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Phase Behavior and Physical Properties of Athabasca Bitumen and Solvent Mixtures

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Phase Behavior and Physical Properties of Athabasca Bitumen and Solvent Mixtures

by

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Abstract

Solvent-aided thermal recovery techniques are gaining prominence for extracting bitumen and heavy oils. These methods involve co-injecting saturated steam and solvent into bitumen reservoirs. The phase behaviour of solvent and bitumen is crucial in designing and optimizing any solvent-assisted in-situ bitumen recovery.

This study investigates vapor-liquid equilibrium (VLE) between various solvents (including dimethyl ether DME, C_1, C_2, C_3, C_4, n- C_5, C_1/n-C_5, C_1/n-C_6, C_1/n-C_7, and C_1/ C_3+n-C_4+n-C_5) and Athabasca bitumen. Parameters such as equilibrium compositions (K-values), liquid-phase density, and viscosity were measured at temperatures up to 260 °C and pressures up to 6 MPa. Methane's solubility in bitumen showed minor temperature dependence (200, 230, and 260 ºC), while ethane, propane, and n-butane exhibited more significant temperature effects.

The study also compared co-injection of DME/steam to traditional steam and steam/butane injections in a 2D sand-pack saturated with Athabasca bitumen. Results indicated DME's efficacy in enhancing bitumen recovery, making DME and steam co-injection promising.

Another focus was the impact of solution gas (methane) on K-values in solvent/live bitumen and solvent dead bitumen systems. In the first stage of experiments, K-values, density and viscosity for methane/bitumen, propane/bitumen, and n-pentane/bitumen were measured. In the next step, methane, pentane, and bitumen were mixed at two concentrations (one with high and the other with low GOR live bitumen). Then K-value, density and viscosity of methane/n-hexane/bitumen and methane/n-

heptane/bitumen system were measured. In the final stage of experimental data collection, K-values, density and viscosity of methane/propane, n-butane, and n-pentane/bitumen system were measured.

The collected experimental PVT data of solvent and bitumen were modeled using PR-EoS, and experimental and calculated k-values of methane, propane, n-butane, n-pentane, n-hexane, and n-heptane data were compared for solvent/live bitumen and solvent dead bitumen system. Also, K-values of methane for methane /solvent(s) /bitumen and methane/bitumen systems were compared to study the effect of methane on the K-values of other hydrocarbon solvents. The results show the variation of methane and n-pentane K-values between various systems are within the experimental error, which means for the modeling and reservoir simulation purposes, we can use the K-values for any of these systems.

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To my parents,

Ebrahim and Shahrbanoo,

my wife, Narges,

and my daughter Lyanna

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Abbreviation

AAD	Average Absolute Deviation
AARD	Absolute Average Relative Deviation
BPI	Binary Interaction Parameter
CSS	Cyclic Steam Stimulation
GOR	Gas-Oil Ratio
MW	Molecular Weight
MAD	Maximum Absolute Deviation
N-solv	Hot solvent injection process
PR EoS	Peng-Robinson equation of state
PVT	Pressure-Volume-Temperature
SAGD	Steam Assisted Gravity Drainage
SOR	Steam-Oil Ratio
SG	Specific gravity
VAPEX	Vapour Extraction

Nomenclature

K	equilibrium K-value
N	Total number of components
P	pressure
R	gas constant
S	Saturation
T	temperature
V	volume
w	mass fraction
x	Mole fraction
y	mole fraction

Z	compressibility factor

Scripts

B	bitumen
c	critical
cal	calculated
corr	correlation
exp	experiment
g	gas
m	mixture
s	solvent
sc	standard condition
t	total

Greek letters

α	coefficient of bitumen density correlation
α	adjustable parameter in Lederer correlation
μ	Viscosity
ρ	Density

CHAPTER ONE:

1 Overview

1.1 Motivations, Objectives, Steps, and Organization

Currently, Canada holds an estimated 186 billion barrels of recoverable oil, with a significant portion existing in the form of natural bitumen commonly referred to as bitumen, tar sands, or oil sands. These reserves are predominantly located in Alberta. While thermal methods are presently the most practical means of heavy oil and bitumen recovery, they come with certain drawbacks such as high greenhouse gas (GHG) emissions and energy consumption.

To mitigate the disadvantages associated with thermal bitumen processes, various solvent-based techniques, both with and without the use of steam, have been proposed and developed. The addition of solvents to steam has shown promise in enhancing the efficiency of in-situ thermal recovery methods by reducing energy intensity and water consumption. Several methods have been introduced, including pure solvent injection (N-Solv), warm vapor extraction (VAPEX)[1], Enhanced Solvent Extraction Incorporating Electromagnetic Heating (ESEIEH)[2,3], and expanding solvent SAGD

(ES-SAGD)[4], among others. These approaches aim to optimize the recovery process while minimizing its environmental impact.

Figure 1-1 shows how by adding 3.5 mass% (24.5 mole%) of butane we can reduce the viscosity of the bitumen from 9 to 5.5 mPa.s at 200 °C. This viscosity reduction is the same as increasing the temperature of bitumen from 200 to 230 °C. This is one the examples of how we can reduce the energy consumption (and as a result GHG emission) by using solvent(s) in the bitumen recovery process.

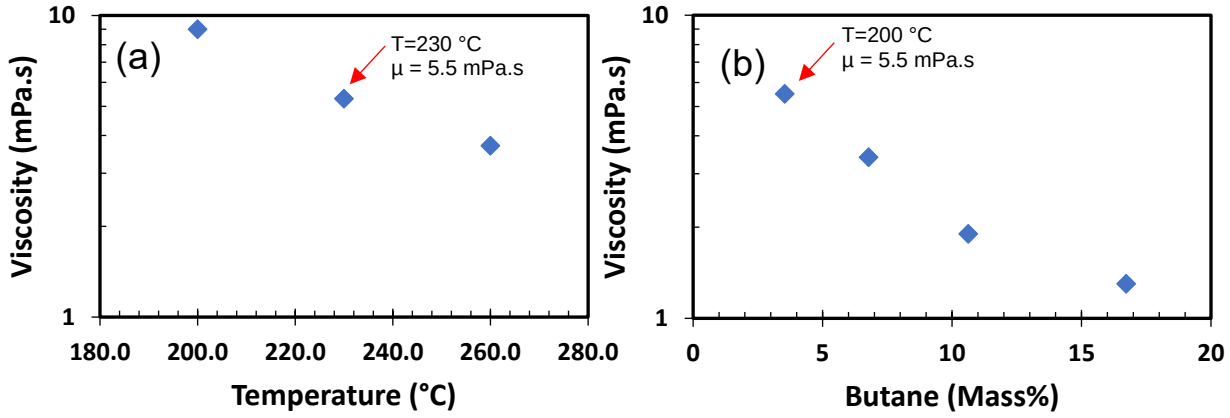


Figure 1-1: Viscosity of bitumen vs a) Temperature and b) Butane concentration.

The presence of gases either from ex-solution of the solution gas from bitumen or generated as a result of aquathermolysis is well-known to retard the SAGD performance[1,2]. An essential challenge in reservoir simulation of thermal recovery processes has been the need for more reliable PVT data (viscosity, density, k-values) that incorporate the effect of solution gas. This challenge becomes more imperative when a solvent is also injected in conjunction with steam.

[1] Hassanzadeh, H., Harding, T.G., Moore, R.G., Mehta, S.A. and Ursenbach, M.G., 2016. Gas generation during electrical heating of oil sands. *Energy & Fuels, 30(9), pp.7001-7013.*

[2] *Hassanzadeh, H., Rabiei Faradonbeh, M. and Harding, T., 2017. Numerical simulation of solvent and water assisted electrical heating of oil sands including aquathermolysis and thermal cracking reactions. AIChE Journal, 63(9), pp.4243-4258.*

There needs to be more experimental data relevant to solution gas/solvent/bitumen systems. The literature does not include a complete set of experimental data for multi-component solvents such as gas condensate and diluents. The quantitative effects of the presence of solution gas on the phase behavior, viscosity and density of solvent-bitumen systems also demand further research. This understanding is a prerequisite for determining the optimal solvent composition for solvent assisted processes. Knowledge of the phase equilibrium properties of solution gas/bitumen/solvent mixtures is essential for designing and optimizing recovery processes for viscous bitumen from the Alberta oil sands.

This study investigates the vapor-liquid equilibrium of light hydrocarbons (methane, ethane, propane and butane)-bitumen mixtures at temperatures above 200 °C, as well as various n-alkane/bitumen and methane/ n-alkane/bitumen systems were studied and their phase behavior and thermophysical properties such as density and viscosity are modeled by various thermodynamic models. Also, the vapor-liquid equilibrium of DME - bitumen mixtures at temperatures up to 190 °C were studied. In addition, the performance of DME as a solvent for bitumen recovery was evaluated by conducting a series of experiments using a 2D sand-pack with steam, DME/steam and butane/steam systems.

We defined the following main steps to accomplish the goals of this work:

1) Designing, fabricating and validating a PVT apparatus to collect comprehensive phase behavior data for multicomponent solvent/bitumen systems with and without solution gas.

2) Measuring the vapor-liquid equilibrium data such as the composition of each phase, density and viscosity of the liquid phase for solvent (DME, methane, ethane, propane, n-C_4, and n-C_5)/bitumen and methane/solvent (n-C_5, n-C_6, n-C_7, and n-C_5+n-C_6+n-C_7)/bitumen mixtures at temperatures and pressures up to 260 °C, and 4 MPa, respectively.
3) Development of a thermodynamic model to predict the solvent(s) K-value and density and viscosity of liquid phase at wide ranges of temperature and pressure.
4) Designing and fabricating a 2D sand-pack model to collect data for steam and solvent/steam co-injection experiments.
5) Evaluating the DME as a solvent for bitumen recovery by conducting a series of experiments using a 2D sand-pack with steam, DME/steam and butane/steam systems.

This work's measured experimental phase behavior data fill the data gaps of live-bitumen/solvent systems. Various experiments were conducted for solvent/bitumen and methane/solvent(s)/bitumen systems to collect, compare and model these various systems.

1.2 Dissertation Outline

This dissertation comprises six chapters. Chapter one includes the introduction, Chapters two to five are the core material of the thesis, followed by conclusions with recommendations presented in Chapter six.

Chapter 2 is dedicated to solubility, modeling and viscosity measurements for methane-, ethane-, propane- and butane/bitumen systems at temperatures up to 260 ºC. This chapter has been published in the Journal of Chemical & Engineering Data.[3]

Chapter 3 presents the experimental phase behavior data and modeling of the dimethyl ether/Athabasca bitumen system. The solubility of DME in bitumen and the density of the liquid phase were represented by PR-EoS, and the viscosity data were correlated by Pederson corresponding state model. This chapter has been published in The Canadian Journal of Chemical Engineering.[4]

The capability of DME as a solvent for bitumen recovery processes was evaluated in chapter 4 by conducting a series of experiments using a 2D sand-pack with steam, DME/steam and butane/steam systems. This chapter has been presented at SPE Canada Heavy Oil Technical Conference.[5]

The effect of methane on the K-values of other hydrocarbon solvents is studied in Chapter 5. In this chapter, the K-value, density, and viscosity of methane / solvent (n-C_5, n-C_6, n-C_7, and n-C_3+n-C_4+n-C_5) / bitumen are measured and modeled. The k-values of methane, n-C_3, and n-C_5 were compared in live and dead bitumen systems.

[3] Haddadnia, A., Sadeghi Yamchi, H., Zirrahi, M., Hassanzadeh, H. and Abedi, J., 2018. New solubility and viscosity measurements for methane–, ethane–, propane–, and butane–Athabasca bitumen systems at high temperatures up to 260° C. *Journal of Chemical & Engineering Data*, *63*(9), pp.3566-3571.

[4] Haddadnia, A., Azinfar, B., Zirrahi, M., Hassanzadeh, H. and Abedi, J., 2018. Thermophysical properties of dimethyl ether/Athabasca bitumen system. *The Canadian Journal of Chemical Engineering*, *96*(2), pp.597-604.

[5] Haddadnia, A., Zirrahi, M., Hassanzadeh, H. and Abedi, J., 2018, March. Dimethylether-a promising solvent for ES-SAGD. Paper presented at the SPE Canada Heavy Oil Technical Conference, Calgary, Alberta, Canada, March 2018. Paper Number: SPE-189741-MS, https://doi.org/10.2118/189741-MS.

Finally, Chapter 6 summarizes the results and contributions of this study and suggests recommendations for future work.

CHAPTER TWO:

2 Phase Behaviour of Methane-, Ethane-, Propane- and Butane- Athabasca Bitumen Systems at High Temperatures[6]

This chapter has been published in a peer-reviewed journal entitled "New Solubility and Viscosity Measurements for Methane-, Ethane-, Propane- and Butane- Athabasca Bitumen Systems at High Temperatures up to 260 ºC". H. Sadeghi Yamchi, M. Zirrahi, H. Hassanzadeh, and J. Abedi co-authored this manuscript. Since this dissertation has been prepared in paper-based format, unavoidably, there are some repetitive parts in each chapter, mainly Chapters 2, 3, and 5, such as experimental setup and characterization descriptions.

This chapter studies vapor liquid equilibrium (VLE) of methane, ethane, propane, and butane/bitumen systems.

2.1 Abstract

One of the important mechanisms in solvent aided thermal recovery processes is viscosity reduction due to dissolution of solvent in the bitumen. This dissolution occurs either with the

[6] Haddadnia, A., Sadeghi Yamchi, H., Zirrahi, M., Hassanzadeh, H. and Abedi, J., 2018. New solubility and viscosity measurements for methane–, ethane–, propane–, and butane–Athabasca bitumen systems at high temperatures up to 260° C. Journal of Chemical & Engineering Data, 63(9), pp.3566-3571.

condensed solvent at the edge of the steam chamber or with direct contact of gaseous solvent and bitumen. Therefore, it is essential to determine the solubility and viscosity of solvent in bitumen for reservoir simulation of solvent-aided thermal recovery processes. In this paper, we report new experimental viscosity and solubility data of methane-, ethane-, propane- and butane- Athabasca bitumen systems at high temperatures (up to 260 ºC). The experimental measurements have been conducted in liquid-vapour equilibrium conditions. Peng-Robinson Equation of State (PR EoS) was employed to model the solubility data. The tuned PR-EoS represented the experimental solubility data of methane, ethane, propane, and n-butane in bitumen with absolute average relative devotion (AARD) of 5.7, 4.1, 7.8 and 4.9%, respectively. The reported data find applications in reservoir simulation studies of the solvent-aided thermal recovery processes.

2.2 Introduction

Introducing solvent to steam has been proposed as a method to improve the economics of the steam assisted gravity drainage (SAGD) by reducing energy intensity and lowering the need for excessive water treatment. The application of various solvents with steam has been widely investigated. Kar et al.[5] studied and analyzed the performance of SAGD and propane-SAGD injection in 2D and 1D physical models. They observed an enhancement in the oil production as well as quality of the produced oil with co-injection of propane and steam due to the better development of the steam chamber.

Sabet et al.[6] performed mathematical studies on solvent-steam co-injection bitumen recovery processes. They conducted that solvents with carbon number range between 7-9 results in earlier onset of convective dissolution of solvent in bitumen. Nourozieh et al.[7] measured and modeled the solubility and saturated-liquid density and viscosity of methane/Athabasca bitumen mixtures for

temperatures up to 190 °C and maximum pressure of 10 MPa. The authors concluded that the effect of solubility of methane into bitumen is negligible at high temperatures.

Simulation studies of solvent and steam injection suggest that higher production rates and ultimate recovery can be achieved. Govind et al.[8] performed simulation studies of ES-SAGD with different solvents at various concentrations and operating conditions. Their work demonstrated that injection of butane can have more advantages compared to the other solvents since it has higher vapor pressure with significant solubility in bitumen. They also suggested that high operating pressure is favourable and the concentration of the co-injected solvents needs to be optimized.

Simulation work carried out by Ardali et al.[9] showed that solvents heavier than butane can improve the heavy oil recovery. In a simulation study, Sheng et al.[10] demonstrated that DME as a water soluble solvent results in higher recovery factor than butane co-injection. Zare et al.[11] also investigated the effect of hydrocarbon solvents co-injection on heavy oil recovery and reported that hexane results in better oil recovery.

One of the essential aspects of solvent-aided processes is to determine how effective a solvent can alter the thermophysical properties of bitumen. In order to determine the impact of solvent on mixture viscosity, solubility of solvents in bitumen need to be measured. A comprehensive review on solvent solubility (methane, ethane, propane and butane) in different bitumen samples has been reported by Zirrahi[12]. Fu et al.[13] reported solubility measurements of methane and ethane in Cold Lake bitumen at 150 °C. Kariznovi et al.[14] reported measured saturated phase densities and viscosities of a bitumen sample with methane and ethane over the temperature ranges of 50 to 190 °C and pressures up to 8 MPa. Badamchi-Zadeh et al.[15] tested the Athabasca bitumen with propane and determined the solubility of solvent as well as the densities and viscosities of the

mixtures for limited range of temperatures of 10 to 50 °C. In a similar approach, Jossy et al.[16] captured the phase partitioning of the propane bitumen systems at low temperatures of 10 and 40 °C. The existence of two phases in propane bitumen mixtures was also reported by Frauenfeld[17].

Detailed phase behaviour experiments of propane and Athabasca bitumen was conducted by Nourozieh et al.[18] over the temperature ranges of 50 to 200 °C and pressures up to 10 MPa. Solubility, density and viscosity measurements were performed, and phase boundaries were detected. Both vapour-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) were observed in their experiments. Han et al.[19] studied vapour-liquid equilibrium (VLE) of supercritical propane and bitumen to investigate the effect of dissolved gases on thermophysical properties of bitumen.

Recently, Zirrahi et al.[20] and Haddadnia et al.[21] measured the solubility of light n-alkanes including C_1, C_2, C_3, n-C_4, and DME for MacKay River bitumen at pressures and temperatures up to 5MPa and 190 °C, respectively. The effect of solvent on thermophysical properties of bitumen was discussed and the investigated solvent-bitumen systems were modelled using the Peng-Robinson EoS.

To the best of our knowledge, solubility and viscosity data of methane-, ethane-, propane-, and butane- Athabasca bitumen mixtures at temperature range of 200-260 °C have not been reported in the literature. In this study, we report new solubility and viscosity measurements of methane-, ethane-, propane- and butane- Athabasca bitumen systems at high temperatures up to 260 °C. These data find applications in reservoir simulation of solvent-aided thermal recovery processes.

In the following sections, experimental setup and procedure will be described and results will be presented and discussed.

2.3 Experimental Details

2.3.1 Material

Research grade (purity higher than 99.995) of methane, ethane, propane and n-butane were purchased from Praxair Canada. All the solvents were used without further purification. Athabasca bitumen from MacKay River formation was provided by an oil producer located in Calgary, Alberta, Canada. The average molecular weight of the bitumen sample has been reported as 512±6.9 g/mol. The detailed data related to density, viscosity, molecular weight, and compositional analysis of the bitumen sample can be found in our previous work from zirrahi et al[22].

2.3.2 Experimental setup

Figure 2-1 shows the schematic diagram of the experimental apparatus. The main component of this apparatus is an equilibrium cell equipped with a magnetic mixer. An in-line Hydramotion viscometer with accuracy of 1% was used to measure the viscosity of the liquid phase. The setup has been placed in a Blue-M oven with accuracy of ±1 ºC. An Isco pump model 500D was used to inject the solvent and keep the pressure constant inside the equilibrium cell. For sampling and liquid phase receiving, a Quizix pump with accuracy of ±0.001 cm^3 was used. A sample cell and a transfer cell placed outside of the oven for receiving the liquid phase and taking the sample in each experiment. For sampling, the Quizix pump received the saturated bitumen phase while the Isco pump were used to charge the solvent into the system to keep the pressure constant to prevent solvent ex-solution. While filling the receiving and sampling cells, viscosity of liquid phase was recorded. The setup was validated with the solubility data of light n-alkanes in bitumen and ethane in toluene reported in the literature for temperatures up to 200 °C[20,23].

