixing and hydrodynamic shearing to liberation bitumen from solid surfaces.

However, it was shown in the inset of Figure 4.7 that a significant decrease in $\gamma_{B/W}$ without any substantial change in $\gamma_{W/S}$ and $\gamma_{B/S}$ with MIBC and EO-PO addition (Figure 4.6) led to a reduction in contact area ΔA. According to Equation 4.2, such a situation eventually resulted in a decrease in ΔG, leading to a lower energy needed to liberate bitumen with the addition of MIBC and EO-PO as observed in Table 4.1 and hence enhanced bitumen recovery as shown in Figure 4.2.

Compared with the case without solvent addition, solvent soaking increased substantially the ultimate bitumen liberation from 25% to around 70%. This finding is in good agreement with the results from the previous studies (Harjai, Flury *et al.* 2012, Zhu, Yan *et al.* 2018). Varying MIBC dosage in the solvent mixture appeared to show a negligible effect on $[DBL]_{ultimate}$, so does the EO-PO addition, despite the reduction in $\gamma_{B/W}$ (Figure 4.6) that would predict an enhance bitumen liberation by the addition of MIBC and EO-PO. It is possible that the addition of MIBC and EO-PO demulsifier may also change $\gamma_{S/W}$, which compensates the effect of changing $\gamma_{B/W}$ on ΔG, showing an overall negligible effect on ΔG and hence the $[DBL]_{ultimate}$.

Overall, bitumen viscosity (Figure 4.5) and $\gamma_{B/W}$ (Figure 4.6) were reduced substantially by the incorporation of MIBC and 1,500 ppm EO-PO for ore pretreatment, which collectively contributed to the optimized bitumen liberation and hence improved bitumen recovery, especially the improved primary bitumen recovery (Figure 4.2).

4.5.3 Effect of Chemical Aids on Bitumen-Water Interfacial Tension and Bitumen Liberation

Flotation is an important integrated part of mineable oil sands processing, as it allows bitumen droplets to be attached to air bubbles and get collected in the form of bitumen froth, after they are liberated from solids (Figure 4.1). A comprehensive evaluation of the effect of solvent and EO-PO on flotation can be provided by studying the bitumen collection rate in flotation. As explicated by Masliyah *et al.* (2010), the bitumen collection rate in a mechanical flotation system, $R_C(t)$, can be written as

$$R_C(t) = -k_s S_b P_c P_a (1 - P_d) n_p \tag{4.3}$$

where, k_s is a flotation parameter associated with the flotation system itself; S_b is the bubble surface area flux; P_c, P_a and P_d stands for the probability of collision, attachment and detachment of bitumen droplets and air bubbles, respectively; and n_p is the number of bitumen droplets.

A good foaming efficiency (corresponding to high S_b) is needed to achieve a satisfactory flotation performance. $C_{foaming}$ and $t_{stability}$ are two indicators used in this study to evaluate the foaming efficiency of flotation operations (Cano-Medina, Jiménez-Islas *et al.* 2011, Oboroceanu, Wang *et al.* 2014). A larger $C_{foaming}$ indicates a larger bubble surface area; while, a greater $t_{stability}$ represents the formation of a more stable foam, respectively: both are favored for flotation operations.

In this study, tailings water from the bench-scale oil sands extraction tests was used to study the effect of chemical additives on flotation efficiency. As shown in Figure 4.8, $C_{foaming}$ and $t_{stability}$ were found to vary substantially with different MIBC content in solvent, suggesting altered foaming characteristics of water by the addition of MIBC. In specific, the two foaming parameters were found positively correlated with MIBC amount in solvent, indicating that within the test range, the foaming efficiency was positively correlated with the MIBC dosage. Such relationship was reasonable as MIBC can reduce water surface tension and assist to generate a large number of bubbles in flotation (Farrokhpay 2011). As for the groups with EO-PO treatment (grey bars), no apparent difference was observed in both

$C_{foaming}$ and $t_{stability}$ comparison to the corresponding ones at same MIBC dosage without EO-PO (white bars). Such phenomenon can be attributed to the relative low amount of free EO-PO in process water. As the propylene oxide segments in EO-PO molecules own relatively strong hydrophobicity, it is likely that the whole EO-PO molecules are attached robustly to the surface of bitumen droplets, leading to a negligible impact of EO-PO addition on water surface tension and foaming characteristics.

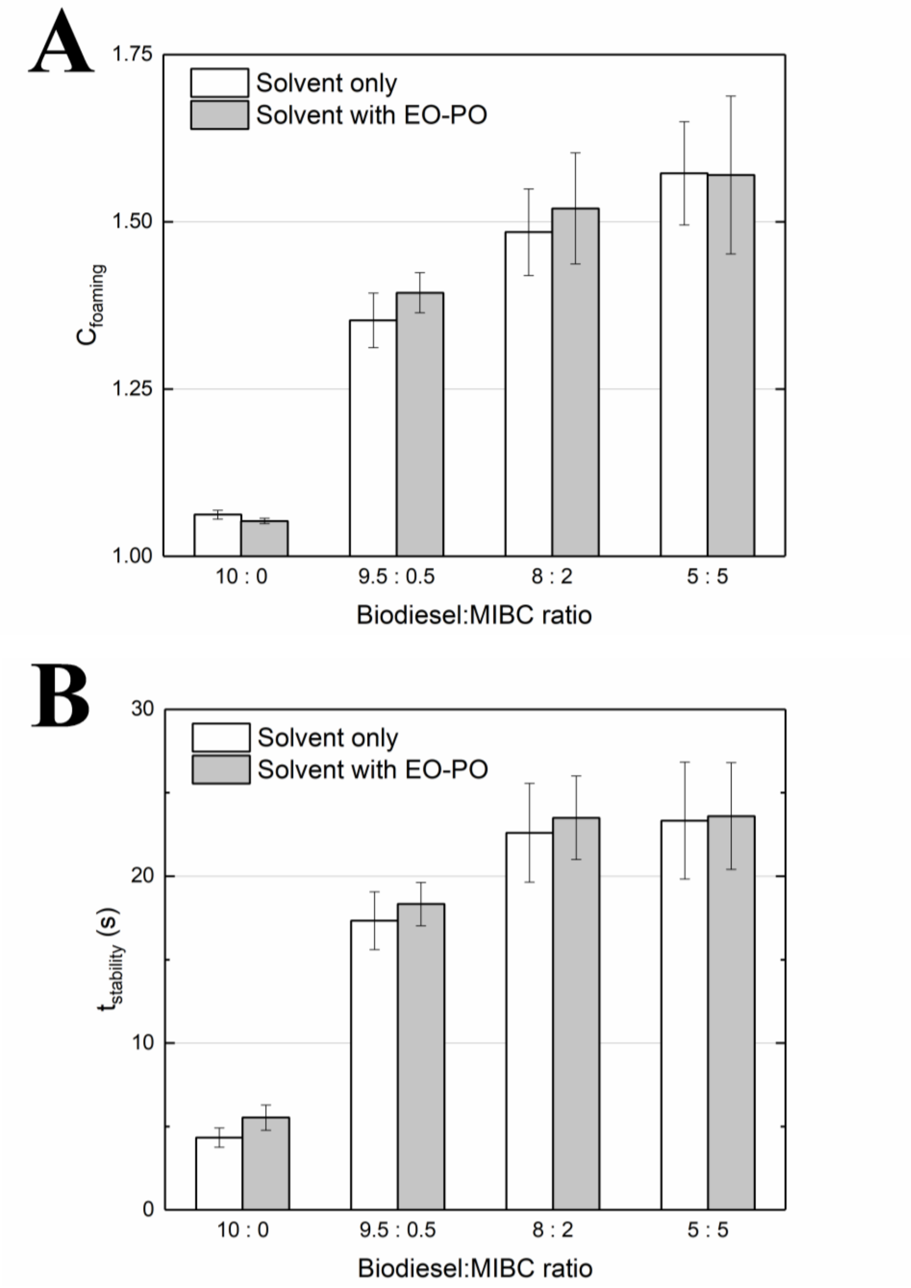


Figure 4.8 (A) Foaming capacity and (B) foaming stability of tailings water, collected from the bench-scale bitumen extraction tests where ores were pretreated with biodiesel-MIBC mixture at specified mass ratio, with or without 1,500 ppm EO-PO.

In addition to the foaming efficiency, increasing the collision probability (P_c) between air bubble and bitumen is also important to improve bitumen recovery. It has been identified that the collision rate between air bubbles and bitumen droplets of size d_a and d_b, is scaled by $\left(\frac{d_b}{d_a}\right)^2$, suggesting that the generation of smaller bubbles and larger bitumen droplets/clusters is favorable for higher collision probability (Yoon and Luttrell 1989). On one hand, the size of air bubble (d_a) appeared to be remarkedly reduced by MIBC addition, as it remarkably increased air bubble surface area flux and helps generate smaller bubbles (Figure 4.6), while d_a appeared to be influenced marginally by the addition of EO-PO. On the other hand, the bitumen droplet size (d_b) in process water was determined by FBRM in this study and the results were shown as C-PSD versus the square-weighted (SQW) chord length. Particularly, the median size (CL_{50}) of the dispersed bitumen droplets was found to shift smaller with increasing MIBC dosage (Table 4.2), indicating the formation of smaller bitumen droplets by MIBC addition. Such trend is reasonable, as under the same agitation energy input, the generation of bitumen-water interfacial area is boosted with smaller $\gamma_{B/W}$ by MIBC addition (Figure 4.6) (2010). Therefore, it is clear that the use of MIBC alone facilitates the emulsification of bitumen that is unfavored for bitumen-bubble collision. However, such drawback could be to some extent alleviated by the use of EO-PO, as the median size of dispersed bitumen droplets was found to boost from 23.7-28.2 μm to over 30 μm (Table 4.2), after the bitumen was blended with 1,500 ppm EO-PO. Such finding can be attributed to the flocculation effect of EO-PO on bitumen emulsions, which facilitated the attachment between different bitumen droplets and hence resulted in increased size of bitumen droplets/clusters. It was also noticeable that though a continuous decrease in CL_{50} of dispersed bitumen could still be observed in this case with increasing addition of MIBC, the extent of such decrease (from 34.6 to 32.2 μm) appeared to be greatly restrained, and the minimum CL_{50} (32.2 μm) among these EO-PO-treated groups was still much greater than the case without EO-PO use (Table 4.2). Overall, with the addition of both MIBC and EO-PO together with biodiesel, the bitumen droplet size (d_b) is enlarged and the air bubble size (d_a) is reduced compared with the basic BA^3BE, which leads to a higher bitumen-air bubble collision rate that hence is favored for bitumen flotation as shown in Equation 4.3.

Table 4.2 Median size (CL_{50}) of bitumen droplets soaked with biodiesel-MIBC mixture of variable mass ratio and with/without EO-PO, at 25°C.

CL_{50} (μm)	**Biodiesel : MIBC ratio***			
	10 : 0	**9.5 : 0.5**	**8 : 2**	**5 : 5**
Solvent only	28.2	27.1	25.1	23.7
Solvent with 1,500 ppm EO-PO	34.6	34.4	33.5	32.2

* Total weight of solvent mixture is 10 wt% of bitumen.

** EO-PO copolymer was added at 1,500 ppm of bitumen.

Once an air bubble collides with a bitumen droplet, a relaxation process is required for the bitumen droplet to spread at the air bubble surface to obtain a successful attachment. Such process is called bitumen aeration, with “induction time” indicating the time required for this relaxation process (2010). In this study, results showed that the induction time was found to be reduced substantially from ~1440 ms to ~900 ms after bitumen was treated with solvent, regardless of the MIBC dosage used (Figure 4.9). Such reduced retention time can be primarily attributed to the solvent-induced viscosity reduction, as reduced bitumen viscosity could allow quicker removal of surfactants from bitumen-air bubble contact area that contributes to faster drainage of the intervening water and quicker spreading of bitumen at air bubble surface (Harjai, Flury *et al.* 2012, Zhu, Yan *et al.* 2018). In addition, the EO-PO addition was found to further reduce the induction time by 80-140 ms, on the basis of solvent addition (Figure 4.9). This phenomenon can be attributed to the effect of amphiphilic polymers on the physical characteristics of bitumen-water interface. As reported in previous studies, amphiphilic polymers (such as EO-PO and EC) are able to penetrate and reduce the stiffness of the interfacial asphaltene films (Feng, Xu *et al.* 2008, Feng, Mussone *et al.* 2009, Feng, Wang *et al.* 2011, Rane, Harbottle *et al.* 2012), which not only provides favorable areas for the flocculation of bitumen droplets, but also benefits the bitumen-air bubble attachment. Therefore, the bitumen-air bubble attachment energy barrier (2010), E_b, was reduced by the addition of solvent and EO-PO. As P_a, the attachment probability of bitumen droplets and air bubbles, is governed by E_b ($P_a = \exp(-E_b/E_k)$, E_k: kinetic energy imparted on colloidal particles by mechanical mixing), it is expected that the use of solvent and EO-PO benefits bitumen flotation.

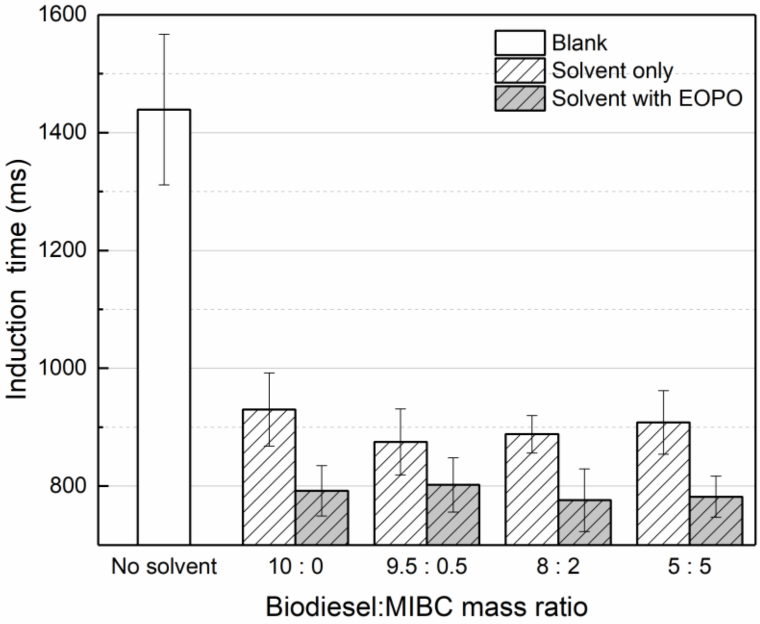


Figure 4.9 Induction time of pure VDF bitumen, and VDF bitumen blended with 10 wt% biodiesel-MIBC mixture of variable mass ratio, with or without 1,500 ppm EO-PO, at 25°C.

The effects of chemical aids (MIBC and EO-PO) on bitumen flotation of a BA^{3}BE process are illustrated in Figure 4.10. As discussed above, on one hand, the use of MIBC reduces the water surface tension, assists to generate smaller and more stable air bubbles, and slightly reduces bitumen droplet size (Figure 4.10B and Figure 4.10D). On the other hand, the use of EO-PO facilitates the flocculation of bitumen droplets, and makes them to be readily attached to air bubbles (Figure 4.10C and Figure 4.10D). In summary, improved bitumen recovery from oil sands slurry is obtained by enhanced bitumen flotation under the synergistic effect of MIBC and EO-PO (Figure 4.2).

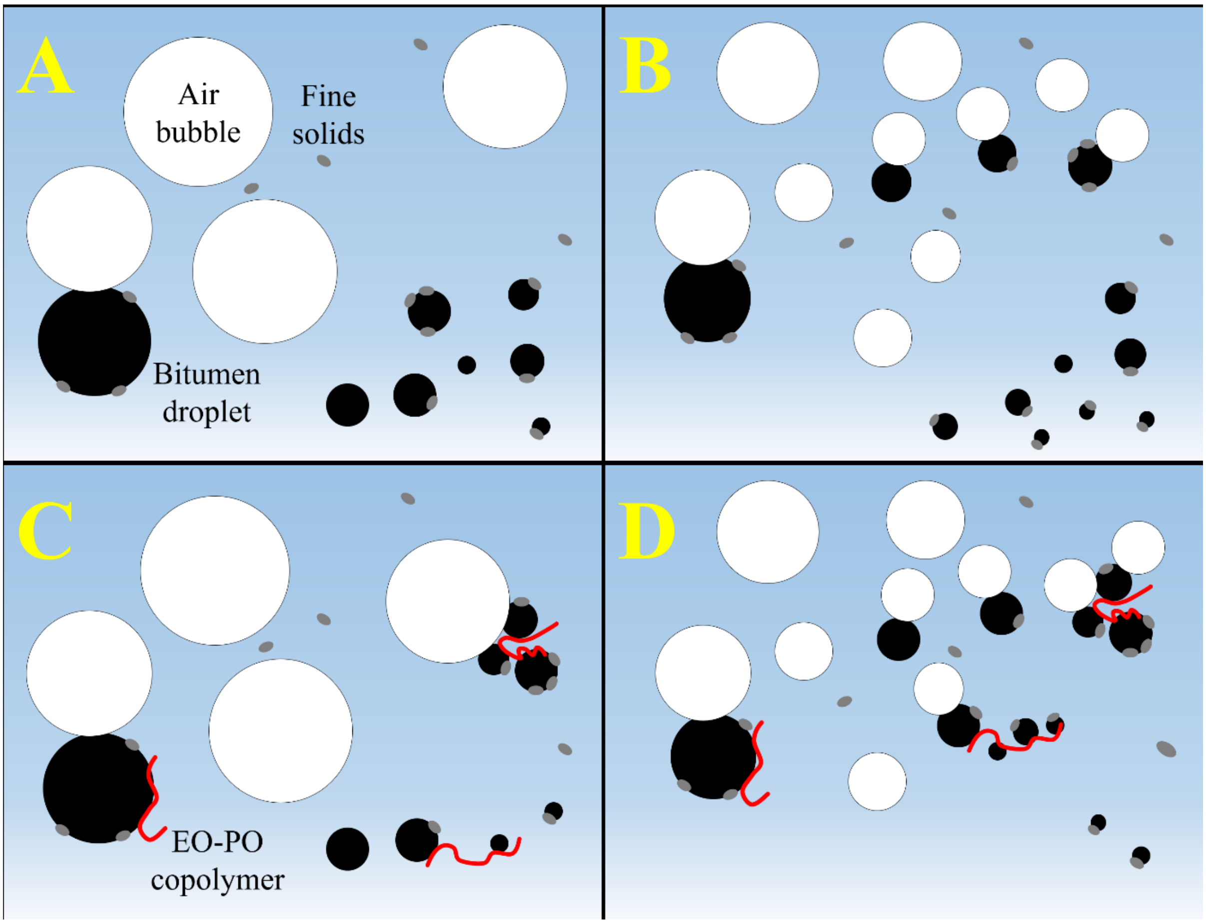


Figure 4.10 Schematic of bitumen flotation in the case of (A) basic BA^{3}BE, (B) BA^{3}BE with MIBC, (C) BA^{3}BE with EO-PO, and (D) BA^{3}BE with both MIBC and EO-PO, at ambient temperature.

4.5.4 Tailings Consolidation

In addition to high bitumen recovery, a rapid and thorough tailings consolidation is another important factor for an ideal processing technique for mineable oil sands. In this study, the tailings collected from the bench-scale extractions in the modified BA^{3}BE were analyzed for their consolidation characteristics, with select cases for comparison, including the blank and the HWBE baseline test. The results were presented in the form of normalized mudline height, $[h/H]$, defined as the mudline height divided by height of the whole tailing versus the elapsed time after vigorous mixing, as shown in Figure 4.11. A hyperbola model proposed by Yaromko (Yaromko 1977), has been found effective in describing the mudline descending and was used in this study, as given in Equation A.4 (in Appendix V). Two important indicators, the initial settling rate, v_{ini}, and the ultimate normalized mudline height, $[h/H]_{ultimate}$, can be derived from Equation A.4, as expressed in Equation A.5 and A.6 with results presented in Table A.5. A higher v_{ini} indicates a more rapid initial tailings consolidation, while a lower $[h/H]_{ultimate}$ represents a more compact sediment obtained in long term. v_{ini} and $[h/H]_{ultimate}$ results are listed in Table 4.3.

As shown in Figure 4.11, with pH adjusted to 9.0 by caustic addition and temperature raised to 40°C for oil sands extraction, the sludge tailings in the HWBE group was found to show the lowest initial settling rate among all test samples, as well as the least compactness of the final sediment (Table 4.3). Such difference was contributed by the increased electrostatic repulsion between dispersed fine solids at high pH (Masliyah, Zhou *et al.* 2004). For the groups with solvent pretreatment, their sludge tailings were found to settle faster (v_{ini} in the range of 1.05-1.65 hr^{-1}) and result in more compact final sediment, compared to the HWBE group. In addition, no clear correlation was found between v_{ini} and the composition of solvent used, a more obvious trend was observed that the tailings of EO-PO treated groups typically gave greater v_{ini} compared to the corresponding case of solvent-only groups. A possible explanation for such difference was that EO-PO could flocculate certain bitumen-contaminated fines, increase the settling velocity of solids and generate drainage channels for water to move upwards, leading to faster settling (Masliyah, Zhou *et al.* 2004). On the other hand, no noticeable variation was found in $[h/H]_{ultimate}$ of all the solvent-treated groups ($[h/H]_{ultimate}$ in the range of 0.349-0.380), suggesting marginally influence of solvent type or EO-PO on the compactness of the final sediment.

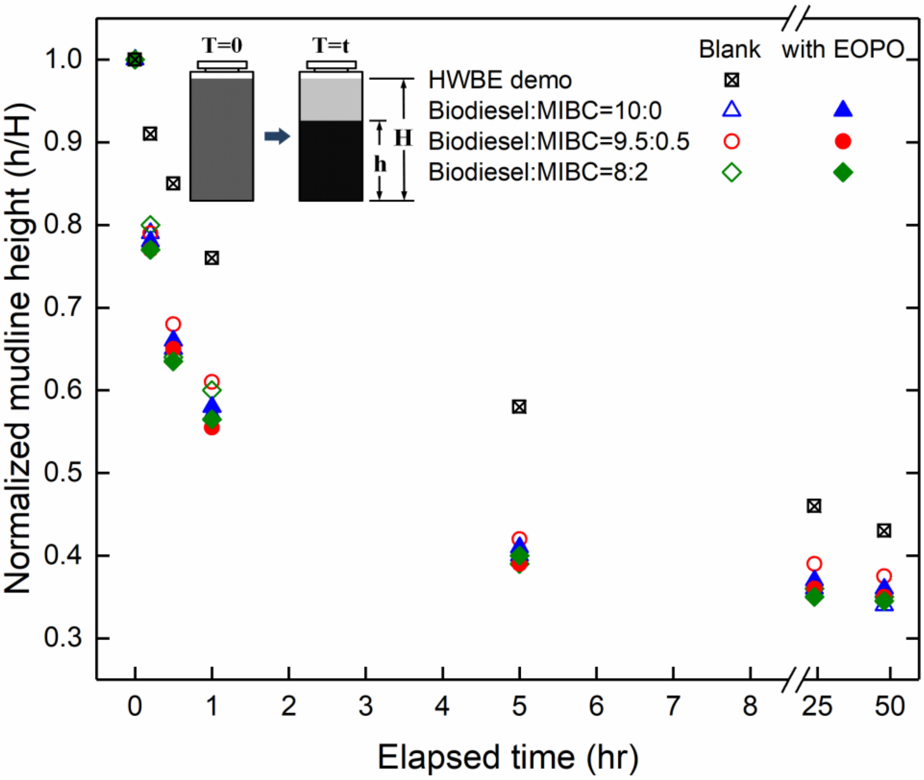


Figure 4.11 Effect of pretreatment additives on sludge tailings settling. Except for HWBE group, oil sands were pretreated with 10 wt% (of bitumen) biodiesel-MIBC mixture of variable mass ratio, with or without 1,500 ppm EO-PO.

