

INVESTIGATION OF ENVIRONMENTALLY FRIENDLY SOLVENTS FOR THE
RECOVERY OF HEAVY OIL AND BITUMEN

A Thesis

by

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ABSTRACT

Solvent injection recovery processes were introduced as a more energy-efficient and environmentally friendly alternative to Steam injection processes. However, BTX chemicals commonly used for crude oil recovery due to their strong solvency and low asphaltene precipitation are acutely toxic and harmful to the environment. These chemicals are easily soluble in water causing groundwater contamination.

In this study, I test the effectiveness of three solvents; Visred, Limonene and Pinene and compare their results to conventional toxic solvents. Visred, although toxic, is chosen as a solvent as it can reduce the amount of solvent injected into the wellbore. Limonene and Pinene are environmentally friendly non-toxic edible solvents. These are also readily available and cheaper than conventional solvents. Three crude samples have been tested in this study: Canadian Bitumen, Californian heavy oil (Cali 1) and Californian extra heavy oil (Cali2).

A total of 15 core flooding experiments including both steam and steam-solvent flooding processes were conducted and the best recovery method for each crude sample was determined based on produced oil quality, displacement efficiency, oil recovered and economic parameters.

This work proves the effectiveness of these solvents in yielding comparable if not more oil recovery than conventional solvents and can be instrumental to heavy oil and bitumen resources across the globe.

DEDICATION

I would like to dedicate this thesis to my family, Ms. Shania Mathews, Mr. Renny Mathews and Mrs. Reena Susan Varghese for their love and support throughout this work.

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Some FTIR and viscosity results presented in the Appendix were conducted in part by Alex Cortes from the department of petroleum engineering.

All other work conducted for the thesis was completed by the student independently.

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NOMENCLATURE

CB	Canadian Bitumen
Cali 1	Californian heavy oil
Cali 2	Californian extra heavy oil
cP	centipoise
BTX	Benzene, Toluene and Xylene
API	American Petroleum Institute
GHG	Greenhouse gases
SAP	Solvent-Aided Processes
CSS	Cyclic Steam Stimulation
SAGD	Steam Assisted Gravity Drainage
SAS	Steam Alternating Solvent
ES-SAGD	Enhanced Steam Assisted Gravity Drainage
CHOPS	Cold heavy oil production with sand
LASER	Liquid Addition to Steam to Enhance Recovery
VAPEX	Vapor extraction
OOIP	Original Oil In Place
CSI	Cyclic Solvent Injection
FTIR	Fourier Transform Infrared Spectroscopy
TGA/DSC	Thermo-gravimetric Analysis/ Differential Scanning Calorimetry

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

The United States Energy Information Administration (EIA) forecasts that the global consumption of petroleum and liquid fuels will average 92.4 million b/d for all of 2020 and will increase in the future. (*Short Term Energy Outlook*, December 2020; Smith, 2020). Hence, the need for research on recovering oil by using more efficient and environmentally friendly methods becomes increasingly important to meet the growing oil demand.

The Organization of the Petroleum Exporting Countries (OPEC) said worldwide oil demand was expected to increase by nearly 10 million barrels per day (b/d) over the long term, rising to 109.3 million b/d in 2040, and to 109.1 million b/d in 2045 (Meredith, 2020). It is not possible to meet this demand with sole reliance on conventional crude oil. Conventional oil can be produced easily at a low cost. Consequently, most of its available resources have been produced and exhausted from developed nations like Canada and so the need arises to develop the Earth's unconventional resources (Alhajji, 2002; Meyer & Attanasi, 2003; Reid, 1984).

Heavy oil and bitumen resources are going to be instrumental in bridging the gap between increasing energy demand and depleting conventional oil resources. The untapped heavy oil and bitumen deposits are over five times than the remaining conventional crude oil reserve, estimated to be over 6 trillion bbl. (Das, 1998; Kovsky, 2006). In addition to its abundance, exploration costs for these resources are almost

nonexistent because of large reserves present in known fields where many producing facilities already exist (Gates & Caraway, 1971).

Heavy oil by standard practice in the US is defined with an API gravity of less than 20° API (Briggs et al., 1988). However, as the flow rate is a much more important factor in the economic exploitation of the reserve, it is proposed that heavy oil be defined as crudes having viscosities more than 100 cP at reservoir conditions (Briggs et al., 1988; Szasz & Thomas, 1965). Under cold production, these crudes would produce at rates less than 10 B/D (Briggs et al., 1988).

Bitumen on the other hand is found in deposits where the permeability is very low and the flow of fluids can only be achieved by fracturing techniques. It is an extremely viscous material, immobile at reservoir conditions (Speight, 2006). Bitumen is generally defined to have API gravity less than 10° API and viscosity greater than 10,000 cP (Briggs et al., 1988; Speight, 2006).

These properties make both heavy oil and bitumen quite difficult to produce, separate and then transport as most pipeline systems require the dehydrated crude to have an API gravity specification of 19° API (Ali, 1976; Argillier et al., 2005; Riveros & Barrios, 2011). However, our interest in these resources remains as the development of high yield hydrocracking refinery processes can convert low-cost viscous oils into valuable fuels (Gates & Caraway, 1971). Hence, it is necessary to enhance heavy oil and bitumen recovery with additional production techniques that reduce its resistance to flow. This can be done by either heat transfer or by diluting the oil with light hydrocarbon solvents (Gupta et al., 2005).

It is important to note that heavy oil recovery produces a large CO₂ footprint. In processes that involve steam, the production of a barrel of heavy oil produces 80 to 140 lb. of CO₂ (Kovscek, 2006). As we move forward into the future, it is vital that generating energy goes hand in hand with sustaining our environment. Hence, it is important to keep CO₂ emissions in check while producing heavy oil.

The oldest and most widely used technique to enhance heavy oil production includes using steam to increase the temperature of the reservoir by heat transfer methods such as conduction and convection (Erpeng et al., 2018; Li & Chen, 2015). This subsequently reduces the viscosity and mobility of heavy oil resulting in oil production primarily by gravity drainage and steam distillation (Hernandez & Trevisan, 2007; Stewart & Udell, 1988; Willman et al., 1961). Other recovery mechanisms that contribute to enhanced oil production include imbibition, wettability alteration wherein oil-wet carbonate rocks become water wet and thermal expansion of the reservoir rock (Tang et al., 2011; Wilson, 2013). In some cases, the dominant recovery mechanism is thermal vis-breaking, which is a permanent reduction in heavy oil viscosity as opposed to the temporary reduction in viscosity that physical heating causes. Vis-breaking occurs as a result of thermal cracking at high temperatures generated by steam (Shu & Hartman, 1986).

Steam injection processes work particularly well in reservoirs with sand thickness greater than 20 feet. Also, in the case of low-pressure reservoirs, it allows excellent calorific content of transported steam which coupled with low depth, guarantee a low loss of heat in injector wells (Riveros & Barrios, 2011). Technologies like CSS

(Cyclic Steam Stimulation), Continuous Steam injection and SAGD (Steam Assisted Gravity Drainage) are the most common and widely proven steam recovery methods. The difference in these methods is largely attributed to their well configuration. The most common form for SAGD involves horizontal well pairs with one well as an injector and the other as a producer. The injector well is usually 5 m above the producer and injects steam into the cold reservoir, creating a steam chamber above the well. The producer well collects the heated oil and condensates (Dou et al., 2007; L. Cunha & J. Cunha, 2005; Nasr et al., 2000). Cyclic steam stimulation utilizes only one vertical well. The well is used to inject steam and produce the heated oil in cyclic intervals. The steam is usually injected and left to soak in the cold reservoir for a few days or weeks, heating the oil and lowering its viscosity (Green et al., 1991; L. Cunha & J. Cunha, 2005; Szasz & Thomas, 1965). Then the well is opened for production. These methods have been very effective in the recovery of heavy oil in thick vertical formations (Szasz & Thomas, 1965).

However, steam generation requires a large source of freshwater for the generation of steam which incurs several environmental concerns (Collins, 2011). It is also not applicable for depths greater than 5000 feet owing to the presence of high pressure (Dou et al., 2007).

Moreover, steam injection produces hydrothermal reactions which can lower the producing potential and permeability of the reservoir. The solubility of minerals like quartz and other silica rises with increasing temperature and pH and therefore steam injection could cause dissolution and mobilization of reservoir minerals resulting in

cavities and subsequent formation collapse in near well-bore regions. Furthermore, as the hot injected fluids containing the dissolved minerals move away from the wellbore, they cool, causing precipitation and deposition if these minerals impairing permeability (McCorrison et al., 1981).

To combat the disadvantages of steam injection, solvent injection processes were introduced by Butler and Mokrys in 1991 for heavy oil recovery. They introduced the VAPEX process which was closely related to the SAGD process. They suggested the use of solvents instead of heat to mobilize the oil (Butler & Mokrys, 1991; 1993). Solvent injections, such as vapor extraction (VAPEX) and cyclic solvent injection (CSI), use a vaporized solvent to extract heavy oil or bitumen deposits. The solvent decreases the crude viscosity and upgrades the crude by depositing in-situ the less interesting heavy ends and extracting a large portion of the lighter ends. A pure light hydrocarbon or a mixture of several pure light hydrocarbons is usually used as the solvent. The diluted oil can be produced by gravity drainage or pressure depletion (Butler & Mokrys, 1991; Cristofari et al., 2008; Deng, 2005; Yazdani & Maini, 2005).

The mechanisms involved in crude recovery by solvent injection include effective diffusion and gravity drainage (Mayorquin & Babadagli, 2015). At high pressures the heavy oil- solvent equilibrium can be divided into 3 layers. The top layer has the highest concentration of solvent and hence has the lowest viscosity even if the solvent was flashed off the heavy crude. The middle layer consists of heavy crude with dissolved solvent. This layer has properties more or less similar to the original crude with reduced viscosity. The bottom layer consists of the least concentration of solvent

and a higher concentration of the heavy components in heavy crude. During production the first two layers are easily produced, leaving behind the bottom more viscous layer. In this way, solvent injection allows for an in-situ up-gradation of the heavy crude (Luo, Yang, et al., 2007). Moreover, the vaporized solvent produces higher driving forces in gravity drainage due to a higher density difference between heavy crude and the solvent (Das & Butler, 1994).

Solvent injections are known to be more energy efficient as they do not consume as much energy as thermal recovery methods (Frauenfeld et al., 2006; Galvão et al., 2014; Jiang et al., 2012). It can be applied to thin reservoirs for which steam processes are deemed to be uneconomical. They can also be applied to low permeability carbonate reservoirs with high heat capacity. In addition, the presence of overburden or underlain aquifer does not hinder the efficiency of solvent-based recovery unlike for steam related processes (Das & Butler, 1994; Pourabdollah & Mokhtari, 2013; Rahnema et al., 2008). Solvent enhanced steam processes also consume lower cold water equivalents than steam processes alone, to achieve the same oil recoveries (Doscher et al., 1979; Galvão et al., 2014). Recovery processes involving solvents alone are not preferred due to their high cost. However, using a solvent as an additive to steam is more cost-effective and yields a higher oil recovery due to improved mobility ratio (Shu & Hartman, 1988).

There are several hybrid processes involving both steam solvent proposed in the literature to improve recovery efficiency and cost-effectiveness. Some of these processes include Enhanced solvent-SAGD (ES-SAGD), Solvent- aided processes (SAP), Steam Alternating Solvent (SAS) and Liquid Addition to Steam to Enhance Recovery

(LASER). The key idea behind ES-SAGD processes is that solvent addition to steam injection would reduce the amount of water and associated water handling and treatment facilities (Gates & Chakrabarty, 2008; Nasr et al., 2003). In both ES-SAGD and SAP, a small amount of solvent is co-injected with steam. They perform better as both dilution and heating mechanisms lead to greater viscosity reduction and better drainage (Gupta et al., 2004).

Gupta et al, 2005 compared recovery rate profiles of SAGD and SAP processes to indicate that SAP produced the bulk of the oil sooner than SAGD which in turn could improve economics for the project (Gupta et al., 2005). In the case of ES-SAGD, the use of solvents that match the condensation of steam are preferred while SAP has no such requirements (Gupta & Gittins, 2006; Nasr et al., 2003). Pentane and butane were found to be optimal solvents for SAP with an optimal injection amount of 10 wt. % (Gupta & Gittins, 2011; Gupta et al., 2010). SAP is quite effective and sustains project capital while greatly reducing energy requirements (Gupta et al., 2015; Gupta & Gittins, 2007). Steam Alternating Solvent (SAS) processes start the process with pure steam injection, followed by solvent injection when the heat loss to overburden becomes significant (Zhao et al., 2005). Steam injection resumes when the chamber temperature reduces. This cycle is repeated until the economic limit (Zhao, 2007).

LASER essentially consists of introducing a diluent as a steam additive in a cyclic mode to improve CSS performance for bitumen recovery (Leaute, 2002). It is expected to perform better than continuous thermal mechanisms (Leaute & Carey, 2007). LASER has the potential to increase oil recovery by more than 5% and decrease

direct GHG emissions by about 25% (Stark, 2013). Ardali et al, 2012, concluded that steam-solvent co-injections had a more favorable economy in comparison to steam alternating solvent processes or pure heated solvent injections (Ardali et al., 2012).

There are several more examples both from field and laboratory in literature wherein solvent injection has been used in combination with known proven techniques to enhance its efficiency. Cristofari et al, 2008 combined solvent injection with in-situ combustion in a two-step process. They applied cyclic solvent injection to heavy viscous oil to reduce its viscosity and extract the lighter crude fractions. This was followed by combustion to clean the wellbore region and thermally stimulate production. An additional bonus to this method involved the consumption of deposited heavy crude fractions as fuel for combustion (Cristofari et al., 2008). Ivory et al, 2010 used solvents as a follow-up process to Cold heavy oil production with sand (CHOPS) in Cold Lake and Lloydminster reservoirs. Typically CHOPS alone recovers about 5-10% of the original oil-in-place (OOIP). Experimental results after six cycles of solvent injection recovered 50% of the OOIP which indicate the viability of Cyclic Solvent Injection (CSI) (Ivory et al., 2010). Mayorquin and Babadagli, 2015 saturated several heavy oil cores with air-solvent mixtures to improve gas diffusivity and accelerate the oxidation process (Mayorquin & Babadagli, 2015).