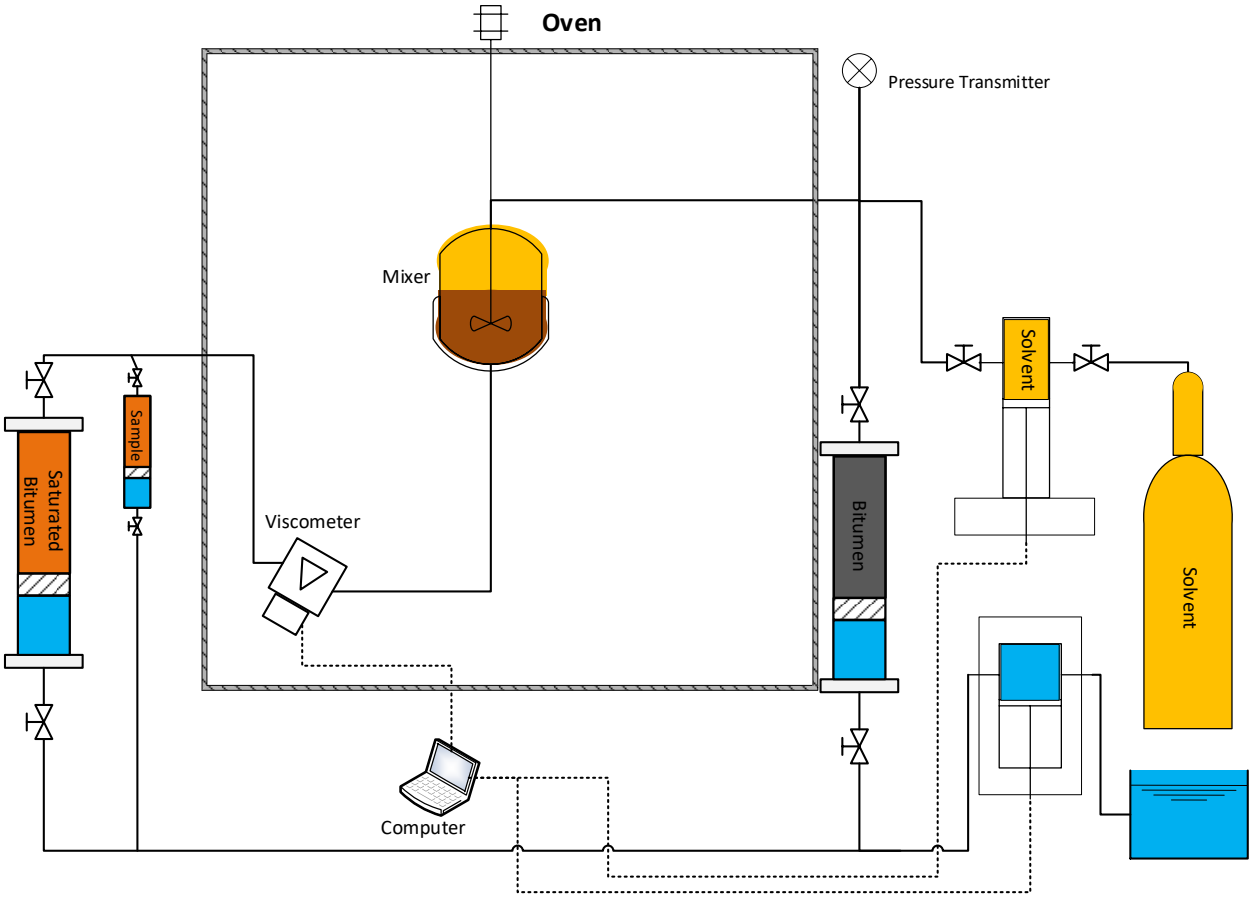


Figure 2-1: Schematic of the implemented experimental setup.

2.3.3 Experimental procedure

Prior to any measurements, all the parts in the system including the equilibrium cell, viscometer and connecting lines were washed with toluene and dried by acetone to prevent any contaminations. The bitumen sample was then charged into the equilibrium cell and the system was purged and vacuumed with the solvent for several times to ensure no air was trapped. In order to saturate the bitumen with solvent (C_1, C_2, C_3, or n-C_4), the oven was first set and brought up to the desired temperature and then the solvent was injected by the Isco pump into the equilibrium cell (mixer cell).While the bitumen sample and the solvent were mixed by the magnetic mixer attached to the equilibration cell, the pump was kept running at a desired constant pressure to make

up for the dissolution of the solvent in the bitumen until the equilibrium was achieved (i.e. the flow rate reading on the pump dropped and remained on zero).

After reaching the equilibrium, the mixing process was stopped, and a two-hour time period was given to allow segregation of possible gas bubbles in the liquid phase. Then, the bitumen-rich phase was discharged from bottom of the cell using the Quizix pump with a very low flow rate of 5 ml/min while the pressure of solvent vapour on top of the cell was kept constant in a way that the equilibrium was not disturbed and the viscosity of the fluid was recorded. Then, a specific amount of the fluid was collected into the sample cell for measurement of the solvent solubility in bitumen.

The sample of solvent-saturated bitumen was flashed at atmospheric conditions and volume of the evolved gas and weight of the remained bitumen were measured and used along with the density of gas at ambient conditions to calculate the solvent solubility. A Chandler engineering gasometer (model 2331) with 0.2 % accuracy was applied to measure the volume of the evolved gas. Sample was heated up to expedite the process and to ensure of thorough evaporation of the gas from the mixture.

2.4 Result and discussion

In the present work, high temperature (>200 °C) experimental data including solubility of light alkanes (methane, ethane, propane, and n-butane) in MacKay River bitumen as well as viscosities of the solvent-saturated bitumen have been measured.

Table 2-1 presents new viscosity data of raw bitumen at temperatures ranging from 200 to 260 °C and pressures as high as 8 MPa. It was found that the viscosity of bitumen at investigated temperatures and pressures can be less than 10 cP and it can be as low as 3.5 cP at 260 °C.

Table 2-1: Viscosity data of raw MacKay Bitumen at temperatures between 200 and 260 °C and pressures between 1 and 8 MPa.[a]

Temperature (°C)	Pressure (MPa)	Viscosity (cP)
200	8	9.7
200	7	9.6
200	6	9.5
200	5	9.3
200	4.5	9.2
200	4	9.1
200	3	9
200	2	8.8
200	1.5	8.7
200	1	8.6
230	8	5.8
230	7	5.7
230	6	5.6
230	5	5.5
230	4.5	5.5
230	4	5.4
230	3	5.3
230	2	5.2
230	1.5	5.2
230	1	5.1
260	8	4.1
260	7	4
260	6	4
260	5	3.9
260	4.5	3.8
260	4	3.8
260	3	3.7
260	2	3.6
260	1.5	3.6
260	1	3.5

[a] Standard uncertainties u are u(T)=0.1 °C, u(P)=0.008 MPa, and the relative expanded uncertainty Ur is Ur(μ)=0.01. (μ is the viscosity of bitumen).

Viscosities of the saturated bitumen with methane, ethane, propane, and n-butane and the corresponding solubilises are reported in Table 2-2 to Table 2-5 and the solubility data are shown in Figure 2-2 and Figure 2-3. The solubility of methane in bitumen was found to be less sensitive to the temperature at the experimental condition but it increases significantly with pressure (Figure

2-2a). For C_2, C_3, and n-C_4 the effect of temperature on the solubility becomes noticeable indicating that the solubility of heavier solvents can decrease with increasing temperature (Figure 2-3).

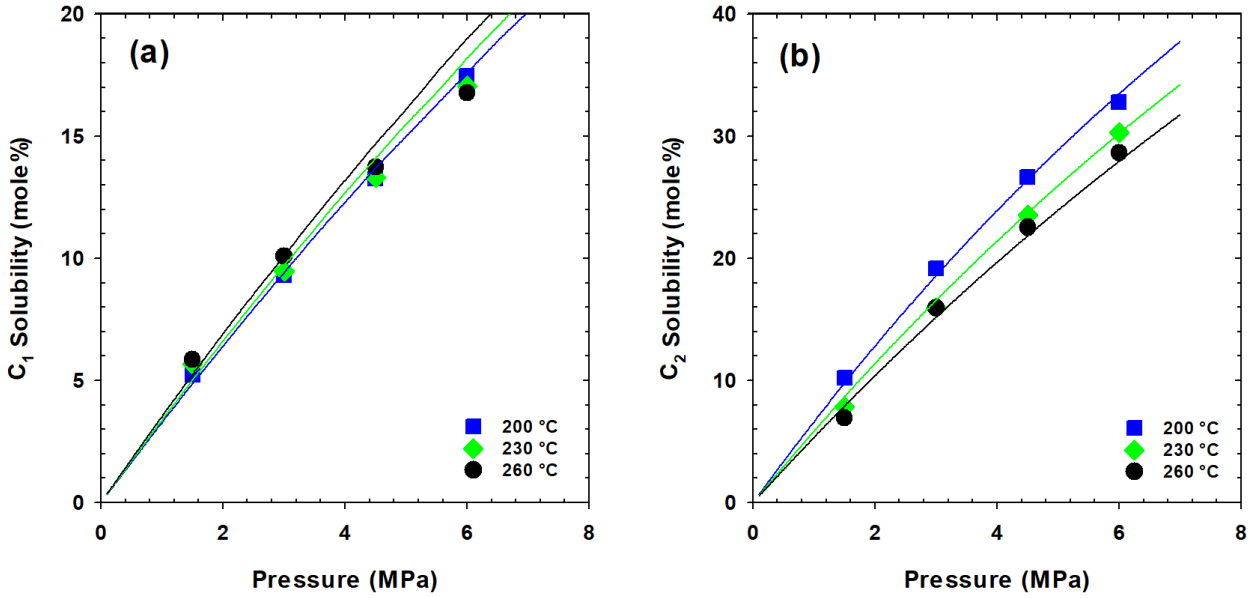


Figure 2-2: Solubility of a) methane and b) ethane in Athabasca bitumen as a function of pressure at various temperatures; ■, ◆, ●, experiment data, — model prediction.

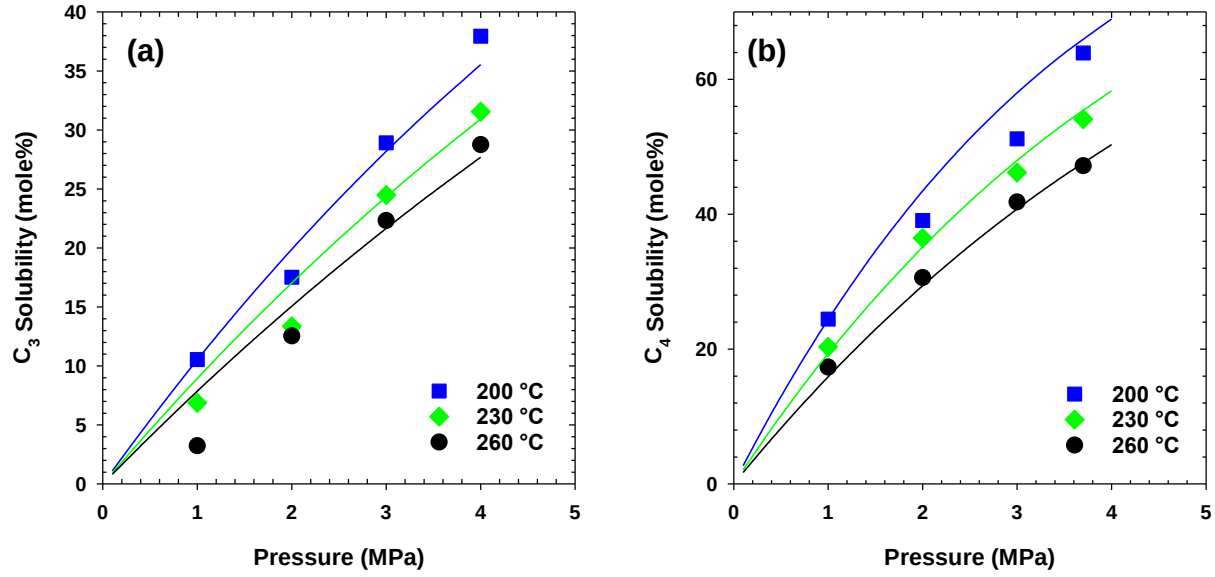


Figure 2-3: Solubility of a) propane and b) n-butane in bitumen as a function of pressure at various temperatures; ■, ◆, ●, experiment data, — model prediction.

The Peng-Robinson equation of state (PR-EoS) was utilized to model and regenerate the experimental solubility data of the solvents in the bitumen. Details of calculations, critical properties, and the acentric factor of the bitumen can be found in reference 18.

$$P = \frac{RT}{V-b} - \frac{a\alpha(T)}{V(V+b)+b(V-b)} \quad \text{2-1}$$

Where

$$a = \frac{0.4572R^2T_c^2}{P_c} \quad \text{2-2}$$

$$\alpha(T) = [1 + k(1 - T_r^{0.5}]^2 \quad \text{2-3}$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad w < 0.49 \quad \text{2-4}$$

$$k = 0.37464 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3 \qquad w \geq 0.49 \quad \text{2-5}$$

Here, T_c, P_c and ω represent the critical temperature, critical pressure, and acentric factor of the bitumen, respectively. The acentric factor and critical temperature of the bitumen were calculated using the correlation provided by Riazi and Al-Sahhaf (1996)[24]. Critical pressure was tuned to match the experimental density of bitumen at room temperature. Additionally, the critical pressure was adjusted to match the experimental density of bitumen at room temperature. The molecular weight of MacKay River bitumen was measured using the freezing point depression method. To apply the PR-EoS for mixture of solvent and bitumen, the classical van der Waals mixing rules were employed, as proposed by Peng and Robinson (1976)[25]:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j (1 - k_{ij})} \quad \text{2-6}$$

$$b = \sum_i x_i b_j \quad \text{2-7}$$

The binary interaction parameter k_{ij} between solvent and bitumen was tuned to match the experimental solvent dissolution in bitumen. Furthermore, the binary interaction parameter between solvent and bitumen was assumed to be linearly dependent on the temperature as follows:

$$k_{ij} = A \times T(K) + B \quad \text{2-8}$$

The parameters A and B for different solvent-bitumen systems were calculated in the following paragraph.

Half of the experimental solubility data was selected and used to tune the model. In the case of methane, it was found that k_{ij} is related to the temperature (T) as $k_{ij} = -1.098 \times 10^{-3} T\,(K) + 0.3366$. As it is shown in the Figure 2-2(a) the model underestimates the experimental data, but this error was found to be low and the absolute average relative deviation (AARD) between the calculated solubility values and experimental data was determined as 5.6% indicating an acceptable agreement between model predictions and the experimental solubility data.

For the case of ethane, the binary interaction parameter was found as a constant value of $k_{ij} = -0.0656$. As illustrated in Figure 2-2 (b) the model can accurately predict experimental data with an AARD of 4.1%.

To regenerate the experimental solubility data of propane in bitumen, $k_{ij} = -4.551 \times 10^{-5}\, T(K) + 0.0088$ was found. The comparison of the model and the experimental data are presented in the Figure 2-3(a). Figure 2-3(a) shows that while the predictions of the PR-EoS at pressures above 3 MPa are in agreement with the experimental data, the predictions at lower pressures show deviation, which results in AARD of 7.9%.

The binary interaction coefficient of butane/bitumen system as a function of temperature was determined as $k_{ij} = -1.222 \times 10^{-4} T - 0.0025$. The comparison between the model and experimental solubility data is shown in Figure 2-3(b). Predictions of the model are in good agreement with the experimental data at higher temperatures of 230 and 260 °C. However, the PR-EoS overestimates the solubility of butane in bitumen at lower temperature of 200 °C. The AARD between the model predictions and the experimental solubility data was found to be 4.9%.

Table 2-2: Solubility of methane in bitumen and viscosities of saturated MacKay bitumen at high temperatures of 200 to 260 °C and pressures between 1.5 and 6 MPa.[a]

Temperature (°C)	Pressure (MPa)	Viscosity (cP)	Solubility (mole%)
200	6	7.1	17.5
	4.5	7.5	13.2
	3	7.9	9.3
	1.5	8.4	5.2
230	6	4.4	17.1
	4.5	4.6	13.3
	3	4.8	9.5
	1.5	5.1	5.7
260	6	3	16.8
	4.5	3.2	13.7
	3	3.3	10.1
	1.5	3.5	5.8

[a] Standard uncertainties u are u(T)=0.1 °C, u(P)=0.008 MPa, and u(x)=0.1 and the relative expanded uncertainty Ur is Ur(μ)=0.01. (μ is the viscosity of methane-saturated bitumen, and x is the mole percent of methane in bitumen.)

Table 2-3: Solubility of ethane in bitumen and viscosities of saturated MacKay bitumen at high temperatures of 200 to 260 °C and pressures between 1.5 and 6 MPa.[a]

Temperature (°C)	Pressure (MPa)	Viscosity (cP)	Solubility (mole%)
200	6	4.6	32.8
	4.5	5.5	26.6
	3	6.2	19.2
	1.5	7.2	10.2
230	6	3	30.3
	4.5	3.5	23.6
	3	3.9	15.9
	1.5	4.5	7.9
260	6	2.3	28.6
	4.5	2.6	22.5
	3	2.9	15.9
	1.5	3.3	6.9

[a] Standard uncertainties u are u(T)=0.1 °C, u(P)=0.008 MPa, and u(x)=0.1 and the relative expanded uncertainty Ur is Ur(μ)=0.01. (μ is the viscosity of ethane-saturated bitumen, and x is the mole percent of ethane in bitumen.)

Table 2-4: Solubility of propane in bitumen and viscosities of saturated MacKay bitumen at high temperatures of 200 to 260 °C and pressures between 1 and 4 MPa.[a]

Temperature (°C)	Pressure (MPa)	Viscosity (cP)	Solubility (mole%)
200	4	3.3	37.9
	3	4.2	28.9
	2	5.4	17.5
	1	6.9	10.5
230	4	2.6	31.5
	3	3.1	24.5
	2	3.8	13.4
	1	4.6	6.9
260	4	2	28.7
	3	2.4	22.3
	2	2.8	12.5
	1	3.1	3.2

[a] Standard uncertainties u are u(T)=0.1 °C, u(P)=0.008 MPa, and u(x)=0.1 and the relative expanded uncertainty Ur is Ur(μ)=0.01. (μ is the viscosity of propane-saturated bitumen, and x is the mole percent of propane in bitumen.)

Table 2-5: Solubility of butane in bitumen and viscosities of saturated MacKay bitumen at high temperatures of 200 to 260 °C and pressures between 1and 3.7 MPa.[a]

Temperature (°C)	Pressure (MPa)	Viscosity (cP)	Solubility (mole%)
200	3.7	1.3	63.9

	3	1.9	51.2
	2	3.4	39.1
	1	5.5	24.4
230	3.7	1.5	54.1
	3	2.1	46.2
	2	2.7	36.5
	1	3.9	20.3
260	3.7	1.4	47.2
	3	1.7	41.8
	2	2.2	30.6
	1	2.9	17.3

[a] Standard uncertainties u are u(T)=0.1 °C, u(P)=0.008 MPa, and u(x)=0.1 and the relative expanded uncertainty Ur is Ur(μ)=0.01. (μ is the viscosity of butane-saturated bitumen, and x is the mole percent of butane in bitumen.)