Table 4.3 v_{ini} and $[h/H]_{ultimate}$ calculated from the fitting parameters of hyperbola function for tailings consolidation, at 25°C.

Biodiesel : MIBC mass ratio*	**EO-PO**	**Results**	
		v_{ini} **(hr^{-1})**	$[h/H]_{ultimate}$
No solvent	Blank	0.41±0.05	0.43±0.02
10:0	Blank**	1.5±0.1	0.34±0.02
	1500 ppm***	1.5±0.2	0.36±0.02
9.5:0.5	Blank	1.3±0.2	0.37±0.02
	1500 ppm	1.6±0.1	0.35±0.02
8:2	Blank	1.4±0.2	0.35±0.03
	1500 ppm	1.6±0.2	0.35±0.02

4.5.5 Tailings Solvent Loss

Minimizing the loss of solvent to tailings is important in the development of a solvent-incorporated oil sands processing technique (Gosselin, Hrudey *et al.* 2010). In this study, the tailings of the optimum extraction group, i.e., Biodiesel : MIBC = 8:2 (w/w) with 1,500 ppm EO-PO (Figure 4.2), was found to contain 1.9% of the biodiesel originally added to the oil sands, as shown in Figure A.10. According to the calculations given in the supplementary information, this indicates an equivalent loss of 1.75 bbl solvent for every 1000 bbl of bitumen produced. In addition, the loss of MIBC to tailings was difficult to quantify in this study, as partial MIBC could be lost during flotation due to its volatility, as indicated by a solvent loss test (Figure A.11).

Overall, the bench-scale extraction of bitumen from mineable oil sands showed that the basic BA^{3}BE technique could be integrated with the use of MIBC and EO-PO, to achieve bitumen recovery to >85% from poor processing ores at a substantially reduced solvent dosage and at ambient temperature, and to produce cleaner diluted bitumen with only ~1/2 the weight of water impurities in the HWBE case, which agreed well with the above-mentioned hypothesis. Although a portion of MIBC was lost in oil sands extraction due to its volatility, a proof-of-concept was provided for the modified BA^{3}BE, which allows synergy of both frother and polymeric demulsifier to enhance bitumen recovery from Athabasca oil sands. To further push forward the development of the modified BA^{3}BE, more studies may be focused on investigating low-volatility frothers. Substituting EO-PO with cheaper and commercially-available alternatives might also be considered.

4.6 Conclusions

Synergy of frother (i.e., MIBC) and polymer demulsifier (i.e., EO-PO copolymer) were for the first time investigated in terms of bench-scale demonstrations, on the top of the basic BA^{3}BE process for enhanced bitumen extraction from Athabasca oil sands. Conducting oil sands extraction in modified BA^{3}BE with the use of MIBC and EO-PO was found to achieve a greater total hydrocarbon recovery at a substantially reduced solvent dosage (10 wt% of bitumen), compared to the optimum case in basic BA^{3}BE technique. In addition, a cleaner diluted bitumen product with a ~50% reduction in water content could be achieved in the optimized method, in comparison to the industrial practice (HWBE). An in-depth investigation on bitumen liberation found that, with the use of MIBC and EO-PO copolymer, bitumen liberation from the Athabasca oil sands samples was substantially improved as collectively contributed by reduced viscosity and decreased bitumen-water interfacial tension, while bitumen flotation was greatly enhanced in various aspects, including improved foaming efficiency, increased bitumen-air bubble collision probability, and reduced induction time for bitumen-air bubble attachment. In addition, the proposed modified BA^{3}BE was found to allow faster solid consolidation and facilitate the generation of more compact final tailing sediment, making the modified BA^{3}BE a promising alternative for Athabasca oil sands processing with enhanced tailings treatment.

Chapter 5 Effect of Biodiesel-Assisted Ambient Aqueous Bitumen Extraction (BA^{3}BE) on Release of Toxic Naphthenic Acids to Tailings

This chapter is part of the following article.

Yeling Zhu, Yi Lu, Qingxia Liu, Jacob Masliyah, and Zhenghe Xu*, Synergy of Chemical Additives to Enhance Bitumen Recovery from Athabasca Oil Sands using Biodiesel-Assisted Ambient Aqueous Bitumen Extraction (BA^{3}BE) Process, manuscript completed

5.1 Abstract

Oil sands processing in Alberta, Canada brings massive volume of toxic oil sands tailings water (OSTW), which is stored in large tailings ponds adjacent to the Athabasca River area. Extensive concerns have been raised on naphthenic acids (NAs; $C_nH_{2n+Z}O_2$), a complex mixture of toxic compounds in OSTW. Most studies on NAs treatment focus on eliminating the already-released NAs after oil sands processing, which limits effectiveness in performance. The novelty of our study is to restrain NAs release during oil sands processing, where solvent-assisted ambient aqueous bitumen extraction (SA^{3}BE) with model solvent (such as biodiesel and decane) is applied. Results demonstrate that compared to the industrial practice (HWBE), processing four common types of ores in SA^{3}BE reduced the total released NAs by 13.9–60.1% in OSTW, especially effective for poor-processing ores (42.4–60.1%). NAs profiles were found to exhibit little variation between OSTW streams from SA^{3}BE and HWBE, categorized in n or Z in formula. Moreover, SA^{3}BE with restrained NAs release during oil sands processing could be readily integrated with the existing NAs treatment technologies to further minimize OSTW NAs.

5.2 Introduction

The oil sands in northern Alberta, Canada, represents one of the largest petroleum resources in the world, with an established reserve of 164 billion barrels of crude bitumen (AER 2018). Approximately 1.27 million barrels of bitumen, the primary goal of the oil sands industry, is produced every day from shallow deposit along Athabasca River area, via open-pit mining coupled with hot water bitumen extraction (HWBE) process (Gosselin, Hrudey *et al.* 2010, 2013). However, produced along with bitumen is an extremely large volume of waste stream – the tailings of mineable oil sands, a mixture comprising oil sands tailings water (OSTW), sand and fine solids (Jordaan 2012). The oil sands tailings are now stored in dozens of engineered tailings ponds adjacent to Athabasca River or its tributaries. These tailings ponds have occupied a total area of 220 km^2 in 2017 and are expected to expand with the continued expansion of surface mining industry (Kent 2017, Canada 2018).

OSTW shows acute toxicity to a number of life forms, with naphthenic acids (NAs) as one of the primary contributors (Frank, Kavanagh *et al.* 2008, Jones, Scarlett *et al.* 2011, Kannel and Gan 2012). NAs are chemically defined as a complex mixture of cycloaliphatic carboxylic acids with the general chemical formula $C_nH_{2n+Z}O_2$, where *n* specifies the carbon number and *Z* refers to the hydrogen deficiency that is related to the degree of cyclization (Brient, Wessner *et al.* 1995). The concentration of NAs in OSTW is found in the range from 2.9 to 100 mg/L (Schramm, Stasiuk *et al.* 2000, Scott, Young *et al.* 2008). Many studies reported that various life forms, including microorganisms, aquatic species, vegetations and mammals (Headley and McMartin 2004, Gentes, Waldner *et al.* 2007, Miskimmin, Fedorak *et al.* 2010, Li, Fu *et al.* 2017), showed toxic responses to exposure of NAs, such as reproduction impairment, developmental delays, immunotoxicity, endocrine disruption, and histological alterations (Garcia-Garcia, Pun *et al.* 2012, Kavanagh, Frank *et al.* 2012, Kavanagh, Frank *et al.* 2013, Marentette, Frank *et al.* 2015). Though there is still a huge knowledge gap in understanding the mechanisms between the structural characteristics of a particular type of NA and its toxic effects, it has been found that the toxicity of OSTW could be substantially alleviated by removal of the NAs (Rogers, Wickstrom *et al.* 2002, Kavanagh, Frank *et al.* 2012, Kindzierski, Jin *et al.* 2012). As a result, it is of great interest to eliminate the NAs in OSTW, from the environmental protection perspective and biodiversity conservation.

OSTW NAs are distinguished from commercial NAs in composition and structure (Marsh 2006, Kannel and Gan 2012). OSTW NAs exhibited relatively stronger resistance to biodegradation by indigenous microorganisms in tailings ponds, especially for the homologues with higher cyclicity (more negative *Z*) (Scott, Mackinnon *et al.* 2005, Han, Scott *et al.* 2008). Currently, there are several methodologies under active investigation for the NA treatment (Brown and Ulrich 2015). Ozonation, in which dissolved ozone is employed for degradation of NAs, was found superior in removing NA species with high carbon numbers and cyclicity, however it could lead to an equivalent or even an increased amount of low molecular weight NA compounds and/or other organics (Scott, Zubot *et al.* 2008, El-Din, Fu *et al.* 2011, Pereira, Islam *et al.* 2013). Another study revealed that the immunotoxicity endpoints of mice macrophages were greater in some ozonated groups than the untreated controls (Garcia-Garcia, Ge *et al.* 2011), suggesting that ozonation might even increase the toxicity of OSTW. The constructed wetlands strategy was piloted a few years ago (Foote 2012, Toor, Franz *et al.* 2013), in which engineered wetlands were built to filter out and/or degrade pollutants in OSTW, mimicking the natural wetlands. This approach was found to allow removal of most of the acid extractable organics (predominantly including NAs) by filtration and microbial degradation (Kannel and Gan 2012, Toor, Franz *et al.* 2013, Li, Fu *et al.* 2017), however the treatment was time-consuming, and certain toxic effects on relevant species still remained in the long-aged OSTW (Kavanagh, Frank *et al.* 2011). Adsorption of NAs using high-surface-area materials (such as petroleum coke and activated carbon) appeared to effectively remove high-cyclicity NAs, however increased contents of vanadium, sulphate and molybdenum were observed in the water after treatment (Zubot 2010). Photolysis (UV radiation) is effective in breaking down large NA molecules into smaller fragments, while its performance in treating turbid oil sands tailings was limited due to the poor penetration of highly energetic radiation (McMartin 2003). It is unfortunate that each of the current methodologies has certain limits (Kannel and Gan 2012, Brown and Ulrich 2015).

It is obvious that all the current NAs treatment techniques aimed at eliminating the existing NAs in tailings ponds. Thus, several questions are raised: where do the NAs come from in the current oil sands industry? And, is it possible to reduce the NAs content before OSTW is sent to tailings ponds? As it is well identified, OSTW NAs come from bitumen (2010). In the current HWBE, a satisfactory bitumen recovery is mostly accomplished at a high pH of 8.5-9 and an elevated temperature of 40-45°C (Masliyah, Zhou *et al.* 2004, 2010, Wang, Harbottle *et al.* 2014). Due to the heavy use of caustic for bitumen recovery, the NAs are severely anionized and become hydrophilic, exhibiting strong tendency to be released from bitumen into the water phase (Figure 5.1), which leads to the enrichment of NAs in OSTW (1998, Headley, Peru *et al.* 2002). Another drawback of using caustic is the increased surface charge of tailings solid, making tailings settling and water reclamation intractable, especially when oil sands feed contains a massive amount of fine solids (Masliyah, Zhou *et al.* 2004, Wang, Harbottle *et al.* 2014).

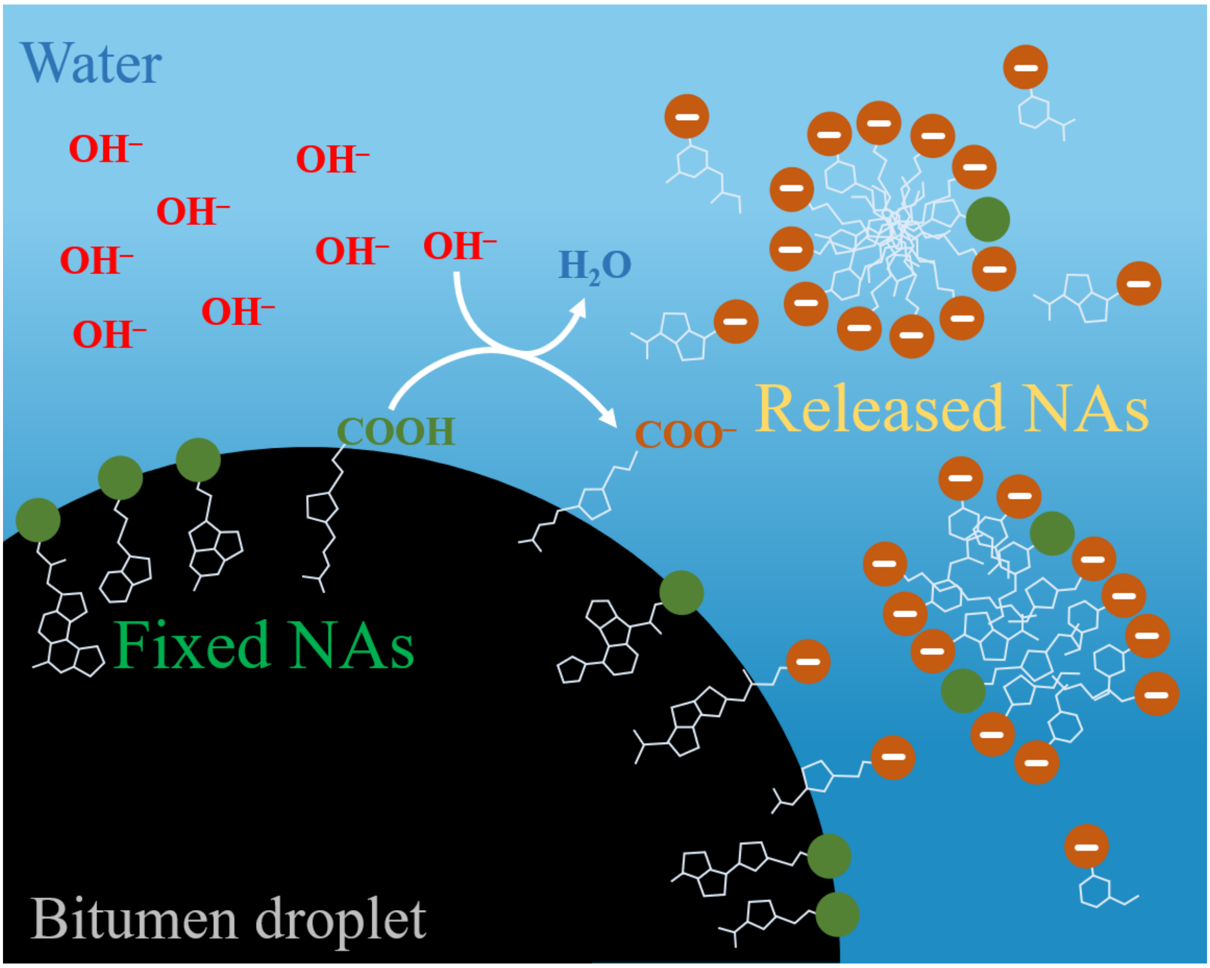


Figure 5.1 Schematic of release of NAs with different n and Z in formula from bitumen to water phase, in the presence of caustic during industrial oil sands slurry conditioning.

We aimed at alleviating NAs release into water phase, by employing a caustic-free extraction method to process mineable oil sands. Solvent-assisted ambient aqueous bitumen extraction (SA^3BE) process has been supported by several bench-scale experiments as a practical technical alternative to HWBE, for satisfactory bitumen recovery (Harjai, Flury *et al.* 2012, Lin, He *et al.* 2015, Russell 2017, Zhu, Yan *et al.* 2018). The fact that SA^3BE allows oil sands processing at near-neutral pH strongly suggests its capability of restraining the NAs liberation from bitumen to the water phase, and thus lowering the concentration of released NAs in OSTW (Harjai, Flury *et al.* 2012, Zhu, Yan *et al.* 2018). As a result, NAs can remain as a part of bitumen product and be treated in downstream refining, where the NAs could be transformed into a part of hydrocarbon product via catalytic hydro-processing.

In this study, SA^3BE was investigated for the first time as a feasible solution to the NAs treatment in mineable oil sands industry. Acid extractable organics (AEOs), primarily consisting of humic acids (Stevenson 1994), was regarded as "unrefined NAs" in early studies (Rogers, Liber *et al.* 2002, Ross, Pereira *et al.* 2012). AEOs were extracted by liquid-liquid extraction from OSTWs at a strong acidic environment (Rogers, Liber *et al.* 2002, Ross, Pereira *et al.* 2012), and were used as the samples in this study for quantitative analysis. NA compounds with different carbon numbers and/or ring numbers were quantified by liquid chromatography coupled with high-resolution mass spectroscopy (LC-HRMS). Bench-scale SA^3BE was conducted and evaluated in NAs release to tailings water, with its performance in bitumen production further compared against a simulated industrial practice. The objective of this study is to provide a proof-of-concept of using a low-toxicity readily-biodegradable solvent (such as biodiesel and decane as model solvents) in SA^3BE to reduce the discharge of pollutive chemicals to water body and to facilitate tailings settling, without sacrificing bitumen production in the mineable oil sands industry.

5.3 Experimental

5.3.1 Chemicals and Reagents

Decane and dichloromethane (DCM, HPLC grade) were purchased from Fisher Scientific, Canada. Acetic acid, 2/3 M sulfuric acid and myristic acid-1-^{13}C (as the internal standard) were purchased from Sigma-Aldrich Canada. 1 M NaOH aqueous solution was purchased from RICCA Chemical (Texas, US). Refined Merichem standard was purchased from Merichem Company (Texas, US). Biodiesel (contains >99 wt% methyl myristate and methyl palmitate) was obtained from Alberta Innovates – Technology Futures (Alberta, Canada). Industrial-grade naphtha was provided by Syncrude Canada Ltd.

To make the bench-scale experiments in this study a good demonstration for a potential technological alternative, four real oil sands for industrial oil sands processing were obtained from Athabasca open-pit mining field (Suncor Canada), noted as Ore SM, SP, SE and SO with their characteristics listed in Table A.6. Process water (PW), directly collected from Syncrude industrial stream, was used as the aqueous medium feed for oil sands extraction process. The process water has a pH of 7.5, and more characteristics can be found in the literature (Zhu, Yan *et al.* 2018).

5.3.2 Oil Sands Tailings Water Sample Collection

OSTW samples were prepared from the bench-scale laboratory experiment using a modified batch extraction unit (M-BEU), following a well-established procedure in the previous studies (Harjai, Flury *et al.* 2012, Zhu, Yan *et al.* 2018). All the types of ores were processed under three conditions: baseline, SA^{3}BE and the caustic-incorporated. To begin with, an extraction was carried out for each ore at ambient temperature using PW (pH adjusted to 7.5 and with no solvent addition), and it was set as the baseline level (colored BLACK in Figure 5.2). In SA^{3}BE process, a small designated amount of solvent (i.e. decane, biodiesel or naphtha) was directly distributed into crushed ores for 20-min conditioning, followed by a conventional aqueous process at ambient temperature (colored BLUE and BLACK in Figure 5.2). The dosage of added solvent was always kept at 10 wt% in respect to bitumen, which was equivalent to 0.97 wt% (set Ore P1 as example) with respect to the total weight of oil sands feed. In the caustic-incorporated demonstrations, oil sands ores were mixed with water and caustic (pH adjusted to 9.0), followed by aqueous process at an elevated temperature of

40°C that was close to the industrial practice. Three additional sets of oil sands extraction with caustic use at (1) 25°C and pH = 9.0, (2) 25°C and pH = 10.5, and (3) 55°C and pH = 9.0, were also conducted in this study, to obtain an in-depth understanding of the roles that caustic and temperature played in the release of NAs to OSTW (colored RED and BLACK in Figure 5.2).

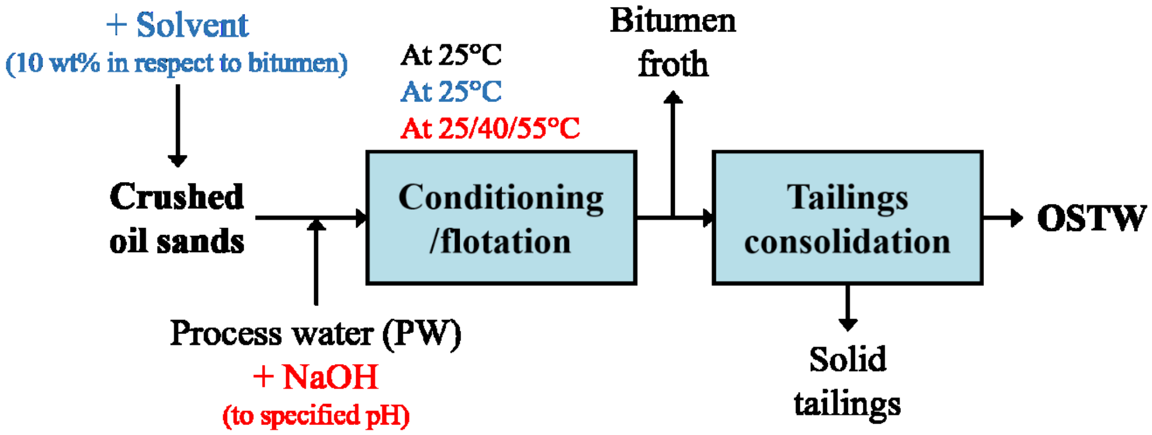


Figure 5.2 Schematic of OSTW sampling from a laboratory-scale oil sands extraction. Descriptions colored in blue/red/black correspond to the steps taken in SA^{3}BE/caustic/both processes.

The influence of ore characteristics was also analyzed by processing the four ores under each set of environmental conditions. All the test conditions applied in the bench-scale oil sands extractions are given in Table 5.1, while each combination of ore type and set of environmental conditions was carried out in triplet, following a well-established extraction procedure (Harjai, Flury *et al.* 2012, Zhu, Yan *et al.* 2018). Abbreviations are adopted in the following discussion, for convenience in referring a specific combination of condition parameters. For example, Set **B** stands for the baselines; Set **BD, DE** and **NF** represent biodiesel-, decane- and naphtha-based SA^{3}BE process, respectively; Set **C** and **EC** correspond to the groups with addition of caustic (pH = 9.0) and excessive caustic (pH = 10.5), respectively. The temperature (°C) of oil sands conditioning was indicated by a suffix

(**-40** or **-55**), otherwise ambient temperature was applied throughout the experiment. All the experiments were carried out at ±0.5°C of the specified temperature and ±0.1 of the specified pH.

Table 5.1 Sets of conditions applied in the oil sands extraction of four types of ores.