Nonetheless, solvent injection processes can be complex. A major contributor to the increased viscosity of heavy oil and bitumen is the presence of large amounts of asphaltene in solubility (Argillier et al., 2005; Luo & Gu, 2005). This solubility can get destabilized due to changes in pressure, temperature or the addition of a solvent. The

type and concentration of the solvent also affect destabilization. Destabilized asphaltenes begin to flocculate and eventually agglomerate into clusters and precipitate out of the fluid. This produces higher-quality deasphalted oil however it may be detrimental to the reservoir as these clusters plug pore spaces, reducing permeability (Monger & Trujillo, 1991; Papadimitriou et al., 2007). The amount of asphaltene precipitated can vary depending on the type of solvent used, ultimately affecting oil recovery and quality (Mohammadzadeh et al., 2010; Mukhametshina et al., 2016). Generally, lower molecular weight solvents are preferred due to their high diffusion coefficient. However, asphaltene precipitation increases with a decrease in carbon number. Hence, it is important to find optimal solvents and application conditions for efficient solvent recovery processes (Moreno-Arciniegas & Babadagli, 2014).

N-alkanes like ethane, propane and butane are commonly used solvents for solvent injection (Das & Butler, 1994; Kaneko et al., 2013). These hydrocarbons are cheap and easily available for use. Redford and McKay, 1980, tested a wide range of hydrocarbons from methane through pentane, natural gasoline, naphtha and synthetic oil. They concluded that methane had very little effect on recovery. However, propane and natural gasoline significantly improved recovery over steam-only processes (Redford & McKay, 1980). Kaneko et al. conducted experiments to check the effectiveness of light gas solvents mainly composed of methane with heavy gas solvents like ethane, propane and butane and found the latter to have greater viscosity reduction and oil recovery (Kaneko et al., 2013). Butler and Jiang, 2000, conducted experiments with propane and butane in the Vapex process. They concluded that propane performed better than butane.

They also reported higher oil recoveries with higher pressures, temperatures and wider well spacing (Butler & Jiang, 2000).

Haghighat and Maini, 2008 conducted several experiments to check whether asphaltene precipitation due to propane injection outweighed the improvement in oil recovery. They concluded that although propane injection resulted in better oil recovery than butane injection at high injection pressures, the consequences to the formation were too severe due to asphaltene clogging (Haghighat & Maini, 2008). As a result, n-alkanes such as propane and butane are not preferred for solvent injection as they cause considerable asphaltene precipitation (Luo, Kladkaew, et al., 2007). Previous experiments show that light aromatic compounds can be useful solvents due to their higher viscosity reduction and low asphaltene precipitation. Ali and Snyder, 1973 conducted experiments to investigate the recovery of bitumen from Athabasca tar sand using solvent, naphtha. Naphtha was chosen as it does not precipitate asphaltene and block formation pores. Also, it is a relatively cheap solvent (Ali & Snyder, 1973). Johnson et al. ran tests on 25 solvents to select a solvent to lower viscosity and prevent asphaltene precipitation simultaneously. The selected solvent contained more than 70% aromatics (Johnson et al., 1975).

The expected properties of a solvent added to a petroleum reservoir containing heavy crude include: Viscosity reduction, breaking of emulsions, removal of organic deposits (paraffin and asphaltenes) and removal of insoluble solids (Gates & Caraway, 1971). Gates and Caraway tested the effectiveness of several solvents ranging from refinery cuts to chemical compounds to find that low molecular-weight aromatic

solvents like toluene, benzene and xylene proved to be most effective in recovering heavy crude (Gates & Caraway, 1971).

However, these chemicals are expensive and hence the need for cost-effective alternatives arises (Gates & Caraway, 1971). Additionally, BTX chemicals are acutely toxic and have relatively high water solubility and low biodegradability, causing aquifer and groundwater contamination. As a result, they are classified as priority pollutants by the U.S Environmental Protection Agency (Agency, 1986; Tsao et al., 1998). These chemicals are not safe to handle due to their low flashpoint (Al-Taq et al., 2019).

Due to the adverse environmental impact these solvents cause, more attention has been diverted to develop environmentally friendly solvents. These solvents are derived from natural and renewable sources (Al-Taq et al., 2019; Berry et al., 2007). Al- Taq et al. performed experimental studies on terpene-based solvents. Terpene is composed of repeating five-carbon isoprene units, grouped as unsaturated aliphatic cyclic hydrocarbon abundant in renewable plant resources such as orange peels (d-limonene), oleoresins from pine plant (alpha and beta-pinene) while others include turpentine, citronella, carotene and many more (Al-Taq et al., 2019; Elochukwu et al.)

Terpenes have low toxicity, high flash point and are readily biodegradable. Additionally, it also possesses high solvency for organic deposits making it a much safer environmentally friendly alternative to BTX solvents. Al- Taq et al. concluded that these terpene-based solvents showed comparable solvency to toluene (Al-Taq et al., 2019). Another study used a corn-based solvent, MS, for oil recovery and compared it to traditional steam injection processes. The study concluded that the corn-based solvent

had the highest recovery and could replace aromatic solvents in solvent injection processes for heavy oil recovery (Ng et al., 2019).

California is one of the world's major heavy oil provinces (Das, 1998; McCullough, 1955). Californian heavy oils contain a large portion of asphaltenes, consequently, their gravities range from about 6° API upwards (McCullough, 1955). Steam stimulation used to be one of the most common methods for heavy oil recovery in the area. During 1970, of the total oil wells completed in California, 77 per cent were drilled in heavy oil fields for steam simulation (Coppel & Newberg, 1972). Solvent stimulation is also used to recover heavy oil. However, California has imposed strict environmental regulations to safeguard its water and air quality (Allen, 1972; Hays et al., 2017; Pickford, 1984). Hence, it is necessary to develop environmentally friendly solvents suitable for the area.

The present work tests the effectiveness of a diluted aromatic solvent, Vis-red, for the recovery of Canadian Bitumen. The study further shows cumulative oil recovered as a result of environmentally friendly solvents such as beta-pine and d-limonene on two types of Californian heavy oils. Limonene is a colorless liquid aliphatic hydrocarbon and is the major component in the oil of citrus fruit peels (Bacanlı et al., 2018; "National Center for Biotechnology Information (2020)," ; Nikfar & Behboudi, 2014). On the other hand, beta-pinene is an organic compound found in plants. It has a woody pine smell ("National Center for Biotechnology Information (2020)."). Limonene and Beta-pinene were chosen as solvents they are easily available near the California oil fields. Their results are compared to conventional processes such as steam, toluene and CO₂

injections. Toluene was chosen due to its strong solvent power and ability to dissolve asphaltene completely as shown in previous literature.

CHAPTER II
MATERIALS AND METHODS

1. Oil samples

Three heavy oil samples have been tested for this thesis, Canadian Bitumen (CB), Californian heavy oil 1 (Cali 1) and Californian heavy oil 2 (Cali 2). Their properties are listed in Table 1.

Table 1: Oil sample properties

Oil Type	Oil Gravity, SG	Oil viscosity (at 20°C), cP	Oil Asphaltene* content, wt. %
C. Bitumen	0.971	236721	43.3
Cali 1	0.75-1.04	874.88	9.505
Cali 2	0.75-1.04	178500	35.3

*Asphaltenes are n-pentane insoluble

These samples are classified based on their viscosity and API gravity in reservoir conditions. As CB has the greatest viscosity, it is classified as bitumen. Cali 1 is classified as heavy oil and Cali 2 is classified as extra heavy oil. Specific gravity (SG) is measured at standard conditions. Asphaltene content was measured according to ASTM D2007-11 (Standard method for SARA) by n-pentane washing. Hence the asphaltenes mentioned in this these are n-pentane insoluble asphaltenes.

2. Solvents

Three solvents have been used for the recovery of heavy oil. The first, Visred, is an aromatic solvent. Limonene and Pinene were chosen as the second and third environmentally friendly solvents due to their high organic solvency and easy

availability in California. Further details on Limonene and Pinene are provided in their MSDS.

3. Medium

The medium used for the core pack was Ottawa sand. The sand reservoir rock has a porosity of 39.1% representing clean sand formations.

4. Viscosity measurement

Viscosity tests were conducted to quantify the viscosity reduction caused by the addition of the solvents to the oil samples. These were compared with the respective base case viscosity of the heavy crude. The viscosity was measured at atmospheric pressure from 35 to 65°C using an HBDV III Brookfield Viscometer (spindle number CPE-51 or CPE-41, depending on tested fluid) through shear stress and shear rate measurements with varying torque (E3116-18). The apparatus was connected to a water bath that heated the oil sample to the set temperature.

5. SARA

SARA experiments were conducted to check for chemical alterations in the crude oil on the addition of the solvents. These experiments were conducted following standard practices mentioned in ASTM D2007 (ASTM-D2007-11; Fan et al., 2002; Kar & Hascakir, 2017). The process is carried out to separate crude oil into its saturate, aromatic, resin and asphaltene fractions. This method is based on the solubility of the crude fractions in different organic solvents (Ramirez-Corredores, 2017; Speight, 2006; Venkatesan & Shu, 1986).

Asphaltenes are separated first from the crude oil by using n-pentane. The deasphalted oil (maltenes) along with n-pentane is then introduced into the SARA separating columns. The upper percolating column, consisting of attapulugus clay, adsorbs resins which are later recovered using a mixture of toluene and acetone. The remaining fractions flow down into the lower percolation column consisting of a layer of attapulugus clay on top and silica gel in the bottom. The silica gel adsorbs the aromatic fraction allowing saturates to flow into a conical flask placed at the bottom. The solvents used for separation are later evaporated from the individual fractions and their weights are determined. The weight of aromatics is determined by mass balance as they cannot be separated from silica gel (ASTM-D2007-11).

6. Core-flooding setup and experimental procedure

The core holder used in the experiment has a volume of 451 cc, resulting in a pore volume of about 176 cc. The core pack was prepared by blending Ottawa sand with 40% PV Water and 60% PV Oil. The sand grains were first mixed with water in a mixing bowl to coat the grains with a water film. Then, the oil was added to the mixture. This method of mixing assures minimum loss of oil to the sides of the mixing bowl.

The core flooding experiments were conducted using a core holder, placed vertically to avoid the effects of gravity (Cristofari et al., 2008). It is a thick-walled stainless steel cylinder measuring 20 cm (7.84 in.) long with an OD of 9.8 cm (3.86 in.) and an ID of 5.41 cm (2.13 in.). The top and bottom portions of the cylinder were sealed with stainless steel caps that were tightly screwed. Copper gaskets were used to ensure

the prevention of leakage. These gaskets were formed using Permatex Ultra Copper paste. A 210 μm mesh screen was placed at the cell outlet to avoid sand production. A thermocouple was inserted in the core holder for experiments involving steam. Measurements from this thermocouple were collected every 2 min and recorded automatically on a laboratory PC.

Figure 1 is a schematic representation of the experimental set-up. As shown in the figure, the bottom end of the core holder is connected via production tubing to a back pressure regulator and separator. The backpressure regulator pressurizes the cell at 75 psi throughout the experiment. For certain experiments, the backpressure was reduced to 45 psi. Production samples were collected every 20 minutes from the outlet of the separator. The injected fluids for the sixteen experiments are listed in Table 2. A solvent pump was used to pump the solvents into the core holder. A water pump first pumped water into a steam generator, from which steam was injected into the core holder for experiments involving steam. The temperature of the steam generator was set at 250°C. The experiments involving solvents and CO₂ were conducted at 20°C to represent typical heavy oil reservoir temperatures (Hamm & Ong, 1995; Mukhametshina et al., 2016).

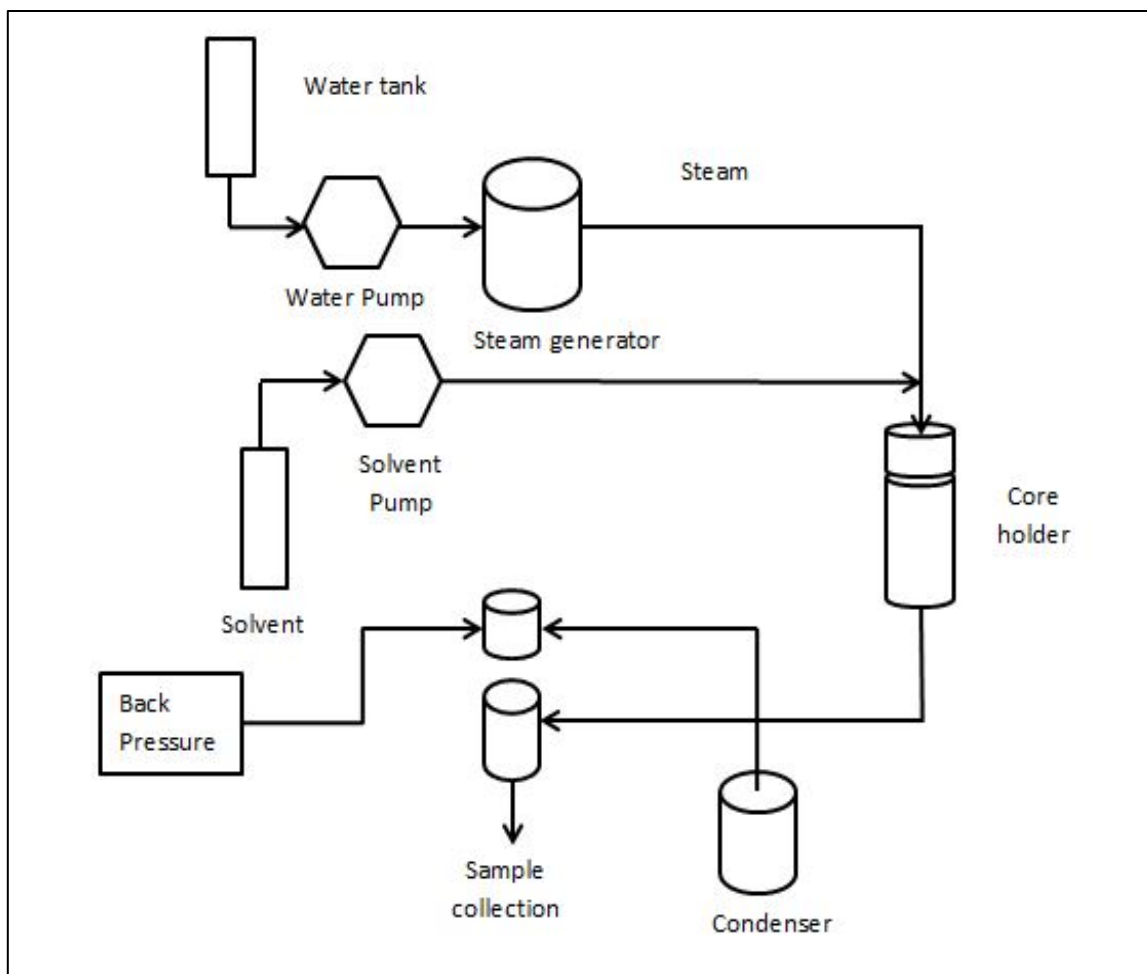


Figure 1: Schematic diagram of the core-flooding experimental setup

7. Visual Post-mortem

The core holder was carefully dismantled to expose the residual core sample after each experiment. The sample was photographed indicating both inlet and outlet positions. This was done to visually estimate how much oil recovery occurred in each experiment.