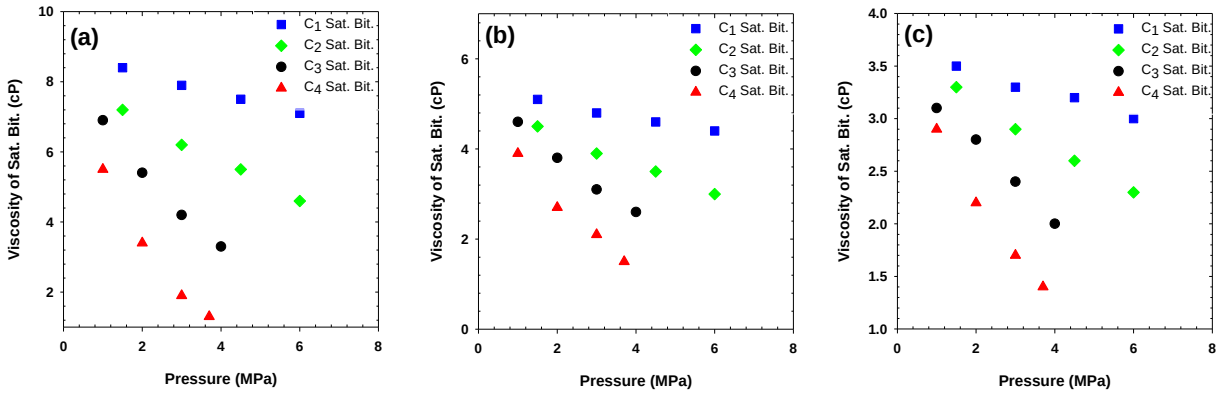


Figure 2-4: Viscosity of the solvent-saturated bitumen versus pressure for different solvents at a) 200, 230, and c) 260 ºC.

Figure 2-4 shows the viscosity of the solvent-saturated bitumen with versus pressure at 200, 230, and 260 ºC for different solvents of methane, ethane, propane, and butane. As expected, the viscosity reduction due to dissolution of solvent in bitumen is more pronounced for heavier solvents (i.e. C_3 and C_4). This is because of higher solvent dissolution in bitumen phase at a desired temperature and pressure. It should also be noted that the higher slope of viscosity curve versus pressure at lower temperatures indicates that the effect of solvent is more pronounced at lower temperature conditions.

2.5 Summary and Conclusions

In this work, solubilities of gaseous solvents including methane, ethane, propane, and n-butane in Athabasca bitumen at high temperatures up to 260 °C were measured and the Peng-Robinson EoS was employed to model the solubility data. In addition, viscosity of the Athabasca raw bitumen as well as the solvent-saturated bitumen viscosities were measured at high temperatures of 200, 230, and 260 ºC and pressures ranging from 1 to 6 MPa. It was found that solubility of methane in bitumen varies slightly with temperature at the experimental condition. However, pressure can highly affect the methane solubility in bitumen. The results showed that the effect of temperature is more evident on solubility of ethane, propane and n-butane in bitumen compared to solubility of methane. It was found that solubility of heavier solvents in bitumen decreases significantly at high temperatures. This is particularly, more evident at higher pressures. The results also revealed that the PR-EoS can regenerate the solubility data of methane, ethane, propane, and butane in bitumen at the experimental condition with AARD errors of 5.7, 4.1, 7.8 and 4.9%, respectively. However, it slightly under-predicts the solubility data. The results revealed that the raw bitumen viscosity can be lowered to less than 10 cP in the temperature range of 200 to 260 °C. This viscosity can further be reduced by several units by saturating the bitumen with a gaseous solvent such as of C_1, C_2, C_3, or n-C_4. The results presented finds applications in solvent-aided recovery processes of bitumen.

CHAPTER THREE:

3 Thermophysical Properties of Dimethyl Ether/Athabasca Bitumen System[7]

This chapter has been published in a peer-reviewed journal entitled "Thermophysical Properties of Dimethyl Ether/Athabasca Bitumen System". B. Azinfar, M. Zirrahi, H. Hassanzadeh, and J. Abedi co-authored this manuscript. Since this dissertation has been prepared in paper-based format, unavoidably, there are some repetitive parts in each chapter, mainly Chapters 2, 3, and 5, such as experimental setup and characterization descriptions.

This chapter studies vapor liquid equilibrium (VLE) of dimethyl ether/ bitumen system.

3.1 Abstract

Solvent-aided thermal recovery processes have recently gained the practical and research interests among other thermal recovery methods due to their reduced environmental footprint and superior energy efficiency. One of the main challenges in design of solvent-based methods is selection of an appropriate solvent that maximizes the bitumen and solvent recoveries. This study attempts to

[7] Haddadnia, A., Azinfar, B., Zirrahi, M., Hassanzadeh, H. and Abedi, J., 2018. Thermophysical properties of dimethyl ether/Athabasca bitumen system. *The Canadian Journal of Chemical Engineering*, *96*(2), pp.597-604.

introduce dimethyl ether (DME) as a non-conventional solvent for heavy oil and bitumen recovery. To investigate the performance of the proposed solvent, thermophysical properties of DME/bitumen is studied. Vapor-liquid equilibrium measurements including solubility, density, and viscosity are performed at three temperatures (100, 125, and 150 °C) and pressures up to 6 MPa. The results were compared with propane/bitumen and butane/bitumen systems. All the measured properties fall between propane and butane systems. The solubility and density data were fairly represented using PR-EoS with AARDs of 10.3 and 1.43 %, respectively, and viscosity data were correlated applying Pederson corresponding state model with an AARD of 10.7 %. The results suggest that DME is a suitable substitute for solvents such as propane and butane in solvent-aided thermal recovery of bitumen from oil sands.

3.2 Introduction

Heavy oil and bitumen are immobile at reservoir condition and cannot be produced using conventional recovery methods. For heavy oil and bitumen production, viscosity should be reduced by increasing temperature or by dilution with a hydrocarbon solvent. SAGD (Steam Assisted Gravity Drainage) and VAPEX (Vaper Extraction) are the major recovery methods in each category. Bitumen mobilization by thermal energy and solvent dilution are employed in these methods, respectively. As the heat transfer is faster than mass transfer (molecular diffusion), the production rate in case of steam injection is higher than solvent alone.[26]

Therefore, steam-based methods are the most common methods for heavy oil and bitumen recovery. High water consumption, energy cost, and environmental issues as the major concerns regarding steam recovery methods motivate attempts to find alternative recovery methods. In the solvent-based methods, as the potential alternatives to the thermal methods, steam is replaced with pure hydrocarbons or mixtures of selected hydrocarbons either partially or totally[27]. The injected hot vapor/liquid hydrocarbons transfer their latent and condensation heats to the immobile viscous bitumen and mobilize it. In other word, in a hybrid process, which utilizes heat and dilution effect, the advantages of both heat and mass transfer are employed. Therefore, Expanding Solvent-SAGD (ES-SAGD) and its derivatives have been developed and proposed to improve SAGD performance by solvent addition to steam[28]. These processes offer higher oil production rate compared to VAPEX and low energy intensity compared to SAGD. The phase behavior and thermophysical properties of solvent/bitumen systems play a crucial role in designing of these processes.

Various hydrocarbon solvents have been suggested considering the cost and the solvent efficiency in dilution and viscosity reduction. There are many studies on performance of different hydrocarbons and bitumen systems in literature[26,29,30]. The major concern about using solvents for

bitumen and heavy oil recovery is their cost. Alternatives to the hydrocarbon solvents that have similar mass transfer rate and solubility in bitumen and heavy oil has to be considered[31]. Recently, DME has been proposed as a non-hydrocarbon solvent for recovery of bitumen and heavy oil. Ignasiak and Yamaoka published a Canadian patent and introduced bitumen or heavy oil recovery method by DME injection[27].

DME, which is often referred as "synthetic LPG", can be produced directly from fossil fuel like natural gas or from renewable sources such as waste, wood, and agricultural products[31,32].

Propane can be produced from LPG or natural gas condensate. However, the limited availability of LPG and condensate in Northern Alberta is the major concern associated with the oil sand industry growth[27]. DME or LPG price is a function of various parameters such as bulk storage, transportation, and distribution costs. Moreover, crude oil price affects the LPG price directly. Larson and Yang compared the DME and LPG price in China and reported that DME is competitive with LPG even when oil price is modest[33].

The other advantages of DME compared to hydrocarbons are, ability of operating at higher temperature, eliminating the need for natural gas pipelining, and capability of applying from shallow to deep reservoirs[27].

DME has attracted worldwide attention as a new fuel for being economical, clean, and environmental friendly. Since DME is similar to LPG products in many aspects such as vapor pressure and density, its handling and transportation is as easy as LPG[31,34,35]. The properties of DME, propane, and butane are compared in Table 3-1. Moreover, with low ignition temperature and high cetane number, DME is suitable for diesel engine fuel (see Table 3-1)[34,35]. DME can be used for household, transportation, power generation and petrochemical feedstock.

Table 3-1: Characteristics of DME, propane, and butane. (Data from GESTIS Substance Database)

Physical property	Propane	DME	Butane
Chemical formula	C_3H_8	C_2H_6O	C_4H_{10}
Molecular weight (gr/mol)	44.10	46.07	58.12
Liquid density at boiling point (kg/m^3)	581.2	735.0	601.1
Gas density at boiling point * (kg/m^3)	2.4170	2.3622	2.7093
Melting point (^oC)	-187.70	-141.50	-138.29
Boiling point (^oC)	-42.1	-24.8	-0.5
Solubility in water at 20 ^oC (g/L)	0.075	70	0.061
Vapor pressure at 20 ^oC (bar)	8.327	5.090	2.081
Flash point (^oC)	-104.0	-42.2	-60.0
Critical pressure (bar)	42.60	53.70	37.96
Critical temperature (^oC)	96.8	126.9	152.0
Ignition temperature (^oC)	470	240	365
Cetane number **	5	55-60	10
Heat of combustion*** (kJ/mol)	-2219.2	-1460.4	-2877.5

*Data from http://encyclopedia.airliquide.com/encyclopedia.asp?GasID=80#MSDS

** Data from[36]

*** Data from National Institute of Standard and Technology (NIST) webBook.

DME was utilized as water soluble solvent with conventional water flooding[37]. DME partitions into hydrocarbon by swelling and mobilizing the oil phase as it is soluble in water because of slight polarity and miscibility with oil. After injection of DME and water, DME-free water was injected for recovering the remained mobile oil and DME. Consequently, the residual oil saturation is reduced in DME enhanced water flooding as compared to waterflood alone. Moreover, DME can be extracted from produced fluid and reused by distillation and adsorption processes[37]. Injecting

an ether with 2-8 carbon atoms and a non-polar hydrocarbon with 2-30 carbon atoms as diluting agent was proposed in bitumen and heavy oil reservoirs[38].

In order to develop the solvent-aided thermal process such as ES-SAGD, the phase behavior of DME/bitumen has to be studied. Solubility of DME in bitumen, density, and viscosity of liquid phase are the crucial data for the phase behavior modeling required for the thermal reservoir simulators. To the best of our knowledge, there is no available phase behavior data on DME/bitumen systems in literature. In this work, the solubility of DME in bitumen as well as viscosity and density of liquid phase are measured at three temperatures (100, 125, and 150 °C) and pressures up to 6 MPa. Finally, the experimental measured solubility and density data are correlated using PR-EoS and experimental viscosity data is correlated using corresponding state model.

The rest of this paper is organized as follows. First, the experimental apparatus and procedures to measure the experimental phase behavior data are described. Then, modeling details are presented. In results and discussion part, the outcomes of experiments and PVT model are described followed by conclusion.

3.3 Experimental Section

3.3.1 Material

The instrument grade dimethyl ether (DME) with purity of 99.5 mol% was supplied by Paraxair. Water- and sand-free Athabasca bitumen sample was provided by an oil company in Alberta, Canada.

3.3.2 PVT Apparatus

The schematic and details of experimental apparatus were presented in our previous work[39]. The apparatus includes one rocking equilibrium cell, a densitometer, a viscometer, an Isco pump, a Quizix pump, one pressure indicator, one transfer cell, and a sample cell. The calibrated densitometer, viscometer, and equilibrium cell were placed in an oven. The transfer and sampling cells are located outside the oven. The ISCO and Quizix pumps are used for solvent injection to the system and transfer the liquid phase from the equilibrium cell to the transfer and sampling cells, respectively.

3.3.3 Experimental Procedure

Before each measurement, the entire system, including cells, densitometer, viscometer, and lines, were washed with toluene and acetone and then vacuumed. Then, the bitumen was charged into the equilibrium cell. The oven temperature has been set to the desired set point. The gaseous solvent was then injected using an ISCO pump at the desired pressure. The feed and solvent were mixed using the rocking system until equilibrium was reached. The ISCO pump was kept running to inject the makeup solvent and maintain the pressure constant during the dissolution of solvent in bitumen. After reaching equilibrium, i.e. the solvent could no longer dissolve in the sample, the equilibrium cell was maintained in the vertical direction for half an hour. Then, the bitumen-rich phase was discharged from the bottom of the equilibrium cell. The liquid phase was passed through

the inline density and viscosity measuring devices and the physical properties were recorded. The liquid sample was taken using the sampling cell and flashed at atmospheric pressure to measure the solubility of gas in the liquid phase. The evolved gas was measured using the Chandler Engineering Gasometer (Model 2331) with an accuracy of 0.2% over the range of the readings. The solvent solubility is calculated using volume of the evolved gas measured by gasometer and density of gas at atmospheric pressure.

3.4 Modeling Section

In this study, the experimental PVT data of Athabasca bitumen were modelled in CMG-WinProp phase behavior software by implementing modified version of PR-EoS (PR 1978)[40].The solubility and viscosity data for DME/bitumen are measured in this work, data of propane/bitumen[29], and butane/bitumen[26] systems reported in the literature have been used to tune the PR EoS.

3.4.1 Solubility

To fit the solubility data, the binary interaction parameters were adjusted. Winprop used the binary interaction exponent (n) as a user input parameter in the following equation,

$$d_{ij} = 1 - \left(\frac{2\sqrt{V_{c_i}^{1/3} V_{cj}^{1/3}}}{V_{c_i}^{1/3} + V_{cj}^{1/3}} \right)^n \qquad (1)$$

where V_c is component critical volume. Considering n as a matching parameter, the experimental equilibrium data were fitted.

3.4.2 Density

To match the bitumen density and solvent-saturated liquid density, the linear temperature dependent volume shift was employed. This method is useful for matching the density data over

the range of temperatures especially for heavy oils[41]. The following equation was used to introduce a temperature dependent Peneloux parameter[42] in PR-EoS[43],

$$S = S_0 + S_1(T - T_{ref}) \tag{2}$$

where, T is the absolute temperature in K, S_0 is the usual Peneloux parameter, and S_1 is a new temperature dependent term determined to comply with the ASTM 1250-80 correlation.

3.4.3 Viscosity

The viscosity data for DME/bitumen, propane/bitumen, and butane/bitumen systems were correlated by Pedersen corresponding state model[44]. The mixture viscosity is calculated by following relation[41],

$$\frac{\mu_{mix}(P,T)}{\mu_o(P_o,T_o)} = \left(\frac{T_{c,mix}}{T_{c,o}}\right)^{-1/6}\left(\frac{P_{c,mix}}{P_{c,o}}\right)^{2/3}\left(\frac{MW_{mix}}{MW_o}\right)^{1/2}\left(\frac{\alpha_{mix}}{\alpha_o}\right) \tag{3}$$

where μ is viscosity, MW is molecular weight, and α is rotational coupling coefficient. The subscripts "*mix*", "*c*", and "*o*" refer to mixture, critical, and reference properties, respectively. The reference substance for this model is methane. The mixture molecular weight is given by,

$$MW_{mix} = b_1(MW_w^{b_2} - MW_n^{b_2}) + MW_n \tag{4}$$

where MW_w and MW_n are weight- and mole- fraction averaged molecular weight, respectively.

The rotational coupling coefficient is calculated as follow:

$$\alpha = 1 + b_3\rho_r^{b_4}MW^{b_5} \tag{5}$$

where ρ_r is the reduced density of the reference substance.

3.5 Results and discussion

The PVT experiments were conducted on DME/bitumen at different temperatures and pressures. The solubility of DME, density, and viscosity of liquid phase were measured at 100, 125, and 150 ºC. In each temperature, according to P-T diagram (Figure 3-1), the experiments were conducted below the vapor pressure to ensure presence of both vapor and liquid phases in the system.

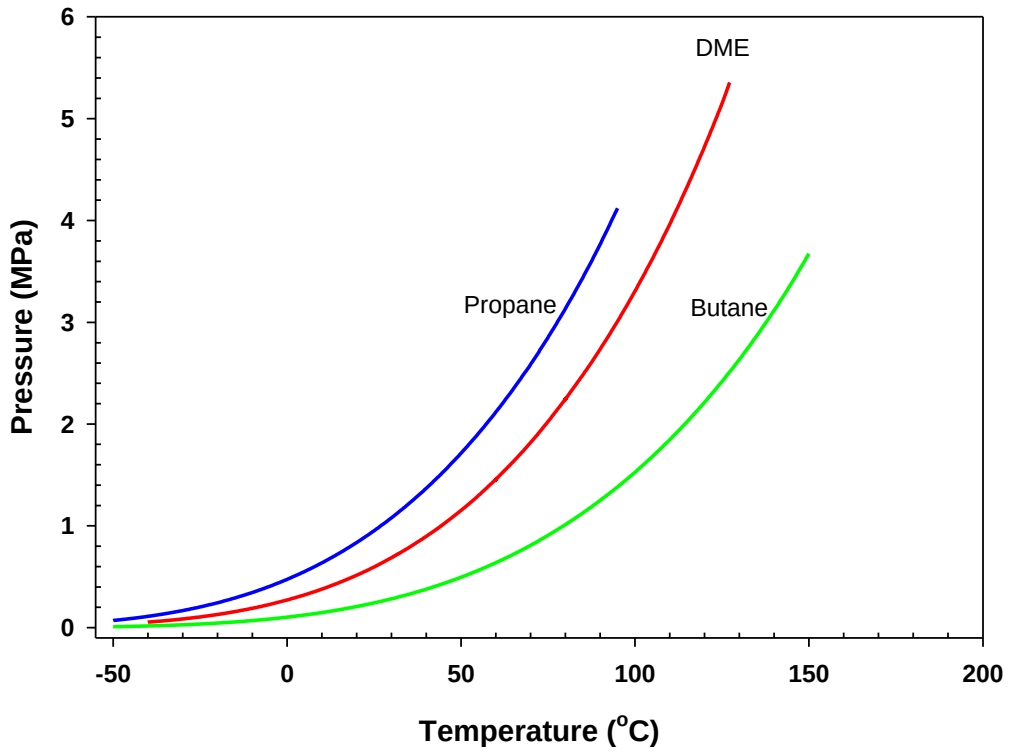


Figure 3-1: Pressure-Temperature (PT) diagrams of DME[45], propane, and butane (data from NIST webBook).

For example, at a temperature of 100 and 125 ºC, the maximum pressure of 3.0 and 4.1 MPa were considered for the experiments, respectively, to avoid formation of liquid/liquid conditions. According to the critical temperature of DME (Table 3-1), DME is supercritical at 150 °C. The

experimental equilibrium properties for vapor-liquid condition of DME/bitumen are presented in Table 3-2.

Table 3-2: Phase behavior data for DME/Bitumen system.

Temperature °C	Pressure MPa	Density kg/m^3	Viscosity mPa.s	Solubility mole fraction
100	3.0	774.6	0.94	0.88
100	2.1	875.6	5.72	0.70
100	1.1	925.5	27.63	0.40
125	4.1	802.1	1.39	0.82
125	3.1	860.8	4.12	0.67
125	2.1	895.7	9.30	0.48
125	1.1	920.8	24.10	0.29
150	6.1	776.6	1.05	0.81
150	5.1	818.1	1.72	0.76
150	4.1	848.9	3.08	0.65
150	3.1	873.5	5.15	0.54
150	2.1	894.5	8.47	0.38
150	1.1	912.4	15.25	0.15

Figure 3-2, panels a to c show the solubility of DME in bitumen, viscosity, and density of liquid phase, respectively. DME solubility in bitumen behaves like hydrocarbon gases. As pressure increases, fugacity of DME in gas phase increases, which results in higher DME solubility in liquid phase as observed in Figure 3-2a. Effect of temperature on solubility of DME in liquid phase can be attributed to the effect of temperature on intermolecular forces in liquid phase. Increasing

temperature decreases the attraction forces between molecules in liquid phase, which results in lower DME solubility in bitumen at high temperature conditions.