Temperature (°C)	**pH**		
	7.5	**9.0**	**10.5**
25	Set **Baseline** Set **BD, DE** and **NF** (SA^{3}BE)	Set **C**	Set **EC**
40		Set **C-40** (HWBE)	
55		Set **C-55**	

In all the extraction experiments, bitumen froth was collected from top of the processed slurry and stored elsewhere as a product stream, which was further examined for its total hydrocarbon content and bitumen quality. The remaining tailings were homogenized and stored in graduated glass bottles, which were then deprived of air by purging with nitrogen and keeping sealed, to minimize oxidation or other weathering effects. The descending of the tailings mudline was recorded over time, for the tailings settling analysis (Zhu, Yan *et al.* 2018). The supernatants of tailings were collected as OSTW samples.

5.3.3 Extraction and HPLC Measurement of Naphthenic Acids

The organic acid fraction was isolated from PW (2000 mL) and OSTW samples (300 mL) by liquid-liquid extraction (Rogers, Liber *et al.* 2002, Ross, Pereira *et al.* 2012). In brief, the pH was adjusted to ~2.0 with the addition of 2/3 M sulfuric acid, mixed with the internal standard and was extracted four times with a total of 800 mL DCM (HPLC grade). The organic phases were combined and evaporated to approximately 10-15 mL in a vacuum distillation apparatus, transferred to a glass sampling vial and further reduced to dryness. For a quality control purpose, 2000 mL of Milli-Q water was also tested as the blank group.

Each sample for LC analysis was prepared by mixing 1 mg of AEOs with 1 mL of 1:100 DCM/MeOH. Samples were chromatographed using an Agilent 1200 SL high-pressure liquid chromatography system with a Kinetex C8 reverse-phase column, 2.1 mm × 50 mm, 1.7 μm d.p. (Phenomenex, Torrance, CA, USA), thermostated at 50 °C, followed by a mass spectrometric detection. An aliquot of 5 μL was injected into the column at a flow rate of 0.5 mL/min. Formic acid (0.1%) in water (mobile phase A) and GC-RESOLV MeOH (mobile phase B) were used as buffer for gradient elution. The mobile phase composition was kept at 10% B over a period of 1 min, followed by a linear gradient to 95% B over a period of 9 min, 95-99% B over a period of 5 min, returned to 5% B over a period of 1 min, and remained at this composition for 4 min.

Mass spectra were acquired in negative mode ionization using an Agilent 6220 Accurate-Mass time-of-flight (TOF) HPLC/MS system (Santa Clara, CA, USA) equipped with a dual sprayer electrospray ionization source with the second sprayer providing a reference mass solution. Mass spectrometric conditions were listed as follows: drying gas, 10 L/min at 300°C; nebulizer, 30 psi; mass range, 100-1100 Da; acquisition rate, ~1.03 spectra/s; fragmentor, 150V; skimmer, 65V; capillary, 3000V; instrument state, 4GHz (High Resolution). Mass correction was performed for every individual spectrum using peaks at m/z = 112.98558 and 1033.98811 from the reference solution. Data acquisition was performed using the Mass Hunter software package (ver. B.04.00.). The Analysis of HPLC-MS data was accomplished using the Agilent Mass Hunter Qualitative Analysis software (ver. B.07.00).

5.3.4 Analysis of NA Profiles, Relative Total NAs and Total AEOs

The peaks of NA homologues (i.e., for a certain combination of n and *Z*) were identified and integrated only when they met all the following three criteria: (1) high-resolution mass measurement (*m/z*) obtained within ±0.015 amu of the theoretical masses of target NAs with n = 10-22, and Z = 0 to Z = -18; (2) retention time observed within ±0.3 min of the same homologue group (if exists) from the Refined Merichem standard; (3) the ratio of intensity of a secondary peak (if exists) to that of the primary peak agreed with the theoretical ratio calculated from the distribution of isotopes.

The absolute quantification of NA homologues was not possible due to lack of appropriate standards for the extremely complex NA samples. A useful method was to present the content of each NA homologue in the form of intensity of the NA homologue's characteristic MS response, normalized by the response of an internal standard, $I(C_nH_{2n+Z}O_2)$, with unit of "A.U./A.U." (Han, Scott *et al.* 2008). The total NAs intensity was therefore determined by summing all the relative peak intensities of all the NA homologues detected in a sample, deducted by that of the background. Due to the relatively high concentrations of almost all $Z = 0$ NAs and three $Z = -2$ NAs (n = 16, 18 and 22) in the laboratory blank samples (Figure A.12), these homologues were exempt from the NA profile presentation and total NAs quantification. Dixon's Q test, which was commonly used in statistics for identification and rejection of outliers, was used in this study to reject any outlier data from the experimental triplet (Rorabacher 1991).

Based on a 5-point calibration curve (concentration range: 0.1–20 µg/mL, r^2 = 0.999) generated from serial dilutions of the internal standard (Figure A.13), the total AEOs content can be determined by calculating the concentration of internal standard in LC sample, as shown in Equation 5.1.

$$c(AEOs) = c(Int.Std.) \times \left[\frac{c(AEOs,LC)}{c(Int.Std.,LC)} - 1\right] \quad (5.1)$$

where $c(AEOs)$ and $c(Int.Std.)$ are the total concentrations of AEOs and the added internal standard initially in OSTW, respectively; $c(AEOs, LC)$ and $c(Int.Std., LC)$ represent the concentration of AEOs sample in LC test, which is precisely equal to 1 mg/mL, and the concentration of internal standard in LC sample that could be calculated from the calibration curve, respectively.

5.4 Results and Discussion

5.4.1 Total NAs Intensity and Total AEOs Content in OSTW Streams

Quantifiable contents of NA homologues were found from all the OSTW streams to have a total intensity in the range of 28.4–189.8 A.U./A.U. (Figure 5.3), all higher than that of the background PW (9.6±1.2 A.U./A.U.). Distinct differences were observed among the liberated NAs of Set **Baseline** (the un-patterned GREY bars) from the four ores, which can be attributed to the intrinsic characteristics of ores. Ore SM, an ore bearing medium-grade bitumen content and certain amount of fine solid, and Ore SE, a poor-processing ore carrying more fine solids, were found to release a comparable amount of total NAs (31.8±1.3 A.U./A.U. and 32.3±0.2 A.U./A.U., respectively); Ore SP, another poor-processing ore, gave a slightly lower release of total NAs (23.2±1.6 A.U./A.U.); Ore SO, a weathered ore originated from a deposit that was exposed to atmosphere and partially oxidized, exhibited the greatest release of total NAs (71.3±2.4 A.U./A.U.).

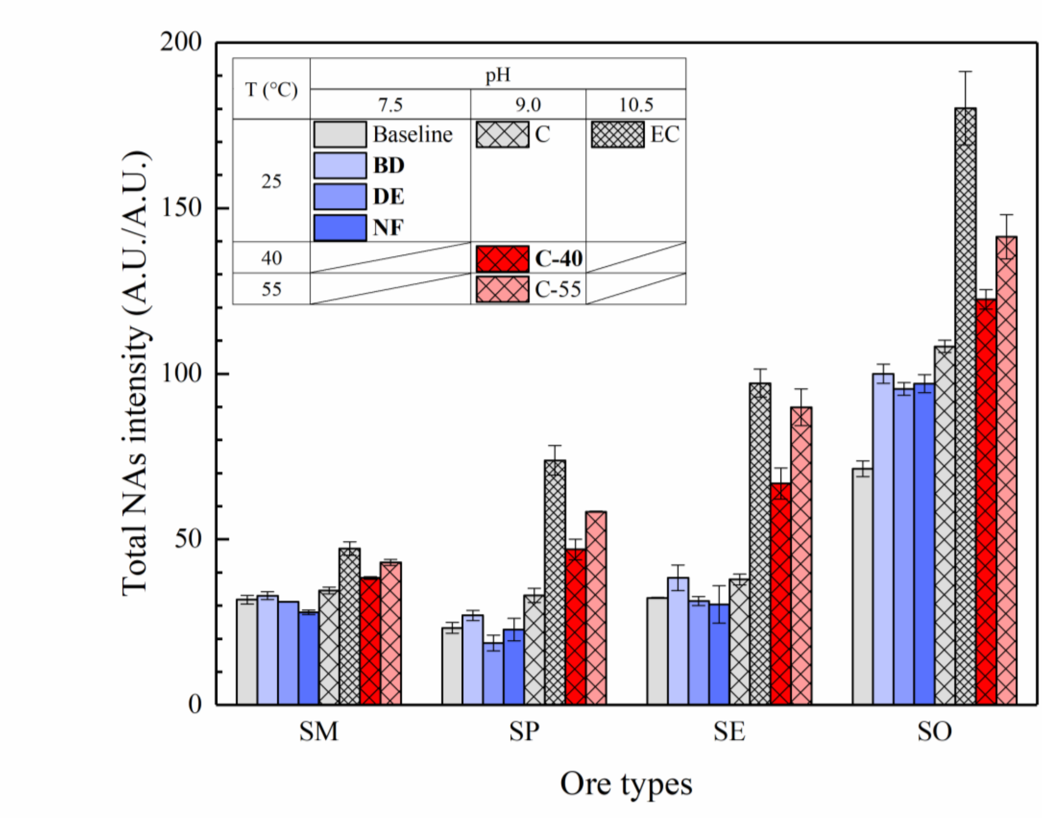


Figure 5.3 Total NAs intensity (with respect to the internal standard) of OSTW samples, obtained from extraction of four oil sand ores under different sets of conditions and with the background deducted.

Though the extent of released NAs was different from ore to ore, clear trends have been found with various sets of extraction conditions for OSTW preparation. A notable observation in processing three of the four ores examined was that the SA^{3}BE groups appeared to allow an equivalent extent of released NAs to the baseline case. For Ore SM, SP and SE, the ratio of the total NAs intensity in Set **BD**, **DE** and **NF** (the BLUE bars) to that of Set **Baseline** was found in the range of 0.81–1.19 (Figure 5.3). This observation was notable, because it suggested that the use of solvent (biodiesel, decane or naphtha) in SA^{3}BE for pretreatment of these three common ores not only scarcely contributed to but, in some cases, even restrained the release of NAs to OSTW, in comparison to the baseline case, where the ores were merely soaked with a comparable amount of PW, at ambient temperature without any additives.

Different from the three un-oxidized ores, the total NAs released in SA^{3}BE was found 1.33–1.40 times of the baseline value in Ore SO, which might be attributed to unique characteristics of the oxidized/weathered ore. Ren *et al.* (Ren, Dang-Vu *et al.* 2008) reported that in weathered ores, the loss of connate water allowed bitumen to have an intimate contact with mineral solids, with certain functional groups (for example, carboxylic acid, hydroxyl and amino groups) acting as bridging molecules. Attachment of these bridging molecules to mineral surfaces was relatively robust and many of them could not be released without certain treatments, such as altered wettability of mineral solids by increasing pH, or increased bitumen mobility with solvent soaking. As a result, the released total NAs intensity given in Set **Baseline** of Ore SO was lower than the corresponding SA^{3}BE cases.

It was noticeable that the total NAs in the industrial baseline (Set **HWBE**, the RED bars), regardless of ore types, was always greater than the corresponding SA^{3}BE ones (the BLUE bars) with the ratio in the range of 1.16–2.50 (Figure 5.3). In other words, the total NAs intensities detected in all SA^{3}BE OSTW samples were reduced by 13.9–60.1% with respect to the corresponding HWBE cases (Figure 5.3), proving that SA^{3}BE provided an effective alternative to substantially restrain the release of NAs during mineable oil sands processing. Especially, such reduction in the total NAs intensity was noted as high as 42.4–60.1% (Figure 5.3) for the two poor-processing ores (Ore **SP** and **SE**).

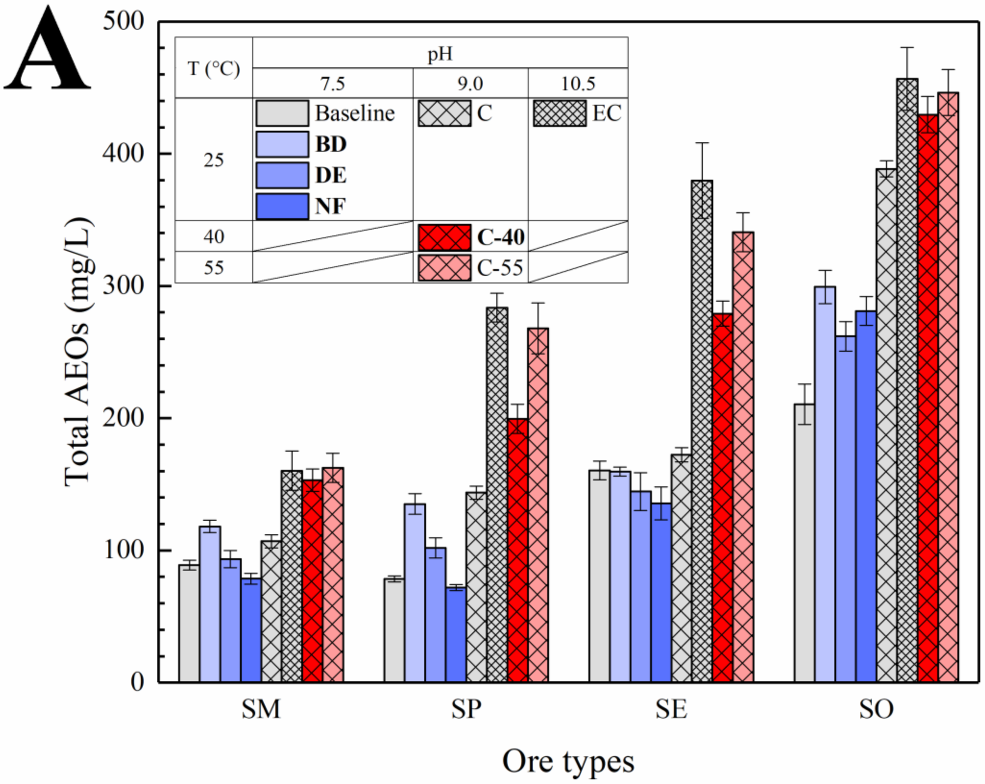
The effects of caustic and temperature on the release of NAs to OSTW were investigated to better understand the high NAs release in the industrial baseline. For the first factor (caustic), continuous increases in the total NAs intensity of OSTW samples were observed at ambient temperature with increased pH from 7.5 to 10.5 (Set **Baseline**, to Set **C** and to Set **EC**, GREY bars with more compact patterns), as shown in Figure 5.3. Varying with the ore type, the total NAs intensity at an elevated pH of 9.0 was found to increase by 8.5–51.7% from the baseline levels, which were further increased to 48.6–218% with an excessive caustic addition and pH = 10.5 (Figure 5.3). Such dependence of liberated NAs on pH agreed well with the hypothesis that with the use of caustic, more NAs at bitumen surface become anionized and migrate into water phase, resulting in the enrichment of released NAs in OSTW (Figure 5.1). In addition to pH, it was also recognized that the content of NAs was positively correlated to operation temperature during extraction experiments. The pH in Set **C**, **C-40** and **C-55** (GREY, RED and PINK bars with the same pattern) remained stable at the industrial level (pH = 9.0). It is important to note that the total NAs intensity increased by 11.1–76.4%, with the conditioning temperature elevation from the ambient (Set **C**) to the industrial practice (Set **C-40**), while this range became 24.7-137% by further elevating the temperature to 55°C (Set **C-55**), as shown in Figure 5.3. Such experimental results agreed with the findings of Bostick *et al.* (Bostick 2002), who investigated the solubility of polar organics using a Gulf of Mexico crude oil with synthetic brine. In their study, the equilibrium concentration of C10-C20 polar organics, most of which were organic acids, was found to continuously increase with elevated temperature in the test range (25–75°C) at the neutral pH (Bostick 2002).

In general, the content of liberated NAs has been found to increase by 20.6%, by adopting the industrial HWBE for bench-scale bitumen production from medium-grade oil sands, compared to the baseline case. The content of NAs liberation was further boosted to 71.7–107%, when poor-processing or oxidized/weathered ores were used as the feed. It revealed that such increases could be essentially attributed to the slurry pH (or, the use of caustic) and operation temperature of HWBE, as the hydration and liberation of NAs was remarkably favored at an elevated pH and temperature. More importantly, the intensity of released NAs in fresh OSTW was substantially reduced by 13.9–60.1%, by substituting HWBE with

SA^{3}BE. A proof-of-concept has thus been demonstrated to support SA^{3}BE as a promising oil sands processing alternative with a reduced energy-intensity due to ambient operation. An apparent reduction in released NA content could be achieved via SA^{3}BE by merely applying a comparatively small dosage (~1 wt% of ore) of readily-biodegradable solvent such as biodiesel and decane, compared to HWBE using caustic at 40°C. Last but not least, the reduction in NAs release via SA^{3}BE was achieved before OSTW was sent to tailings ponds, suggesting that SA^{3}BE could be integrated with other downstream NA treatment methods, such as the ozonation method, the constructed wetlands strategy, etc., to accomplish further improvement in the NA treatment.

AEOs were found to contain thousands of acidic compounds (including NAs), with many carrying sulfur, nitrogen, and multiple oxygen atoms (Barrow, Witt *et al.* 2010, Grewer, Young *et al.* 2010, Headley, Peru *et al.* 2010). AEOs, regarded as "unrefined NAs" in the early studies (Stevenson 1994, Rogers, Liber *et al.* 2002, Ross, Pereira *et al.* 2012), were recognized as a possible contributor to the complexity of OSTW toxicity (Hagen, Katzenback *et al.* 2013). Although AEOs were not the major focus of this study, their total concentration was also quantified and presented as a supplement to give a comprehensive evaluation of the OSTW toxicity. Results showed that AEOs with concentrations in the range of 71.9–457 mg/L were observed in all the samples (Figure 5.4A). The variation of AEOs content with extraction conditions was found to follow a similar trend as the total NAs intensity. For example, the total AEOs in the industrial baseline (Set **HWBE**), regardless of ore types, were always greater than the corresponding SA^{3}BE ones (Set **BD**, **DE** and **NF**) with the ratio in the range of 1.30–2.77 (Figure 5.4A). Like NAs, it was also found that the release of AEOs was promoted at increased pH and temperature. Released AEOs were found to increase by 7.4–84.6% or 80.1–261% with pH increased from 7.5 (Set **Baseline**) to 9.0 (Set **C**), or to 10.5 (Set **EC**), respectively, while elevating temperature from the ambient (Set **C**) to 40°C (Set **C-**

40), or to 55°C (Set **C-55**) gave a boost in the AEOs concentration by 10.6–61.9% or 14.8-97.6%, respectively. In addition, it was interesting to observe that the released AEOs appeared to possess a strong proportional relationship with the corresponding total NAs intensity, among samples from the same type of ore (Figure 5.4B). This finding was notable, as it revealed that variation in extraction conditions (solvent, pH and temperature) within the experimental range showed weak selectivity in extracting NAs and other compounds of AEOs. In other words, SA^{3}BE was capable of not only reducing NAs release to OSTW, but also correspondingly lowering the content of other toxic AEO compounds by 26.3–74.6%, in comparison with the industrial practice (HWBE).



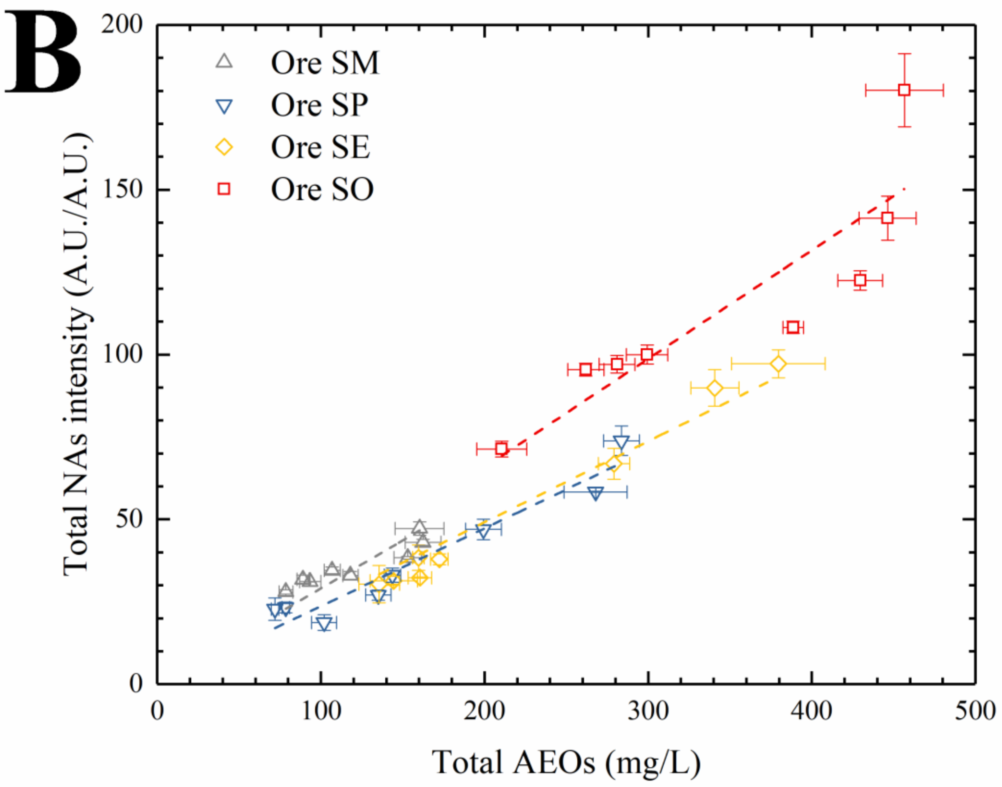


Figure 5.4 (A) Total AEOs concentration, and (B) its correlation with total NAs intensity of the identical OSTW samples, obtained from extraction of four oil sand ores. Total AEOs of the background (PW), 18.6±0.2 mg/L, has been deducted from the total AEOs of each sample. Dashed lines in (B) specified the proportional fitting of total NAs intensity and total AEOs obtained from the same type of ores. Fitting lines have slopes of SM: 0.291, SP: 0.236, SE: 0.246 and SO: 0.329, with unit of L/mg and $R^2 \geq 0.982$.

5.4.2 NA Profiles

The previous discussion supported that the total concentration of released NAs could be greatly restrained by using SA^3BE for oil sands processing. However, it is well known that NA homologues with different *n* and *Z* demonstrate a great variability in toxicity and resistance to biodegradation. For example, NAs with high molecular weight and cyclicity were generally believed to be more recalcitrant to microbial degradation (Han, Scott *et al.* 2008). Therefore, a reduction in the total NAs concentration of a sample does not necessarily mean an improvement in its biodegradability. A careful examination of NA profiles between OSTW streams obtained in SA^{3}BE and HWBE is of vital importance to elaborate a specific range of n and/or Z of NAs that contribute to their difference in the total NAs concentration.

In this study, liquid chromatography coupled with high-resolution MS provided profiles specific for the NA homologues. Since there were two variables (n and Z) for NA homologues ($\mathrm{C}_n\mathrm{H}_{2n+Z}\mathrm{O}_2$), for convenience in comparison, NA profiles were presented in the form of categorizing NA homologues in either n-series with intensity of each proportion calculated by Equation 5.2, or Z-series with intensity of each proportion calculated by Equation 5.3.

$$I(\boldsymbol{n}) = \sum_{\boldsymbol{Z}} I(C_{\boldsymbol{n}}H_{\boldsymbol{2n+Z}}O_{\boldsymbol{2}}) \tag{5.2}$$

$$I(\boldsymbol{Z}) = \sum_{\boldsymbol{n}} I(C_{\boldsymbol{n}}H_{\boldsymbol{2n+Z}}O_{\boldsymbol{2}}) \tag{5.3}$$

where $I(\boldsymbol{n})$ and $I(\boldsymbol{Z})$ represent the total intensities of NA homologues with identical carbon number n and identical hydrogen deficiency Z, respectively. The NA profiles could then be demonstrated in the form of cumulative distribution.