8. Residual oil determination

The residual oil was determined using two procedures: Pentane wash and TGA/DSC.

Pentane Wash

The first part involves washing the spent rock with n-pentane to separate maltenes from asphaltenes and sand. Two samples of the spent rock (50 grams), taken from both inlet and outlet positions of the core pack are placed in clean beakers and mixed with 80 mL of n-pentane. N-pentane dissolves the maltenes and leaves behind n-pentane insoluble asphaltene and sand particles (ASTM-D2007-11; Fan et al., 2002). The mixture is then thoroughly mixed (until homogeneous) with a glass rod and kept to rest for 30 minutes, stirred once at the 15-minute mark. A conical flask, funnel and a 25 μm filter paper is set-up to filter the mixture into the conical flask. Small amounts of n-pentane are added to the funnel to aid filtration. After filtration, asphaltenes and sand will be left on the filter paper. The n-pentane is allowed to completely evaporate from both the filter paper and the deasphalted oil before weighing. A complete weight balance should be done to ensure the accuracy of the method.

The second part of the process includes toluene washing to separate asphaltenes from sand. Toluene is used to separate asphaltenes from sand because it is an asphaltene solvent (Kar & Hascakir, 2015; Speight, 2006). A portion of the residue left on the filter paper from Part 1 (approximately 30 grams) is transferred into clean beakers and mixed with 80 mL of toluene. This mixture is thoroughly mixed and left to rest for 30 minutes with occasional stirring. It is then filtered through a 2 μm filter paper into a conical flask. The remaining sand mixture is washed and filtered repeatedly using 40 mL of toluene

for every wash. The asphaltenes are left behind on the filter paper. A complete weight balance gives the amount of asphaltenes and maltenes in the sample. The results from both inlet and outlet positions are averaged and then up-scaled to represent the whole core.

Thermo-gravimetric Analysis/ Differential Scanning Calorimetry (TGA/DSC)

Water content in the production samples and residual oil in the core was measured by using NETZSCH Thermo-gravimetric Analysis/ Differential Scanning Calorimetry (TGA/DSC). Produced oil samples were subjected to heating under nitrogen injection till reaching 700 °C at a constant heating rate of 10 °C/min whereas residual core samples were subjected to heating under nitrogen injection till reaching 900 °C at a constant heating rate of 20 °C/min (ASTM-International-E1131-20; ASTM-International-E1356-08, 2014). A sudden weight loss seen in the TGA curve accompanied by a simultaneous endothermic peak in the DSC curve around the temperature range of 70 to 120°C represents water content in the production samples. The residual oil was calculated from the total weight loss depicted in the TGA curve for residual core samples.

9. Emulsion Characterization

Emulsion characterization was done using an optical microscope, the Meiji Techno Japan microscope and a ProgRes CT5-Camera. The slides were prepared from produced fluid samples taken every 20 minutes for each experiment. Each slide was viewed with 40X, 100X, 400X and 1000X magnifications lens to better understand the emulsion characteristics of the sample.

A total of 16 core flooding experiments were conducted with different combinations of injected fluids on three different oil samples (**Table 2**). Representative porous media was created and used for the core pack. Post-mortem analysis such as Visual Post-mortem of the residual core, emulsion characterization of the produced fluids and residual oil determination tests from the residual core samples were carried out.

Table 2: List of experiments with their respective injected fluids and rates

Crude	Experiment	Solvent	Injection rate, mL/min
Canadian Bitumen (C.B.)	E1	Steam	18
	E2	Visred	2
	E3	Toluene	2
	E4	Steam-Toluene	18:2
	E5	Steam- Visred	18:2
Cali 1 (Heavy Oil)	E6	CO ₂	2000
	E7	Limonene	2
	E8	CO ₂ -Limonene	2000:2
	E9	Phase 1: CO ₂	2000
		Phase 2: Limonene	2
	E10	Pinene	2
E11	CO ₂ -Pinene	2000:2	
Cali 2 (Extra Heavy Oil)	E12	Pinene	2
	E13	Limonene	2
	E14	CO ₂ - Limonene	2000:2
	E15	CO ₂ - Pinene	2000:2
	E12 repeat	Pinene	2
	E13 repeat	Limonene	2
	E16	CO ₂	2000

CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

1. Effect of solvents on Crude viscosity

In this section, we investigate the effect of the various solvents on all three samples of crude. The solvents were each added to the crude in a 1:1000 by volume ratio. The viscosities of the mixtures were compared to the bulk viscosity.

As shown in Figure 2, for the case of Canadian Bitumen, the greatest viscosity reduction was achieved by Toluene. This is due to the high organic solvency of toluene. Limonene and Visred also achieved considerable viscosity reduction.

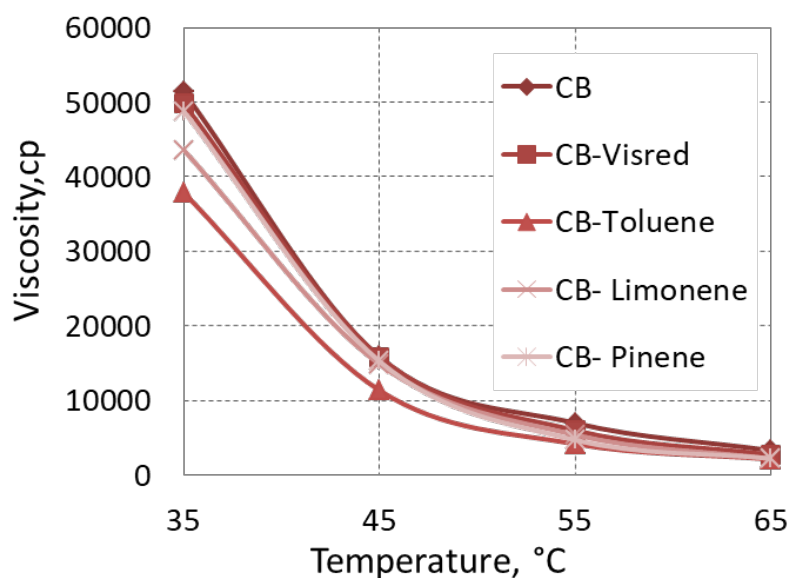


Figure 2: Effect of solvent on Canadian Bitumen viscosity

Similarly from Figure 3, the greatest viscosity reduction for Cali 2 was seen with Toluene followed by Limonene and Pinene. Figure 4 shows that the greatest viscosity reduction for Cali 1 was achieved by Limonene followed by Pinene. These results are summarized in Table 3.

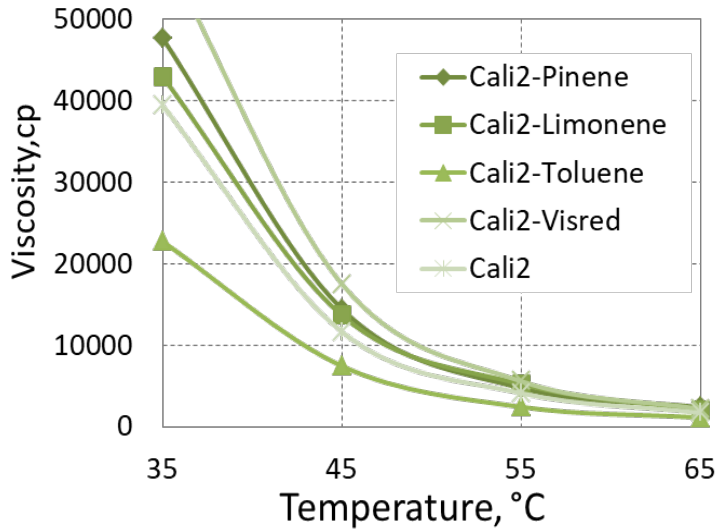


Figure 3: Effect of solvent on Cali 2 viscosity

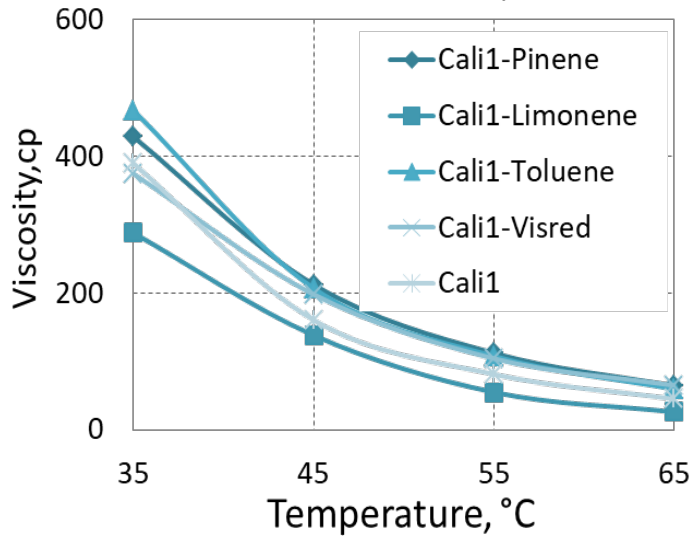


Figure 4: Effect of solvent on Cali 1 viscosity

Table 3: Summary of the effect of solvent on crude

Solvent/Crude name	Canadian Bitumen	Californian extra heavy oil	Californian heavy oil
Bulk sample	51,395	39,391	390
With Visred	49,822	58,554	374
With Toluene	37,859	22,721	467
With Limonene	43,587	42,939	288
With Pinene	48,801	47,651	429

2. Core flooding results on Canadian Bitumen

Produced Oil content

Emulsion characterization was conducted on production oil samples taken every 20 minutes from each of the core flooding experiments. They were visualized with the Meiji Techno Japan-Microscope under 100x magnification and a ProgRes CT5-Camera. An image from each of the five experiments on Canadian Bitumen is depicted in Figure 5. The resulting images for Canadian Bitumen show experiments E1 (Steam), E4 (Steam-Toluene) and E5 (Steam-Visred) contain higher water content i.e., stronger emulsion formations.

Emulsion stability is dependent on the existence of polar components and their interactions with emulsion. In this case, the main polar components are water, asphaltenes and resins (Kar & Hascakir, 2015). Consequently stronger emulsion formations are indicative of higher asphaltene content. Experiments involving steam are

expected to form stronger emulsions as steam promoted more severe emulsion formations than liquid water (Ng et al., 2018). Additionally, as the stability of emulsion increases, separating oil from the emulsion (emulsion breaking) becomes more difficult and consumes more energy (Kar & Hascakir, 2015). Thus stronger emulsions indicate lower oil quality and result in lower oil recovery.

According to Kokal in 2005 smaller average size of emulsion droplets result in longer residence time (Kokal, 2005). This implies a larger separation setup. Thus from Figure 5, it is evident that the lowest oil quality was achieved by sole steam injection (E1). On the other hand, images of samples from E2 (Visred) showed very little to no water content. Hence, produced oil quality was best with a sole injection of visred.

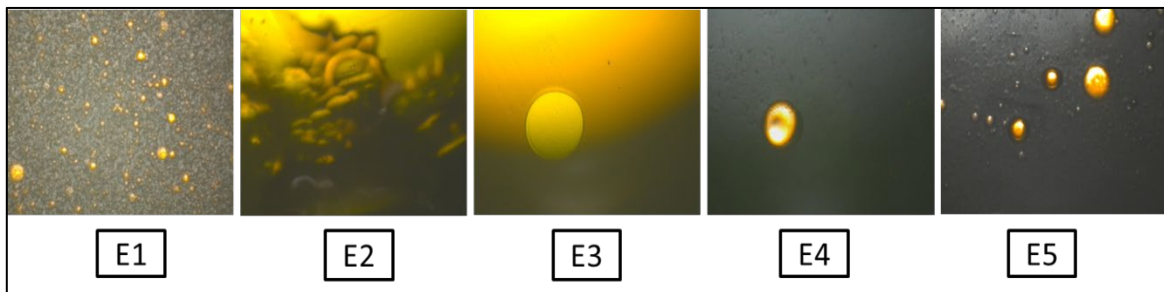


Figure 5: Summary of Emulsion characterization for experiments E1-E5

Post-mortem results

Spent rock analyses were conducted on each of the experiments to determine residual oil and displacement efficiency. Spent rock images of Experiments 1-5 are provided in Figure 6. As evident in the figure, the sole injection of visred resulted in the lightest color implying the highest oil recovery. However, a co-injection of steam and visred yielded the lowest oil recovery, as seen from a very dark post-mortem sample,

indicating that visred reacts adversely in the presence of water. This could be due to phase trapping in the core. We observe a lighter area with sole injections of visred and toluene as they have a higher solubility than steam and result in higher sweep efficiency (Mukhametshina et al., 2016). It is important to note that visred achieves similar results to toluene in almost half the time. As a result, visred reduces the number of Pore volumes (PVs) injected into the sample.