The higher viscosity and density reduction was observed at lower temperatures (Figure 3-2b and c). The crossover was observed for viscosity and density at different temperatures and pressures. Effect of DME solubility on viscosity and density of bitumen is more pronounced at low temperatures. However, at high temperature (150 ºC) where the DME solubility is less, the viscosity and density reduction is lower than low temperature (100 ºC). For example, at 100 ºC, the liquid phase viscosity was reduced from 27.93 to 0.64 mPa.s, by increasing the pressure from 1.1 to 3 MPa. However, by increasing the pressure from 1.1 to 6.1 MPa at 150 ºC, viscosity was decreased from 15.25 to 1.05 mPa.s.

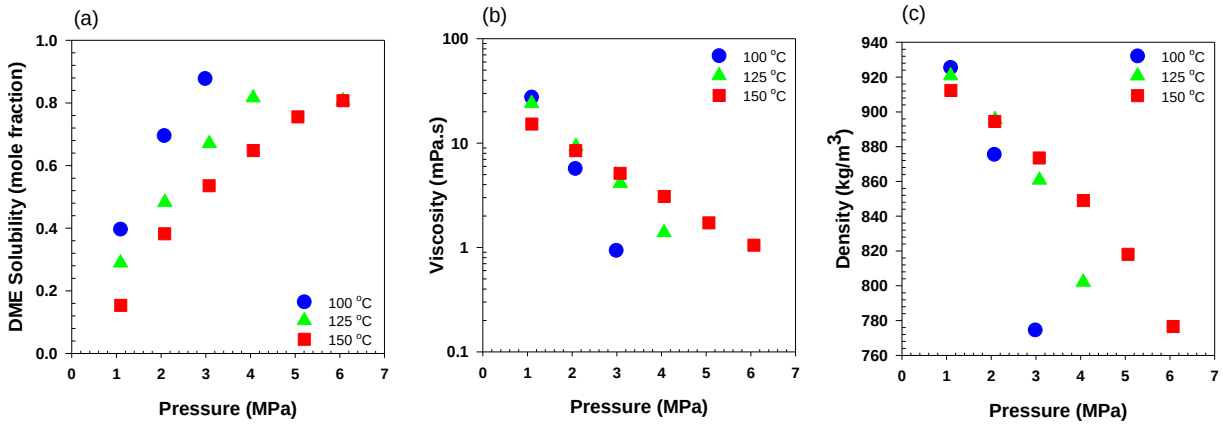


Figure 3-2: Vapour-liquid equilibrium data for DME/bitumen including, (a) DME solubility in bitumen; (b) liquid phase viscosity; and (c) Liquid phase density.

The measured equilibrium data of DME/bitumen, propane/bitumen, and butane/bitumen including solubility, viscosity, and density are compared to evaluate the capability of DME as solvent for bitumen and heavy oil recovery. The data for propane/bitumen and butane/bitumen were obtained from [26,29], which were conducted previously on the same bitumen in our research lab. The density

and viscosity data of bitumen at different temperatures and pressures followed by SARA (Saturate, Aromatic, Resin, Asphaltene) composition of bitumen were summarized in Appendix A[29,46].

Figure 3-3 (a-c) compare the solubility of solvent in bitumen, viscosity, and density of liquid phase for DME/bitumen, propane/bitumen, and butane/bitumen systems at 100 ºC, respectively.

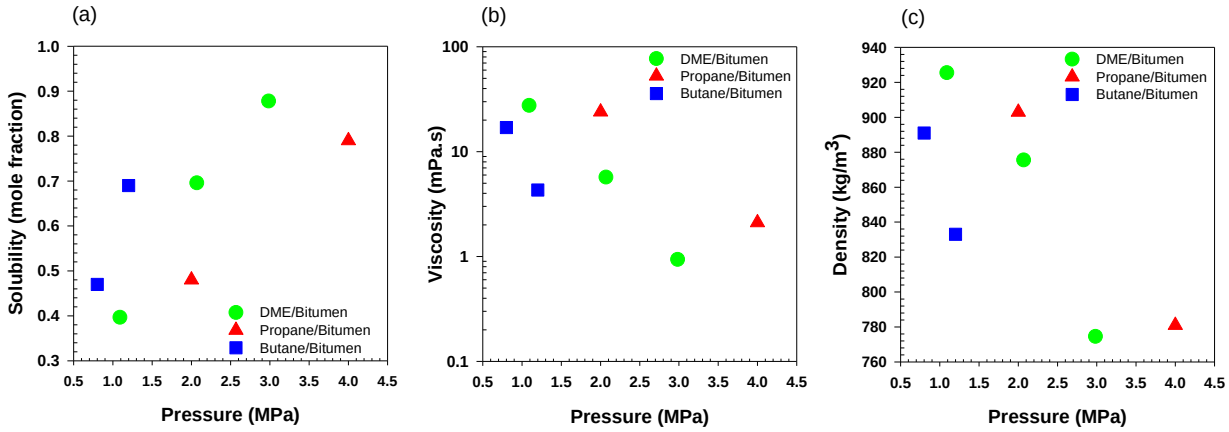


Figure 3-3: Vapour-liquid equilibrium data at 100 ºC for DME/bitumen, propane/bitumen, and butane/bitumen including, (a) solubility in bitumen; (b) liquid phase viscosity; and (c) Liquid phase density.

As shown in Figure 3-3 (a), the DME solubility falls within solubilities of propane and butane. Moreover, the viscosity and density reductions of bitumen in case of DME are higher than those of propane and lower than butane. For example, at the temperature of 100 °C and pressure about 2 MPa, propane-saturated liquid viscosity is 23.9 mPa.s[29] while DME-saturated liquid viscosity is 5.72 mPa.s. The viscosity reduction is an important factor in solvent-based recovery methods and DME can improve the viscosity reduction. This finding suggests that DME has potential to be used in solvent-based recovery methods as an alternative to hydrocarbons. The same trends were also observed at 150 ºC (Figure 3-4). As it was expected, at the higher temperature (150 ºC) the difference in equilibrium properties of solvent/bitumen mixtures were decreased compared to lower temperature (100 ºC).

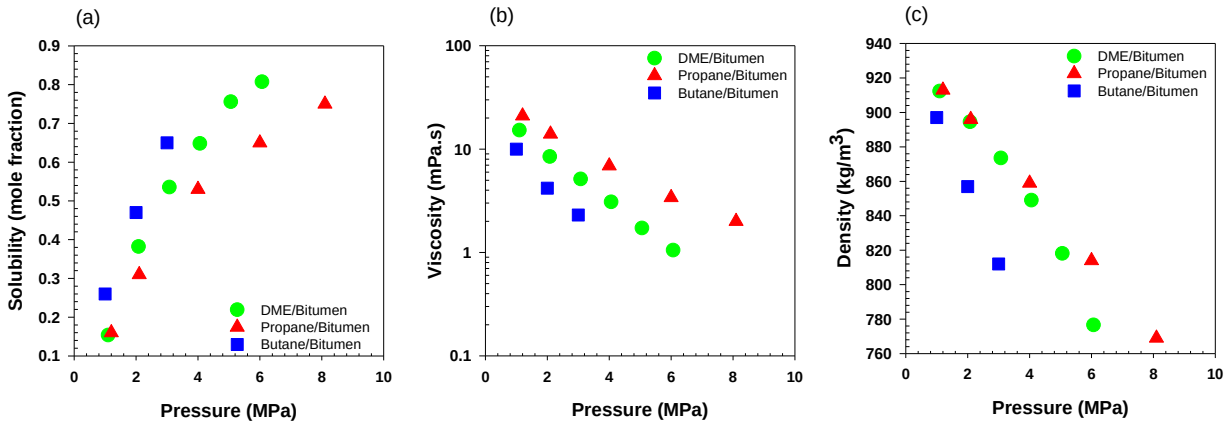


Figure 3-4: Vapour-liquid equilibrium data at 150 ºC for DME/bitumen, propane/bitumen, and butane/bitumen including, (a) solubility in bitumen; (b) liquid phase viscosity; and (c) Liquid phase density.

In order to build a fluid model for reservoir simulation, tuning of EoS using experimental PVT data is required. CMG-WinProp phase behavior software was employed to generate the phase behaviour model by matching the equilibrium experimental data. In this work, the thermodynamic model was generated for three systems including DME/bitumen, propane/bitumen, and butane/bitumen.

The matched density and viscosity of raw bitumen are shown in Figure 3-5 (experimental data from [47]).

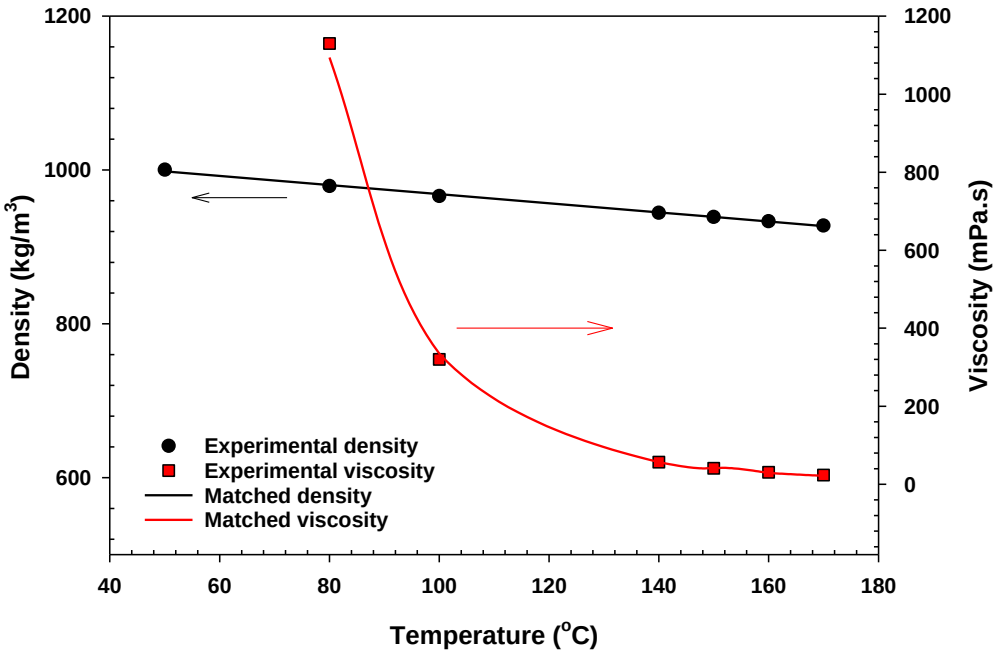


Figure 3-5: Matched and experimental data of density and viscosity of raw bitumen, experimental data of raw bitumen are obtained from[46].

It is common to use bitumen as a single component in thermal reservoir simulation due to computational burden of multicomponent thermal models. In this work, bitumen was also considered as a single component. Table 3-3 summarizes the bitumen component properties for PR-EoS. The critical properties and acentric factor have been calculated in WinProp using Twu[47] and Lee-Kesler[48] correlations, respectively.

Table 3-3: Bitumen properties for PR-EoS.

Component	MW (g/mol)	T_c (˚C)	P_c (MPa)	ω	SG
Bitumen	540	746.93	1.022	1.17	1

Comparison between the experimental and calculated solubility data for DME/bitumen, propane/bitumen, and butane/bitumen systems at different temperatures and pressures are shown

in Figure 3-6 (a-c). The solubility data were represented with AARDs (Average Absolute Relative Deviation $= \frac{1}{n}\sum_{i=1}^{n} | (x_{calc} - x_{\exp}) / x_{\exp} |$ of 10.3, 7.07, and 8.35 % for DME, propane, and butane solubility in bitumen, respectively.

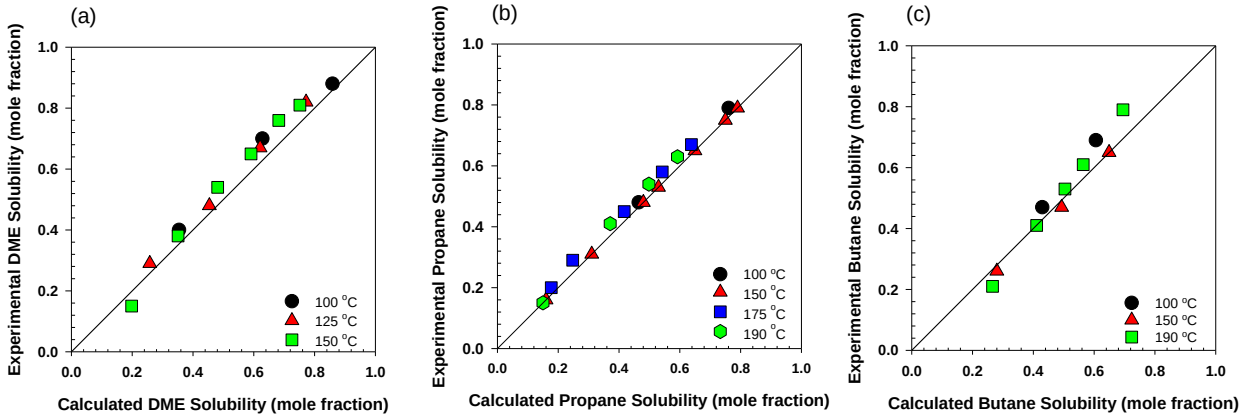


Figure 3-6: Deviation between calculated and experimental solubility data for (a) DME/bitumen, (b) propane/bitumen, and (c) butane/bitumen systems. Experimental data for propane/bitumen and butane/bitumen systems were obtained from [26,29].

The calculated and experimental k-values versus pressure are plotted in Figure 3-7 for DME/bitumen system. The calculated k-value (lines) and experimental data (symbols) for each temperature are in the same color.

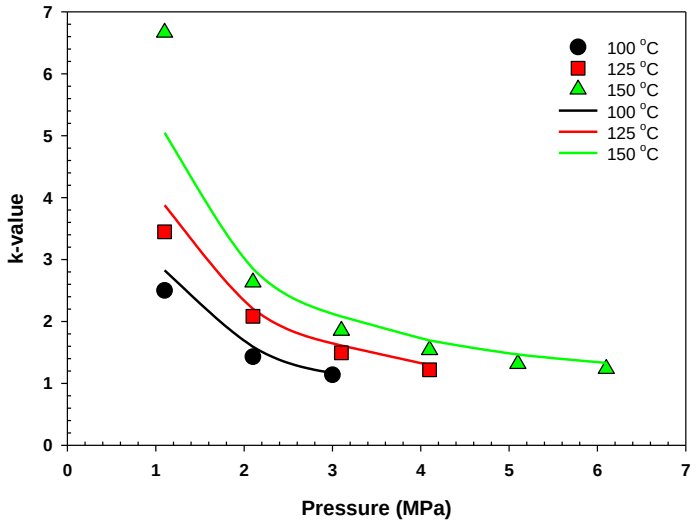


Figure 3-7: Measured and predicted k-values for DME/bitumen system.

The experimental solubility data of solvent in bitumen was used to determine the k-value at each temperature and pressure. Using the generated model, the k-values can be interpolated or extrapolated for the desired temperature and pressure conditions where experimental data are not available.

The measured liquid density of DME/bitumen, propane/bitumen, and butane/bitumen systems were predicted by the AARD of 1.43, 0.65, and 1.27 %, respectively. The deviation from experimental data is plotted in Figure 3-8, which show the well-representation of experimental density data.

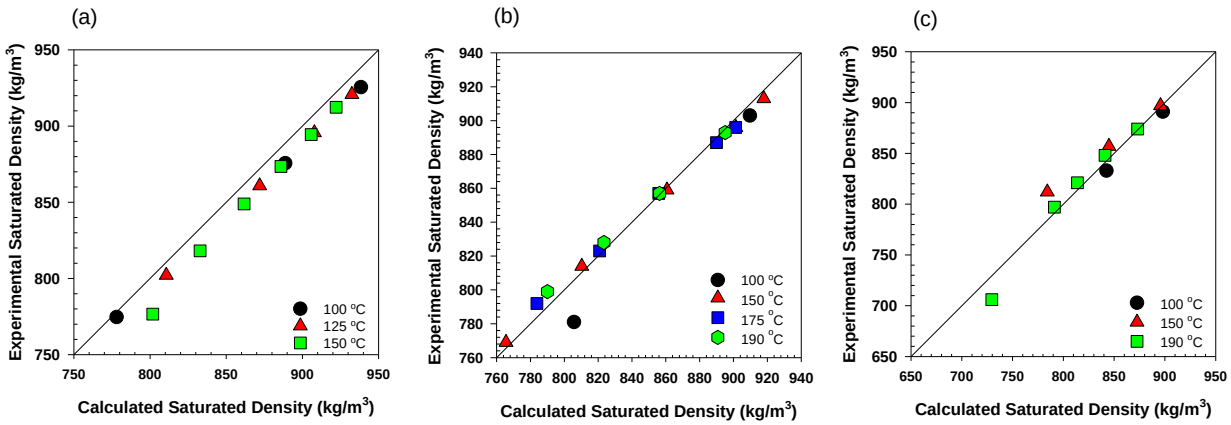


Figure 3-8: Deviation between calculated and experimental liquid density data for (a) DME/bitumen; (b) propane/bitumen; and (c) butane/bitumen systems. Experimental data for propane/bitumen and butane/bitumen systems were obtained from [26,29].

The experimental viscosity data were fitted applying modified Pedersen method with AARD of 10.7, 9.3, and 8.7 % for DME/bitumen, propane/bitumen, and butane/bitumen systems, respectively. The fitted Pederson coefficients are summarized in Table 3-4.

Table 3-4: The fitted parameters of Pedersen corresponding state model.

System	b_1	b_2	b_3	b_4	b_5
DME/Bitumen	0.0001304	2.3147	0.005902	2.2163	0.4726
Propane/Bitumen	0.0001565	2.3562	0.008854	2.2163	0.4242
Butane/Bitumen	0.0001565	2.2660	0.008854	1.4776	0.5245

The value of AARDs and correlated viscosity data in Figure 3-9 show that modified Pederson model can regenerate the experimental viscosity data with acceptable accuracy.

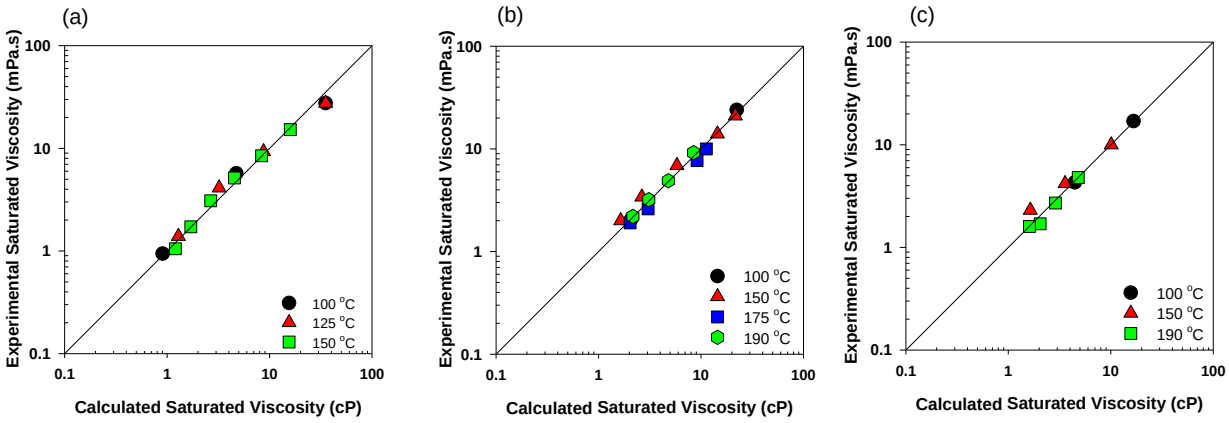


Figure 3-9: Deviation between calculated and experimental liquid viscosity data for (a) DME/bitumen; (b) propane/bitumen; and (c) butane/bitumen systems. Experimental data for propane/bitumen and butane/bitumen systems were obtained from [26,29].