It was observed that the NA profiles from all the streams, including background samples and OSTW samples, followed similar trends. Profiles of baseline, SA^{3}BE and HWBE samples are presented in Figure 5.5, while profiles of all test samples are given in Figure A.14. An overall Gaussian-like distribution of homologues was noted in all the n-series NA profiles (gradient GREEN-YELLOW-RED) with a center around n = 16–18, while it was interesting that an evident bimodal distribution was observed in all the Z-series NA profiles (gradient YELLOW-BROWN), with the two maxima located around Z = -4, -6 and Z = -12 (Figure 5.5

and Figure A.14). A similar distribution was reported in bitumen-derived naphthenic acids by Martin et al (Bataineh, Scott *et al.* 2006, Ross, Pereira *et al.* 2012).

The background (PW) in this study can be roughly regarded as diluted aged OSTW, as it comprised around 70% reclaimed water from tailings ponds, balanced with river water that has a NAs concentration 1-3 orders of magnitude lower than OSTW (Brown and Ulrich 2015). Therefore, it was reasonable that the profiles of the background expressed certain similarities to those of fresh OSTW samples from the four types of ores (Figure 5.5). Moreover, the major difference relied on the relatively low proportions of low molecular weight (n = 10–14) and ring-deficient (Z = -2, -4 and -6) NA homologues in the background samples, which could be attributed to: (1) NAs with low n tended to possess less alkyl branching and lower cyclicity (less negative Z), and thus more susceptible to biodegradation (Rontani and Bonin 1992, Holowenko, MacKinnon *et al.* 2002, Clemente, MacKinnon *et al.* 2004, Quagraine, Headley *et al.* 2005, Scott, Mackinnon *et al.* 2005), and (2) NAs with higher cyclicity (more negative Z) were more resistant to biodegradation (Han, Scott *et al.* 2008). An interesting observation was that the background shared the greatest similarity in NA profiles with Ore SO among the four types of ores (Figure 5.5), probably because the weathering/oxidizing effect of the oxidized ore, to a certain extent, acted equivalently as the aging effect on bitumen-derived NA species. For instance, the proportions of high-n (n = 19–22) and ring-deficient ($Z \geq -6$) NAs from Ore SO were much lower than the rest three types of ores but close to the background (Figure 5.5), as a result of loss of long aliphatic branches and relatively faster degradation of ring-deficient NAs during ore weathering, which as well occurred during the aging of fresh OSTW.

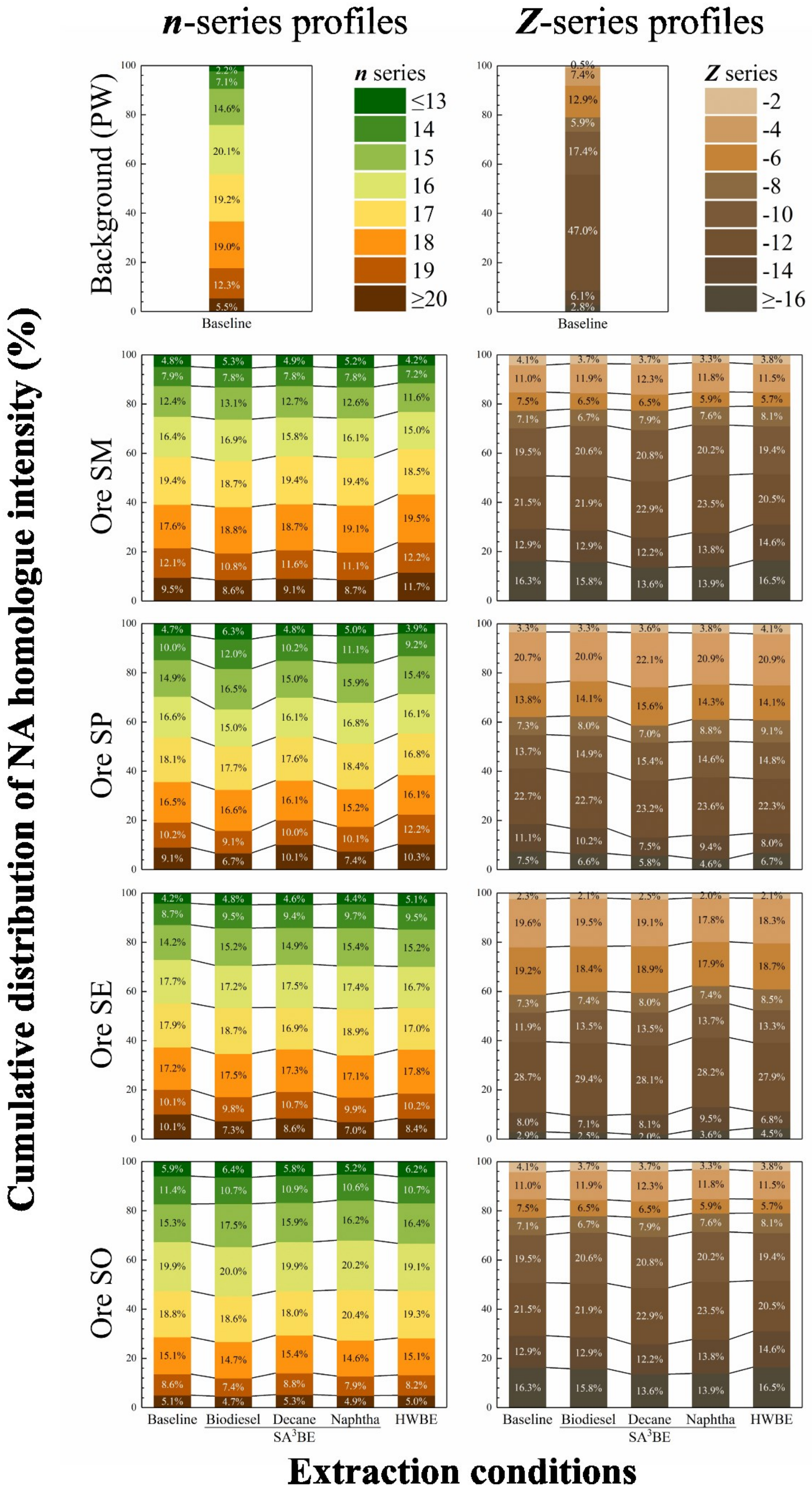

n-series profiles
Z-series profiles
Cumulative distribution of NA homologue intensity (%)
Background (PW)
100
80
60
40
20
0
2.2%
7.1%
14.6%
20.1%
19.2%
19.0%
12.3%
5.5%
Baseline
n series
≤13
14
15
16
17
18
19
≥20
0.5%
7.4%
12.9%
5.9%
17.4%
47.0%
6.1%
2.8%
Baseline
Z series
-2
-4
-6
-8
-10
-12
-14
≥-16
Ore SM
4.8% 5.3% 4.9% 5.2% 4.2%
7.9% 7.8% 7.8% 7.8% 7.2%
12.4% 13.1% 12.7% 12.6% 11.6%
16.4% 16.9% 15.8% 16.1% 15.0%
19.4% 18.7% 19.4% 19.4% 18.5%
17.6% 18.8% 18.7% 19.1% 19.5%
12.1% 10.8% 11.6% 11.1% 12.2%
9.5% 8.6% 9.1% 8.7% 11.7%
4.1% 3.7% 3.7% 3.3% 3.8%
11.0% 11.9% 12.3% 11.8% 11.5%
7.5% 6.5% 6.5% 5.9% 5.7%
7.1% 6.7% 7.9% 7.6% 8.1%
19.5% 20.6% 20.8% 20.2% 19.4%
21.5% 21.9% 22.9% 23.5% 20.5%
12.9% 12.9% 12.2% 13.8% 14.6%
16.3% 15.8% 13.6% 13.9% 16.5%
Ore SP
4.7% 6.3% 4.8% 5.0% 3.9%
10.0% 12.0% 10.2% 11.1% 9.2%
14.9% 16.5% 15.0% 15.9% 15.4%
16.6% 15.0% 16.1% 16.8% 16.1%
18.1% 17.7% 17.6% 18.4% 16.8%
16.5% 16.6% 16.1% 15.2% 16.1%
10.2% 9.1% 10.0% 10.1% 12.2%
9.1% 6.7% 10.1% 7.4% 10.3%
3.3% 3.3% 3.6% 3.8% 4.1%
20.7% 20.0% 22.1% 20.9% 20.9%
13.8% 14.1% 15.6% 14.3% 14.1%
7.3% 8.0% 7.0% 8.8% 9.1%
13.7% 14.9% 15.4% 14.6% 14.8%
22.7% 22.7% 23.2% 23.6% 22.3%
11.1% 10.2% 7.5% 9.4% 8.0%
7.5% 6.6% 5.8% 4.6% 6.7%
Ore SE
4.2% 4.8% 4.6% 4.4% 5.1%
8.7% 9.5% 9.4% 9.7% 9.5%
14.2% 15.2% 14.9% 15.4% 15.2%
17.7% 17.2% 17.5% 17.4% 16.7%
17.9% 18.7% 16.9% 18.9% 17.0%
17.2% 17.5% 17.3% 17.1% 17.8%
10.1% 9.8% 10.7% 9.9% 10.2%
10.1% 7.3% 8.6% 7.0% 8.4%
2.3% 2.1% 2.5% 2.0% 2.1%
19.6% 19.5% 19.1% 17.8% 18.3%
19.2% 18.4% 18.9% 17.9% 18.7%
7.3% 7.4% 8.0% 7.4% 8.5%
11.9% 13.5% 13.5% 13.7% 13.3%
28.7% 29.4% 28.1% 28.2% 27.9%
8.0% 7.1% 8.1% 9.5% 6.8%
2.9% 2.5% 2.0% 3.6% 4.5%
Ore SO
5.9% 6.4% 5.8% 5.2% 6.2%
11.4% 10.7% 10.9% 10.6% 10.7%
15.3% 17.5% 15.9% 16.2% 16.4%
19.9% 20.0% 19.9% 20.2% 19.1%
18.8% 18.6% 18.0% 20.4% 19.3%
15.1% 14.7% 15.4% 14.6% 15.1%
8.6% 7.4% 8.8% 7.9% 8.2%
5.1% 4.7% 5.3% 4.9% 5.0%
4.1% 3.7% 3.7% 3.3% 3.8%
11.0% 11.9% 12.3% 11.8% 11.5%
7.5% 6.5% 6.5% 5.9% 5.7%
7.1% 6.7% 7.9% 7.6% 8.1%
19.5% 20.6% 20.8% 20.2% 19.4%
21.5% 21.9% 22.9% 23.5% 20.5%
12.9% 12.9% 12.2% 13.8% 14.6%
16.3% 15.8% 13.6% 13.9% 16.5%
Baseline
Biodiesel
Decane
Naphtha
HWBE
SA^{3}BE
Extraction conditions

Figure 5.5 NA profiles of the background (PW) and select OSTW streams, qualified and quantified by LC-HRMS. Data were categorized in n- (carbon number, colored in gradient GREEN-YELLOW-RED of the left column) series or Z- (hydrogen deficiency, colored in gradient YELLOW-BROWN of the right column) series, and classified in extraction conditions.

Changes in the extraction conditions were found to induce minor alterations in the NA profiles (Figure 5.5 and Figure A.14). In specific, the *n*-series profiles appeared to have a consistent pattern among 6 sets of conditions (excluding Set **BD** and Set **EC**) for the same type of ore, while a low-*n* shift was observed in biodiesel-incorporated SA^3BE (Figure 5.5), indicated by the increases in $n \leq 16$ and decreases in $n \geq 19$ proportions of NA profiles (especially for Ore SM and SP). Such a low-*n* shift demonstrated SA^3BE to exhibit certain preference to release low-*n* NA homologues that were expected to be more susceptible to biodegradation. Caustic addition was noted to contribute to an increased proportion of high-*n* (n = 19–22) NA homologues, especially at pH = 10.5 (Figure A.14), while temperature appeared to make subtle difference to NA profiles.

Similarly, an examination of the *Z*-series profiles revealed no evident statistical difference among 6 sets of conditions (excluding Set **DE** and Set **EC**), suggesting that changes in the extraction conditions (solvent, caustic and temperature) within the experimental range provided minor selectivity in the release of NA homologues during oil sands processing. For decane-incorporated SA^3BE, a slight less-negative-*Z* ($Z \geq -6$) shift was observed (Figure 5.5), especially for Ore SM and SP. This finding suggested SA^3BE could preferentially extract ring-deficient NA homologues that were likely less resistant to biodegradation, compared to HWBE. For caustic-incorporated groups, a more obvious more-negative-*Z* shift were noted compared to other sets of the same ore (Figure A.14), suggesting that regardless of ore types, caustic addition not only contributed to more NA release (Figure 5.3), but also allowed a preferential release of low-*Z* NAs, compared to the rest groups over the same ore.

NA profiles provided a straightforward support that OSTW samples collected from SA^{3}BE revealed similar NA profiles with respect to HWBE, while slightly distinguished from the latter in preference to extract low-*n* and less-negative-*Z* NA homologues that are believed to be readily-biodegraded. Therefore, it can be deduced that the acute toxicity of OSTW samples contributed by NAs was reduced in SA^{3}BE compared to HWBE, in an extent approximately proportional to the relative reduction of the total NAs intensity, which was 13.9–60.1% as determined in the previous section.

5.5 Conclusions

This work represents the first comprehensive study of OSTW NAs derived from processing mineable oil sands in a novel extraction method (SA^{3}BE) with readily-biodegraded model solvent (biodiesel and decane). It demonstrates that compared to the industrial practice (HWBE), SA^{3}BE features a reduction in the reject of total NAs intensity by 13.9–60.1% in fresh OSTW, especially for the two poor-processing ores with the reduction as high as 42.4–60.1%. More importantly, such reduction is achieved before OSTW is sent to tailings pond, suggesting that this method can be probably integrated with other downstream NAs treatment methods (such as ozonation, constructed wetlands strategy, etc.) to accomplish further improvement for the NA treatment. Furthermore, NA profiles were found to have a comparable pattern under different extraction conditions, suggesting that the release of most intractable and toxic NA species can be correspondingly reduced along with the total NAs. In general, this study has provided a bench-scale proof-of-concept in supporting SA^{3}BE as a promising alternative to process mineable oil sands with less negative environmental impacts, especially in restrained release of toxic compounds and massively reduced GHG emissions.

Chapter 6 Contributions of This Study and Recommendations for Future Research

6.1 Contributions of This Study

Biodiesel-assisted ambient aqueous bitumen extraction (BA^{3}BE) technique was for the first time proposed and developed to separate hydrocarbon resources from oil-bearing minerals, i.e., mineable oil sands. BA^{3}BE technique uses a small quantity of biodiesel as a conditioner for feedstock pretreatment combined with a caustic-free water extraction processing, to achieve bitumen production from mineable oil sands at ambient temperature. Investigation of the sub-processes of oil sands processing revealed that the use of solvent in BA^{3}BE allows enhanced bitumen liberation from oil sands mineral surfaces into bulky aqueous, as well as improved bitumen aeration performance, giving an increased bitumen recovery. In addition, the incorporation of certain chemical aids with BA^{3}BE, including frother and polymer demulsifier, was found to further improve bitumen flotation, especially on foaming capacity, foaming stability and bitumen-air attachment, which provided a further boost to bitumen recovery and led to a cleaner bitumen product of less water content.

As supported by bench-scale experiments in this study, BA^{3}BE technique was capable of producing bitumen from real poor-processing Athabasca oil sand ores at ambient temperature. The bitumen recovery obtained in the novel BA^{3}BE was comparable to or better than the case of hot water bitumen extraction (HWBE), a technique widely employed in the industrial processing of mineable oil sands. It is notable that processing oil sands in BA^{3}BE required substantially reduced energy input for operation, as it was operated at a temperature much lower than the industrial practice (40-45°C), which is of vital significance in terms of energy consumption, cost management and greenhouse gas (GHG) emissions.

Improved tailings settling was also achieved using BA^3BE, indicating a faster water recycling and land reclamation, compared to HWBE. Beyond that, BA^3BE was also capable of reducing the release of toxic natural naphthenic acids (NA) from oil sands into tailings water, which was supported by a comprehensive quality and quantity evaluation of NA species in tailings streams obtained from extraction of 4 Athabasca oil sands. Experimental results revealed that no statistical difference was found among NA profiles of different extraction methods (room temperature benchmark, HWBE, BA^3BE, etc.), while BA^3BE gave substantial reduction in the concentration of total released NAs, suggesting its effectiveness in reducing toxicity of tailings water and negative environmental impacts.

6.2 Recommendations for Future Research

Future research should fill the following knowledge gaps:

- **Use alternative frother.** Methyl isobutyl carbinol (MIBC) was used as a processing aid for BA^3BE in Chapter 2. As a proof-of-concept, the results of using MIBC supported that using a frother can substantially improve the flotation efficiency and hence the bitumen recovery. However, MIBC can be lost due to high volatility and MIBC itself is not welcomed in industrial operations due to its unpleasant odor. Therefore, it is hypothesized that alternative frother, such as pine oil, is likely to serve as a promising processing aid for BA^3BE due to its low volatility and subtle odor.
- **Address biodiesel recovery concerns.** The current BA^3BE design uses biodiesel in its pure status for ore pretreatment, and hence it is important to recover biodiesel in the same purity for continuous oil sands operation. However, if either naphtha or paraffins, common solvents for froth treatment in current industry, is still used in BA^3BE, there may be concerns that a portion of biodiesel species with low boiling

point will be recovered together with the froth treatment solvent, making the separation of one from the other extremely difficult.

One possible solution is using biodiesel froth treatment for BA^{3}BE. Thus, biodiesel is used for both ore pretreatment and froth treatment, and it is hypothesized that the solvent recovered from diluted bitumen is high purity biodiesel, which is favored for continuous oil sands treatment.

Another possible solution is using certain biodiesel type whose boiling point range does not overlap with other solvent. In this case, the separation of biodiesel and froth treatment solvent is hypothesized to be operated conveniently. In addition, this method also applied to the probable use of pine oil, as it is easier to separate all of the three solvent streams if all their boiling points are essentially different.

- **Use MIBC and EO-PO for naphtha-based hybrid extraction of mineable oil sands.** Chapter 4 revealed that using frother and demulsifier greatly improve the performance of BA^{3}BE, especially in terms of improved flotation efficiency, enhanced bitumen recovery, and restrained generation of water emulsions. It is hypothesized that an equivalent improvement can also be observed when these two chemical aids are used in the naphtha-based hybrid extraction. Current study on naphtha-based hybrid extraction is limited by low bitumen recovery, which is probably improved by the incorporation of frother and demulsifier.
- **Economic viability studies and life cycle analysis.** This thesis focuses mainly on developing and optimizing hybrid extraction for mineable oil sands. To obtain a comprehensive evaluation for its commercialization, the economic viability, impact of downstream processes, and life cycle analysis should be further studied, such as the determination of CAPEX, OPEX, and energy intensity.

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Appendix I: Summary of typical solvent extraction (SE) techniques for mineable oil sands processing in the last decade (2009-2019)

Solvent type*	Operating temperatures	Solvent dosage (S/O or S/B**)	Bitumen recovery	Solid/liquid separation	Main features	Reference
• D-limonene, soy methyl esters, and glycol ether esters	10°C	Unspecified	85-97% (expected)	Centrifugation	• Specified solvents are injected into an oil well to enhance recovery of bitumen or crude. BioSpan materials are investigated for their performance in bitumen viscosity reduction.	(Chesky 2016)
• Synthetic turpentine • Terpineol blends (α-, β- and γ-terpineol)	About 96°C	S/O = 1, 2 (w/w)	~100% by synthetic turpentine at S/O = 2	Filtration	• Filtration for slurry treatment. Cake washed with ethanol for removal of residual solvent. • Extra energy intensity rises from use and recovery of ethanol.	(Fan, Shafie *et al.* 2015)
• Primary solvent: Solvesso 150 • Secondary solvent: methanol.	25°C	S/O = 0.165-0.316 (w/w), for primary solvent. S/O = 0.1-0.162 (w/w), for secondary solvent.	99%	Pressure filtration	• A first solvent and a second solvent are used for solvent extraction and recovery of first solvent from tailings purpose, respectively. • Methanol recovery can reach up to 94%.	(Duyvesteyn 2014, Duyvesteyn, Joshi *et al.* 2014, Duyvesteyn, Kift *et al.* 2014, Kift, Joshi *et al.* 2015)
• Butane, pentane, hexane, heptane or other aliphatic solvents	0-40°C	S/B = 0.7-1.1 (w/w)	> 90% (theoretical value)	Filtration	• Separate oil sands using solvent into a solid-depleted stream and a solid-enriched stream. The solid-depleted stream is further treated with fresh solvent to obtain a second solid-depleted stream. All solid-enriched streams undergo filtration to recovery residual bitumen. • Bitumen is considered exempt from solids.	(Ploemen, Colenbrander *et al.* 2014)

• Dimethyl sulfide and other organic solvent	10-30°C	Unspecified	> 94%	Filtration, vacuum evaporation	• Oil sands ores soaked with solvent are drained on a porous support followed by thermal/vacuum drying. • Dimethyl sulfide can greatly reduce the viscosity of bitumen during slurry preparation.	(Milam, Tegelaar *et al.* 2014)
• Aliphatic solvent (such as propane, butane, pentane, hexane and heptane)	0-25°C	Unspecified	Unspecified	Unspecified	• Hot water is used for displacing and vaporizing solvent in a sealed vessel while the gangue is removed by a conveyor underwater.	(House, Kift *et al.* 2014)
• Cyclohexane	24 ± 0.5°C	S/O = 1.67 (w/w), for the entire process	Unspecified	Settling	• An optimum water content has been found for oil sands extraction using cyclohexane: inadequate water leads to migration of fines into product bitumen, while excessive water forms emulsion and carries fines to product bitumen. • Incomplete coverage of the organic existed on the surface of fines/clays.	(Nikakhtari, Wolf *et al.* 2014)
• Mixtures of toluene, heptane and hexane.	Unspecified	Unspecified	95-98% (expected)	Filtration	• Filtration cakes are prepared for enhanced extraction performance and easy removal of tailings.	(Peuker 2014)
• Mixture of aromatic solvent (such as Solvesso 100/150 or a light end of bitumen) and paraffinic solvent (such as pentane)	Unspecified	Unspecified	Unspecified	Filtration, decantation	• Oil sands mixed with aromatic solvent to produce a first stream of bitumen, followed by addition of paraffinic solvent to produce a second stream of bitumen. Asphaltene precipitation is prevented during the first stage of separation.	(Kift and Joshi 2013)
• Toluene, cyclohexane, diesel oil, gasoline	80°C	Unspecified	93.50%	Centrifugation	• Performance evaluation of single- and multi-stage counter-current extraction on Xinjiang oil sands. Results show oil sands particles should have a dimension of < 450 micrometer to increase recovery	(Yu, Wang *et al.* 2013)