TGA/DSC analysis to determine residual oil consists of using weight loss percentage at the oil decomposition temperature. However, this method is not representative of the entire residual core as a very small sample is taken for TGA/DSC analysis. Hence, in this work, residual oil is determined through a complete mass balance of the process. The displacement efficiency (volume per cent of the whole core) is provided in Table 4. The initial oil saturation was 60 vol. %.

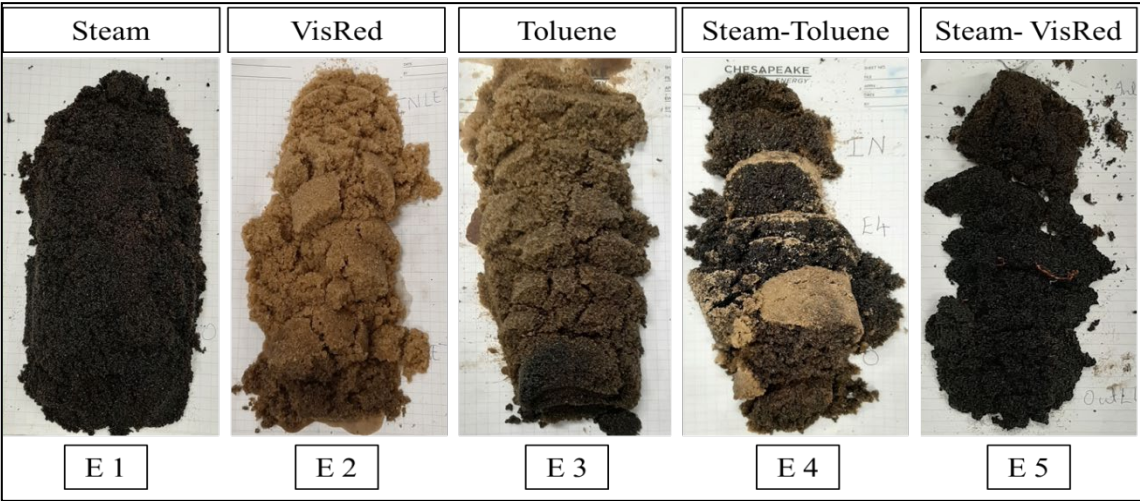


Figure 6: Post-mortem images for Canadian Bitumen

Table 4: Post-mortem results for Canadian Bitumen

Experiment number	Solvent Injected	Displacement efficiency, vol. %	Experiment run time, min
E1	Steam	17.4	196
E2	Visred	28.9	93
E3	Toluene	28.7	143
E4	Steam-Toluene	13.4	112
E5	Steam-Visred	0.95	125

Economic parameters

To check for economic viability, three parameters were evaluated; oil recovery in terms of bbl./acre.ft, the number of pore volumes injected and cost of solvent. Cost calculations were determined by taking the cost of toluene and visred as 0.055 and 0.057 \$/ml. As our interest lies in solvent cost, we omit the price of steam in these calculations. These prices were obtained from commercial vendors as of March 2021. Their results are summarized in Table 5. These results are illustrated in Figures 7-9.

Table 5: Economic calculations for Canadian Bitumen

Experiment number	Solvent injected	Oil recovery, bbl./acre.ft	Cost of solvent , \$	PVs injected
E1	Steam	454	0	-
E2	Visred	752	0.9	1.1
E3	Toluene	747	0.6	1.6
E4	Steam-Toluene	349	0.7	1.3
E5	Steam-Visred	25	0.7	1.4

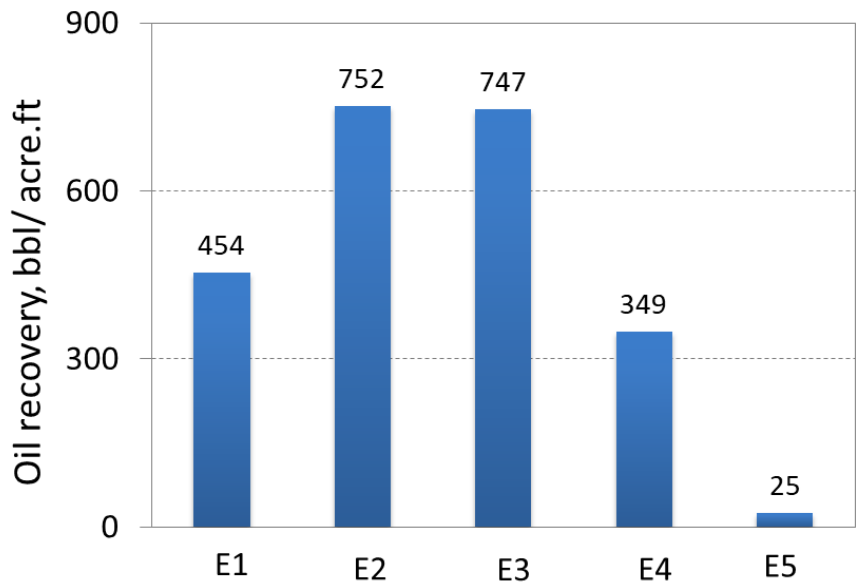


Figure 7: Oil recovery for Canadian Bitumen, bbl./acre.ft

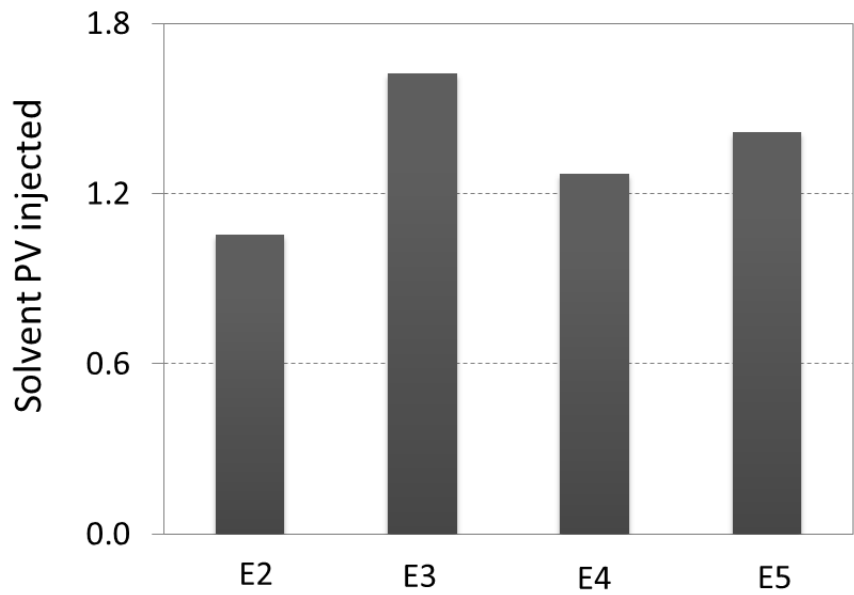


Figure 8: Solvent PV injected for Canadian Bitumen

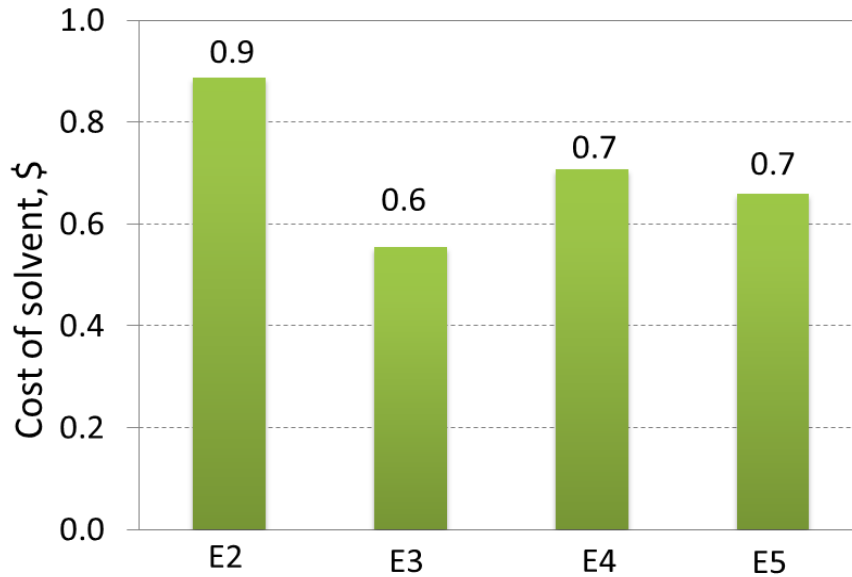


Figure 9: Solvent cost for Canadian Bitumen

Figure 7 indicates that Visred achieved the highest oil recovery. In addition, it also requires the minimum number of PVs injected. Figure 9 indicates that the cost of visred injection is higher than that of toluene however, as the amount of pore volume required is almost half of that of toluene, it is still a viable option. Overall, considering oil quality, recovery, PVs required and cost of solvent, sole injection visred is the best recovery method for Canadian Bitumen.

3. Core flooding results on Californian Heavy Oil (Cali 1)

Produced Oil content

TGA/DSC analyses were conducted on produced oil samples to determine water and solvent percentages by applying a constant heating rate (10 °C/min) under air injection until reaching 700 °C. The DSC curve indicates an endothermic peak at the same temperature values where the weight loss is observed in the TGA graph which is

due to evaporation(Kar & Hascakir, 2015). This weight loss in TGA graphs at varying temperatures is used to calculate water and solvent content. Several control experiments were conducted in order to determine the evaporation temperature range for solvents and water. The control experiments are included in the Appendix. Water evaporation was determined to occur from around 100-120°C and solvent from around 125-160°C.

Oil wt. % was calculated from the following equation:


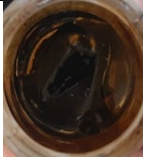


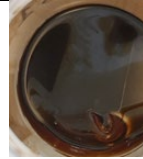

$$O(\text{wt. \%}) = 1 - S(\text{wt. \%}) - W(\text{wt. \%})$$

Where S = Solvent weight percentage, %

W = Water weight percentage, %

Two samples were tested from every experiment and averaged to obtain the results in Table 6. It was concluded that co-injections of carbon dioxide and solvent yielded higher oil wt. % in produced oil samples than solvent injections alone.

Table 6: Produced oil analysis for Californian heavy oil (Cali 1)

Experiment number	E1: CO ₂	E2: Limonene	E3: CO ₂ -Limonene	E4: CO ₂ then Limonene	E5: Pinene	E3: CO ₂ -Pinene
Images						
Solvent wt. %	-	51.5	29.7	43.6	52	55
Water wt. %	30	20	12.7	11.7	20	12
Oil wt. %	70	28.5	57.5	44.6	28	33

Post-mortem results

Spent rock images for Californian heavy oil are presented in Figure 9. Both solvents did well with Cali 1. Post-mortem image from E6 (CO₂ alone) however is still dark indicating that most of the oil was still left behind in the core.

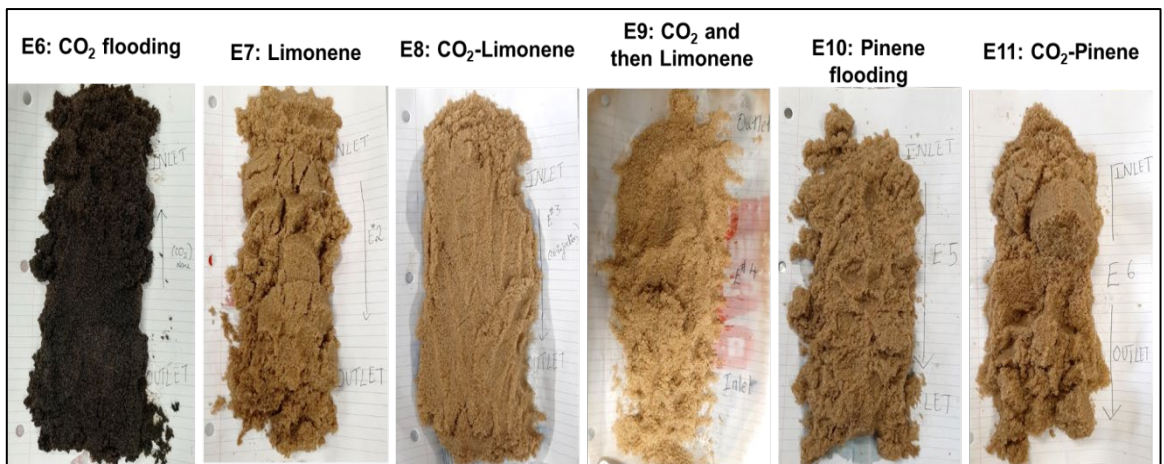


Figure 10: Post-mortem images for Californian heavy oil

Similar to spent rock analyses for Canadian Bitumen, a complete mass balance was done in order to determine oil recovered in terms of displacement efficiency, vol. %. The results for Cali 1 are depicted in Table 7. From the table, we see that the highest displacement efficiency was obtained from E8 i.e., co-injection of CO₂ and Limonene. Additionally, we see that CO₂ alone (E6) performed worst and hardly recovered oil. This is because CO₂ when injected below the minimum miscible pressure (MMP) is not soluble with the crude and results in immiscible flooding (Zhang et al., 2018). Although immiscible flooding in addition to miscible can yield higher recoveries, it is not very effective alone. Co-injections of CO₂ and solvents performed better than solvents alone due to the presence of both miscible and immiscible drive mechanisms.