The results show that DME has comparable dilution effect in lowering viscosity of bitumen as of propane and butane. The result also suggests that DME has potential to be utilized as an alternative to costly hydrocarbons for solvent-based heavy oil and bitumen recovery. Study of nonconventional solvents such as DME needs further examination from reservoir engineering and operational aspects. It has been reported that DME alone may lead to DME loss in water in the reservoir and cause compatibility issues with seal materials in process equipment and pumps[38]. Such operational aspects need further investigations.

3.6 Summary and conclusion

In this work, DME as a potential alternative to low boiling point hydrocarbons such as propane and butane was suggested. To examine the ability of DME to be used instead of hydrocarbons, the vapor-liquid equilibrium data for DME/Athabasca bitumen at the ranges of temperature and pressure were measured. The measured data including solubility, density, and viscosity were compared to those of propane/bitumen and butane/bitumen systems. The measured DME solubility is more than propane and less than butane. The same trends were observed for density and viscosity measurements. Using modified PR-EoS, phase composition and densities were predicted. The experimental viscosity data was also correlated using modified Pederson corresponding state model. All the modeling results in which bitumen was considered as one pseudocomponent led to acceptable AARDs.

The results show that DME with greater solubility and viscosity reduction compared to propane has the potential to be considered as an alternative to hydrocarbons in solvent-aided processes. It is expected that DME with capability of dissolving water and polar compounds requires less energy for recycling and improves the bitumen mobilization.

Appendix 3.A: Bitumen properties

Table 3.A1. Density data of bitumen at different temperatures and pressures[46].

T (^oC)	P (MPa)	ρ (kg/m^3)
190	2.01	907.6
174.6	2.01	917.3
150.3	2.02	932.7
125	1.99	947.9
100.6	2.02	962.6
89.8	2	969.1
79.9	2.01	974.9
69.9	2.01	980.9
60.1	2	986.7
49.9	2.01	992.9
23	1.99	1009.3
190	4	909.5
174.6	4.06	918.6
150.3	4.01	934.3
125	4	949.4
100.6	4.06	964
89.8	3.99	970.3
79.9	3.99	976.1
69.9	4	982
60.1	4.01	987.8
49.9	4	994
23	4.02	1010.1

190	6	911.5
174.6	6.01	920.8
150.3	5.98	935.9
125	6	950.8
100.6	6.02	965.3
89.8	6.01	971.6
79.9	5.99	977.2
69.9	6.01	983.2
60.1	6.01	989
49.9	6.01	995
23	6	1011
190	8	913.3
174.6	8	922.5
150.3	8.02	937.5
125	8.01	952.3
100.6	8.02	966.6
89.8	8	972.8
79.9	8.01	978.5
69.9	8	984.4
60.1	8.01	990.1
49.9	8.01	996.1
23	8	1012
190	10.01	915.2
174.6	10.01	924.1
150.3	10	939

125	10.01	953.7
100.6	10.01	967.8
89.8	10	974.1
79.9	9.99	979.6
69.9	10.01	985.5
60.1	10.01	991.3
49.9	10	997.2
23	10.01	1012.9

Table 3.A2. Viscosity data of bitumen at different temperatures and pressures [46].

T (^{o}C)	P (MPa)	μ (mPa.s)
52.7	2.01	14640
62.8	2	5560
72.4	2.01	2440
83	2.01	730
92.7	2	372
102.9	2.01	222
103.4	2.02	223
127.1	1.99	72.8
151.6	2.02	32.2
175.5	2.01	16.2
190.4	2.01	11.8
52.7	4	15900
62.8	4.01	6150

72.4	4	2590
83	3.99	786
92.7	3.99	396
103	4.06	234
103.4	4.07	237
127.1	4	76.5
151.6	4.01	33.5
175.5	4.06	16.8
190.4	4	12.2
52.7	6.01	17100
62.8	6.01	6700
72.5	6.01	2760
83	5.99	839
92.7	6.01	421
103	6.01	246
103.4	6.03	251
127.1	6	80.3
151.6	5.98	34.9
175.5	6.01	17.5
190.5	8	13.1
52.7	10	19700
62.8	10.01	7710
72.5	10.01	3220
92.8	10	477
103	10.03	274

103.4	10	280
127.2	10.01	88.8
151.6	10	37.7
175.5	10.01	18.8
190.6	10.01	13.6

Table 3.A3. SARA analysis of bitumen[29].

Sample	Saturates	Aromatics	Resins	Asphaltenes
Bitumen	12.26	40.08	36.53	11.13

CHAPTER FOUR:

4 Co-injection of Steam and Dimethyl Ether in 2D Sand-Pack[8]

This chapter has been published in SPE Canada Heavy Oil Technical Conference entitled "Dimethyl ether-A Promising Solvent for ES-SAGD". M. Zirrahi, H. Hassanzadeh, and J. Abedi co-authored this manuscript. This chapter studies the DME as a solvent for bitumen recovery by conducting a series of experiments using a 2D sand-pack with steam, DME/steam and butane/steam systems.

4.1 Abstract

Co-injection of solvent with steam is one of the promising methods to recover bitumen. The major operational cost for these projects is related to steam generation, water treatment and solvent. Propane and butane have shown desirable performance as solvent. In this work, we introduce Dimethyl ether (DME) as an alternative solvent because of its lower cost compared to propane and butane.

[8] Haddadnia, A., Zirrahi, M., Hassanzadeh, H. and Abedi, J., 2018, March. Dimethyl ether-a promising solvent for ES-SAGD. Paper presented at the SPE Canada Heavy Oil Technical Conference, Calgary, Alberta, Canada, March 2018. Paper Number: SPE-189741-MS, https://doi.org/10.2118/189741-MS.

We evaluate the capability of DME as a solvent for bitumen recovery processes. To investigate the performance of solvents, a series of experiments were conducted using a 2D sand-pack saturated with Athabasca bitumen. In these experiments, co-injection of steam with DME was compared with steam and steam/butane injections. The steam injection was conducted at 1 MPa and solvent concentration of 5 vol.% was tested in solvent/steam co-injection experiments. The cumulative bitumen production and bitumen production rate for each scenario were measured and compared with SAGD.

Experimental results revealed that using butane and DME as the additives to steam will improve the bitumen recovery. DME showed a performance close to butane. Since the cost of DME is lower than butane, it can be expected that production cost with DME injection is lower than butane. Considering that vapour pressure and density of DME are close to LPG products, its handling and transportation is as easy as LPG. Moreover, availability of DME is another advantage compared to butane. DME can be produced from natural gas or from renewable sources such as waste, wood, and agricultural products using well-established processes. A mobile production unit can be used to convert the produced solution gas to DME, which can reduce the methane emission and the costs of solvent injection.

4.2 Introduction

Bitumen and heavy oils are the key energy sources to compensate the declining rate of production of conventional oil reservoirs. Canada's oil sand reserves, estimated at 171.4 billion barrels, are among the largest known hydrocarbon deposits in the world[49]. Thermal recovery processes such as Steam Assisted Gravity Drainage (SAGD) and Cyclic Steam Stimulation (CSS) are the practical methods for heavy oil and bitumen recovery. In these methods, steam is injected into reservoirs to heat and mobilize the bitumen and heavy oil. These thermal recovery methods require large amounts of steam (cold water equivalent) per unit volume of the oil produced. Large amounts of natural gas must be burned to produce the steam resulting in significant greenhouse gas emissions.

Recently, solvent-aided recovery processes such as Expanding-Solvent SAGD (ES-SAGD) and Liquid Addition to Steam for Enhanced Recovery (LASER) have been developed to increase the energy efficiency of the thermal processes. In these methods, viscosity reduction is the result of both heating and solvent dissolution in bitumen. Field experiences of solvent-aided thermal recovery methods have been different. Many successful and promising projects have been reported. At the same time, many failures have also been reported[30,50]. There are many key technical and economic considerations for design of a successful ES-SAGD. Capital and operational costs of the injected solvent are the main elements. Heavier solvents (e.g. C_{5+}) are more expensive than light solvents. On the other hand, higher solvent loss is expected for the heavier solvents compared to the light ones (C_1-C_4). Source of hydrocarbon solvents is limited. Therefore, a cheap and abundant solvent with accessibility would be a desirable alternative. Dimethyl ether (DME) as a candidate has gained increasing interest as solvent for bitumen recovery processes[51–53].

In this work, first, we perform a screening of possible solvents, which can be produced from natural gas. Then, we compare the phase behaviour properties of DME-bitumen system with propane- and butane-bitumen systems. Next, we evaluate the performance of the DME/steam injection processes to recover bitumen using a 2D sand-pack model.

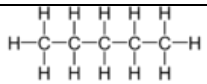
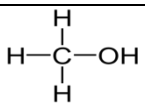
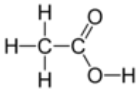
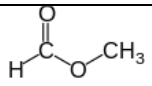
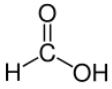
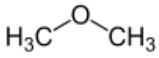
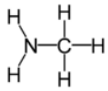
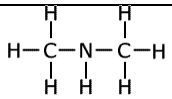
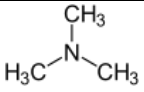
4.3 Natural Gas Derivatives as Potential Solvents

Chemicals that can be produced from the natural gas using established processes can be considered as secure and desirable candidates for solvent. Table 2-1 summarizes the molecular structure, boiling point and safety information of natural gas derivatives. Pentane is also given in this table for a comparison between safety information of pentane as a typical solvent and natural gas derivatives as potential solvents. Chemical processes to produce these components have been well established. These chemical components have different solubility in water. Some of them such as methanol and amines are completely miscible with water while dimethyl ether (DME) has low solubility in water (~71 g/L at 20 °C) compare to others. There is a lack of experimental solubility data for these chemical components in heavy oil and bitumen. Formaldehyde, ethers and amines have significant solubility in hydrocarbons. However, there are serious safety and health issues for application of formaldehyde. The mole fraction of methylamine in decane and nonane at 273 K and 1 atm is 0.413 and 0.353, respectively [54]. Solubility of amines in normal alkanes decreases by increasing chain length of hydrocarbon molecules. It also increases by increase of aromaticity of hydrocarbon fluid. Solubility of dimethylamine in hexane has been reported 0.473 mole% at 293 K and 1 atm. Amines that are gaseous at atmospheric condition results in easy separation of amine from the produced bitumen. However, amines are corrosive and their application as solvent in ES-SAGD process increases the capital cost related to piping and surface facilities.

Formic acid is soluble in water but it is partially soluble in hydrocarbons. Acetic acid is completely miscible with water. It has a $-CH_3$ group in its structure resulting in significant solubility in hydrocarbons. Acetic acid can be a potential solvent because of its high boiling point close to that of water. However, its corrosive nature and health and safety issues should be considered. Ammonia is another chemical that may have potential for solvent injection processes. However, application of ammonia in field is associated with high health risks.

Dimethyl ether (DME) can be the best choice as the potential solvent for ES-SAGD. The price of DME is usually about 65-90% of the liquefied petroleum gas (LPG)[55]. No health issue associated with DME has been reported in the literature. During recovery and injection of DME, drained DME can be used as fuel gas in steam generators. DME has significant solubility in bitumen and heavy oils to decrease the oleic phase viscosity. For simulation of an ES-SAGD, k-value of DME in aqueous and oleic phases in the temperature and pressure range of steam chamber as well as density and viscosity of oleic phase at different DME concentration are necessary that should be measured experimentally.

Table 4-1: Name, structure and properties of natural gas derivatives.

Name	Structure	Boiling Point (°C)	Material Safety Data Sheet (MSDS) Information*		
			Health	Fire	Reactivity
Pentane		36	1	4	0
Methanol		64.7	1	3	0
Formaldehyde		-19	3	4	0
Acetic acid		118	3	2	0
Methyl formate		32	2	4	0
Formic acid		100.8	3	2	1
Dimethyl ether		-24	1	4	1
Methylamine		-6.6	3	4	0
Dimethylamine		7-9	3	4	0
Trimethylamine		3-7	2	4	0
Ammonia		-33.34	3	1	0

*For description of each code see NFPA 704: Standard System for the Identification of the Hazards of Materials for Emergency Response.

4.4 Solubility and Physical Properties of DME-Bitumen System

An appropriate solvent for ES-SAGD process should have significant solubility in bitumen at high temperature conditions to decrease the oleic phase viscosity. We measured the solubility of DME in Athabasca bitumen as well as density and viscosity of bitumen rich phase. Details of the experimental apparatus and measurement procedure can be found elsewhere[52]. These data were compared with the experimental solubility, density and viscosity data of propane- and butane-Athabasca bitumen system at same temperature and pressure conditions. Figure 2-1 shows the P-T diagram of propane, butane and DME obtained from NIST Chemistry Webbook[56] and Wu and Yin [57]. This figure shows that saturation pressure of DME is higher than butane and lower than propane at a desired temperature. Higher saturation pressure indicates wider pressure range for solvent to be in vapor phase in the steam chamber. A higher saturation pressure also increases the solvent recovery factor, which is the crucial parameter for a successful ES-SAGD process.

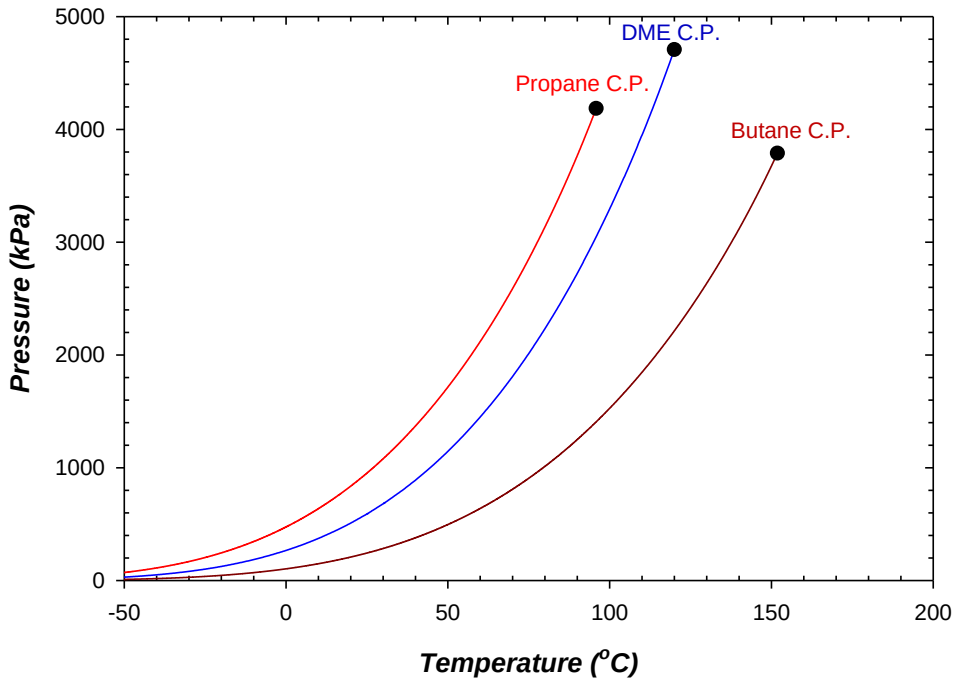


Figure 4-1: P-T diagram for propane, butane and DME. Experimental data for propane and butane were obtained from NIST Chemistry Webbook[56]. The data for DME was obtained from Wu and Yin [57].

Solubility of DME, propane and butane in Athabasca bitumen as well as density and viscosity of bitumen rich phase are shown in Figure 4-2 and Figure 4-3. As shown in Figure 4-2, solubility of DME falls between those of propane and butane. Similarly, the effect of DME dissolution on viscosity of bitumen rich phase follows the same trend as shown in Figure 4-3. Density of Athabasca bitumen saturated with DME, given in Figure 4-3, is very close to propane-bitumen system. Higher density and lower viscosity are desired in an ES-SAGD process.

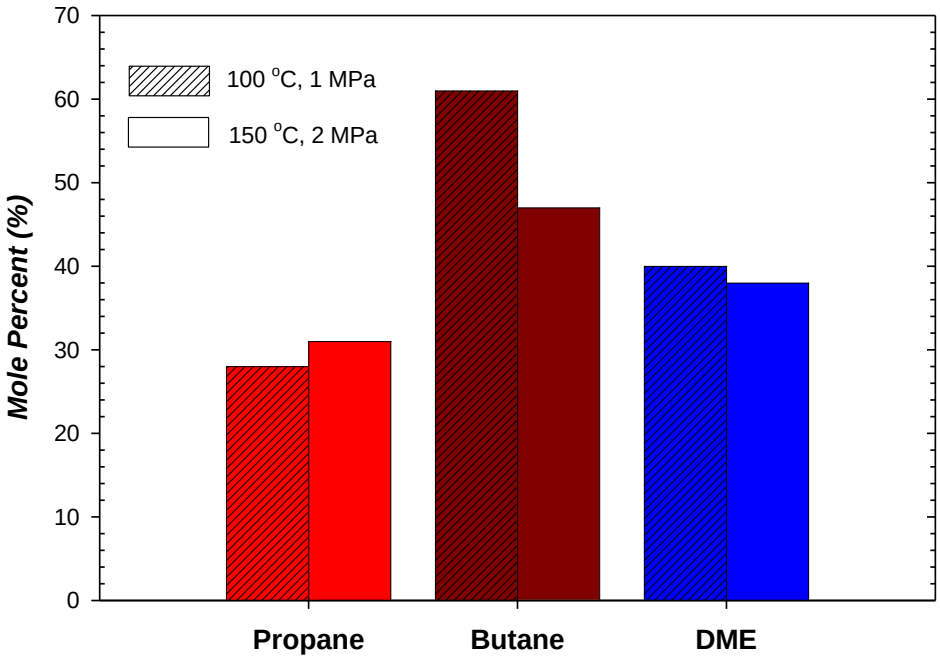


Figure 4-2: Solubility of propane, butane and DME in Athabasca bitumen.

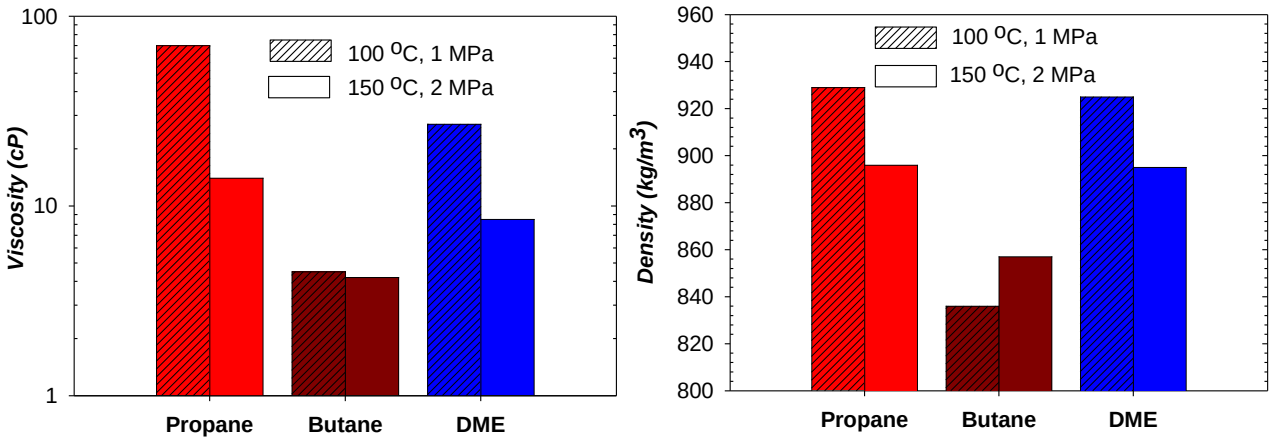


Figure 4-3: Viscosity and density of bitumen phase saturated with propane, butane and DME.