• Light aliphatic solvents (hexane, toluene, xylene, naphtha, etc.)	50, 62, 80°C	S/O = 2 (w/w)	> 90%	Settling, centrifugation	• Oil sands slurry prepared with solvent is reshaped by agglomerator into agglomerates, which are further removed by a classifier. The leftover is treated under elevated temperature and/or pressure to generate bitumen, asphaltenes and fines.	(Filby, Aviezer *et al.* 2013)
• Mixture of polar and non-polar solvent. Such as acetone and pentane (v/v, 3:7) blend	21-22°C	S/O = ~1 ml g^{-1}	86%	Settling	• Mixture of polar and non-polar solvent shows a superb solvent power that allows faster penetration of solvent into oil sands matrix than that using individual solvent. The new solvent blend achieves a bitumen recovery equivalent to that of toluene and xylene.	(Chakrabarty 2010)
• Mixture of carbon disulfide, paraffin wax and naphthalene	20°C	Unspecified	Unspecified	Unspecified	• Oil sands is treated with a countercurrent flow of solvent mixture. The extracted bitumen is further upgraded in a hydrotreater. • Carbon disulfide (B.P. = 46.3°C) is recovered at relatively low temperature.	(Stauffer 2013)
• N-pentane, cyclopentane, hexanes, toluene	25°C	S/B = 1-6 (w/w)	90% from high grade ore at S/B = 6; 70% from low grade ore at S/B = 4	Pressure/centrifuge filtration, vacuum evaporation.	• Extraction carried out by multistage washing using different solvents. Specially-designed pressure vessel is occupied to allow centrifugation and vacuum filtration. • Solvent residue in tailings (filtration cake) was considered to be reduced to the requirement (4 bbl loss per 1000 bbl bitumen) after applying vacuum evaporation.	(Wu and Dabros 2012)
• Turpentine mixture containing different content of terpineols	96°C	33-100%	S/O = 2 (w/w)	Filtration	• Oil sands mixed with turpentine mixtures for slurry preparation followed by filtration. Liquid effluent is collected as product, and filter cake is further washed with ethanol for drying purpose.	(Fan, Shafie *et al.* 2013)
• Mixture of 65-90% hydrophobic solvent and balanced hydrophilic solvent	~60°C	Unspecified	Unspecified	Settling	• High speed flow of solvent mixture is used to fluidize oil sands for enhanced separation of bitumen. • After separation of bitumen-abundant stream from slurry, bitumen-free stream is dried by elevating the temperature to up to >100°C.	(Podlipskiy 2013)

• Pentane	25°C	S/B = 1.6-2.5 (w/w)	Unspecified	Filtration, gas stripping	• Separate oil sands using solvent into a solid-depleted stream and a solid-enriched stream. Bitumen derived from eluent of solid-enriched stream contains > 40 wt% asphaltenes. • Purge gas is used to reduce tailings solvent retainment.	(Lankshear 2013)
• Mixture of 60-80 wt% heptane, 2.5-3.5 wt% toluene and 24-32 wt% diethyl ether	60-93°C	Unspecified	Unspecified	Unspecified	• The methodology is designed for in-situ oil sands processing but could be also applied for mineable oil sans as claimed. • Solvent mixture is injected into oil sands reservoir to reduce viscosity and density of heavy oil for enhance recovery. As claimed, the specified solvent mixture appeared to have better diluting effect on bitumen than conventional diluents, such as natural gas condensates, diesel and naphtha.	(Thompson and Grace 2013)
• Toluene • Cyclohexane • Methyl cyclohexane • Ethylbenzene • Xylenes • Isoprene • Limonene • N-heptane and toluene (w/w, from 3:7 to 9:1) blends	24°C	S/O = 1, 1.67 (w/w), for the entire multistage process	91.4% by isoprene; 53.0% by limonene; > 95% by other solvents	Filtration	• Extraction carried out by different solvents in a multistage process including rotary mixers and vibration sieving. • Fines content was less than 2.9 wt% of extracted bitumen, except for n-heptane-rich group. • It was claimed that cyclohexane was the best among all candidates, as it makes a compromise among satisfactory recovery (94.4%), low tailings solvent content (5 mg solvent residue / 1 kg tailings) and clean bitumen product (1.4 wt% fines in bitumen).	(Nikakhtari, Vagi *et al.* 2013)
• Primary solvent: aliphatic solvents • Secondary solvent: hydrocarbon solvents (preferably 3-9 carbon atoms)	5°C	S/B = 1.5-2.1 (w/w)	Unspecified	Settling, Pressure filtration	• Separate oil sands using mixed solvent into a solid-depleted stream and a solid-enriched stream. The solid-enriched stream is further treated with fresh solvent to obtain a second solid-enriched stream, which is filtered to remove solids. All liquid streams are collected as product.	(Ploemen, Ringstrom *et al.* 2013)

• N-pentane	5-25°C	S/B = 1.2-4.1 (w/w)	92%	Filtration, gas stripping	• Separate oil slurry into a first and second bitumen-enriched stream and a bitumen-depleted stream. The solvent used for first separation is separated from the second solvent. • Purge nitrogen is used for recovery of tailings solvent.	(Ploemen, Maria *et al.* 2013)
• Propane	36.7°C	S/O = 0.5-2 (w/w)	86-100% from low grade ore (9% bitumen) 90-100% from high grade ore (13.7% bitumen)	Vacuum evaporation to remove propane from gangue	• Pressurized propane (11.4 atm) is evenly distributed to oil sands. Solvent with bitumen could be expelled out from oil sands matrix by adjusting the globule sizes of solvent and oil sands sizes.	(Phillips 2013)
• Terpene, limonene, liquid carbon dioxide	< 27°C	S/O = 0.1-10 (w/w)	Unspecified	Gas stripping	• Oil sands ores are pre-dried using heated air followed by mixing with non-aqueous extractant. The liquid-soaked solids are treated with gas stripping to produce dry tailings	(Bohnert and Verhulst 2013)
• Aromatic solvent (with B.P. lower than 400°C)	30-75°C	S/B = 0.5-4 (v/v)	Unspecified	Pressure filtration	• Solvent flows through an oil sands layer packed in a sealed vertical column. Water and gas are used to remove the solvent afterwards.	(Joshi, Kift *et al.* 2013)
• Dimethyl sulfoxide, glycol ethers	80°C	S/O = 1 (w/w)	70.4-100%	Filtration, vacuum evaporation.	• Oil sands are mixed with specified solvent to release bitumen at elevated temperature. 100% recovery was observed for group using DMSO at S/O = 1 (w/w) at conditioning temperature of 80°C and conditioning time of 15 min.	(Fan and Shafie 2013)

• N-pentane and other aliphatic hydrocarbon solvents (3-9 carbon atoms)	35-120°C	S/B = 1.2-5 (w/w)	Unspecified	Filtration, gas stripping	• Oil sands slurry prepared with solvent is loaded to form packed bed for drainage with pressurized filtration. The pressure above the filter cake is > 1.7 atm, while the pressure below is < 1.2 bar. • Purge gas could be used to dry tailings	(Ploemen, Schoonebeek *et al.* 2013)
• Pentane	25°C	S/B = 1.5-2.5 (v/v)	90-99 % (anticipated)	Pressure filtration	• Multi-stage solvent washing is applied to oil sands layer packed in a confined pressure column to create a bitumen-enriched solvent. • Water is used to wash the gangue for solvent recovery.	(Kift, Hoffman *et al.* 2013)
• Heptane and toluene (w/w, 3:7, 7:3, 9:1 and 10:0) blends	25°C	S/O = 1 (w/w), for the entire process	85-90% from medium grade ore; 80-85% from high grade ore	Settling	• Increasing heptane-to-toluene ratio made a negligible and a slightly negative effect on bitumen recovery, from high grade and medium grade ore, respectively. • Product extracted by pure heptane contained higher fine solid content. • A transition layer, considered to be mainly composed of asphaltenes and fine solids, was formed between supernatant diluted bitumen and tailings sludge after settling, especially when heptane-rich solvent was used for extraction.	(Hooshiar, Uhlik *et al.* 2012)
• Hydrocarbon solvent	10-40°C	S/B = 0.5-3 (v/v)	Unspecified	Unspecified	• Oil sands undergo continuous crushing and mixing with solvent to form a solvent-wet crushed bituminous material, from which bitumen can be separated.	(Kift and Joshi 2012)
• Heavy solvent (C10-C20) and light solvent (C5-C7)	50°C	S/B = 1-1.5 (w/w)	96.40%	Vacuum filtration, inert gas stripping	• Dense oil sands slurry is prepared by mixing heavy solvent and oil sands, followed by addition of light solvent before further solid-liquid separation.	(Wu, Jones *et al.* 2012)
• Cyclohexane, may be partially loaded with bitumen.	22°C	S/O = 0.672 (w/w), water added at 4.8 wt% on basis of oil sands	Unspecified	Settling	• (Expected) use of pipeline agglomerator allowed improved operation safety, improved mixing of water and extraction liquid and flexibility to have long residence time.	(Adeyinka, Alvarez *et al.* 2012)
• Carbon disulfide	20°C	Unspecified	Unspecified	Unspecified	• Carbon disulfide is injected in countercurrent to oil sands flow. • The retail price of carbon disulfide is high.	(Stauffer 2012)

- Primary solvent: aromatic solvent. - Secondary solvent: volatile hydrocarbon.	20°C	S/B = 1.75, for first solvent. S/B = 0.79, for second solvent.	99%	Pressure filtration, heat stripping	- First solvent (aromatic) is used to extract bitumen, followed by use of a second solvent (volatile) to recover the remaining first solvent in the tailings.	(Duyvesteyn and Kift 2012)
- Solvent mixture with special requirement for Hansen solubility parameters	> 35°C	S/O = 1 (w/w)	80%	Filtration	- Hydrocarbon mixtures with desired Hansen solubility parameters and low boiling points allow production of high-quality bitumen.	(Diefenthal, Jordan *et al.* 2012)
- N-heptane and toluene (v/v, 3:1) blend	25, 40, 55°C	S/O = 2-15 (ml /g)	Unspecified	Centrifugation	- Importance of operating factors: solvent dosage > agitation rate > contact time > temperature. - Recovery of asphaltenes was more sensitive to temperature and contact time than other fractions. - 3-7 wt% bitumen particles, mostly composed of asphaltenes, coexisted with clay after extraction.	(Li, He *et al.* 2012)
- Turpentine, α-terpineol	96°C	S/O = 1, 2 (w/w)	~100% at S/O = 2 ~70% at S/O = 1	Filtration	- Acceptable recovery could only be achieved at a high temperature of 96°C. At 15°C and S/O =0.5, only up to 4.5% of bitumen was recovered at best solvent choice.	(Fan and Shafie 2012)
- Disbit (Aromatic 150 loaded with 30 wt% bitumen)	Unspecified	S/B = 2.25 (w/w)	94.10%	Settling, cyclone	- Countercurrent cyclone array apparatus occupied for higher recovery.	(Kift, Joshi *et al.* 2012)
- Primary solvent (light aromatic solvent): Solvesso 150, naphtha - Secondary solvent: methanol, pressurized propane, heptane	25°C	S/B = 2 (v/v), for primary solvent. S/B = 1.5, 2 (v/v), for secondary solvent.	80-90%	Settling and pressure filtration, inert gas stripping.	- Primary solvent was used to extract bitumen. Secondary solvent was used for recovery of the remaining first solvent from tailings. The second solvent left in tailings could be recovered by an optional third solvent. Liquid stream is expelled from tailings with nitrogen purge at 3 bars. - High energy intensity of solid/liquid separation treatment.	(Duyvesteyn and Kift 2010, Duyvesteyn and Kift 2011)

• Primary solvent: light aromatic solvent • Secondary solvent: volatile hydrocarbons	10-60°C	Unspecified	Unspecified	Filtration, thermal stripping	• Oil sands are mixed with light aromatic solvent for slurry preparation, followed with filtration to produce bitumen-enriched stream and bitumen-depleted stream. The latter stream is further mixed with volatile hydrocarbons for higher bitumen recovery.	(Duyvesteyn, Morley *et al.* 2010, Duyvesteyn, Morley *et al.* 2011)
• Mixture of tetrahydrofuran and ethyl alcohol (1:0-1:0.2, v/v)	Unspecified	Unspecified	Unspecified	Unspecified	• Oil sands carried against steam of solvent to produce diluted liquid bitumen. The drained bitumen-enriched solvent is sent back to evaporator for recycle.	(Wei, Xie *et al.* 2011)
• Primary solvent: C6-C7 (cyclo)alkanes • Secondary solvent: pentane, heptane, cyclohexane blend or blend of above	30°C	S/O = 0.6 (w/w), for primary solvent. Unspecified for secondary solvent.	Unspecified	Settling	• The addition of a first solvent and a second solvent is for sand/clay agglomeration and deasphaltening purpose, respectively. • Producing two product streams: partially-deasphalted oil and solid-rich asphaltene stream. • Oil stream meets refinery requirement (solid < 400 ppm, water < 200 ppm).	(Adeyinka, Speirs *et al.* 2011, Adeyinka, Speirs *et al.* 2011)
• Aromatic solvent (such as Aromatic 150) and polar solvent (such as methanol)	30-40°C	S/B = 3.3 (w/w), for combined primary and secondary solvent	86.8-98 %	Settling, pressure filtration	• Oil sands are treated with aromatic solvent to produce diluted bitumen and primary tailings. The primary tailings are mixed with polar solvent to recover bitumen. • Extraction is tested in various types of apparatuses, including sealed vessel and vertical column. • The remaining solvent in final tailings is recovered by water.	(Duyvesteyn, Joshi *et al.* 2011)
• Propane or butane	50°C	Unspecified	Unspecified	Pressure filtration	• Studies on the effect of temperature and pressure on extraction of oil sands. Extraction operated at ~15 atm to keep light paraffinic solvent as liquid. Using butane as solvent at lower temperature appeared to be most effective.	(Pathak, Babadagli *et al.* 2011)
• Mixture of 65-95% cyclohexane and balanced ethanol	25°C	S/O = 26 (w/w)	46.8-99.3%, controlled by solvent blend ratio	Centrifugation, filtration	• An azeotropic mixture of cyclohexane and ethanol is used for oil sands slurry preparation. Centrifugation is occupied for enhanced solid-liquid separation.	(O'Neil and Osaheni 2011)

• D-limonene	Unspecified	Unspecified	Unspecified	Unspecified	• Vortex provided by eddy pump is considered to significantly improve the bitumen liberation from oil sands with terpene solvents. High pressure is employed for slurry preparation. • The use of environmentally friendly solvent.	(Rapp 2010)
• Hexane, kerosene	121°C	S/B = 6 (v/v)	Unspecified	Filtration	• Oil sands are treated with solvent for bitumen recovery. Water is used for gangue cooling and solvent recovery.	(Hastings 2010)

* Researches or patents lacking of processing details or experimental data is not involved here.

** S/O, S/B: ratio of solvent over oil sands, and ratio of solvent over bitumen.

Appendix II: Summary of typical hybrid extraction (HE) techniques for mineable oil sands processing in the last decade (2009-2019)

Solvent type*	**Operating temperatures**	**Solvent dosage (S/O, S/B or W/B**)**	**Bitumen recovery**	**Solid/liquid separation**	**Main features**	**Reference**
• Biodiesel	25°C	S/O < 0.02 (w/w)	75-90 %	Settling	• Room temperature processing. • Biodegradable solvent use at low dosage. • Recovery subtly dependent on ore types.	(Zhu, Yan *et al.* 2018)
• N-pentane	25°C	S/O = 0.672 (w/w), for the entire process, W/O unspecified	> 99 %	Pressure filtration	• Enhanced bitumen recovery and reduced solvent dosage by using counter-current continuous wash/extraction. Decantation of supernatant of solvent sludge promotes filtration performance. • Tailings solvent removal by water washing.	(Ploemen, Schoonebeek *et al.* 2014, Kift, Hoffman *et al.* 2015)
• D-limonene, terpene.	50-70°C	W/B = ~30-90 (w/w) and S/B = 0.6-1.8 (w/w)	73-98 %	Settling, filtration	• D-limonene and steam are directly injected into ore to produce slurry. Coarse tailings are treated with filtration to remove water. The fines contained are further cleared in a polishing step.	(Ophus 2013)
• Mixture of citrus terpene, non-ionic liquid surfactant, acetone and/or isopropyl alcohol	25°C	Unspecified	Unspecified	Filtration, gas/thermal stripping	• Oil sands mixed with specified solvent mixture to extract bitumen at ambient temperature.	(Bauer and Calvert 2013)
• Kerosene	25°C	S/B = 0.05-0.15 (w/w)	Up to 92 %	Settling	• High bitumen recovery could be achieved at low solvent dosage (S/B up to 0.15). Kerosene was found to facilitate bitumen liberation and aeration during extraction.	(Harjai, Flury *et al.* 2012)
• Blend of pentane and hexane	10, 15°C	W/O = 0.5 (w/w) and common S/B = 2.2 (w/w)	89.3 %	Settling	• Oil sands pre-mixed with water were found to allow best extraction performance with solvent at low temperature.	(Wolff 2011)

* Researches or patents lacking of processing details or experimental data is not involved here.

** S/O, S/B, W/B: ratio of solvent over oil sands, ratio of solvent over bitumen, and ratio of water over bitumen, respectively.

Appendix III: Other techniques for mineable oil sands processing

Other techniques under active study for mineable oil sands processing include 1) ionic liquid assisted extraction (ILAE), 2) switchable-hydrophilicity solvent-based extraction (SHSE), 3) supercritical fluid extraction (SFE), 4) pyrolytic process (PP), 5) cryogenic processing (CP), and 6) microbial-enhanced oil recovery (MOR), which are briefly introduced in the following subsections.

A-III.1 Ionic liquid assisted extraction (ILE)

Ionic liquid assisted extraction (ILE) refers to the method that ionic liquids (such as *trihexyl (tetradecyl) phosphonium chloride* (Lago, Francisco *et al.* 2013)) are used for enhanced bitumen extraction from oil sands. Methods employing the use of analogue ionic liquids, such as deep eutectic solvents (Pulati, Lupinsky *et al.* 2015), can also be classified in this category due to similar mechanisms. A more general definition of ionic liquids (ILs) is a group of materials composed of organic cations and anions, with melting temperature below 100°C, while in technical development of ILE for oil sands processing, the ILs engaged typically stay as liquid at much lower operation temperatures (such as room temperature). Currently, ILs are becoming attractive for several industrial processes (Plechkova and Seddon 2008), due to excellent chemical and thermal stability, high non-flammability, and extremely low vapor pressure (Welton 1999). Recent studies focused on ILs' good performance on bitumen and heavy oil production from unconventional oil resources (Williams, Lupinsky *et al.* 2010, Li, Sun *et al.* 2011, Lago, Francisco *et al.* 2013, Sakthivel, Velusamy *et al.* 2014, Pulati, Lupinsky *et al.* 2015).

ILs are almost immiscible with bitumen, and the way they take effect in bitumen extraction from oil sands is drastically different from that of typical nonaqueous solvents described previously (Painter, Williams *et al.* 2009). Theoretically, the effect of ILs on bitumen extraction was believed to be attributed to the strong electrostatic interactions between ILs and sand/clay surfaces, which reduces the adhesive interaction between bitumen and sand by around one order of magnitude (Hogshead, Manias *et al.* 2010). For example, the use of a typical IL, $[Bmmim][BF_4]$, allowed an improved bitumen recovery of 95% with toluene as diluent. With the assistance of IL, the bitumen liberation was observed to undergo more completely, leading to the reject of clean solids and fines that are exempt from bitumen (Li, Sun *et al.* 2011). Another solvent, called basic solvent, can be added together with ILs for oil sands conditioning, to dilute bitumen for good processability. In addition, with assistance of microwave heating, using ILs that own surface-active characteristics has shown potential to demulsify the W/O emulsions that are present in diluted bitumen, which is preferable for bitumen upgrading or refining (Lago, Francisco *et al.* 2013).

A typical bench-scale ILE process is illustrated in Figure A.1 (Painter, Williams *et al.* 2009). The ILs are added to crushed oil sands for pretreatment. Generally, certain amount of organic solvents is also added to merge bitumen droplets for dilution purpose, while proper agitation is deployed to facilitate bitumen liberation from solids and clays. The heterogeneous slurry formed gradually separates into two distinct phases: 1) diluted bitumen phase atop, which contains little clays and fine minerals as examined by infrared spectra (Li, Sun *et al.* 2011, Pulati, Lupinsky *et al.* 2015) and is supposed to be ready for downstream processes, and 2) heterogeneous IL-solids mixture, which can be further separated into IL phase and IL-rich sediment via centrifugation and/or filtration (Painter, Williams *et al.* 2009, Williams, Lupinsky *et al.* 2010, Li, Sun *et al.* 2011, Pulati, Lupinsky *et al.* 2015).

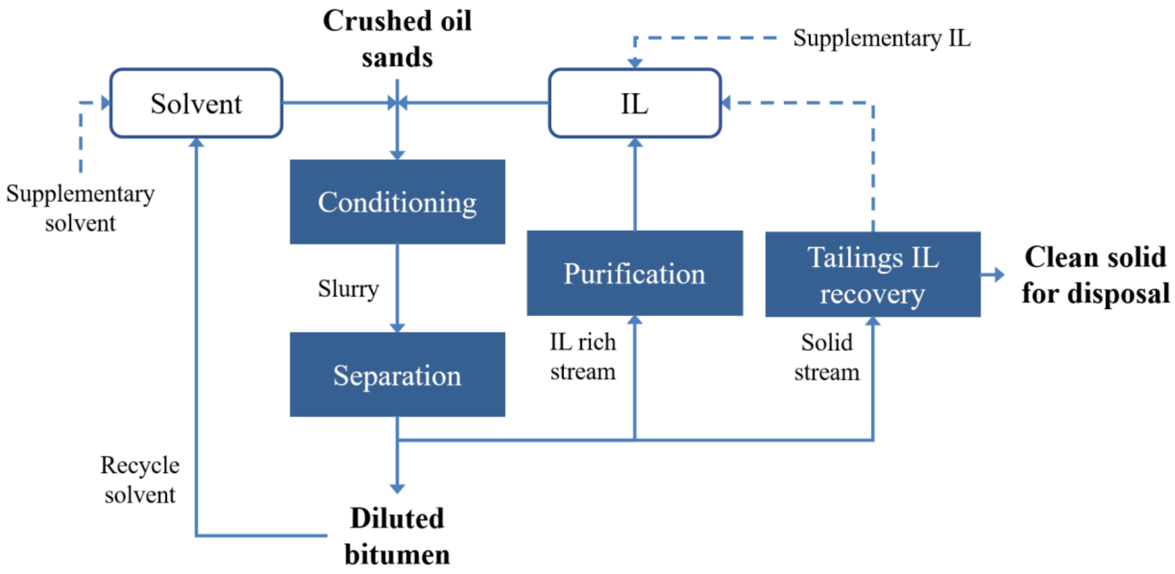


Figure A.1 Schematic of a bench-scale ILE process (modified from (Painter, Williams *et al.* 2009)). Dashed lines specify minor flows.