Table 7: Post-mortem results for Cali 1

Experiment number	Solvent Injected	Displacement efficiency, vol.%	Experiment run time, min
E6	CO ₂	6.4	480
E7	Limonene	35	300
E8	CO ₂ - Limonene	44.5	287
E9	First: CO ₂ Second: Limonene	27.2	360
E10	Pinene	31.3	320
E11	CO ₂ - Pinene	32	180

Economic parameters

In order to check for economic viability, three parameters were evaluated; oil recovery in terms of bbl./acre.ft, the number of pore volumes injected and cost of solvent. Cost calculations were determined by taking the cost of limonene and pinene as

0.02 and 0.068 \$/ml. The price of carbon dioxide is taken as zero. These prices were obtained from commercial vendors as of March 2021. Their results are given in Table 8.

These results are illustrated in Figures 11-13.

Table 8: Economic calculations for Cali 1

Experiment number	Solvent injected	Oil recovery, bbl./acre.ft	Cost of solvent , \$	PVs injected
E6	CO ₂	167	0	*
E7	Limonene	912	0.10	3.4
E8	CO ₂ - Limonene	1158	0.10	3.3
E9	First: CO ₂ Second: Limonene	709	0.08	4.1
E10	Pinene	816	0.31	3.6
E11	CO ₂ - Pinene	834	0.54	2.0

*Note: PVs of CO₂ injected is 5444 PV.

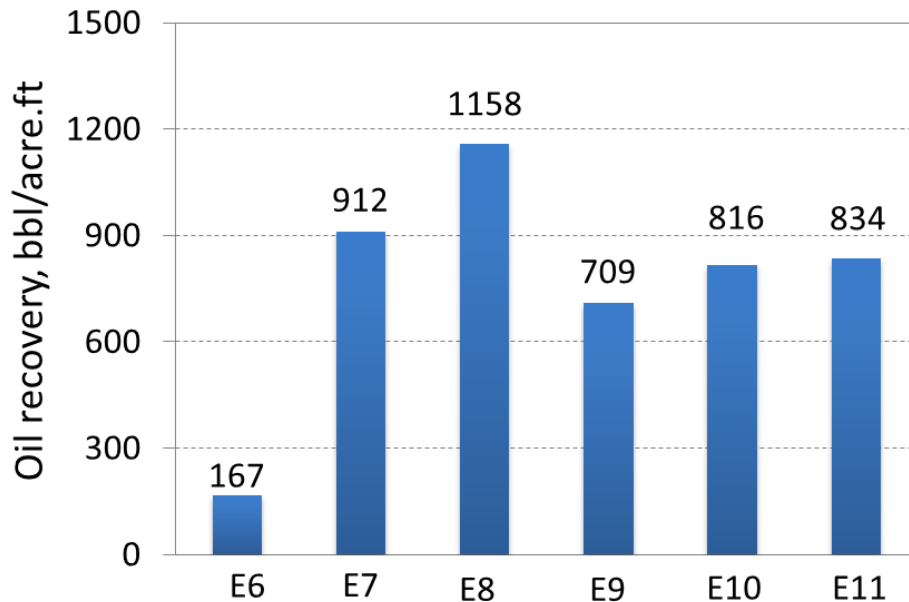


Figure 11: Oil recovery for Californian heavy oil (Cali 1), bbl./acre.ft

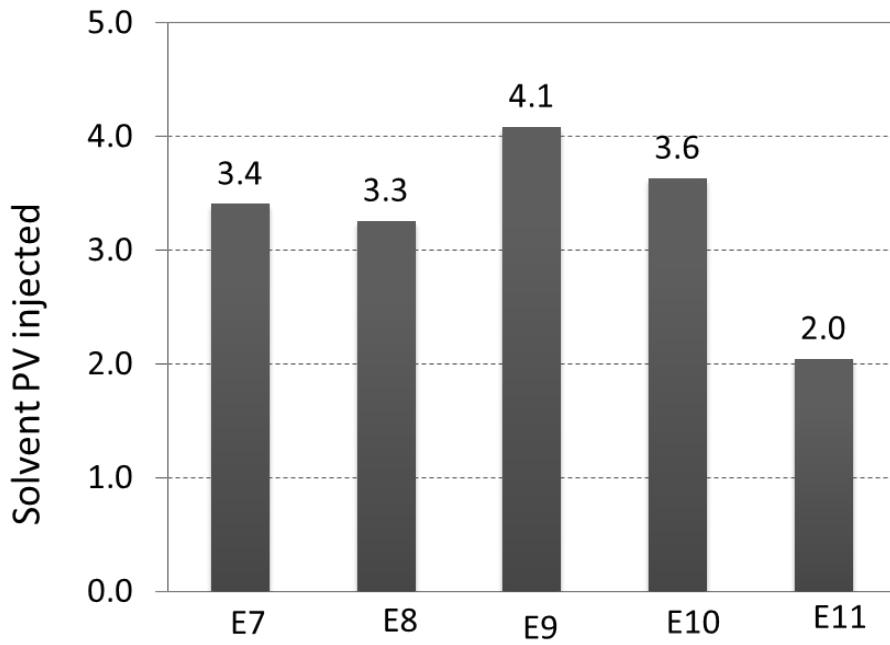


Figure 12: Solvent PV injected for Cali 1

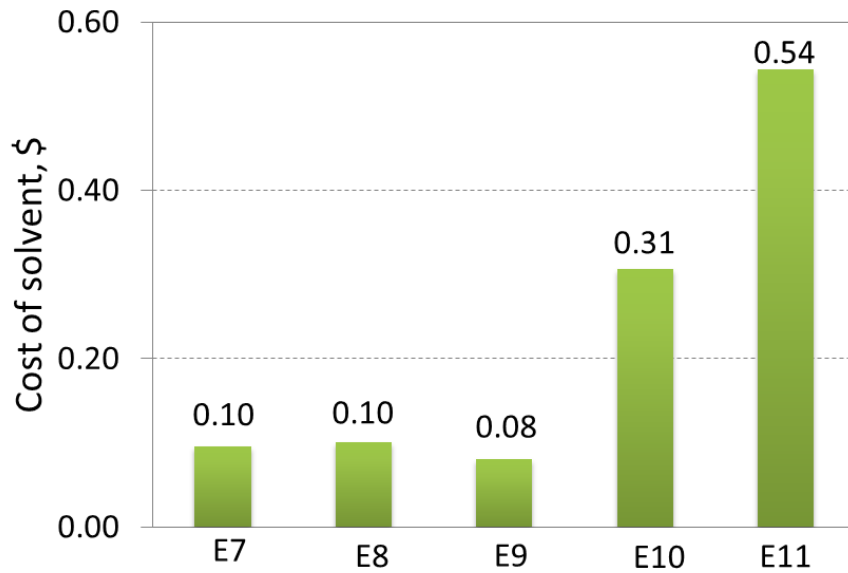


Figure 13: Solvent cost for Cali 1

According to Figure 11, the highest oil recovery was achieved in E8 (CO₂ + Limonene). Although E11 (CO₂ + Pinene) has the lowest number of PV injected, it has the highest cost for the solvent. Hence it is not a desirable recovery method. Considering all three parameters, E8 (CO₂ + Limonene) seems to be the best option for Californian heavy oil.

4. Core flooding results on Californian Extra Heavy Oil (Cali 2)

Produced Oil content

Similarly to produced oil analysis of Cali 1, TGA/DSC analyses were conducted on produced oil samples to determine water and solvent percentages by applying a constant heating rate (10 °C/min) under air injection until reaching 700 °C. The DSC curve indicates an endothermic peak at the same temperature values where the weight loss is observed in the TGA graph which is due to evaporation(Kar & Hascakir, 2015). This weight loss in TGA graphs at varying temperatures is used to calculate water and solvent. Water evaporation was determined to occur from around 100°C and solvent from around 120-130°C.

Oil wt. % was calculated from the following equation:

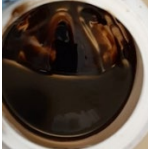
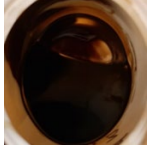

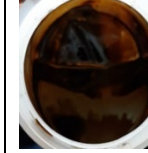
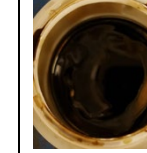
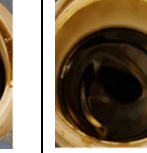
$$O(\text{wt. \%}) = 1 - S(\text{wt. \%}) - W(\text{wt. \%})$$

Where S = Solvent weight percentage, %

W = Water weight percentage, %

Two samples were tested from every experiment and averaged to obtain the results in Table 9.

Table 9: Produced oil analysis for Californian extra heavy oil (Cali 2)

Expt. number	E12: Pinene	E13: Limonene	E14: CO₂-Limonene	E15: CO₂ - Pinene	E12R: Pinene	E13R: Limonene
Images						
Solvent wt. %	49.5	45	61.5	59.5	46.5	44.5
Water wt. %	29.5	19	12.5	17	31	32
Oil wt. %	21	36	26	23.5	22.5	23.5

Post-mortem results

Spent rock images for Californian extra heavy oil are presented in Figure 14. As the viscosity of Cali 2 is much higher than that of Cali 1, the solvents did not respond as well as for Cali 1. However, sole injections of the solvents (limonene and pinene) did better than their co-injections with CO₂. Both limonene and Pinene injections were repeated due to issues with the solvent pump during Limonene injection which caused the experiment to end abruptly.

Post- mortem analyses were conducted by complete mass balance to find the displacement efficiencies of the experiments. The results are reported in Table 10. From the table, it is evident that Pinene injections had relatively higher displacement efficiencies.

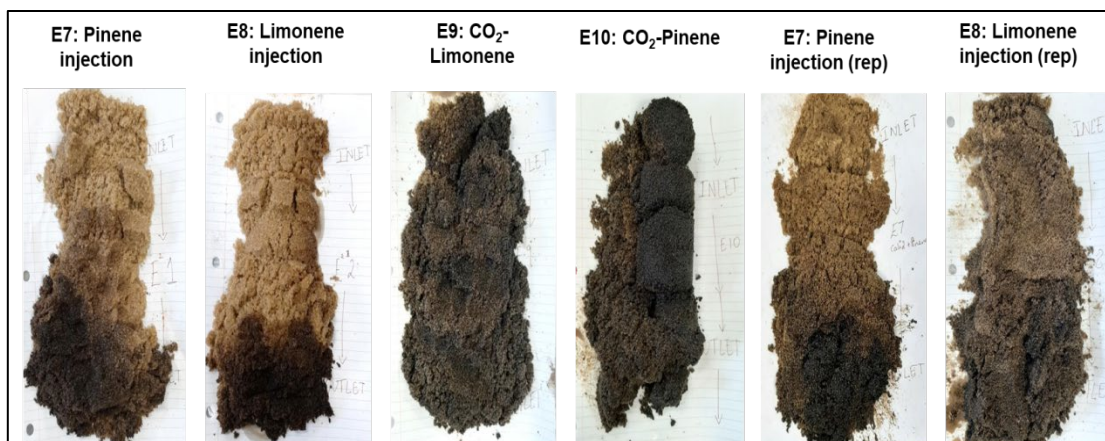


Figure 14: Post-mortem images for Californian extra heavy oil (Cali 2)

Table 10: Post-mortem results for Cali 2

Experiment number	Solvent Injected	Displacement efficiency, vol. %	Experiment run time, min
E12	Pinene	26.8	230
E13	Limonene	22.5	260
E14	CO ₂ - Limonene	7.5	220
E15	CO ₂ - Pinene	12.3	220
E12 rep	Pinene	28.6	260
E13 rep	Limonene	24.5	300

Economic parameters

I evaluated three parameters to check economic viability; oil recovery in terms of bbl./acre.ft, the number of pore volumes injected and cost of solvent. Cost calculations were determined by taking the cost of limonene and pinene as 0.02 and 0.068 \$/ml. The price of carbon dioxide is taken as zero. These prices were obtained from commercial vendors as of March 2021. The results are summarized in Table 11 and illustrated in Figures 15-17.