DME can also be a candidate as a solvent in the processes in which a heated solvent is injected into bitumen reservoir (e.g. Nsolv). In this process, pressure of the system is the saturation pressure of the solvent at injection temperature. Therefore, the injected solvent in the chamber can be in vapour or liquid states depending on the injection temperature. The solubility of the solvent in bitumen, density and viscosity of solvent saturated-bitumen were calculated at different temperatures (T) and the corresponding saturation pressure ($P=P^{sat}$ at T). The details of calculations can be found in our previous work [52]. Figure 4-4 shows the solubility of propane, DME and butane versus temperature. This figure shows that DME has higher solubility compared to propane and butane at a constant injection temperature. Viscosity and density of the bitumen phase at each temperature and the corresponding saturation pressure are shown in Figure 4-5. This figure shows that lower viscosity and density for the DME-bitumen system compared to propane- and butane-bitumen systems. The results suggest that DME has potential to show superior performance than propane and butane in heated solvent injection processes. Since there is no lab or filed experience on hot DME injection, this should be evaluated in lab scale and field scale.

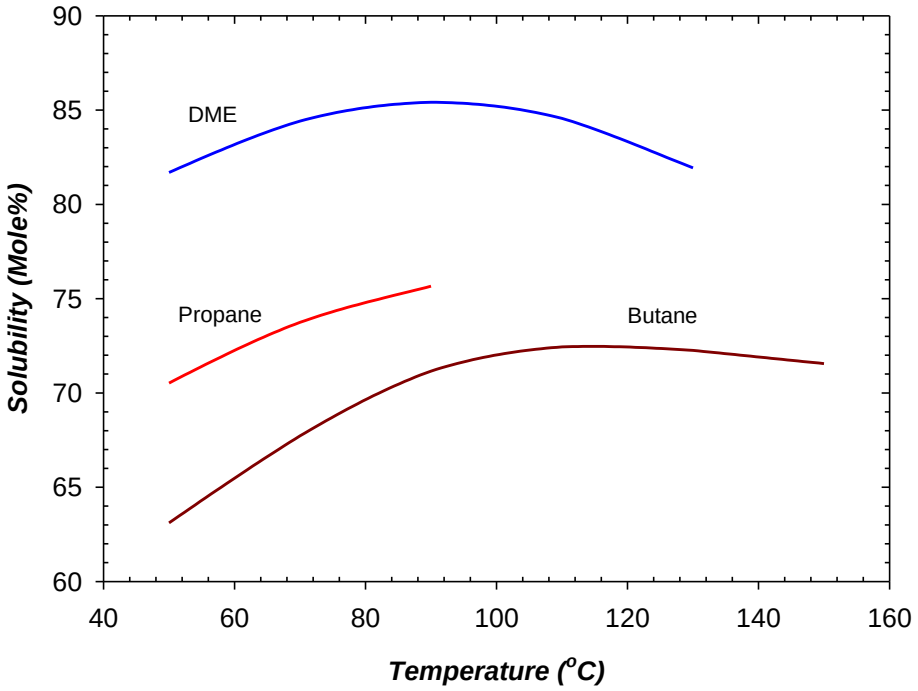


Figure 4-4: Solubility of DME, propane and butane versus temperature at their saturation pressure.

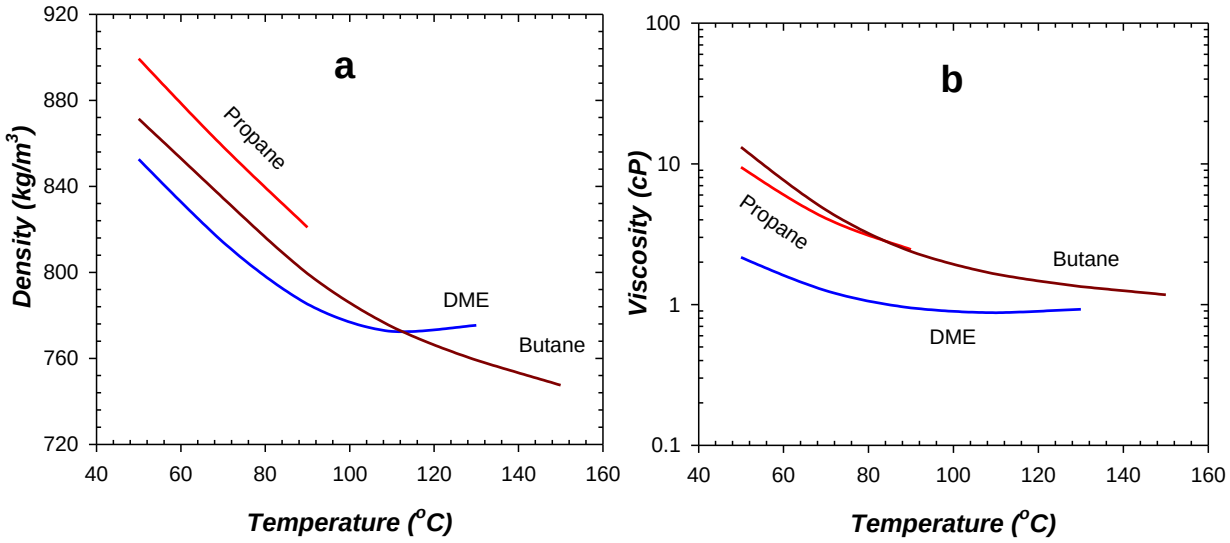


Figure 4-5: Viscosity and density of DME-, propane- and butane-bitumen systems versus temperature at the corresponding saturation pressure.

4.5 Experimental details of solvent/steam co-injection

Figure 4-6 shows schematic of the 2-D sand-pack physical model implemented in this work to evaluate the performance of solvent/steam co-injection. The dimensions of sand-pack are 1W×6D×20L inch. Total 17 k-type thermocouples were distributed in the sand-pack as shown in Figure 4-7. The temperature distribution was used to evaluate and monitor the growth of steam chamber during the experiments. To reduce the heat loss of the sand-pack, two pieces of the linen phenolic with thermal conductivity of 0.3 W/m·K (1W×6D×20L inch) are used to separate steel side plates from the system.

The sand pack was meticulously filled with sand (ASTM mesh size of 12/20 which will result in permeability of 555 D[58])and was shaken for the entire day. To prepare it for experimentation, the sand pack underwent a CO_2 flooding process for 3 hours at 50 psig (~0.345 MPa) inlet pressure. During this stage, the outlet was left open to the atmosphere, effectively displacing any residual air from within the sand pack. To ensure optimal conditions, the sand pack was then subjected to vacuuming for an entire day, eliminating as much CO_2 as possible before water imbibition. This preparatory step laid the foundation for accurate porosity measurement.

Next, the sand pack was carefully saturated with distilled water until reaching full capacity. Using the Quizix pump, the sand pack was pressurized to 500 psig (3.45 MPa). Then the sand pack was heated via heat tape wrapped around its exterior until it reached a consistent temperature of 70 ℃. Once the desired heat level was achieved, the sand pack was flooded with hot bitumen. This step was vital in establishing the initial oil saturation (S_{oi}). The flooding process was extended beyond one pore volume (PV) of the sand pack to ensure thorough saturation and the elimination of any remaining water.

As part of the process, the displaced water was carefully collected and cooled, allowing for precise measurements of the irreducible water saturation (S_{wirr}) of the sand pack. The dead volume of tubes was taken into account, ensuring accurate results and minimizing any potential discrepancies. Upon completion of the oil flood, assessment revealed the sand-pack porosity to be 37%, while the initial water saturation was determined to be 9%.

The sand pack was brought to room temperature, and the model's pressure was precisely maintained at 1.5 MPa using a back-pressure regulator (BPR). An in-house control system was designed to manage the BPR, minimizing any pressure deviation from the desired working pressure. Injection and production ports are clearly illustrated in Figure 4-7. The injection port was positioned on top of the production port maintaining a measured distance of 5 cm between them. Additionally, the production port was thoughtfully placed just 1 cm from the bottom of the sand pack.

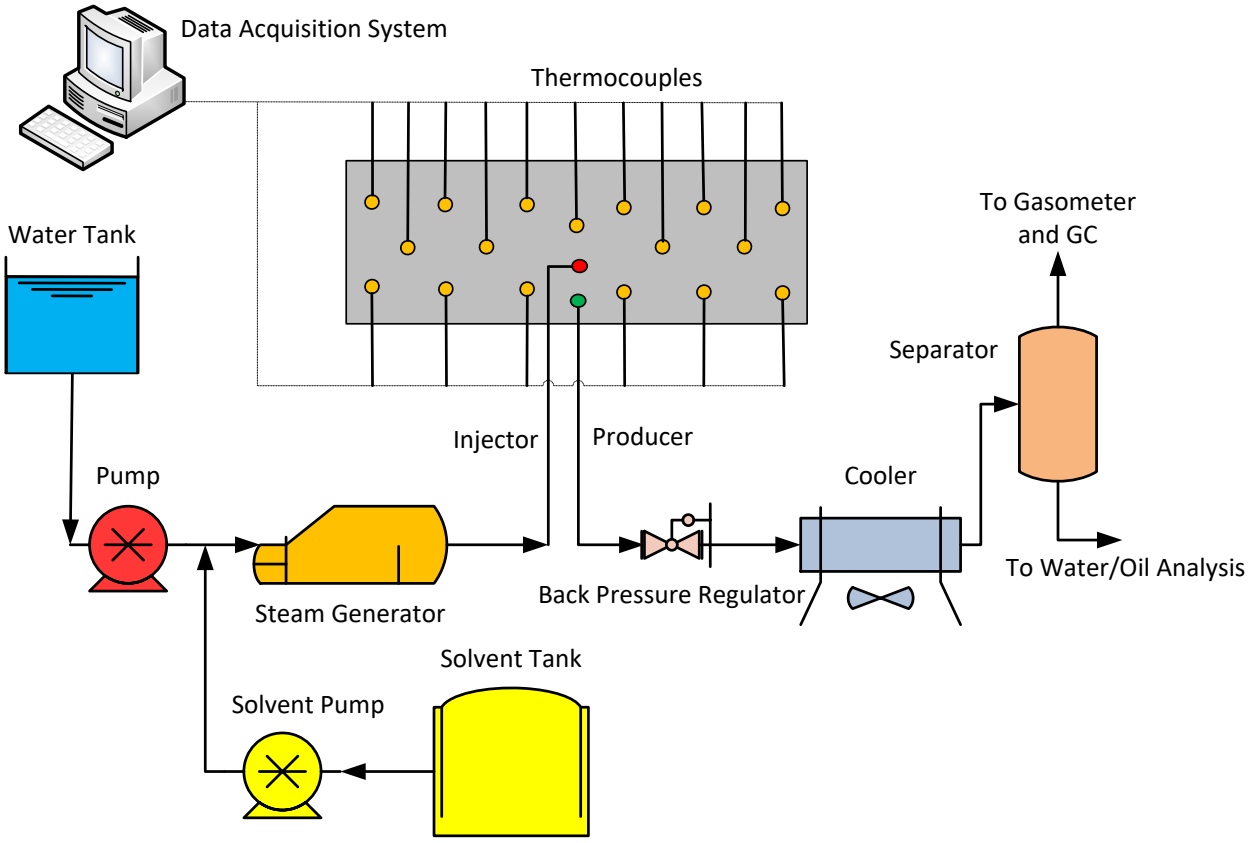


Figure 4-6: Schematic diagram of the 2D sand-pack experimental apparatus.

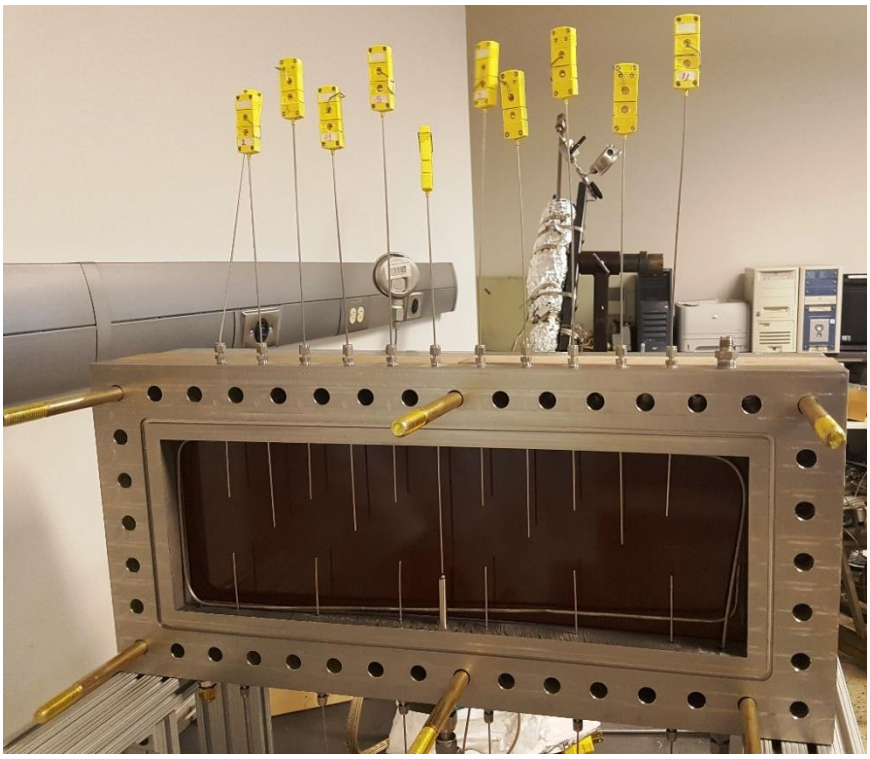


Figure 4-7: Distribution of thermocouples within the 2D sand-pack.

Water was injected using a Vindum Engineering pump into a steam generator. Solvent was injected using a ISCO pump at constant rate. The pressure of the sand-pack was kept at 1 MPa using a back pressure regulator. The produced fluid was collected after passing through a cooler.

Before the steam injection, the steam was circulated to warm-up the injection and production lines. The steam was injected at a rate of 15 ml/min (cold water equivalent) into the sand-pack. The produced fluid, which was a water-oil emulsion, was diluted with toluene/heptane mixture (50 vol%). Then, the oleic and aqueous phases were separated using centrifuge (10 min at 4000 rpm).

The solvent (butane and DME) was added to the steam in a proportion corresponding to 5 vol% of solvent-steam mixture. In all cases, rate of cold water was kept constant. Figure 4-8 (a and b) shows the cumulative oil production and oil production rate for SAGD and ES-SAGD (butane and

DME solvents) processes. The panel (a) of this figure shows that co-injection of DME increases the oil recovery. Butane injection has higher improvement compared to DME.

Panel (b) shows the oil production rate versus time for different steam/solvent injection processes. This figure reveals a delay in the peak of oil production when solvent is co-injected with steam. This is expected since the latent heat of steam decreases in the presence of the injected solvent.

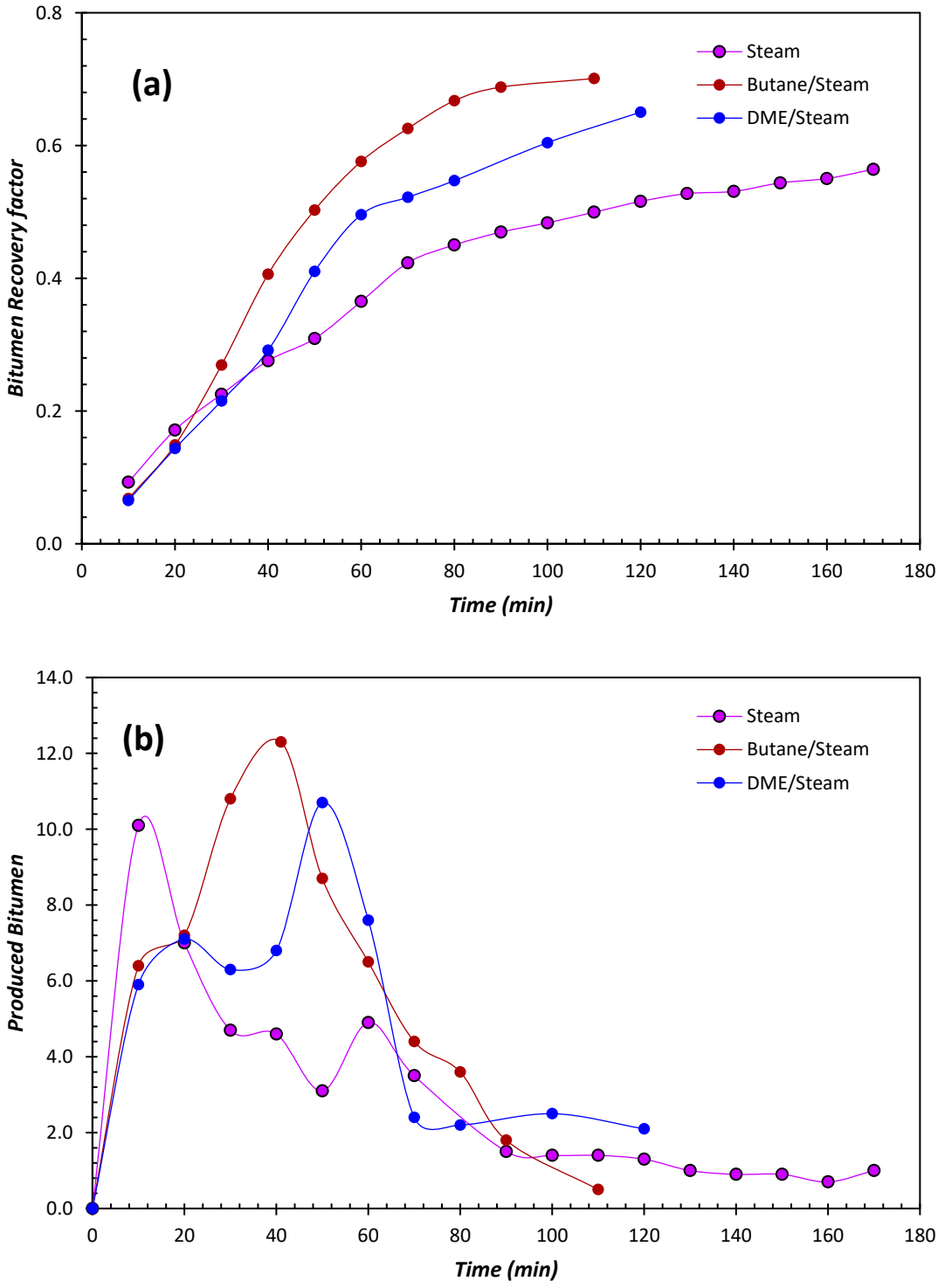


Figure 4-8: Bitumen recovery factor (a) and oil production rate (b) of steam and solvent/steam injection processes.

Figure 4-9 shows the temperature distribution in the sand-pack model for SAGD and ES-SAGD processes. It can be found that the high temperature zone is wider in case of steam injection. Co-injection of butane- and DME-steam result in reduced size of the steamed zone. This observation highlights a lower energy intensity for the solvent/steam injection processes. It also reveals the potential of solvent additives such DME to improve the energy efficacy of SAGD.