The IL phase can be recycled and reused after removal of clays and fines, while some experiments suggested that the direct reuse of the IL rich phase without purification also allowed a stable bitumen recovery efficiency for up to 5-10 consecutive cycles (Painter, Williams *et al.* 2009, Li, Sun *et al.* 2011). However, the sediment traps a small portion of IL which must be reclaimed. In preliminary demonstrations, such process was accomplished by washing the sediment with a certain portion of water and then the dissolved IL was recovered from the aqueous effluent by distillation (Painter, Williams *et al.* 2009, Painter, Williams *et al.* 2010, Li, Sun *et al.* 2011, Pulati, Lupinsky *et al.* 2015).

A-III.2 Switchable-hydrophilicity-solvent-based extraction (SHSE)

Switchable solvent based extraction process refers to an innovative extraction approach in which the extraction medium is a unique solvent whose certain properties (for example, polarity, ionic strength, hydrophilicity and viscosity (Jessop, Mercer *et al.* 2012)) can be reversibly switched between two or more distinct forms by a simple change in the system. In general, most industrial chemical engineering processes involve multiple steps, and the solvent used in previous step may not be the most suitable for the next step, which brings about a series of energy-intensive processes, especially the removal of previous solvent. Therefore, switchable solvent has apparent advantages over traditional solvents as the former can be switched to serve multiple purposes; the properties of switchable solvent can be tuned as expected to meet the requirement for each industrial step. Switchable hydrophilicity solvent (SHS) is a group of switchable solvents that their hydrophilicity can be substantially changed and reversibly triggered by certain stimuli. One of the examples is CO_2-triggered SHSs, on which Jessop (Jessop, Heldebrant *et al.* 2005, Jessop, Phan *et al.* 2010, Jessop, Kozycz *et al.* 2011, Jessop, Mercer *et al.* 2012, Jessop, Phan *et al.* 2013, Vanderveen, Durelle *et al.* 2014) did quite a number of fundamental works in the last decade. Briefly speaking, the nature of CO_2-triggered SHSs is that, a series of chemicals selected from amide, diamine, imide, guanidine(Jessop, Mercer *et al.* 2012) that are normally in low hydrophilicity and polarity form can be switched to high hydrophilicity and polarity form in the presence of CO_2, and such transformation can be mostly reversed once CO_2 is removed, as shown in Figure A.2 (Jessop, Mercer *et al.* 2012).

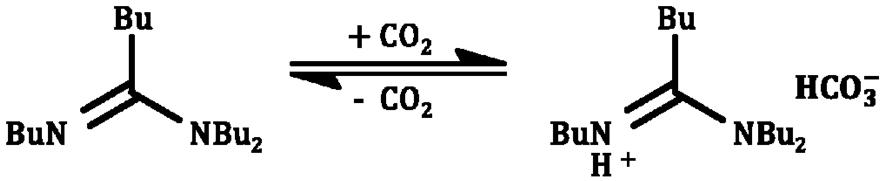


Figure A.2 A switchable hydrophilicity solvent (N,N,N'-tributylpentanamidine) switches between its forms of (left) low hydrophilicity and (right) high hydrophilicity, triggered by the presence/removal of CO_2, Modified from Jessop's work (Jessop, Mercer *et al.* 2012).

Such features make SHSs useful in extraction and separation of hydrophobic materials, including soybean oil (Phan, Brown *et al.* 2009), algae oil (Samorì, Torri *et al.* 2010) and phenols (Fu, Farag *et al.* 2014) from soybean flakes, alga and lignin bio-oil, respectively. For example, oil entrapped in solids can be solubilized by and merged in *cyclohexyldimethylamine* ($CyNMe_2$) (Holland, Wechsler *et al.* 2012), a typical SHS. After solids are deprived of oil and removed from the system, the oil rich SHS can be treated with wash water and CO_2, which increases the hydrophilicity of $CyNMe_2$ and makes it transferred to aqueous phase, leaving pure oil phase separated atop to be collected. For reclamation of $CyNMe_2$, inert gases (for example, N_2) were bubbled into aqueous effluent to remove CO_2, allowing $CyNMe_2$ to regain its hydrophobicity and be separated from water. The recycled SHS and water can be used for the next extraction processes.

Jessop proposed a possible SHS-based extraction strategy specifically for oil sands processing, as illustrated in Figure A.3. In his design, SHS is supposed to act as good nonaqueous solvent to facilitate extraction of bitumen from solid matrix. This is similar to the effect of solvent in SE, while the difference relies on the separation and recovery of SHS. By treating with injected water (contains CO_2), SHS is hydrophilicized and anticipated to be readily separated from diluted bitumen. The regeneration of low-hydrophilicity SHS and processing water can be achieved by removing CO_2 from the system.

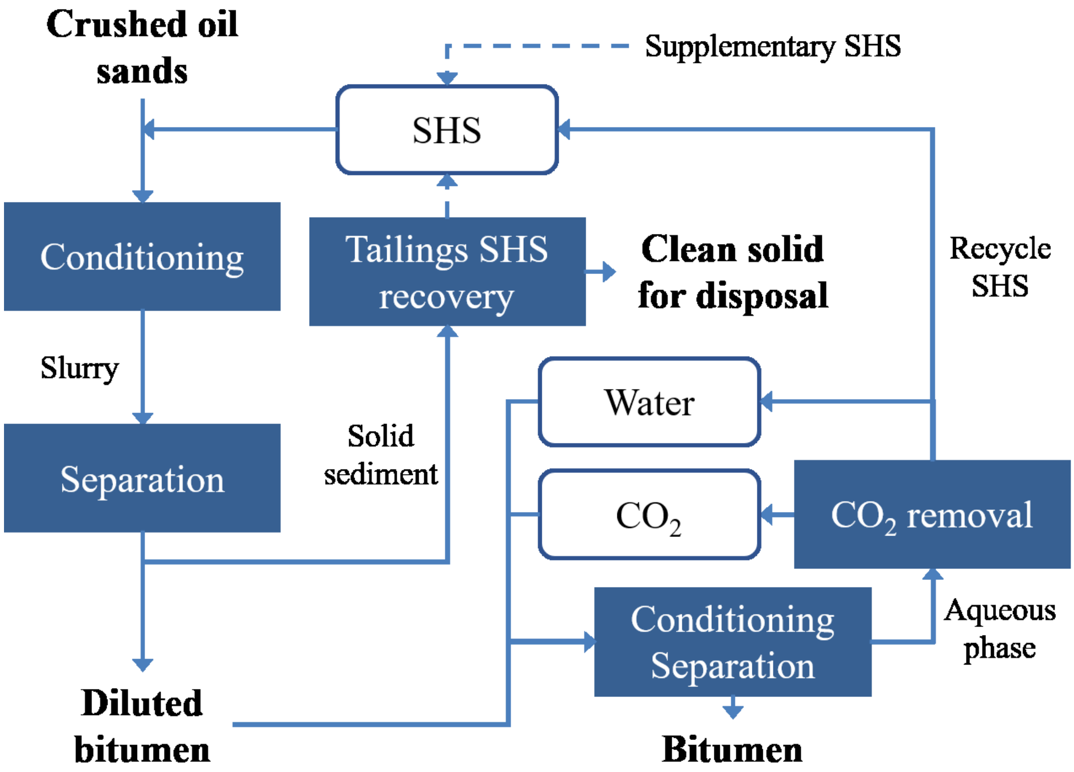


Figure A.3 The schematic of a SHS-based process, obtained from the work of (Holland, Wechsler *et al.* 2012). Dashed lines specify minor flows.

A-III.3 Supercritical fluid extraction (SFE)

Supercritical fluid extraction (SFE) refers to a process where supercritical fluid is used as extraction medium for bitumen recovery purpose from oil sands. When a chemical element or compound is above the *critical parameters* (that is, *critical temperature* T_c and *critical pressure* P_c), it transforms into supercritical fluid (sc-fluid) and gains a series of interesting properties (Kiran, Debenedetti *et al.* 2012), including increased diffusivity, substantially reduced surface tension and significantly decreased viscosity. Typically, when contact with porous or stacked solids, sc-fluid not only diffuses into solid matrix, solubilizes and extract target product more rapidly, but may also penetrates into tiny pores of the matrix that are typically considered non-accessible (Kiran, Debenedetti *et al.* 2012), both of which are of special interests in extraction processes.

SFE has been proposed for the extraction of bitumen from bituminous deposits since 1970s (Williams and Martin 1978). Many factors have been found to affect the extraction performance of bitumen from oil sands; while, temperature, pressure and type of fluid are among the most important. Typically, extraction using sc-fluid at higher pressure and lower temperature tends to result in higher bitumen recovery (Subramanian and Hanson 1998). As for fluid type, a series of fluids have been proposed for SFE based extraction of bitumen from oil sands, including CO_2 (Schucker 1995, Brough, Riley *et al.* 2010, Bohnert and Verhulst 2013), N_2 (Poska 1982), water (Paspek 1985, Berkowitz and Calderon 1990, Meng, Hu *et al.* 2006), hydrocarbons (Poska 1982, Scinta and Hart 1983, Subramanian and Hanson 1998, Rose, Monnery *et al.* 2001) or mixtures, among which supercritical CO_2 ($scCO_2$) is the most widely and commonly investigated (Rudzinski and Aminabhavi 2000) for its low price and low toxicity. In general, $scCO_2$ and supercritical aliphatic hydrocarbons tend to extract maltenes and reject the majority of the asphaltenes out of bitumen (Gupta and Shim 2006). More asphaltenes can be extracted when aromatic solvents are added to the extraction medium. For example, Subramanian showed that the extracted bitumen from Utah oil sands using sc-propane was deprived of asphaltenes (Subramanian and Hanson 1998), while McGrady reported the co-extraction of certain asphaltenes with maltenes when toluene was incorporated as conditioner to the extraction medium (Brough, Riley *et al.* 2010).

Proper bitumen upgrading has been found viable during SFE process of oil sands (Scinta and Hart 1983, Paspek 1985, Hong and Duyvesteyn 2011, McGrady, Brough *et al.* 2014). It is interesting that the critical parameters of many fluids are comparable to those that are required by bitumen upgrading/refining (Kiran, Debenedetti *et al.* 2012). Moreover, the strong permeability, rapid diffusion and enhanced solid-fluid contact provided by sc-fluid greatly benefit upgrading processes, such as cracking (Hong and Duyvesteyn 2011, Morimoto, Sugimoto *et al.* 2014) and catalytic hydroprocessing of bitumen (Scinta and Hart 1983, Piskorz, Radlein *et al.* 1996, Brough, Riley *et al.* 2010, McGrady, Brough *et al.* 2014) in the presence of hydrogen donors. More specifically, the behavior of sc-fluid based bitumen upgrading process is to some extent similar to that of liquid-phase cracking in delayed coker that allows higher yield of high-value liquid hydrocarbons and lower yield of low-value light petroleum ends, due to enhanced hydrogen abstraction and suppressed β-scission reactions (Gray 2010). A number of studies on extracting crude oil and bitumen products using supercritical fluid technology has been reviewed by Rudzinski *et al.* (Rudzinski and Aminabhavi 2000).

Though SFE allows enhanced conditioning of oil sands slurry for rapid mass and heat transfer, it is currently far from industrialization, primarily due to limited bitumen recovery it allows, high CAPEX and high OPEX. In specific, early SFE trials for oil sands processing generally gave limited bitumen recovery, which is commonly believed as a result of using solvent of low solubility parameters as processing medium. For instance, Subramanian, *et al.* (Subramanian and Hanson 1998) used supercritical propane as medium to process Utah oil sands. The result showed a complete recovery of maltenes that made up ~45 wt% of the whole bitumen, while the majority of asphaltenes were left in residual solids. As for processing cost, by comparing the T_c and P_c of liquids studied for SFE process of oil sands, it is clear that the commercialization of SFE technique for large-scale extraction operation requires massive investment on constructing and maintaining large-scale high-pressure apparatuses and high cost for supercritical fluid processing, which call for ultra-high CAPEX and high OPEX. Considering the fact that the warm water (40-45ºC) based extraction process in current mineable oil sands industry, only when the high cost for SFE process can be reimbursed by the benefits it brings, can SFE techniques become a viable choice for mineable oil sands industry.

A-III.4 Pyrolytic process (PP)

Pyrolytic process (PP), or pyrolysis, is a thermochemical process of materials at elevated temperatures. Pyrolysis is generally conducted in anaerobic conditions (or without any oxidizers) but can also be processed with the presence of controlled amount of oxygen (or air) in a few cases. A variety of chemical reactions and physical processes may occur simultaneously in a pyrolysis process of hydrocarbons, typically including decomposition (thermal cracking), coking and phase transformation. Pyrolysis has been a common practice used for converting complex low-value or waste carbonaceous materials, such as coal (Khan 1988, Solomon, Fletcher *et al.* 1993), heavy oil (Woebcke and Johnson 1988, Ambalae, Mahinpey *et al.* 2006), biomass (Zhang, Chang *et al.* 2007, Bridgwater, Gerhauser *et al.* 2011), waste plastics (Panda, Singh *et al.* 2010), and scrapped rubber (Schulz 2003, Islam, Haniu *et al.* 2008), into fuels or other commercially desirable products.

Pyrolysis has long been studied in North America as an approach towards the oil shale (Kirby 1923) and oil sands industry (Peck and Tomkins 1949, Matheson 1952) for crude production. Pyrolysis specialized for these solid hydrocarbon sources has alternative names in history, such as destructive distillation (Peck 1949), carbonization (Eger 1961), dry distillation (Owen, Haddad *et al.* 1985), coking (Towler 2010), etc. Specifically for mineable oil sands industry, bitumen has been found to undergo a series of complex thermochemical processes under pyrolytic conditions (Pakdel and Roy 2003, Gray 2010). For example, typical pyrolytic reactions of the asphaltene components in bitumen at elevated temperature (typically start at 200-300ºC) include the loss of hydrogen-rich alkyl groups that contributes to the generation of the volatile fractions, and the addition reaction of polycyclic aromatic molecules that leads to the coke formation (Gray 2010). A complete pyrolytic process of oil sands (or bitumen) eventually results in two major groups of products: (1) light petroleum ends and oil, which are in gas or liquid phase and can be collected atop, and (2) coke, which is in solid phase mixed with gangue solids (rocks, sands, clays, etc.). In a general pyrolytic process of oil sands, the feedstock is not limited to crushed oil sands, but a number of other hydrocarbon-enriched intermediates derived from oil sands are also suitable. For example, the bitumen-rich concentrate from water based extraction process of oil sands (Steinmetz 1969, Hanson, Miller *et al.* 1982, Hanson, Miller *et al.* 1983), the effluent from the SE process of oil sands (Hanson 1978, Hanson, Miller *et al.* 1983) or a mixture of these two streams (Cha, Duc *et al.* 1991) can all be the feed for pyrolysis.

Pyrolysis of oil sands (or bitumen) is an endothermic process. The coke carried within the pyrolytic residual may be combusted to provide partial energy required for the next batch (Odell 1952, Berg 1959). The remaining energy gap could be filled by providing external energy input, such as electric energy (Salnikov 1968), microwave energy (Balint, Pinter *et al.* 1983), and nuclear energy (Wu, Zhou *et al.* 2010).

The two-stage pyrolysis has become one of the most popular techniques in pyrolytic hydrocarbon recovery from oil sands and oil shale. Such method comprises two key stages – the pyrolysis stage and the combustion stage (Berg 1959, Steinmetz 1969, Tse 1970, Seader and Jayakar 1979), as shown in Figure A.4 and described in the following.

- **Pyrolysis stage**. Crushed oil sands (or other hydrocarbon-enriched intermediates) are heated by being mixed with hot clean sands in a pyrolysis reactor, where the bitumen undergoes cracking and distillation, generating vaporized hydrocarbons to be collected and coke-rich residue. This process is typically conducted at a relatively low temperature (below 500ºC). Several pyrolysis reactor types can be engaged, such as fluid coking reactor and fixed bed coking reactor. The coke-rich sands produced need be deprived of volatile gas by steam stripping, to prevent explosive reaction in the next stage.

- **Combustion stage**. The coke-rich residue is fed to a combustion reactor, where the entrapped coke is combusted in the presence of fresh air, to provide the energy heating up the sands, resulting in hot stackable solids of relatively high temperature (typically >500 ºC) and exhaust gas. A controlled amount of the hot clean sands produced in the second stage is fed back to the pyrolysis reactor to provide heat for continuous processing. The exhaust gas contains toxic and harmful gases, which require further treatment (especially removal of sulfur). The rejected clean stackable solids are suitable for landfill back to mining pits.

The major challenges with a pyrolytic processing of oil sands rely on limited processing capability and poor processability. In perspective of mechanisms, using pyrolytic processing for oil sands (Figure A.4) is to some extent similar to the fluid (or fluidized) coking of bitumen, which has been well-developed and commercialized for bitumen upgrading (Edelman, Lipuma *et al.* 1979). In fluid coking, raw bitumen is directly used as feed for pyrolysis, with coke circulating and functioning as both heat source and heat transfer intermediate. Nevertheless, if oil sands are used as feed, over 80 wt% of the feed would be occupied by the gangue solid while the bitumen only accounts for 7-15 wt%. As a result, large quantities of solids are processed and heated in the two reactors as shown in Figure A.4, which limits the processing capability of reactors. Processability is the other concern, as in fluid coking, the size of heat transfer intermediate (coke) is well controlled within a narrow range to maintain a satisfactory fluidization, which is ideal for heat and mass transfer. However, for the case of direct oil sands PP, the size of heat transfer intermediate (rock, sands, clays) is widely distributed, making it difficult and complicated to achieve a good heat and mass transfer during pyrolysis.

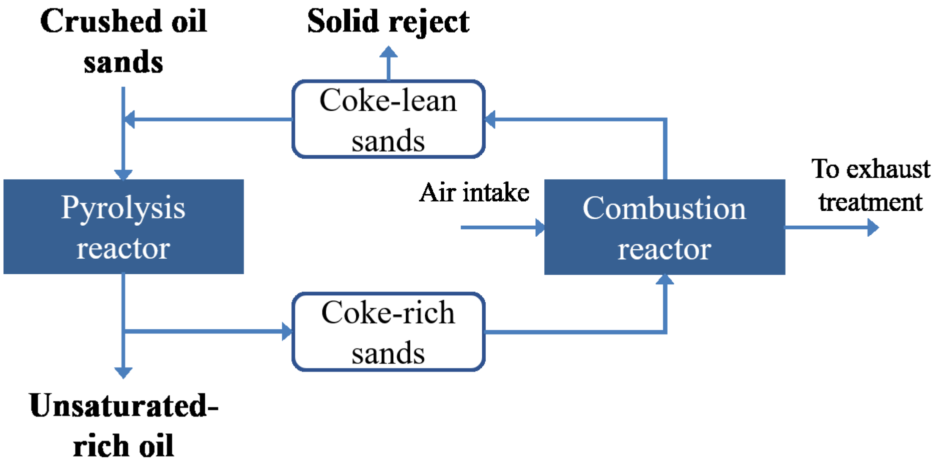


Figure A.4 The schematic of a two-stage pyrolytic process, modified from the work of (Tse 1970).

A-III.5 Cryogenic processing (CP)

Cryogenic processing (CP) refers to a group of methods where oil sands processing is operated at an extremely low temperature (typically in the range of -60 to -20°C) (Bergougnou and Kalina 1963). Typical cooling sources used for CP include nitrogen (Welmers, Bergougnou *et al.* 1978, Angelov and Shibley 1985), cold air (Leon 2011) and liquid/solid carbon dioxide (Angelov and Shibley 1985, Leon 2011). The mechanism of CP is that, when temperature is reduced to certain extent equivalent or below the glass transition temperature (T_g, which is around -20 °C (Masson and Polomark 2001)) of bitumen, all the constituents of oil sands become solid, and bitumen becomes brittle and fragile. By mechanical crushing, such ‘frozen’ ore can be comminuted into smaller fragments, where the separation of bitumen from ore matrix is facilitated under a series of effects (Welmers, Bergougnou *et al.* 1978, Leon 2011, Bousquet and Halais 2013), including:

- Mechanical energy provided by crusher/grinder.
- Enhanced brittleness of bitumen at temperature equivalent or below T_g.
- Enhanced fragmentation of bitumen due to interfacial stress at bitumen/solids interface, which arises from the difference in thermal expansion coefficients of bitumen and other constituents and becomes increasingly appreciable at further decreased temperatures.
- For Athabasca oil sands, the commonly-believed water layer existing at sand/bitumen interface should transform into ice layers at such temperature, which is considered beneficial to the flaking and liberation of bitumen from gangue.

Cryogenic crushing produces a solid stream consisting of sands, bitumen powder and ice flakes. Direct separation of bitumen from such stream (that is, dry-CP) can be achieved by pressure sieving (Leon 2011), while more commonly investigated is the wet-CP, where fragmented bitumen is solubilized by solvent and further separated from gangue materials. Therefore, the wet-CP can be regarded as a modified SE process, with cryogenic crushing for ore pretreatment. However, compared to SE, the efficiency of solvent-induced dilution is expected more restrained in wet-CP, due to higher viscosity and reduced diffusion coefficient of solvent in cryogenic conditions.

CP reveals an important information that oil sands can be processed in a cryogenic environment with a bitumen recovery of up to 90% (Park and Allen 1976, Welmers, Bergougnou *et al.* 1978, Bousquet and Halais 2013). This information is of special interest to Canada's mineable oil sands operators, as in the Athabasca River area where their mining pits and plants are located, generally 150-210 days out of a year have a day-average temperature below 0°C, among which 90 days even have a day-average temperature below -20°C.

However, several factors limit the commercialization of CP processes. Firstly, mechanical processing of massive rigid solids in cryogenic condition requires high OPEX for energy consumption and facility maintenance. The storage and use of certain cooling sources, such as liquid carbon dioxide (Bousquet and Halais 2013), could substantially increase the CAPEX and is the limiting factor for the processing capability. Secondly, dry-CP has been found not competent to support a satisfactory bitumen-solid separation that makes it commercially competitive. For example, Welmers proposed a CP process that is entirely mechanical-based and gives a coarse bitumen recovery of around 90%, however even the most enriched bitumen product still contains up to 40 wt% of gangue solid (Welmers, Bergougnou *et al.* 1978). Thirdly, the use of solvents for bitumen/tailings separation in wet-CP definitely brings about similar problems as SE does.

A-III.6 Microbial-enhanced oil recovery (MOR)

Microbial-enhanced oil recovery (MOR) process refers to oil recovery process where microbial (bacteria, fungi, etc.) activities or their metabolic products are utilized for enhanced recovery of oil (ZoBell 1947, Lazar, Petrisor *et al.* 2007, Sen 2008). MOR has been proven successful to improve oil production in tens of field trials in the US, China, Australia, etc. (Lazar, Petrisor *et al.* 2007, Sen 2008). Though the mechanisms of MOR are not fully discovered (Lazar, Petrisor *et al.* 2007), several hypotheses have been proposed, including:

- Microbial activities facilitate biodegradation of big oil molecules into smaller ones, which increased oil's mobility (Widdel and Rabus 2001).
- Microbes produce bio-surfactants that reduce the $\gamma_{B/W}$ and increase the wettability of solids (Urum and Pekdemir 2004).

- Microbial activities could produce tiny gases, which reduces the viscosity of oil and may provide additional pressure as driving force for liberation and/or expulsion of oil.