Table 11: Economic calculations for Cali 2

Experiment number	Solvent injected	Oil recovery, bbl./acre.ft	Cost of solvent , \$	PVs injected
E12	Pinene	699	0.43	2.6
E13	Limonene	585	0.10	3.4
E14	CO ₂ - Limonene	195	0.13	2.5
E15	CO ₂ - Pinene	319	0.45	2.5
E12 rep	Pinene	745	0.70	1.6
E13 rep	Limonene	639	0.10	3.4

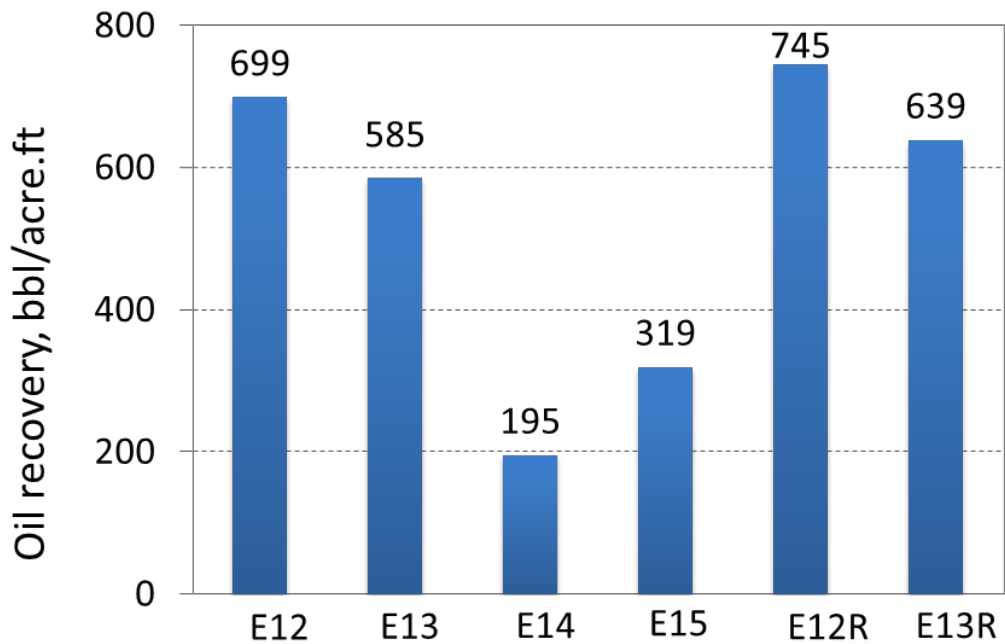


Figure 15: Oil recovery for Californian extra heavy oil (Cali 2), bbl./acre.ft

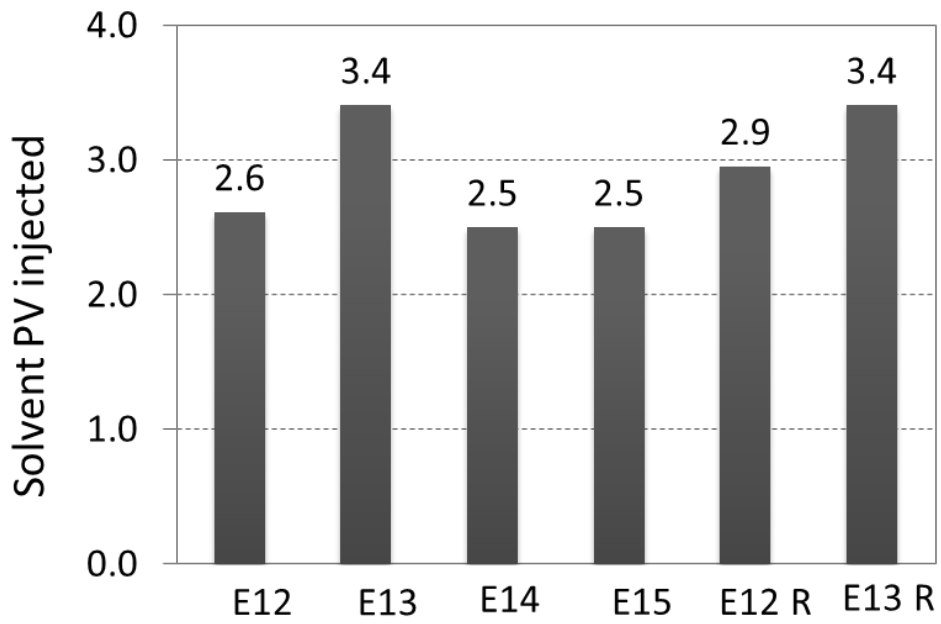


Figure 16: Solvent PV injected for Cali 2

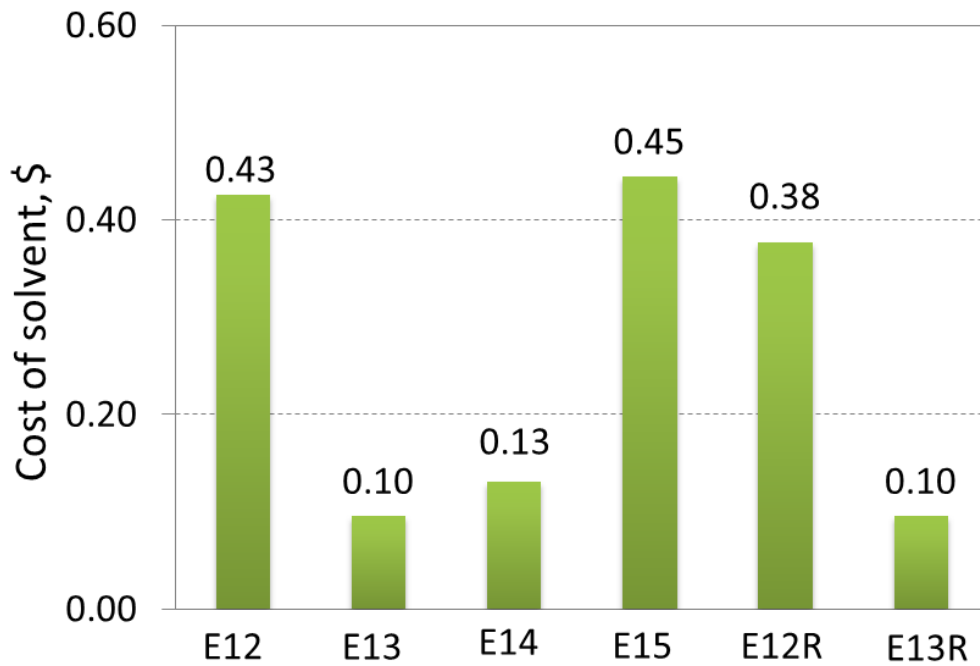


Figure 17: Solvent cost for Cali 2

According to Figure 15, the highest oil recovery was achieved by the sole injection of Pinene (E12 R) closely followed by the sole injection of Limonene (E13 R). The pore volume required for injection was slightly lower for E12 R compared to E13 R. However, we see that cost of Pinene injection is almost three times that of Limonene. Hence, the recommended recovery method for Californian extra-heavy oil is a sole injection of Limonene.

CHAPTER IV

CONCLUSIONS

A total of 15 core flooding experiments were conducted to check the effectiveness of three aromatic solvents; limonene, pinene and visred in comparison with conventional solvents like toluene, steam and carbon dioxide. The experiments involved both solvent and steam-solvent flooding. Three different crudes were studied namely, Canadian Bitumen (CB), Californian heavy oil (Cali 1) and Californian extra heavy oil (Cali 2). Limonene and Pinene were chosen as solvents as they are environmentally friendly non-toxic edible solvents that are easily available at a low cost in California. Visred was chosen as a solvent as it can be used in smaller quantities than conventional toxic aromatic solvents like benzene, toluene and xylene.

The oil recovery, produced oil quality, displacement efficiency and economic parameters were evaluated for each experiment and the best recovery method was found for every crude sample. It was found that Visred injection alone was the best recovery method for Canadian Bitumen as it produced better oil quality and higher oil recovery. However, co-injection of visred and steam performed poorly indicating that visred reacts adversely with water. In the case of Californian heavy oil, co-injection of limonene and carbon dioxide was chosen due to high oil recovery and relatively lower cost of solvent. Californian extra heavy oil responded much better to sole solvent injections than co-injections with carbon dioxide. The best recovery method was chosen as the sole injection of limonene due to lower cost and high oil recovery.

Ultimately, the experimental results conclude that these environmentally friendly solvents yield oil recoveries comparable to that of conventional solvents. Hence these solvents can reduce the environmental damage caused by conventional toxic chemicals. Therefore this study is a breakthrough for many heavy oil and bitumen reservoirs around the world.