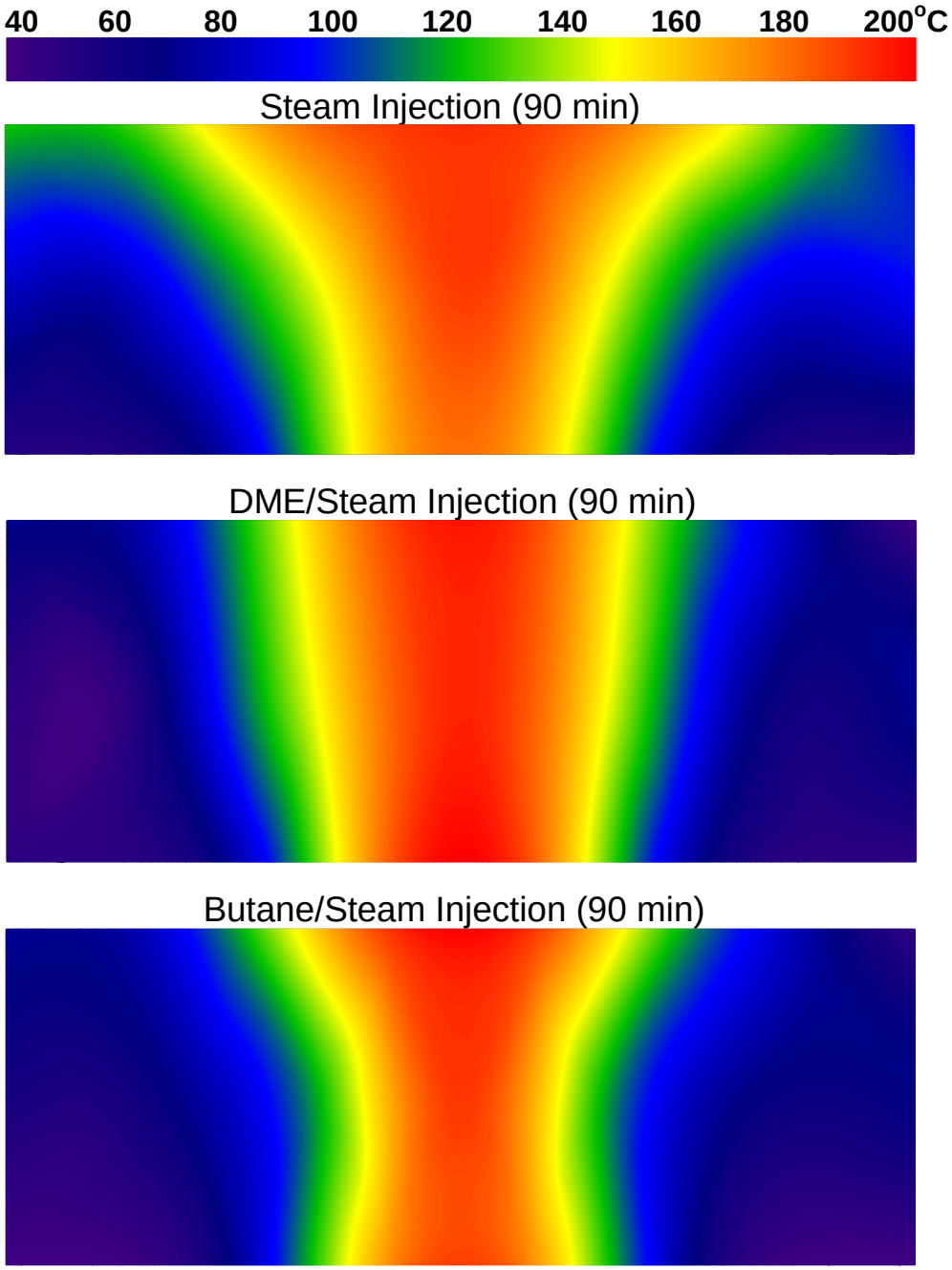


Figure 4-9: Temperature distribution within the 2D sand-pack in steam and solvent/steam injection processes.

4.6 Summary and Conclusion

Chemical derivatives from natural gas was introduced as the potential solvents for solvent-aided thermal recovery methods. DME was suggested as the potential candidate. Saturation pressure,

solubility in bitumen and effect on viscosity and density of bitumen was investigated and compared with propane and butane. Results showed substantial dissolution of DME in bitumen leads to significant viscosity reduction of the bitumen rich phase.

Steam and solvent/steam co-injection tests were conducted to evaluate the capability of DME as a solvent for bitumen recovery. Results showed that DME improves the bitumen recovery. The results show that co-injection of DME and steam is promising for bitumen recovery. Further studies are needed to evaluate the energy intensity and solvent recovery of DME co-injection with steam.

CHAPTER FIVE:

5 Phase Behaviour of Methane/Solvent(s)/Bitumen System

5.1 Abstract

The phase behaviour of solvent and bitumen is crucial in designing and optimizing any solvent-assisted in-situ bitumen recovery. One of the primary solvents considered for these processes is n-alkane.

This study presents experimental and modeling results on the phase behaviour of C_1/bitumen, C_3/bitumen, n-C_5/bitumen, C_1/n-C_5/bitumen, C_1/n-C_6/bitumen, C_1/n-C_7/bitumen, and C_1/ C_3+n-C_4+n-C_5/bitumen systems are performed. The measured data includes liquid viscosity, liquid density, and mole fraction of components in vapour and liquid phases were measured at a pressure range of 1−4MPa and a temperature range of 70 – 230 °C. PR-EoS is tuned using the measured solubility data from the experiments, and the K-values of each solvent are modeled.

The measured data are correlated with the correlations used in commercial thermal reservoir simulators. Accepted agreements were found between all the predicted properties and experimental data of the solvent/ bitumen, solvent/live bitumen, and multi-component solvent/live

bitumen system. The data and the parametrization approach find applications in the design and optimization of solvent-aided thermal recovery of bitumen.

5.2 Introduction

Currently, 186 billion barrels of recoverable oil are in Canada in which most of them are in form of natural bitumen (called bitumen, tar sands, or oil sands) located in Alberta. Thermal methods are currently the most practical heavy oil and bitumen recoveries methods. However, they are prone to high GHG emission and energy consumption.

To address the disadvantages of thermal bitumen processes, solvents with and without steam have been proposed and developed. Adding solvent to steam can improve the performance of in-situ thermal recovery by decreasing the energy intensity and water consumption[59]. Pure solvent injection (N-Solv)[60], warm vapour extraction (VAPEX)[1], Enhanced Solvent Extraction Incorporating Electromagnetic Heating (ESEIEH)[2,3] and, expanding solvent SAGD (ES-SAGD)[4] are some examples of these methods.

The phase behaviour of solvent and bitumen are the key factor to design and optimize any solvent assisted in-situ bitumen recovery and one of the main solvents considered for these processes are n-alkane. There is a distinct lack of enough experimental data and mechanistic knowledge relevant to solution gas/solvent/bitumen systems[61]. The literature does not include a complete set of experimental data for multi-component solvents such as gas condensate and diluents. The quantitative effects of the presence of solution gas on the phase behaviour, viscosity and density of solvent-bitumen systems also demand further research. This understanding is a prerequisite for the determination of the optimal solvent composition for solvent assisted processes. Knowledge

of the phase equilibrium properties of solution gas/bitumen/solvent mixtures is essential for the design and optimization of recovery processes for viscous bitumen from the Alberta oil sands.

The application of various solvents with steam has been widely investigated. Kar et al.,[62] studied and analysed the performance of SAGD and propane-SAGD injection in 2D and 1D physical models. They observed an enhancement in the oil production as well as quality of the produced oil with co-injection of propane and steam due to the better development of the steam chamber.

Souraki et al.,[63] conducted several laboratory experiments to compare the efficiency of SAGD versus ES-SAGD method in terms of some economical indicators such as: oil production rate and cumulative steam-oil-ratio (CSOR). They used three different n-alkane (n-C_5-C_7) solvents in their experiments and reported that the performance of n-C_5 for ultimate oil recovery was better than other two solvents. Both n-C_5 and n-C_6 had high production oil rate and low CSOR. Despite the results of n-C_7 were not as effective as the other two solvents, its performance was still comparable to SAGD process.

Hascakir[64] performed experimental study of SA-SAGD process using asphaltene insoluble or soluble solvents. By comparing the results of propane, n-hexane, carbon dioxide and toluene, Hascakir[64] concluded that CO_2 can yield not only high oil recovery but also results in superior oil quality. Nourozieh et al.,[65] measured and modeled the solubility and saturated-liquid density and viscosity of methane/Athabasca bitumen mixtures for temperatures up to 190 °C and maximum pressure of 10 MPa. The authors concluded that at higher temperatures the effect of solubility of methane into bitumen is negligible.

Mohammadzadeh et al.,[66] investigated the pore-scaled aspects of Solvent-Aided SAGD using glass-etched micromodels. They tested n-C_5 and n-C_6 as the solvent additive to the steam and

observed a higher production performance in the case of n-C_6 compared to n-C_5. Increasing the solvent concentration led to higher pore scale sweep efficiency due to the effective viscosity reduction via mass transfer for both cases.

Previous reservoir simulation studies of solvent and steam injection suggest that higher production rates and ultimate recovery can be achieved. Govind et al.,[67] performed simulation studies of ES-SAGD with different solvents at various concentrations and operating conditions. Their work demonstrated that injection of butane can have more advantages compared to the other solvents since it has higher vapor pressure with significant solubility in bitumen. They also suggested that high operating pressure is favourable and the concentration of the co-injected solvents needs to be optimized.

Simulation work carried out by Ardali et al.,[68] showed that solvents heavier than butane can improve the heavy oil recovery. In a simulation study, Sheng et al.,[69] demonstrated that DME as a water soluble solvent results in higher recovery factor than butane co-injection. Zare et al.,[70] also investigated the effect of hydrocarbon solvents co-injection on heavy oil recovery and reported that hexane results in better performance.

One of the essential aspects of solvent-aided processes is to determine how effective a solvent can alter the thermophysical properties of bitumen[71]. In order to determine the impact of solvent on mixture viscosity, solubility of solvents in bitumen need to be measured. Mehrotra and Svrcek [72] reported the solubility of methane and ethane in various bitumen at temperatures up to 100 °C. Fu et al.,[73] reported solubility measurements of methane and ethane in Cold Lake bitumen at 150 °C. Kariznovi et al.,[74] also reported measured saturated phase densities and viscosities of a bitumen sample with methane and ethane over the temperature ranges of 50 to 190 °C and pressures up to

8 MPa. Badamchi-Zadeh et al.,[75] tested the Athabasca bitumen with propane and determined the solubility of solvent as well as the densities and viscosities of the mixtures for limited range of temperatures of 10 to 50 °C. In a similar approach, Jossy et al.,[76] captured the phase partitioning of the propane bitumen systems at low temperatures of 10 and 40 °C. The existence of two phases in propane bitumen mixtures was also reported by Frauenfeld et al.,[77].

Detailed phase behaviour experiments of propane and Athabasca bitumen was conducted by Nourozieh et al.,[78] over the temperature ranges of 50 to 200 °C and pressures up to 10 MPa. Solubility, density and viscosity measurements were performed, and phase boundaries were detected. Both vapour-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE) were observed in their experiments. Han et al.,[79] studied vapour-liquid equilibrium (VLE) of supercritical propane and bitumen to investigate the effect of dissolved gases on thermophysical properties of bitumen.

Zirrahi et al.,[80] and Haddadnia et al.,[81] measured the solubility of light n-alkanes including C_1, C_2, C_3, n-C_4, and DME for MacKay River bitumen at pressures and temperatures up to 5MPa and 190 °C, respectively. The effect of solvent on thermophysical properties of bitumen was discussed and the investigated solvent-bitumen systems were modelled using the Peng-Robinson EoS.

Gao et al[82] studied the phase behaviour of Athabasca bitumen and n-hexane mixtures at temperatures up to 160 °C. They measured density and viscosity of the mixtures and determined that no liquid-liquid separation happened at operating conditions even for solvent concentrations greater than 90 mole%. It was then concluded that the entire injected solvent can be available for bitumen dilution at the edge of steam chamber leading to more efficient co-injection process.

Johnston et al.,[83] experimentally investigated phase behavior of bitumen and n-pentane mixtures at temperatures up to 280 °C and pressures up to 14 MPa. They illustrated phase boundaries and saturation pressures of bitumen-pentane mixtures.

Volumetric properties of Athabasca bitumen and n-hexane mixtures at temperatures and pressures as high as 190 ºC and 10 MPa, respectively, were measured by Kariznovi et al.,[84]. Nourozieh et al.,[85,86] also reported viscosities of bitumen diluted by n-pentane and n-hexane at temperatures up to 200 °C and pressures as high as 10 MPa.

In a conducted study by Haddadnia et al.,[87] viscosities and densities of Athabasca bitumen diluted by n-pentane and n-hexane were measured. The effect of variations of solvent mass fraction ($0.05 \leq \omega \leq 0.5$), temperature ($30 \leq T \leq 190$ °C), and pressure ($2 \leq P \leq 8$ MPa) on PVT properties of solvent-bitumen systems were investigated. The study proposed appropriate mixing rules and the generalized parameters to predict the viscosity and density of diluted bitumen with solvent with great accuracy.

Yamchi et al.,[88] conducted LLE measurements for propane + n-butane/bitumen mixtures in temperature range of 21 to 80 °C and constant pressure of 3.4 MPa. The authors also conducted another study[89] for the LLE measurements for DME/bitumen system and they reported the saturation pressure of the mixture as well as composition of DME, viscosity and density of the light phase.

There is a lack of experimental data on k-value and physical properties of live-bitumen/solvent systems. In a recent study by Bamzad et al.,[61] density, viscosity, and K-values of the live bitumen/multicomponent solvent system with solvent composition of n-C_4, n-C_5, n-C_6, n-C_8 and, n-C_{10} at pressure range of 1-6 MPa and temperature range of 70-230 °C were measured. In another

study, Bamzad et al., reported the experimental measurement and thermodynamic modeling of vapor-liquid equilibrium data of C_1/bitumen, CO_2/bitumen, C_1/ CO_2/bitumen, C_1/diluent/bitumen, and C_1/ CO_2/diluent/bitumen systems[90]. To the best of my knowledge, there is no other experimental data of k-value, liquid phase density and viscosity for live-bitumen/solvent systems in open literature. Therefore, this research new measurements and model the obtained data using an EoS approach has been conducted to fill the existing knowledge gap.

Different n-alkane/bitumen systems were studied and their phase behaviours and thermophysical properties such as density and viscosity are modeled by various thermodynamic models.

5.3 Experimental Details

5.3.1 Materials

Research grade (purity higher than 99.9%) of methane, propane, n-butane, n-pentane, n-hexane and n-heptane were purchased from Praxair and VWR. All the solvents were used without further purification. MacKay River bitumen was provided by an oil producer located in Calgary, Alberta, Canada. Average molecular weight of the bitumen was reported at as 512±6.9 g/mol. Other details including density, viscosity, molecular weight, compositional analysis, and detail characterizations of the bitumen sample can be found in our previous works [91–93].

5.3.2 Experimental setup

Figure 2-1 shows the experimental apparatus implemented in this study to measure viscosity, density, and composition of liquid and vapour phase for bitumen / solvent and live bitumen / solvent(s) system. This setup can operate at maximum temperature and pressure of 300 °C and 10 MPa, respectively. This PVT system consists of densitometer, viscometer, rocking equilibrium cylinder, high temperature back pressure regulators and a visual cell, which are located inside an oven with accuracy of ±1 ºC. Pressure transmitter, bitumen or live bitumen and solvent feeding cells, density and viscosity data acquisition unit and Quizix pumps are located outside of the oven.

The equilibrium cell and all lines and connections were washed with toluene and dried by acetone. After that, the system was purged with helium then placed under vacuum over night. Prior to each experiment the lines was filled with helium at the same pressure of the experiment to prevent any disruption on the pressure of the equilibrium cell while opening the valves to transfer vapour and liquid phases.

For the bitumen/solvent system, predetermined volume of bitumen was transferred from feeding cell to equilibrium cell at the temperatures between 60 to 80 °C to reduce the viscosity of bitumen. In the next step, the oven was set to reach the desired temperature and then a predetermined volume of solvent added to the hot bitumen with a very low flowrate (1 -2 ml/ minute). After feeding the system with solvent and bitumen, the pump was kept running at a desired constant pressure to make up for the dissolution of the solvent in the bitumen until the equilibrium was achieved. The mixture was considered at equilibrium condition when the pressure, temperature and volume were all constant for a minimum of six hours.

After the mixing, the equilibrium cell was kept in vertical position for two hours, the sampling line was purged with liquid phase and then 10 to 20 cc sample was collected while the keeping the pressure of the system at constant value. Collected samples were used for compositional analysis.

For the live bitumen/solvent(s) system, prior to any experiment, specific amount of bitumen, methane and solvent(s) was mixed by rocking the feeding cell separately at 100 °C and 10 MPa for two weeks. The pressure of the feeding cell was set at 10 MPa to make sure the mixture is in single liquid phase. Few samples from the prepared live bitumen and solvent mixture were taken and their composition were analysed to make sure they are mixed properly and verifying our liquid compositional analysis methodology.

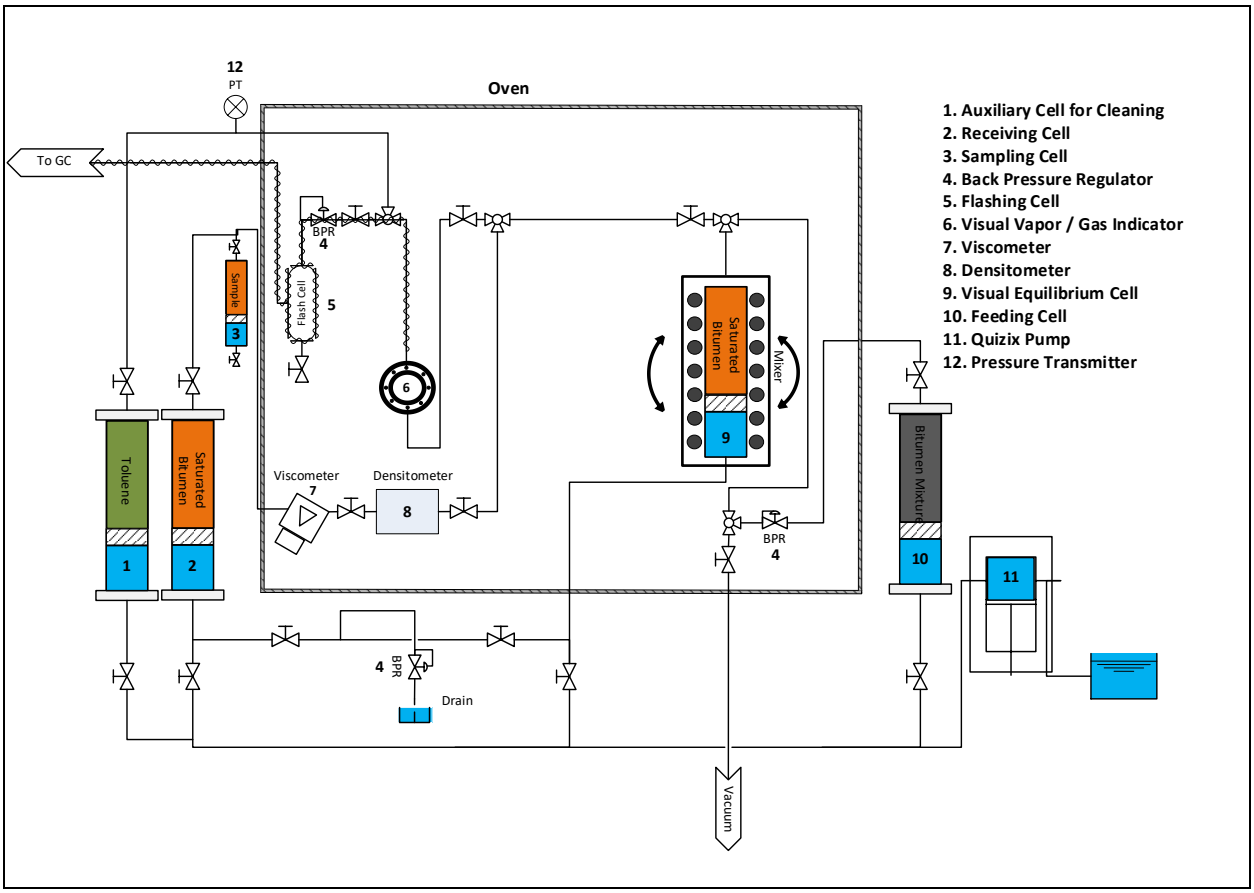


Figure 5-1: The schematic diagram of the apparatus for the phase behavior study of methane/solvent(s)/bitumen/ systems.