Investigation on using MOR process for Alberta mineable oil sands can date back to 1970's, when Zajic and Gerson investigated the generation of bio-surfactants derived from more than 80 microbial cultures (Zajic and Knettig 1976, Margaritis, Zajic *et al.* 1979), and used them to process Athabasca oil sands with cold water as medium (Gerson, Zajie *et al.* 1976). The results showed that after soaked in water with bio-surfactants at a concentration of 0.02 vol% for 48 hrs, oil sand ore released about 90% of the total bitumen, and over 99% of the liberated bitumen could either be accumulated in big droplets or float on the surface of processing water (Gerson, Zajie *et al.* 1976). Such values were comparable to that of using *Petrostep-A-50*, a commercial surfactant. In addition, the formation of intractable emulsified bitumen was greatly restrained to less than 0.5% of the total bitumen when using bio-surfactant; in contrast, the use of *Petrostep-A-50* resulted in massive generation of emulsified bitumen, which accounted for 7% of the total bitumen, which could be attributed to the presence of microorganism-originated demulsifiers in the former case (Zajic and Cooper 1984). More recently, Ding *et al.* revealed that weathered oil sands ores soaked with microbial culture solution and a strain of *Pseudomonas aeruginosa* allowed bitumen recovery of 70% and 98% after an incubation period of 7 and 20 days, respectively (Ding, Zhang *et al.* 2014). It was found that the pH of the culture solution increased from 6.6 to 8.2 along within the first 14 days of the whole incubation period, which was beneficial for bitumen liberation from solid surface. Further analysis on the processing slurry revealed that the content of water-wet fines increased from 5.5% (of the total fines) in the original weathered ore, to 55.2% in that of the microbial-treated group. Such finding suggested that more fines were deprived of organic matters after microbial activities and the concentration of solid impurities in oil phase was reduced (Ding, Zhang *et al.* 2014).

A-III.7 Summary

A summary of select operation parameters and Pros/Cons of the other technologies for mineable oil sands processing is given in Table A.1.

Table A.1 Summary of other techniques for mineable oil sands processing

Technique	Solvent (dosage*)	Operating Temperature	PROS	CONS
Ionic liquid assisted extraction (ILE)	IL (1.5-3) and conventional solvent (0.5-3.5)	Room temperature or above	• Reduced water intake • Less fines/clays in bitumen product	• High cost of IL • IL recovery from tailings • IL contamination in bitumen • Toxicity of IL • Solvent induced hazards
Switchable hydrophilicity solvent extraction (SHSE)	SHS (0.426)	Room temperature or above	• Operation safety	• SHS recovery from diluted bitumen and tailings • Water removal from diluted bitumen
Supercritical fluid extraction (SFE)	Supercritical fluid (circulated)	Above T_c	• Upgrading-integrated processing	• Extremely high CAPEX and OPEX • Recovery of catalyst
Pyrolytic processing (PP)	Not applicable	Typically > 400°C	• Upgrading-integrated processing • Clean stackable waste solid produced • Low water usage • Intractable ores	• High CAPEX • Technological difficulties in operation • Exhaust gas treatment
Cryogenic processing (CP)	Dry process: not applicable; Wet process: cold organic solvent (in average ~1)	Between -60°C and -20°C	• No water/solvent used, no fluid tailings produced in dry process	• Extremely high CAPEX and OPEX • Complex operation • Limited bitumen/gangue separation in dry process • Solvent-induced hazards in wet process
Microbial-enhanced oil recovery (MOR)	Solvent-free process; microbial metabolism solution is used (dosage varies with microbial used)	Room temperature or above	• (Anticipated) reduced environmental impacts	• Lack of fundamental understanding • Long incubation period; limited production

* Parts of solvent (in weight) required for processing a unit part of oil sands ore.

Appendix IV: Supplementary information of Chapter 3

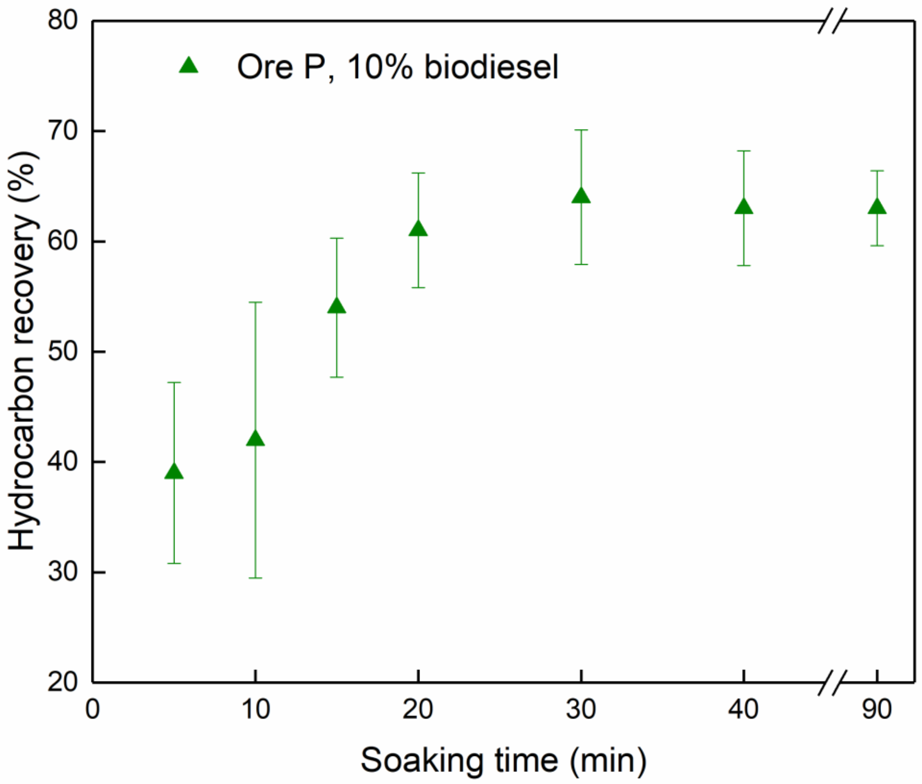
A-IV.1 Soaking time at ambient temperature

The dependence of solvent soaking performance on soaking time is examined using a mutual diffusion model between solvent and Athabasca bitumen. That is, a relatively large volume of the light solvent is initially placed onto a relatively large volume of bitumen, where the mutual diffusion of these two is presented by the concentration of the solvent versus location elapsed time (Zhang, Fulem et al. 2007, Sadighian, Becerra et al. 2011, Fadaei, Shaw et al. 2013).

Shaw *et al.* (Zhang, Fulem et al. 2007) reported that after 30 min blending, the affected depths (the concentration of the minor component > 10%) within bitumen and pentane were found to be 1.3 mm and 3.0 mm, respectively. For a common oil sands ore (10% bitumen), when the maximum size of ore is around 20 mm (bench-scale case), the corresponding thickness of distributed solvent is found to be 0.18 mm; in contrast, when the maximum size of ore is around 2 inches (or 51 mm; industrial case), the thickness of distributed solvent is found to be 0.45 mm.

On the one hand, since the solvent thickness in both cases is less than 2.2 mm, it is hypothesized that all the solvent added can be sufficiently soaked with bitumen. On the other hand, though the affected depth in bitumen (1.3 mm) is not comparable to the size of maximum ore size (20 mm or 51 mm), it is likely that the unaffected bitumen can be further blended with the soaked portion in the downstream mechanical agitation and achieve a more homogeneous solvent distribution.

In addition to the theoretical calculation, a series of bench-scale oil sands extractions with increasing soaking time were conducted. Results revealed that bitumen recovery increased with increasing soaking time and reached a plateau after 20 min, as shown in the following figure. Thus, 20 min soaking time at ambient temperature is considered sufficient for bench-scale extraction to achieve a satisfactory homogeneity of biodiesel and bitumen for good bitumen recovery.



To sum up, 20-30 min soaking time is considered sufficient to achieve satisfactory conditioning of solvent and bitumen, leading to good bitumen recovery. Also, a similar time scale for was used in another bench-scale study (Harjai, Flury et al. 2012).

For the reader’s information, the estimation of soaking time applied here can also be used for estimating larger demonstrations and industrial scale-ups, where the affected depth in bitumen needs be determined due to its dependence on ore characteristics and mechanical crushing applied.

A-IV.2 Liberation kinetics

He *et al.* (He, Lin et al. 2014) reported that bitumen-water interfacial tension ($\gamma_{B/W}$) and viscosity (μ) can be considered as the driving force for bitumen liberation and the inertia, respectively. His study supported that the bitumen liberation rate is dominated by the ratio of $\gamma_{B/W}$ over μ_B, while the ultimate degree of bitumen liberation mainly depends on $\gamma_{B/W}$.

In this study, the effect of biodiesel on bitumen liberation kinetics is also studied by a similar methodology. The results are listed in the following table.

Solvent dosage (%)	$\gamma_{B/W}$ (mN/m)	μ (Pa s)	$\gamma_{B/W}/\mu$ (10^{-3} m/s)	$v_{norm,\ DBL}$ (10^{-3} s^{-1})	$[DBL]_{ultimate}$ (%)
0	18	2.2×10^3	8.1	40.1	11.3
10	12.8	8.5×10^1	1.5×10^2	140.6	66.8
20	10.1	1.1×10^1	9.2×10^2	265.2	85.2

The table shows that, the increasing proportion of solvent initially added to bitumen reduced both $\gamma_{B/W}$ and μ, but more significantly for the reduction of the latter. Such a continual increase in the ratio of $\gamma_{B/W}/\mu$ led to a higher bitumen liberation rate constant, despite the reduction in $\gamma_{B/W}$. On the other hand, the reduction in $\gamma_{B/W}$ at increasing solvent use meant a thermodynamically favored tendency of bitumen liberation, which was supported by an increase in the $[DBL]_{ultimate}$.

In overall, both bitumen liberation rate constant and ultimate bitumen liberation agree well with the work completed by He *et al.* (He, Lin et al. 2014).

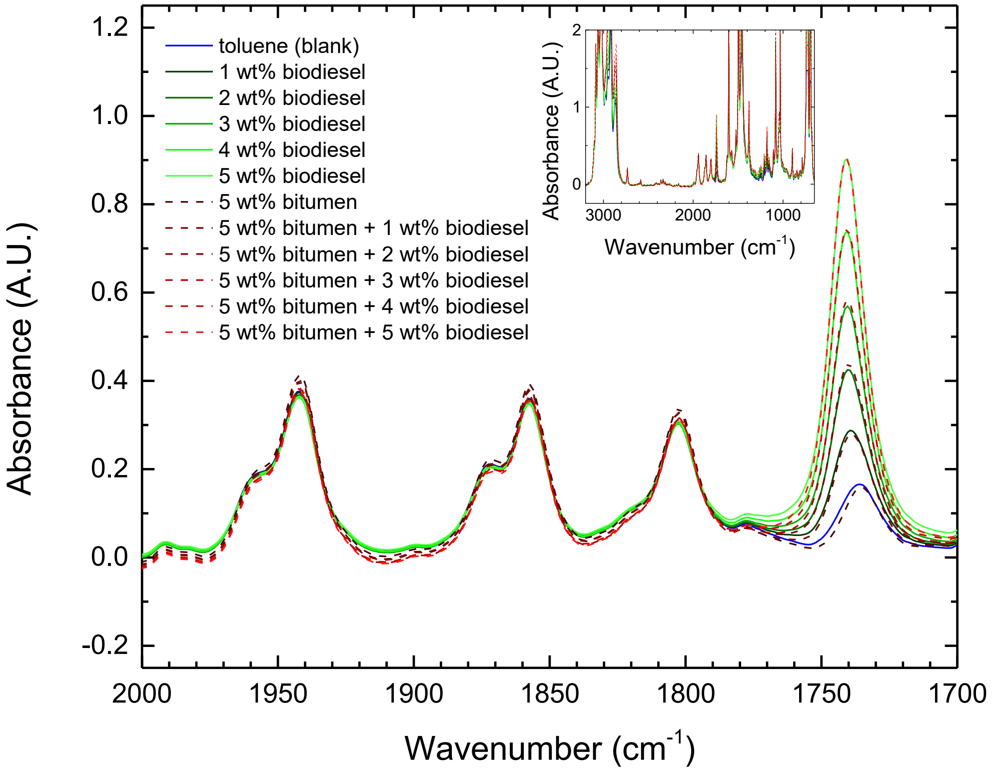


Figure A.5 FTIR patterns of biodiesel in toluene solution, without and with 5 wt% bitumen. Toluene solutions of biodiesel have a concentration range of 0 ~ 5 wt.%.

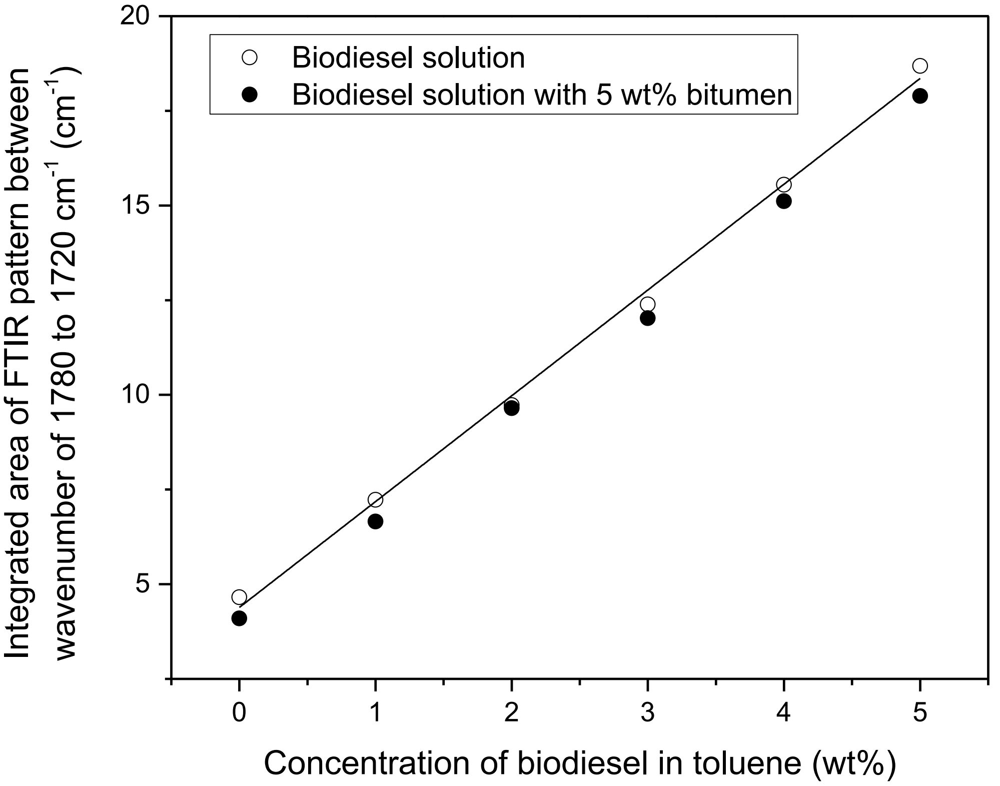


Figure A.6 Integrated area of FTIR patterns at the characteristic peak 1745 cm^{-1}.

Linear fitting of data of biodiesel in toluene solutions, giving a correlation coefficient of 0.9964, provides a satisfactory estimation of biodiesel concentration in the presence of bitumen.

Appendix V: Supplementary information of Chapter 4

Table A.2 Characteristics of oil sands ore used in this study

Bitumen	**Water**	**Solids**	**Fines***
9.12	4.94	85.94	42

* defined as mineral solids with sized less than 44 μm and expressed as fraction of total solids.

Table A.3 Densities of bitumen soaked with 10 wt% solvent mixture at specified ratio*

Biodiesel : MIBC mass ratio	**Density** (g/mL)**
10 : 0	1.0107
9.5 : 0.5	1.0096
8 : 2	1.0065
5 : 5	1.0020

* pure VDF bitumen has a density of 1.0245 g/cm^3.

** negligible difference was found between the samples with and without 1,500 ppm EO-PO copolymer addition.

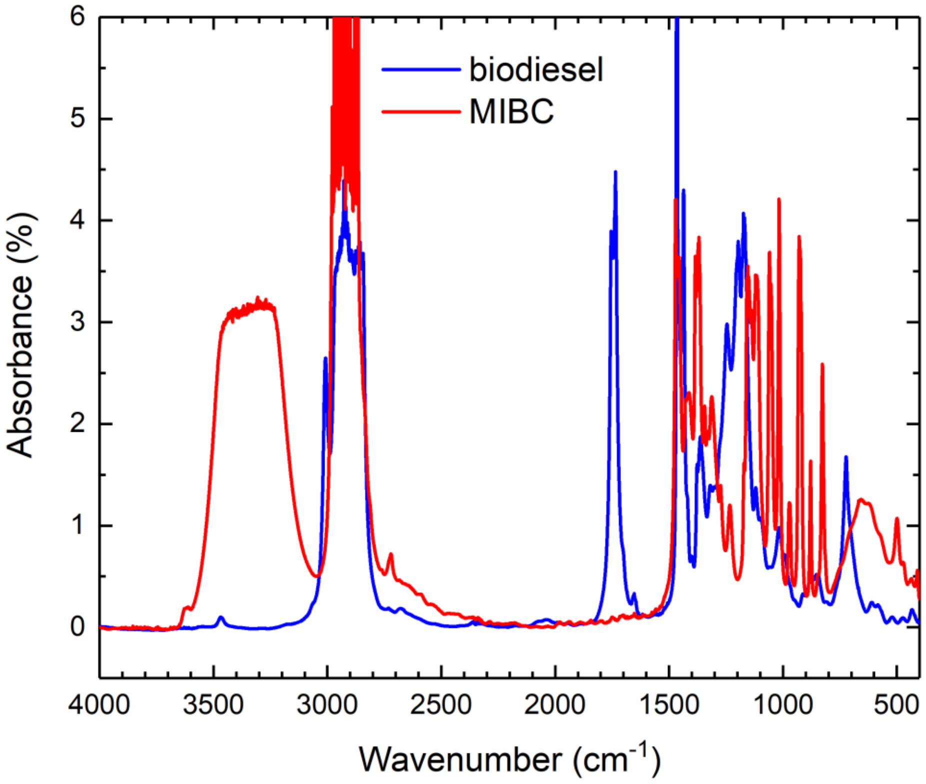


Figure A.7 FTIR spectra of biodiesel and MIBC used in this study

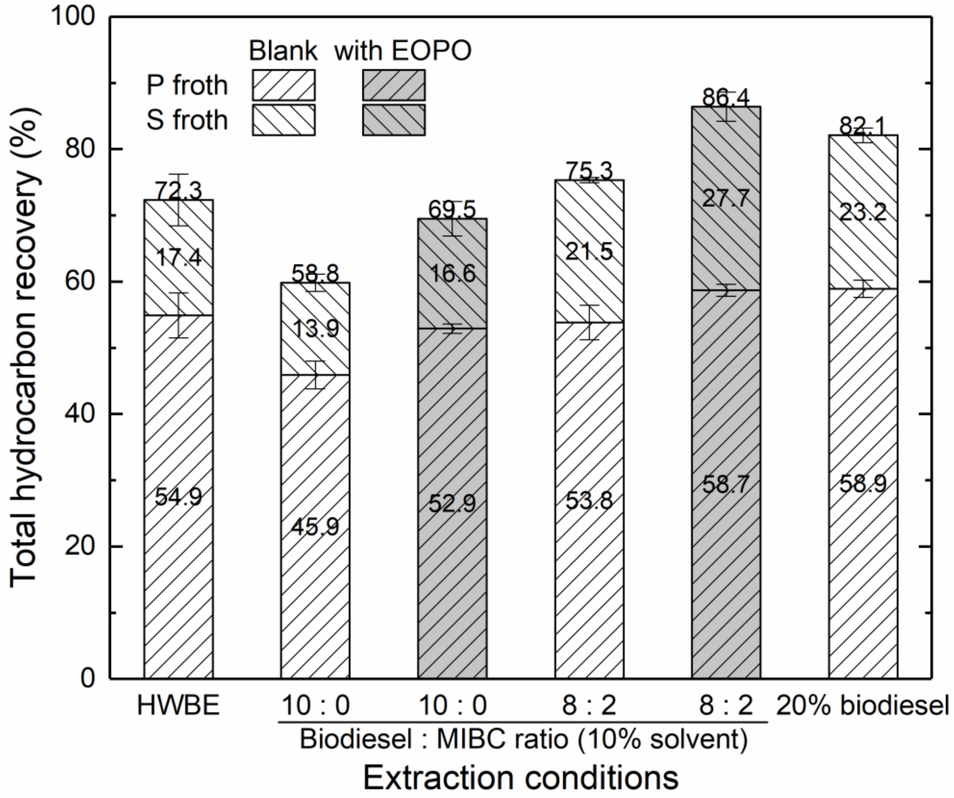


Figure A.8 Comparison of total hydrocarbon recovery between HWBE, four 10 wt% solvent addition groups and 20 wt% biodiesel addition group. Labels specify bitumen recovery from each stream (center of bars) or combined recovery (top of bars). Oil sands were pretreated with 10 wt% (of bitumen) biodiesel-MIBC mixtures at specified mass ratio, with or without 1,500 ppm EO-PO

$$DBL(t) = \frac{mt}{n+t}\ (\%) \qquad \text{Equation A.1}$$

$$[DBL]_{ultimate} = \left(\frac{mt}{n+t}\right)_{t\to\infty} = m\ (\%) \qquad \text{Equation A.2}$$

$$v_{norm,\ DBL} = \left[\frac{d(DBL)}{dt}\right]_{t=0} \Big/ [DBL]_{ultimate} = \frac{1}{n}\ (s^{-1}) \qquad \text{Equation A.3}$$

Table A.4 Fitting parameters of hyperbola function (Equation A.1) for bitumen liberation

Biodiesel : MIBC mass ratio*	**EO-PO**	**Fitting Parameters**		
		m	***n***	***R^2***
No solvent	Blank	24.8±0.4	43.5±3.5	0.986
10 : 0	Blank	70.8±0.6	7.8±0.8	0.983
	1500 ppm**	70.7±0.4	4.6±0.4	0.990
9.5 : 0.5	Blank	69.8±0.4	4.4±0.4	0.990
	1500 ppm	70.4±0.3	3.0±0.2	0.995
8 : 2	Blank	70.8±0.3	3.3±0.3	0.992
	1500 ppm	72.1±0.3	2.7±0.2	0.996

* Except for “No solvent” group

** Concentration of EO-PO copolymer with respect to bitumen content

$$[h/H] = \frac{\alpha t}{\beta + t} + 1$$ Equation A.4

$$v_{ini} = \left[-\frac{d(h/H)}{dt}\right]_{t=0} = -\frac{\alpha}{\beta}\ (hr^{-1})$$ Equation A.5

$$[h/H]_{ultimate} = \left(\frac{\alpha t}{\beta + t} + 1\right)_{t \to \infty} = \alpha + 1$$ Equation A.6

Table A.5 Fitting parameters of hyperbola function (Equation A.4) for tailings consolidation