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APPENDIX A

CHARACTERIZATION OF CRUDE SAMPLES

1. Canadian Bitumen

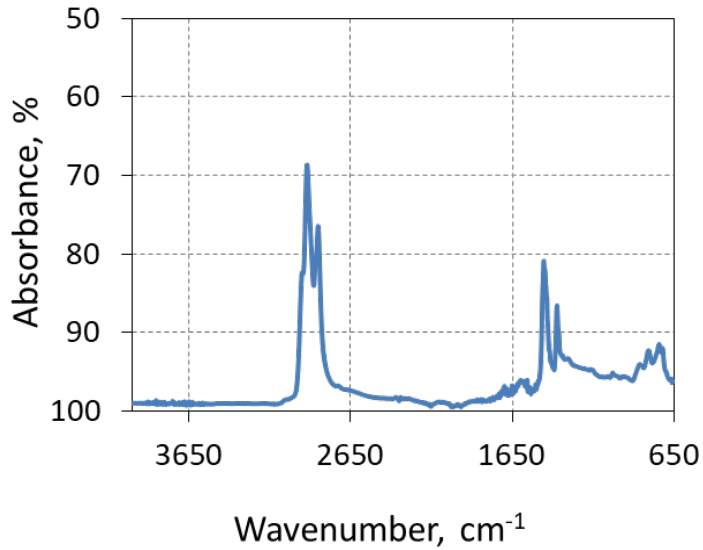


Figure 18: FTIR of Canadian Bitumen

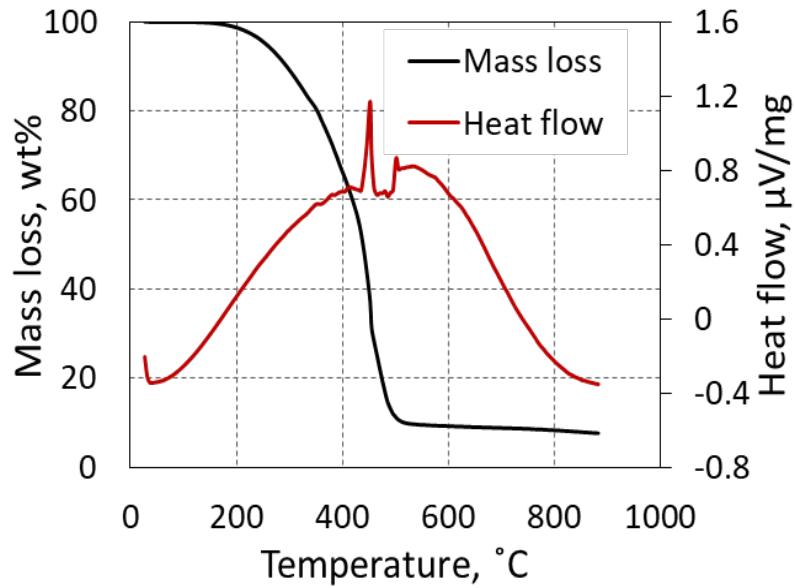


Figure 19: TGA/DSC analyses of Canadian Bitumen under Nitrogen*

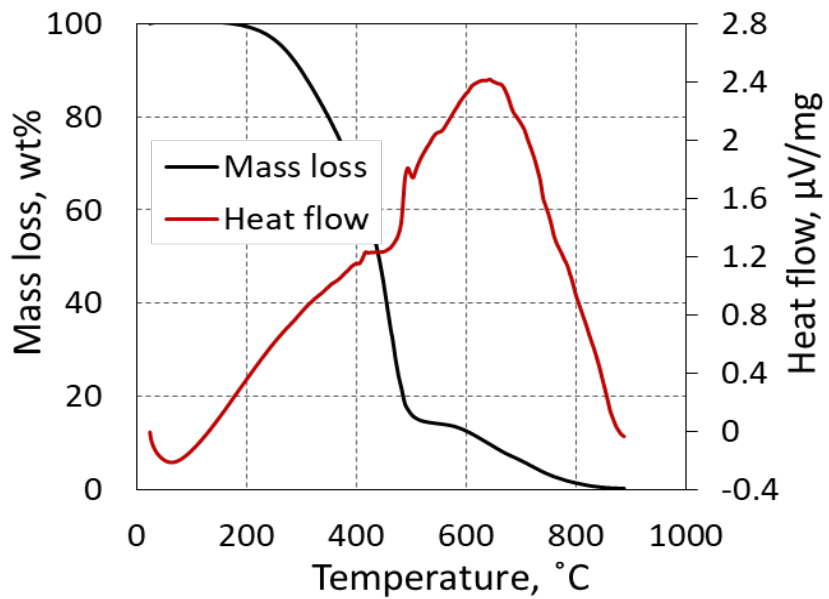


Figure 20: TGA/DSC analyses of Canadian Bitumen under Air*

2. Californian Heavy Oil (Cali 1)

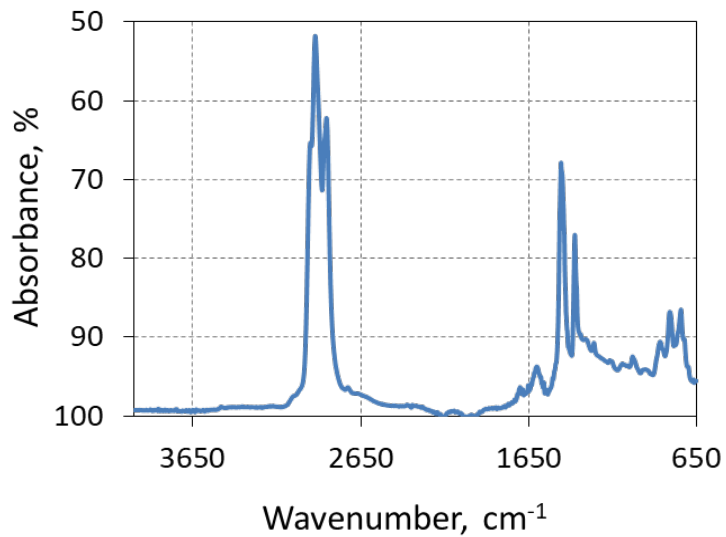


Figure 21: FTIR of Cali 1

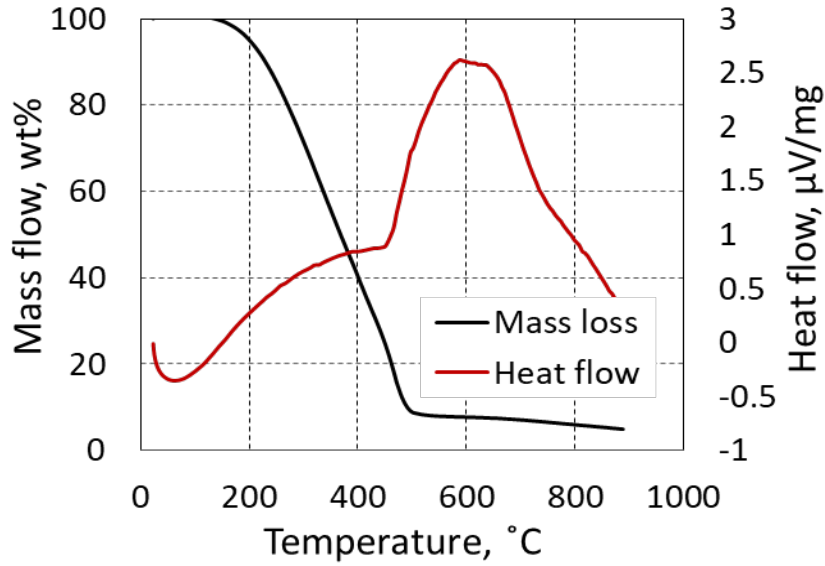


Figure 22: TGA/DSC analyses of Cali 1 under Nitrogen*

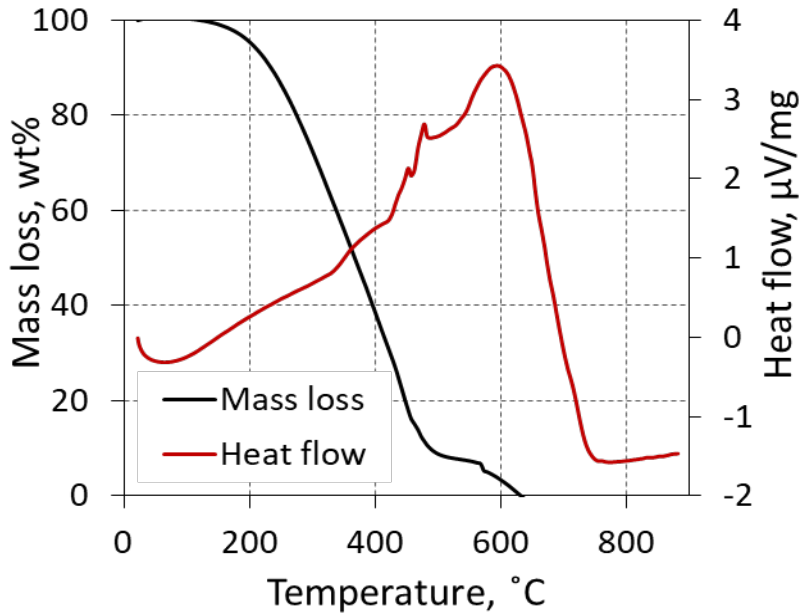


Figure 23: TGA/DSC analyses of Cali 1 under Air*

3. Californian Extra Heavy Oil (Cali 2)

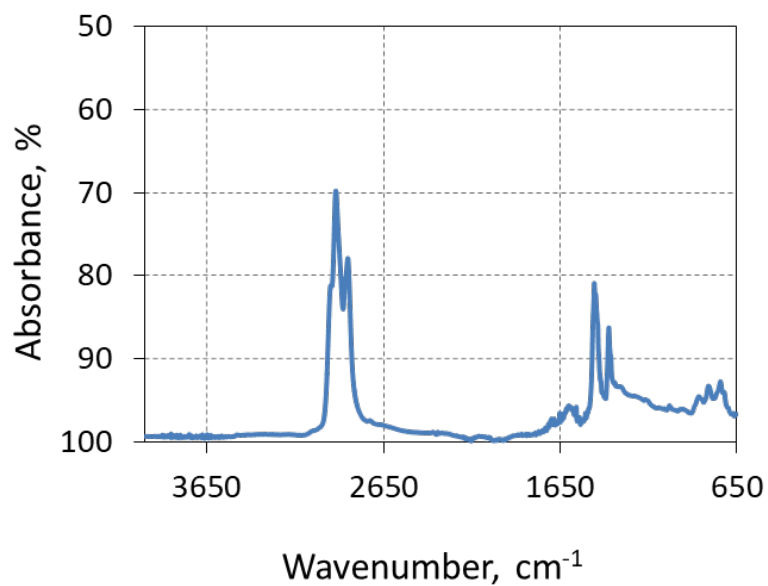


Figure 24: FTIR of Cali 2

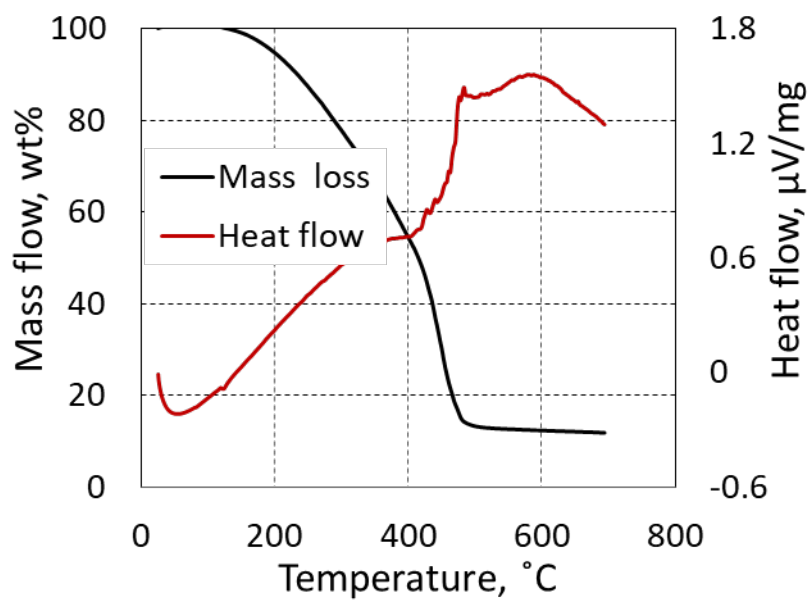


Figure 25: TGA/DSC analyses of Cali 2 under Nitrogen*

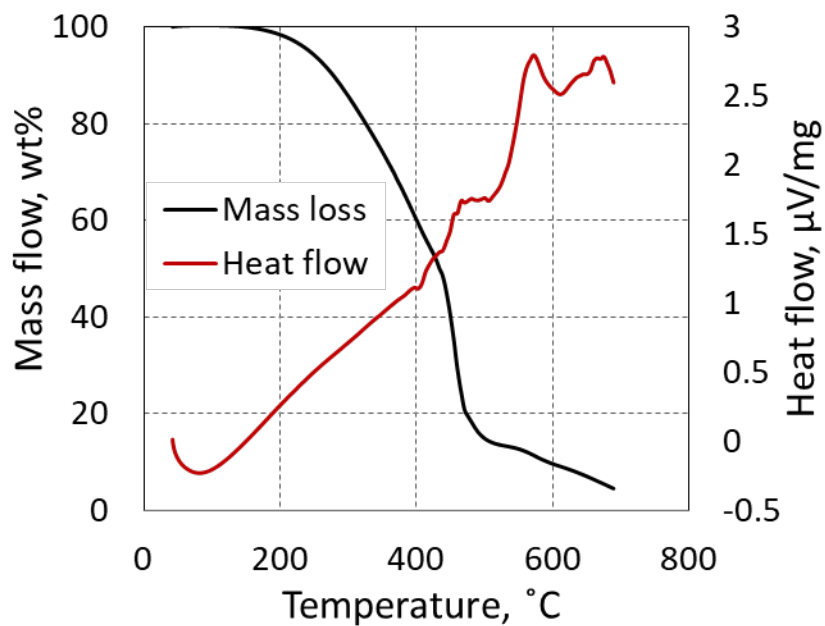


Figure 26:TGA/DSC analyses of Cali 2 under Air*

Table 12: Summary of TGA/DSC analyses for all three crude samples

Sample	Decomposition temperature, °C
Canadian Bitumen	~ 500
Californian extra heavy oil (Cali 2)	~ 470
Californian heavy oil (Cali 1)	~ 480

*All TGA/DSC graphs in this section were conducted at 20°C/min until 900°C.

APPENDIX B
CHARACTERIZATION OF SOLVENTS

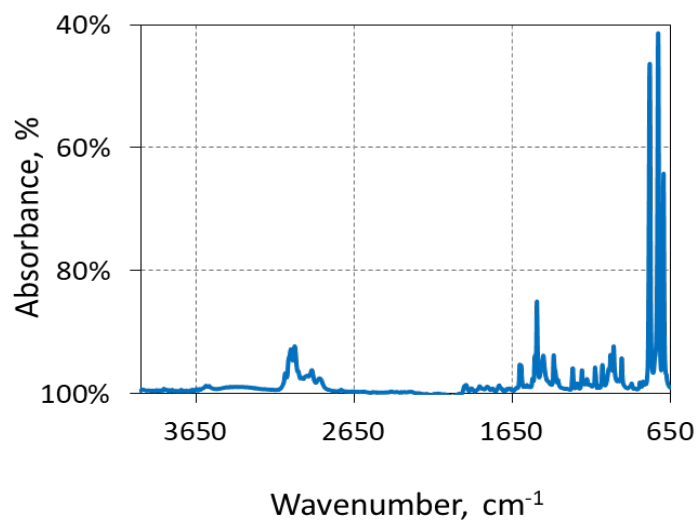


Figure 27: FTIR results of Visred

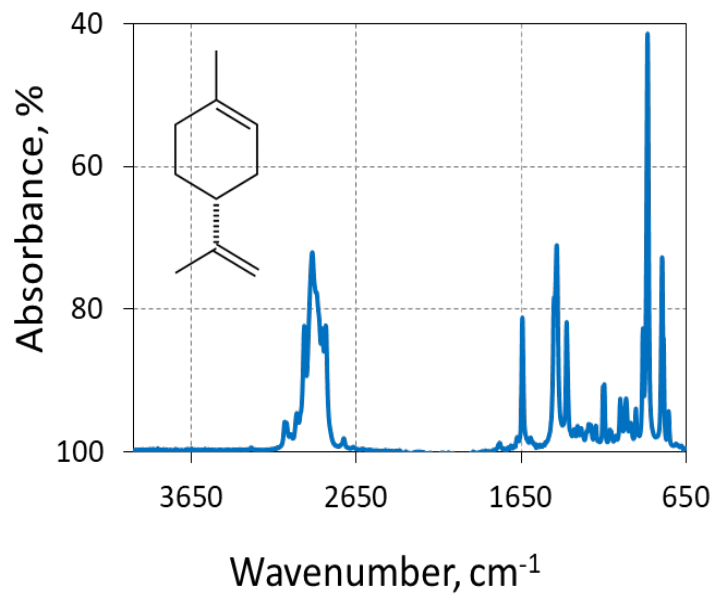


Figure 28: FTIR results of Limonene

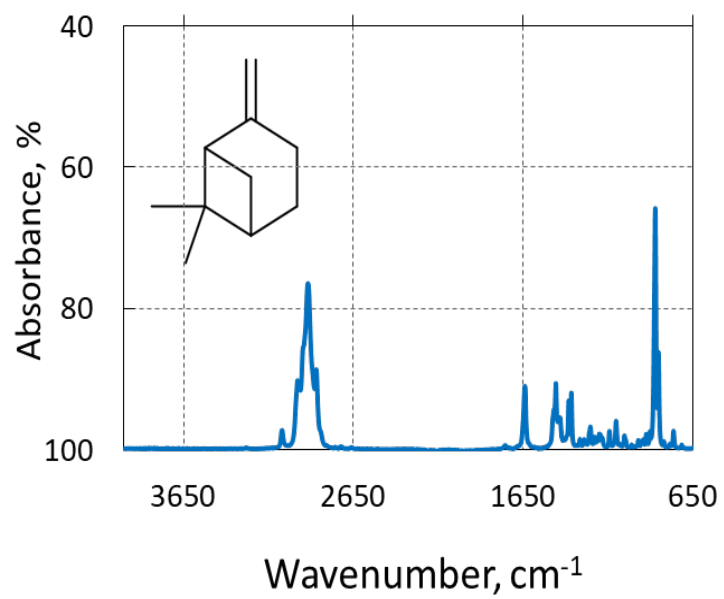


Figure 29: FTIR results of Pinene

APPENDIX C

CONTROL EXPERIMENTS FOR DETERMINATION OF WATER AND SOLVENT

CONTENT

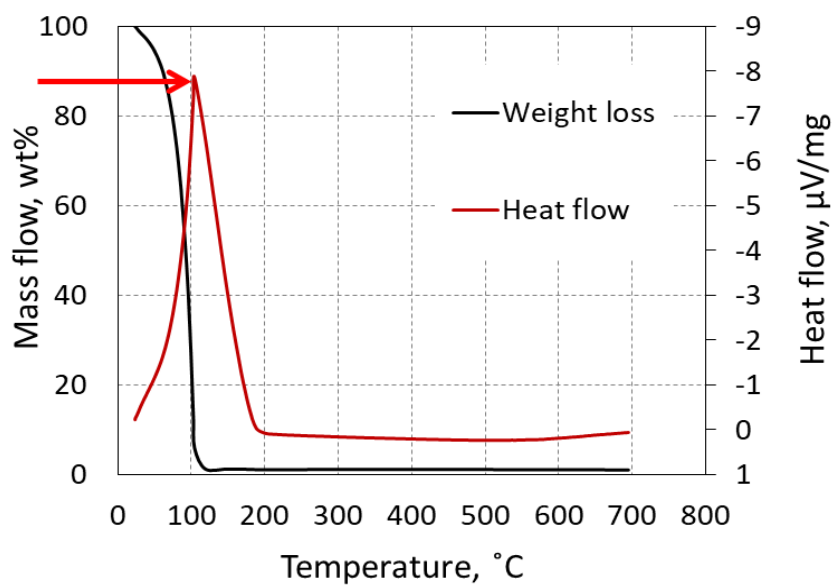


Figure 30: TGA/DSC graph of Water

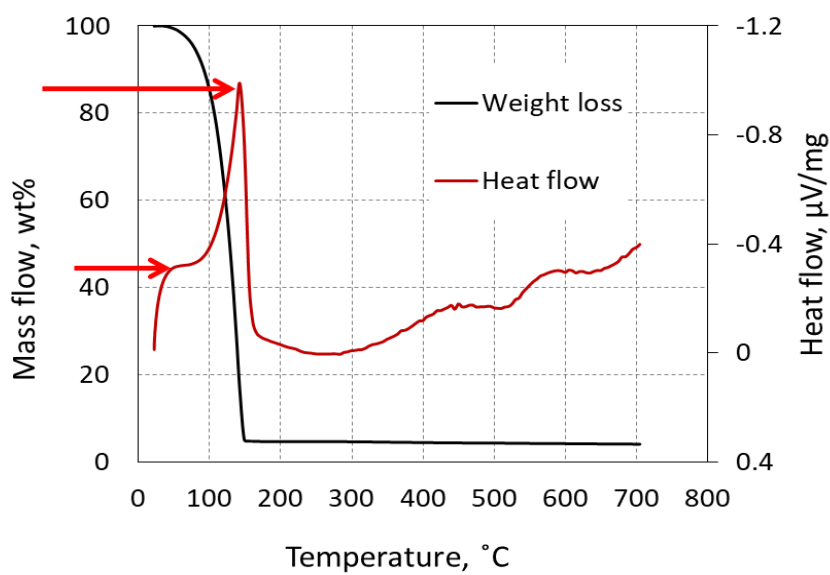


Figure 31: TGA/DSC graph for limonene

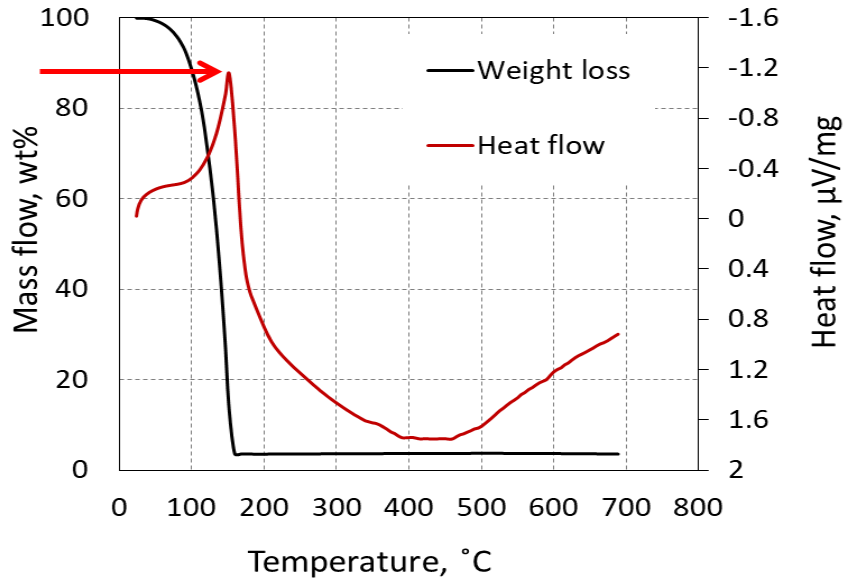


Figure 32: TGA/DCS graph for Pinene

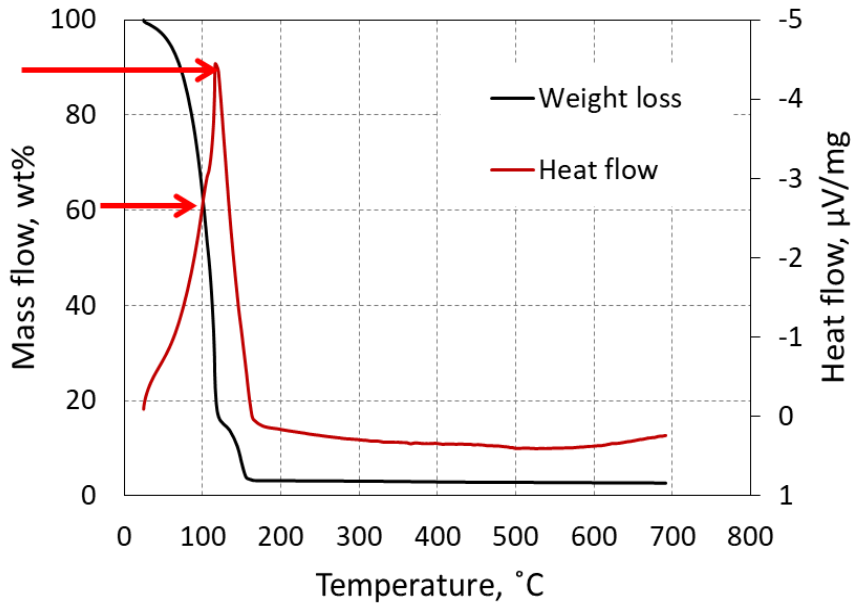


Figure 33: TGA/DSC graph for Limonene-Water mixture (1:1)

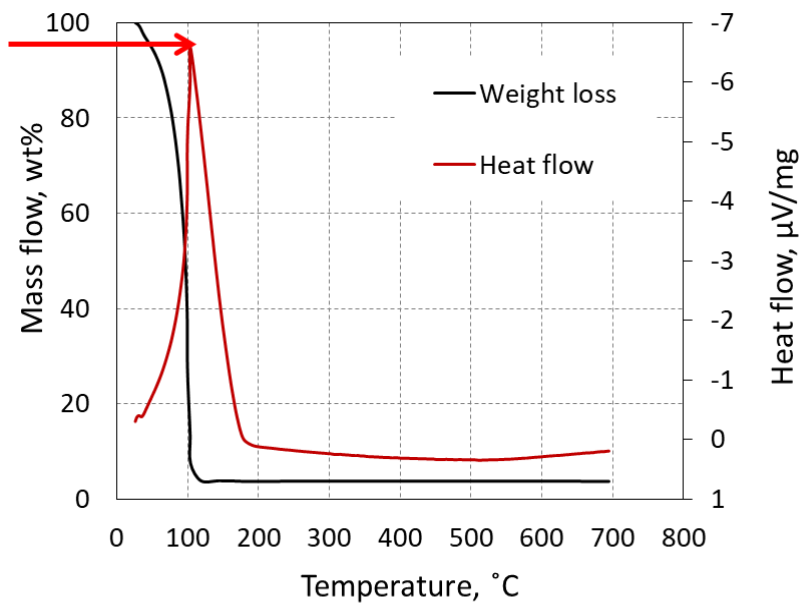


Figure 34: TGA/DSC graph for Pinene-Water mixture (1:1)

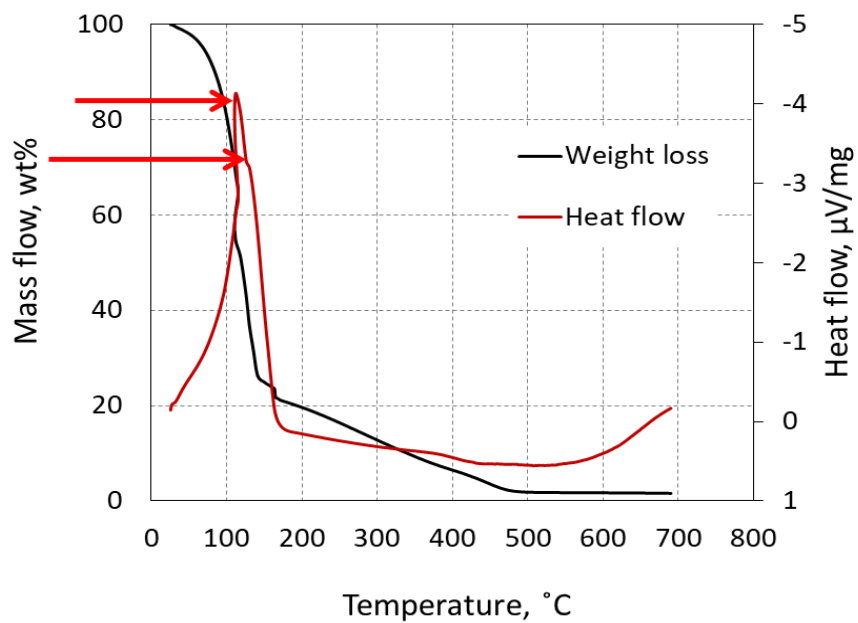


Figure 35: TGA/DSC graphs for Limonene-Water-Oil 1 (1:1:1)

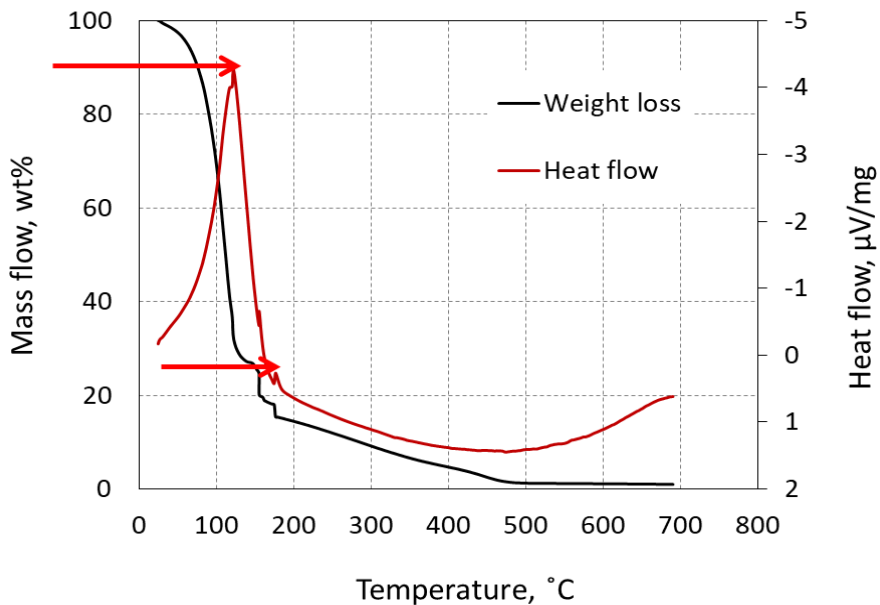


Figure 36: TGA/DSC graphs for Pinene-Water-Oil 1 (1:1:1)

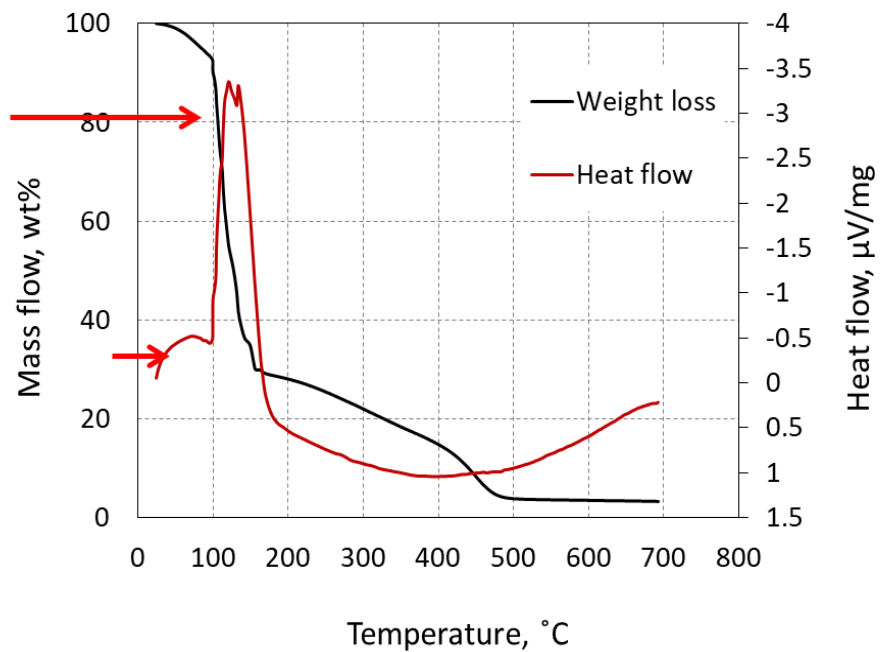


Figure 37: TGA/DSC graphs for Limonene-Water-Oil 2 (1:1:1)

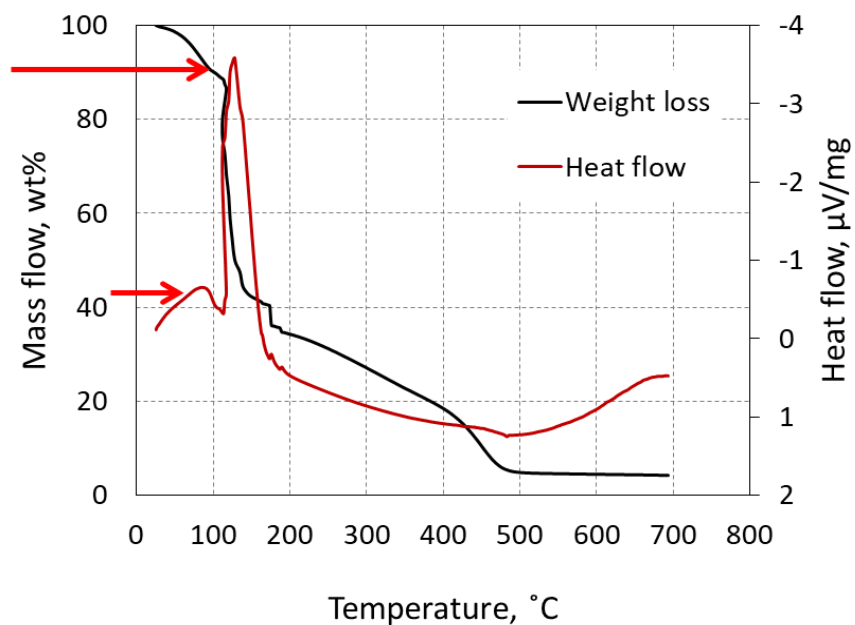


Figure 38: TGA/DSC graphs for Pinene-Water-Oil 2 (1:1:1)

Table 13: Summary of evaporation temperature ranges obtained from control experiments

Experiment type	Temperature range for Water loss	Temperature range for Solvent loss
CO2 injection on Oil 1	100-130	NA
Limonene injection on Oil 1	100-120	120-160
Pinene injection on Oil 1	100-120	150-160
Limonene injection on Oil 2	60-100	120
Pinene injection on Oil 2	70-100	120-130