Biodiesel : MIBC mass ratio*	**EO-PO**	**Fitting Parameters**		
		α	**β**	**R^2**
HWBE	Blank	-0.563	1.383	0.994
10:0	Blank	-0.649	0.447	0.997
	1500 ppm**	-0.637	0.435	0.996
9.5:0.5	Blank	-0.620	0.480	0.991
	1500 ppm	-0.650	0.394	0.997
8:2	Blank	-0.651	0.484	0.990
	1500 ppm	-0.648	0.383	0.994
5:5	Blank	-0.632	0.604	0.991
	1500 ppm	-0.635	0.400	0.996

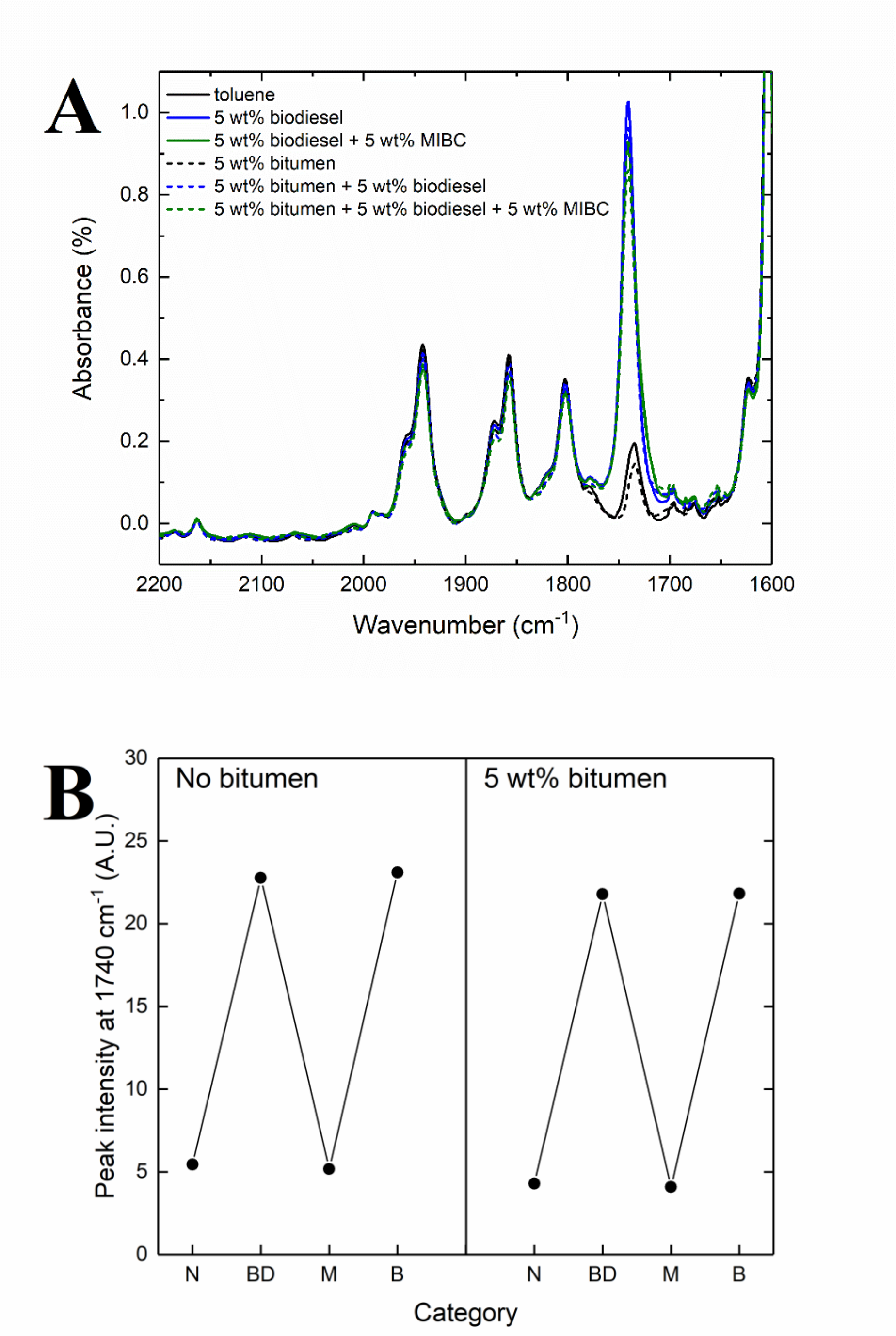


Figure A.9 (A) FTIR patterns of biodiesel with characteristic peak at 1740 cm^{-1}, which was subtly influenced by the presence of up to 5 wt% bitumen and/or MIBC; (B) dependence of peak intensity at 1740 cm^{-1} of FTIR patterns on the presence of: *N* – none, *BD* – 5 wt% biodiesel only, *M* – 5 wt% MIBC only, *B* – 5 wt% of both chemicals.

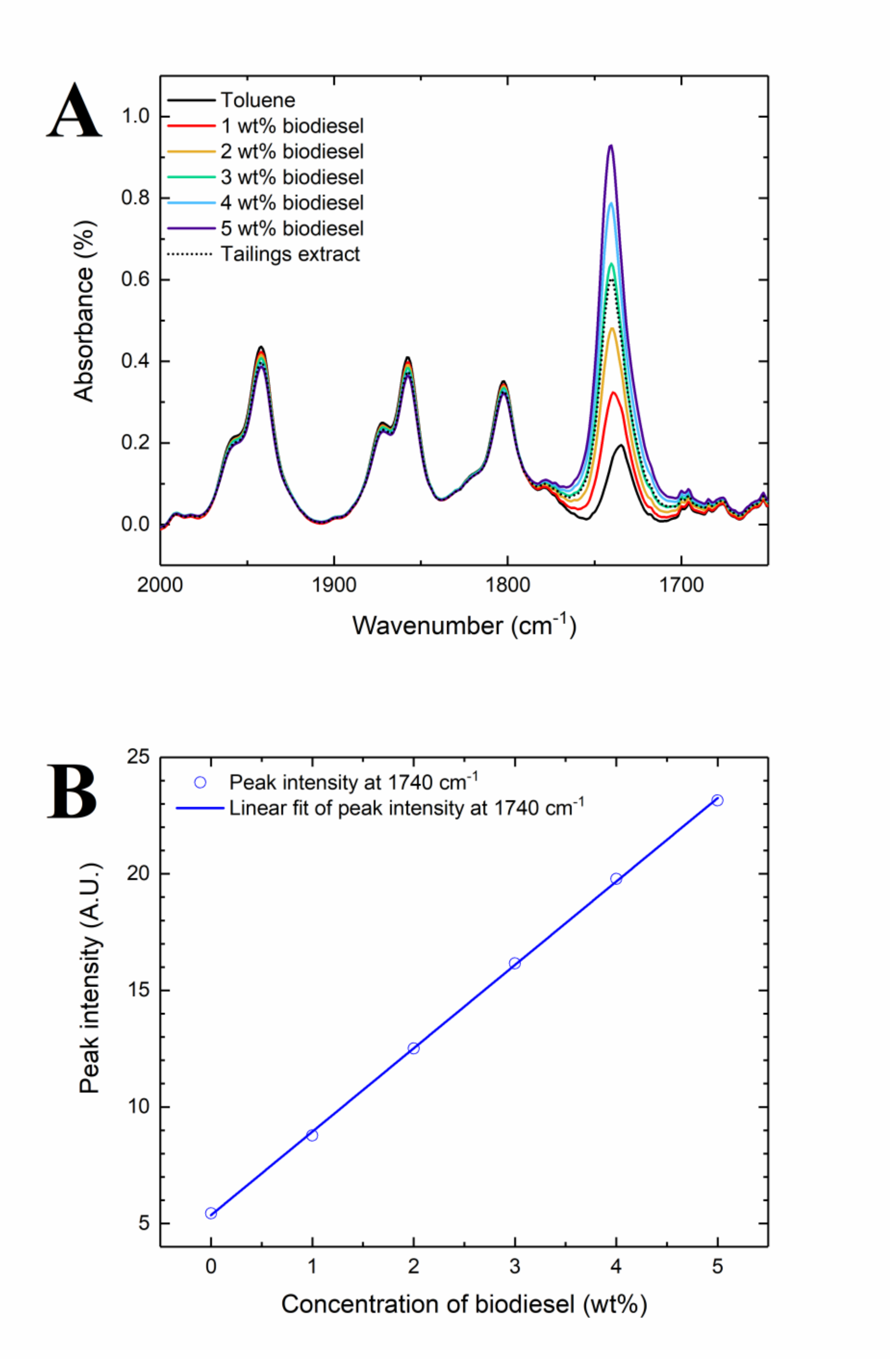


Figure A.10 (A) FTIR patterns of the serial dilutions of biodiesel in toluene solutions; (B) dependence of peak intensity at 1740 cm^{-1} on the concentration of biodiesel.

A linear correlation was confirmed between the peak intensities at 1740 cm^{-1} and the concentrations of biodiesel in sample (Figure A.10A and Figure A.10B), with fitting parameters presented below.

$$I(1740\ cm^{-1}) = 5.356 + 3.578 \times \eta(biodiesel), R^2 = 0.999$$

Where, $I(1740\ cm^{-1})$ represented peak intensities at 1740 cm^{-1}; $\eta(biodiesel)$ stood for weight percentages of the corresponding chemicals.

In the quantification of lost solvent in tailings, the oil sand tailings were first refluxed by toluene and concentrated to $m(solution) = 2.37\text{g}$, followed by integrating the two characteristic peaks of its FTIR spectra (dotted curve in Figure A.10A). It was assumed that all the bitumen and solvent in the feed went to either the froth stream or tailings stream, that is, no bitumen or biodiesel was lost due to attachment to the internal wall of M-BEU or during sample transfer. In addition, it was easy to obtain the following relationships between masses of biodiesel and sample

$$m(biodiesel) = m(solution) \times \frac{\eta(biodiesel)}{100\%}$$

Thus, the mass of lost biodiesel can be calculated as

$$m(biodiesel) = (2.37g) \times \left[\frac{-1.496+0.2795\times I(1740\ cm^{-1})}{100\%}\right] = 0.0681\ g$$

The ratio of lost biodiesel was found as

$$R(biodiesel\ loss) = \frac{0.0681\ g}{3.648\ g} \times 100\% = 1.9\%$$

The loss of biodiesel could also be calculated as per bitumen produced, as

$$\frac{Solvent\ loss}{1000\ bbl} = \frac{m(solvent\ loss)}{m(froth) - [m(solvent\ added) - m(solvent\ loss)]}$$

, which was found to be 1.75 bbl total solvent loss per 1000 bbl of bitumen produced.

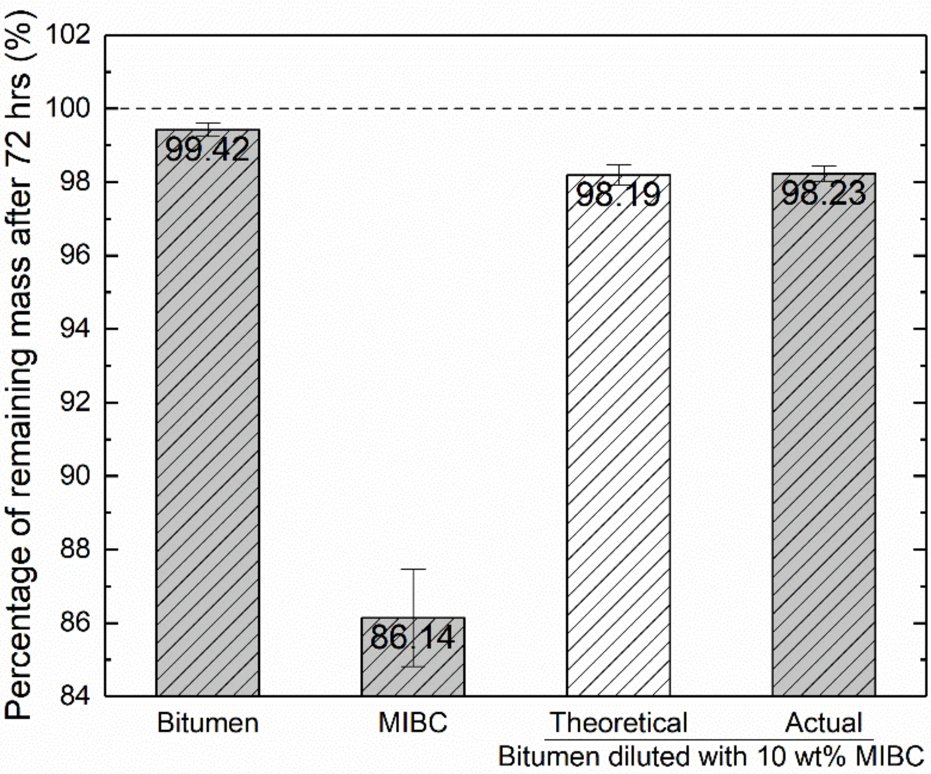


Figure A.11 Percentage of mass loss of VDF bitumen, pure MIBC and diluted bitumen with 10 wt% MIBC (in grey bars), being stored in sampling bottles (lids removed) for 72 hours. The theoretical loss of the diluted bitumen (white bar) was calculated from the loss of the two individual components.

Loss of MIBC due to evaporation from diluted bitumen was found to up to ~13.86 ±1.32% at ambient temperature in fume hood for 72 hrs, while the loss of MIBC and bitumen appeared to be irrelevant as the actual loss of 10 wt% MIBC-diluted bitumen was close to that of the theoretical value. This finding suggested the relatively high volatility of MIBC, implying that the evaporation of MIBC during bitumen flotation and froth storage is not negligible, making total MIBC loss difficult to be determined.

Appendix VI: Supplementary information of Chapter 5

Table A.6 Characteristics of oil sand samples used in this study

Label	**Content (wt%)**			
	Bitumen	**Water**	**Solids**	**Fines***
SM (medium-grade ore)	9.7	6.2	84.1	25
SP (poor-processing ore)	9.9	3.5	86.6	33
SE (poor-processing and poor-grade ore)	8.7	5.3	86.0	43
SO (oxidized/weathered ore)	12.1	2.5	85.4	12

* Fraction of fines (defined as mineral solids with sizes less than 44 μm) in solids.

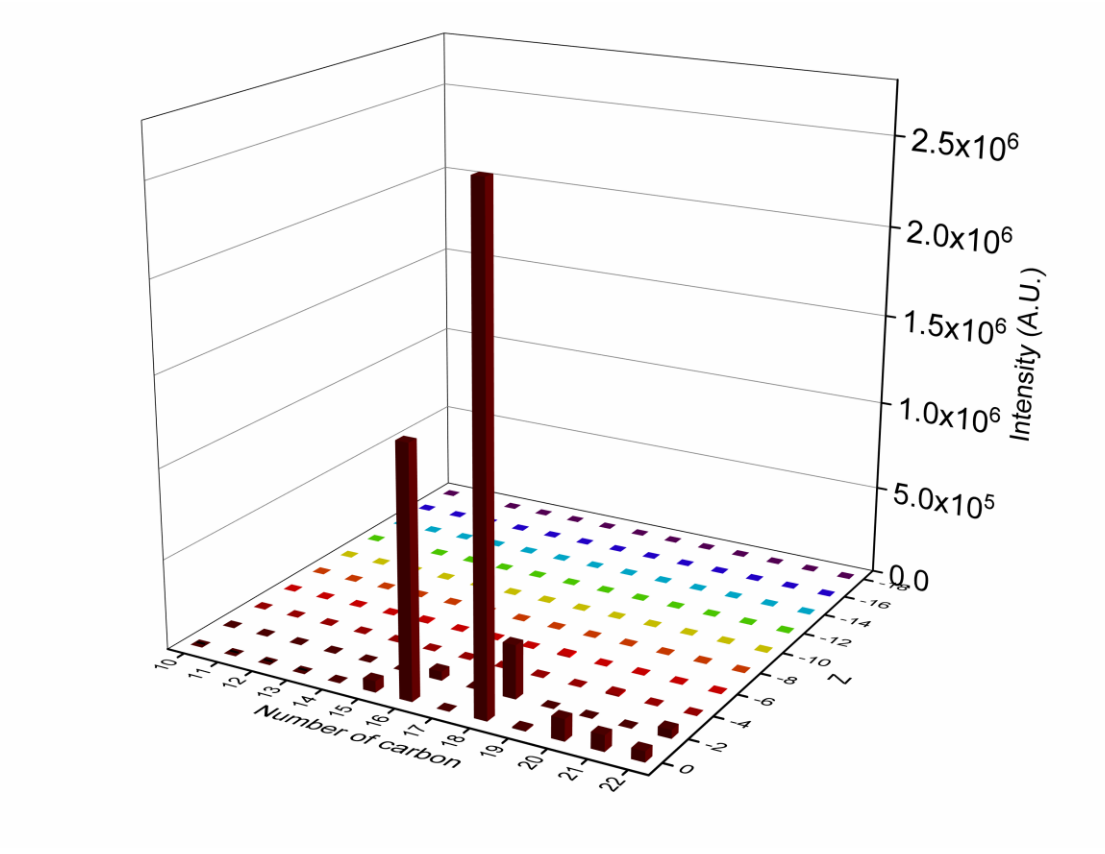


Figure A.12 NA profile of laboratory blank sample

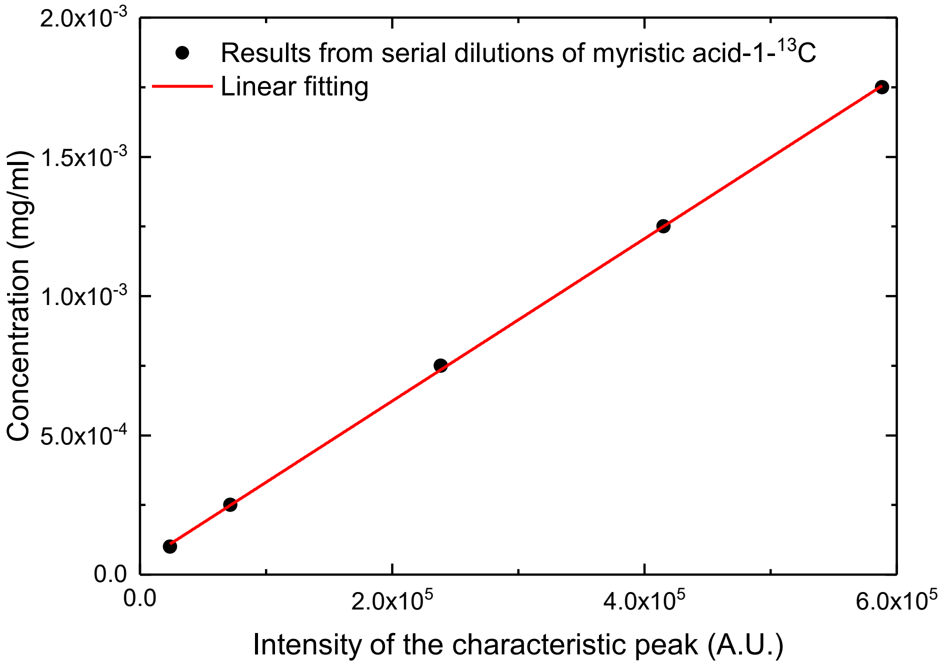


Figure A.13 5-point calibration from serial dilution of the internal standard

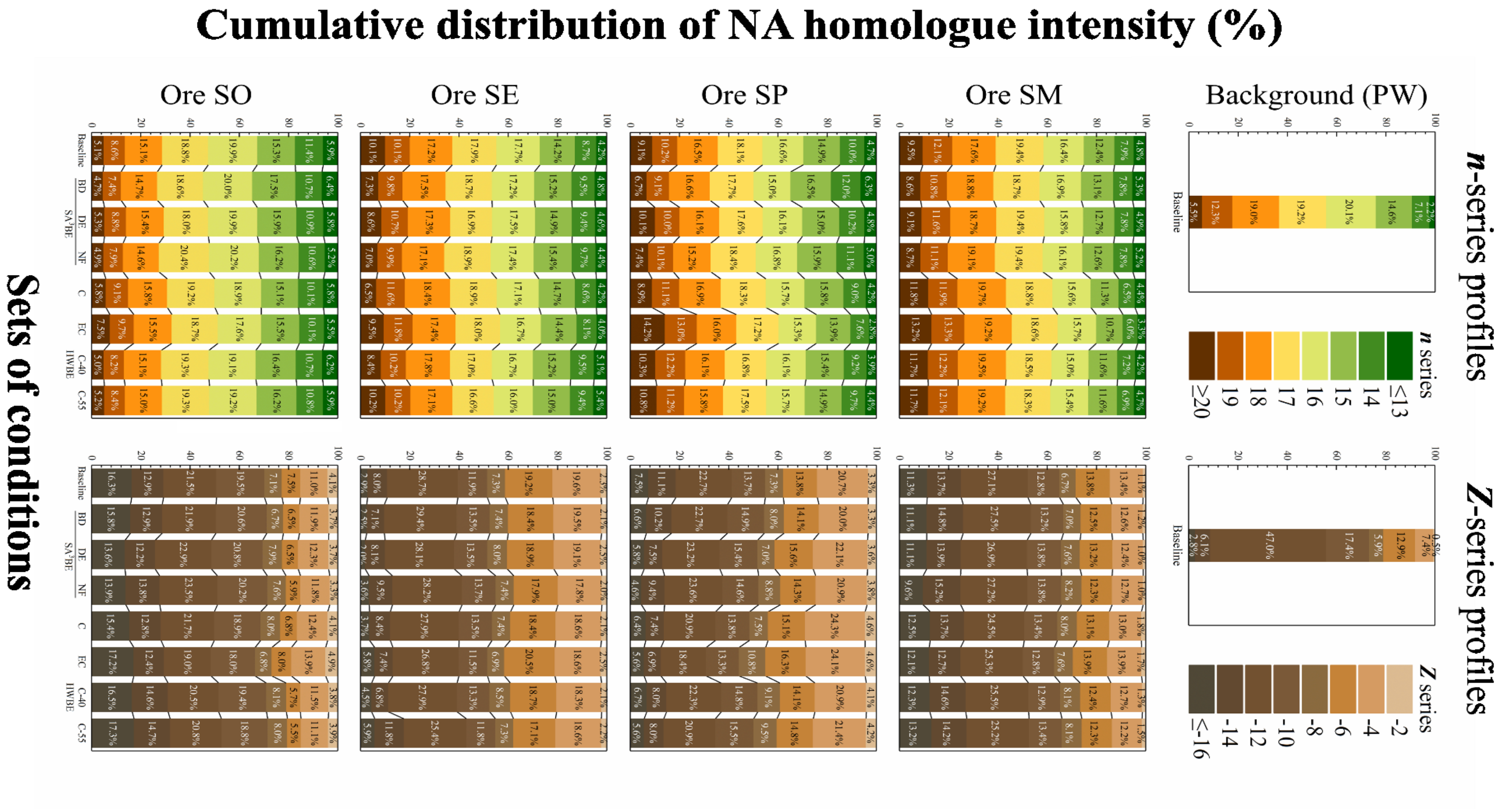


Figure A.14 NA profiles of the background (PW) and all OSTW samples, qualified and quantified by LC-HRMS. Data were categorized in *n* (carbon number, colored in gradient GREEN-YELLOW-RED of the left column) series or *Z* (hydrogen deficiency, colored in gradient YELLOW-BROWN of the right column) series, and classified in extraction conditions.