After preparing the mixture (bitumen, methane, and solvent), the oven was set to reach the desired temperature then a predetermined amount of mixture was injected into the equilibrium cell. The volume of the equilibrium cell could be altered by displacing the water and moving the piston inside it. After charging the equilibrium cell with the mixture, the back pressure regulator and pump was set to a desired constant pressure until the equilibrium was achieved. The mixture was considered at equilibrium condition when the pressure, temperature and volume were all constant for a minimum of six hours.

In the next step, the equilibrium cell was kept in a vertical position for two hours to ensure there were no bubbles in the liquid phase. First, the gas in the equilibrium cell was discharged by passing it through a densitometer, a visual cell, and a back pressure regulator (BPR). The gas phase was analyzed using a GC-3900 unit (Varian) equipped with a flame ionization detector (FID). The GC column used was a wall-coated open tubular (WCOT) type (CP-Sil 5 CB: 10 m × 0.15 mm × 2 μm), which was provided by Agilent Technologies (Figure 5-2)

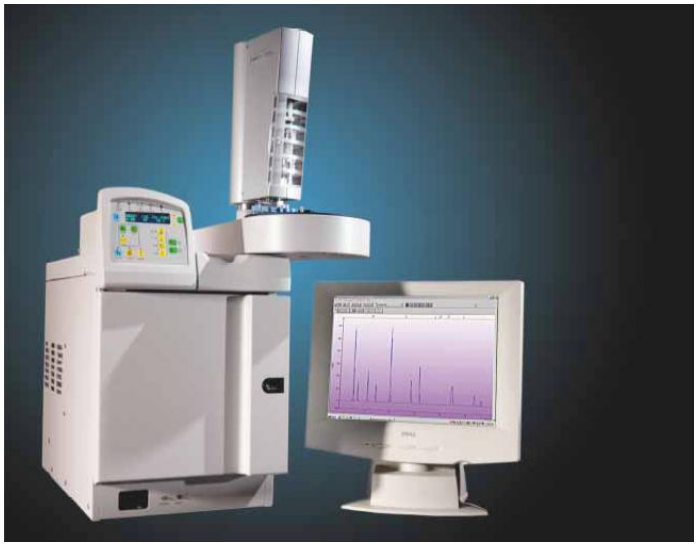


Figure 5-2: Varian 3900 gas chromatograph (from www.asap4u.nl/pdf/varian/3900.PDF).

To ensure there is no condensation on the tubing wall during the vapour phase sample collection, all the gas tubes and the corresponding back pressure regulator are kept at 300°C. The densitometer and visual cell will indicate the phase change between vapour and liquid. After the vapour phase sample collection, the liquid phase was discharged for viscosity and density measurement. To keep the pressure constant, receiving cell and BPR on the left side of the PVT setup were used to receive the sample at constant pressure. A sample from liquid phase (10 to 20 ml) was taken to find its composition.

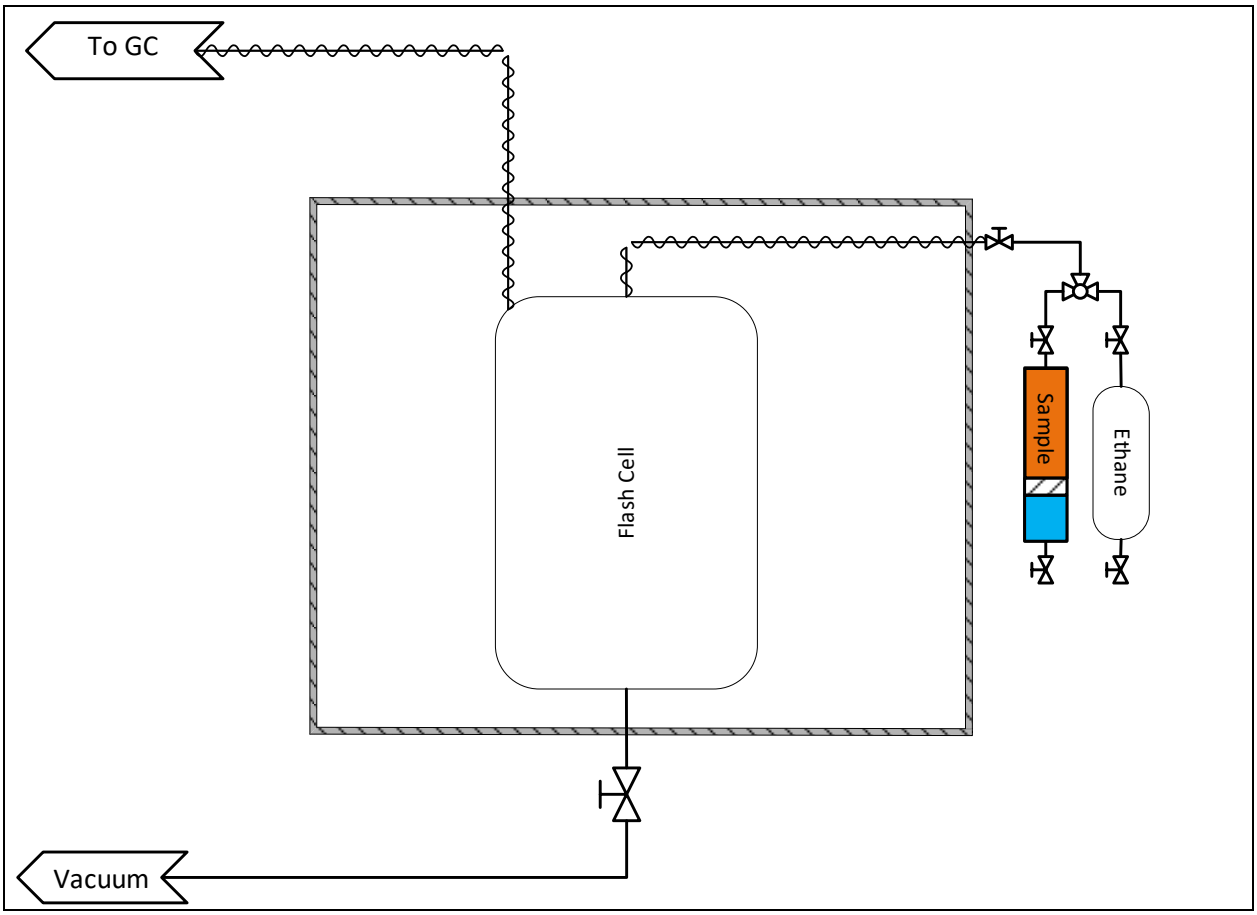


Figure 5-3: The schematic diagram of the apparatus for the compositional analysis of liquid samples.

As shown in Figure 5-3, liquid phase sample was flashed inside a vacuum cell at 250°C and a predetermined amount of ethane was added to the cell and the gas phased was analysed by GC.

$$Solvent\ Mass = \frac{Ethane\ Mass\ \times Solvent\ mass\%}{Ethane\ mass\%} \qquad 5\text{-}1$$

The compositional analyses for the evaporated hydrocarbons completed using ASTM D2887 and by using equation 5-1, we calculated the mass of methane, solvent(s) and their concentrations will be calculated using total mass of sample, where solvent and ethane% were obtained from GC analysis. Composition of each gas and liquid sample was analyzed at least 5 times to ensure

the accuracy of the compositional analysis. Also, prior to each experiment, the liquid phase composition analysis was verified by analysing several methane, solvent and bitumen mixtures.

The described PVT apparatus was utilized to measure the K-value and thermophysical properties of methane/bitumen and various solvents including propane, n-butane, n-pentane, n-hexane and n-heptane systems.

5.4 Result and discussion

The experimental apparatus described in the previous section was applied to measure k-values (for methane, propane, n-butane, n-pentane, n-hexane, and n-heptane), density and viscosity of liquid phase for methane/bitumen, propane/bitumen, n-pentane/bitumen, and methane / solvent(s) / bitumen systems were measured. The pressure and temperature ranges of experiments were between 1-4 MPa and 70 to 230 °C, respectively. Density and viscosity of MacKay River bitumen were measured and reported in Table 2-1.

Table 5-1: Experimental density and viscosity data of MacKay River bitumen.

T	P	Density	Viscosity	T	P	Density	Viscosity
	1	981.3	1293		1	906.4	11.3
	2	981.9	1332		2	907.4	11.5
70	3	982.6	1375	190	3	908.3	11.8
	4	983.3	1415		4	909.2	12
	5	983.8	1450		5	909.6	12.1
	1	954.2	141.2		1		5.6
	2	955.0	145.8		2		5.7
110	3	955.8	150	230	3		5.8
	4	956.4	154.4		4		6
	5	957.2	158.6		5		6.1
	1	931.7	30.5				
	2	932.6	31.3				
150	3	933.3	32				
	4	934.2	32.7				
	5	934.9	33.4				

In the first stage of experiments, K-values, density and viscosity for methane/bitumen, propane/bitumen, and n-pentane bitumen were measures. Table 5-2, Table 5-3 and Table 5-4 show the measured experimental values for K-values, density, and viscosity of the liquid phase.

Table 5-2: Experimental K-value, density, and viscosity data of methane/bitumen system.

T (°C)	P (MPa)	ρs (kg/m^3)	Viscosity(cP)	K-value of methane	methane (mol%)
70	2	976.2	940	12.34	8.10
	3	973.6	830	8.37	11.94
	4	973	744	5.21	19.20
110	1	952	124.1	25.78	3.88
	2	949.8	111.7	13.43	7.45
	3	948	101.8	9.25	10.81
	4	945.9	93.2	7.19	13.91
150	1	929.3	28.8	29.77	3.36
	2	927	26.8	13.88	7.21
	3	925.1	25.2	9.79	10.22
	4	924.4	23.8	7.97	12.55
190	1	904.5	10.4	32.19	3.11
	2	902.4	10	14.68	6.81
	3	900.60	9.6	10.24	9.77
	4	899.60	9.3	7.89	12.68
230	1		5.3	31.89	3.14
	2		5.1	15.24	6.56
	3		4.9	10.63	9.41
	4		4.8	8.20	12.19

Note: Standard uncertainties u are u(T) = 0.288 K, u(P) = 0.003 MPa, and the combined expanded uncertainties U are U(μ) = 0.55 U(ρ) = 0.44 (level of confidence = 0.95).

Table 5-3: Experimental K-value and density data of n-pentane/bitumen system.

T (°C)	P (MPa)	ρs (kg/m^3)	K-value of n-pentane	n-pentane (mol%)
125	0.4	915.4	3.65	27.38
	0.8	851.9	1.76	56.74
150	0.4	899.6	3.60	27.81
	0.8	855.8	1.98	50.42
	1.2	775.3	1.38	72.48
175	0.8	865.9	2.49	40.13
	1.2	832.1	1.97	50.64
	1.6	787.6	1.55	64.69
	2.1	705.7	1.37	72.98
200	0.8		3.02	33.09
	1.6		1.94	51.61
	2.5		1.44	69.36
	2.9		1.34	74.70
230	.8		4.85	20.63
	1.6		2.59	38.62
	2.5		1.83	54.70
	2.9		1.69	59.00

Note: Standard uncertainties u are u(T) = 0.288 K, u(P) = 0.003 MPa, and the combined expanded uncertainties U are U(μ) = 0.55 U(ρ) = 0.44 (level of confidence = 0.95).

Table 5-4: Experimental K-value, density, and viscosity data of propane/bitumen system

T (°C)	P (MPa)	ρs (kg/m^3)	Viscosity(cP)	K-value of propane	propane (mol%)
70	1	937.5	121	2.32	43.02
	2	860.8	11	1.47	67.94
110	1	932.1	51.2	3.61	27.69
	2	906.3	22.5	2.34	42.71
	3	869.9	9	1.62	61.67
	4	830.9	4.8	1.44	69.67
150	1	915.5	18.5	5.25	19.06
	2	896.8	11.5	2.86	34.99
	3	879.5	7.7	2.26	44.27
	4	861.2	5.2	1.90	52.58
190	1	894.8	8.4	6.47	15.45
	2	880.7	6.3	3.57	27.99
	3	867.5	4.9	2.70	36.97
	4	853.7	3.8	2.25	44.36
230	1		4.6	7.98	12.53
	2		3.8	4.42	22.65
	3		3.2	3.23	30.99
	4		2.7	2.60	38.46

Note: Standard uncertainties u are u(T) = 0.288 K, u(P) = 0.003 MPa, and the combined expanded uncertainties U are U(μ) = 0.55 U(ρ) = 0.44 (level of confidence = 0.95).

In the next step, methane, pentane, and bitumen were mixed at two different concentrations. First mixture with 6, 50, 42 mole% and the second mixture with higher methane concentration at 15, 50, 35 mole% of methane, n-pentane, and bitumen, respectively. The mixture was used as feed,

and K-values of methane and n-pentane as well as density and viscosity of the liquid phase at each temperature and pressure were measured. Table 5-5 and Table 5-6 show the measured data for each of the mixtures.

Next, K-value, density and viscosity of methane/n-hexane/bitumen and methane/n-heptane/bitumen system was measured by preparing 15, 50 and, 35 mole% of methane, n-hexane or n-heptane, and bitumen as feed for the PVT apparatus. Measured K-values, density and viscosity of each system were reported in Table 5-7 and Table 5-8.

In the final stage of experimental data collection, K-values, density and viscosity of methane/propane, n-butane, n-pentane/bitumen system measured. A mixture of 10, 15, 20, 15 and, 40 mole% of methane, propane, n-butane, n-pentane, and bitumen was prepared as our feed for the experimental measurement. Table 5-9 shows the measured data.

Table 5-5: Experimental K-value, density, and viscosity data of methane/ n-pentane /bitumen system (using 15, 50, 35 mole% of methane, n-pentane, and bitumen as our feed).

				Phase Composition (mol%)					
				K-value		Liquid		Gas	
T (°C)	P (MPa)	ρs (kg/m^3)	Viscosity(cP)	C1	n-C5	C1	n-C5	C1	n-C5
70	1	897.7	23.6	25.31	0.38	3.10	55.72	78.56	21.44
	2	891.9	21	15.44	0.23	5.65	55.82	87.30	12.70
	3	881.2	19.1	9.22	0.16	9.94	53.03	91.67	8.33
110	1	880.8	9.7	27.45	0.92	1.91	51.47	52.53	47.47
	2	866	6.9	15.05	0.54	4.68	54.28	70.50	29.50
	3	860.6	6.1	10.22	0.41	7.65	53.69	78.15	21.85
	4	856.6	5.7	8.08	0.34	10.16	52.90	82.13	17.87
150	1	876.4	6.7	27.53	1.45	1.25	45.05	34.54	65.46
	2	852.3	4.1	15.73	0.97	3.19	51.59	50.18	49.82
	3	840.7	3.3	10.35	0.72	5.91	53.94	61.18	38.82
	4	835	3	8.37	0.63	8.00	52.86	66.95	33.05
190	1	871.9	5.3	30.44	2.39	0.88	30.64	26.72	73.28
	2	844.3	3	14.40	1.46	2.44	44.43	35.14	64.86
	3	825.9	2.2	10.24	1.12	4.47	48.49	45.77	54.23
	4	817.4	2	8.27	0.99	6.01	50.67	49.68	50.32
230	1	NA	3.5	28.91	3.38	0.82	22.55	23.67	76.33
	2	NA	2.5	15.40	2.10	1.79	34.51	27.64	72.36
	3	NA	1.9	9.99	1.54	3.33	43.16	33.32	66.68
	4	NA	1.5	7.80	1.28	4.90	48.08	38.24	61.76

Note: Standard uncertainties u are u(T) = 0.288 K, u(P) = 0.003 MPa, and the combined expanded uncertainties U are U(μ) = 0.55 U(ρ) = 0.44 (level of confidence = 0.95)

Table 5-6: Experimental K-value, density, and viscosity data of methane/n-pentane/bitumen system (using 6, 50, 42 mole% of methane, n-pentane, and bitumen as our feed).

				Phase Composition (mol%)					
				K-value		Liquid		Gas	
T (°C)	P (MPa)	ρs (kg/m^3)	Viscosity(cP)	C1	n-C5	C1	n-C5	C1	n-C5
70	1	896.8		28.10	0.41	2.78	53.97	78.05	21.95
110	1	877.6		29.67	0.93	1.71	52.92	50.85	49.15
	2	869.1		15.73	0.52	4.60	53.20	72.34	27.66
150	1	868.5		27.84	1.57	0.93	47.25	25.87	74.13
	2	849.5		15.39	0.99	3.13	52.60	48.12	51.88
190	1	865.4		28.35	2.38	0.58	35.04	16.50	83.50
	2	837.4		15.47	1.52	1.78	47.84	27.51	72.49
	3	823.3		10.77	1.16	3.79	51.18	40.82	59.18
230	1			29.05	3.40	0.46	25.53	13.31	86.69
	2			14.79	2.01	1.29	40.25	19.14	80.86
	3			9.91	1.58	2.61	46.93	25.87	74.13
	4			7.68	1.31	4.50	50.14	34.54	65.46

Note: Standard uncertainties u are u(T) = 0.288 K, u(P) = 0.003 MPa, and the combined expanded uncertainties U are U(μ) = 0.55 U(ρ) = 0.44 (level of confidence = 0.95)

Table 5-7: Experimental K-value, density, and viscosity data of methane/n-hexane/bitumen system (using 15, 50, 35 mole% of methane, n-hexane, and bitumen as our feed).

				Phase Composition (mol%)					
				K-value		Liquid		Gas	
T (°C)	P (MPa)	ρs (kg/m^3)	Viscosity(cP)	C1	n-C6	C1	n-C6	C1	n-C6
70	1	882.0	18.5	29.00	0.17	3.12	56.08	90.48	9.52
	2	877.7	16.8	15.92	0.10	5.94	52.47	94.59	5.41
	3	873.8	15.2	10.45	0.08	9.19	51.37	96.10	3.90
110	1	862.0	6.5	29.83	0.43	2.55	56.39	76.01	23.99
	2	857.9	5.8	15.98	0.25	5.40	55.22	86.27	13.73
	3	853.2	5.4	10.68	0.18	8.43	54.26	90.07	9.93
	4	849.1	5	8.28	0.17	10.98	52.81	90.89	9.11
150	1	848.0	3.8	28.88	0.90	1.83	52.47	52.74	47.26
	2	834.8	3	15.82	0.55	4.44	54.40	70.23	29.77
	3	829.4	2.7	11.47	0.42	6.76	53.65	77.55	22.45
	4	825.5	2.5	8.58	0.36	9.51	50.71	81.59	18.41
190	1	847.9	3.2	29.01	1.63	1.19	40.19	34.42	65.58
	2	820.7	2	15.85	0.97	3.20	50.77	50.76	49.24
	3	810.0	1.7	10.73	0.73	5.71	52.96	61.20	38.80
	4	802.9	1.6	8.09	0.60	8.47	52.46	68.59	31.41
230	1		2.8	29.70	2.40	0.93	30.17	27.68	72.32
	2		1.7	15.03	1.44	2.45	43.88	36.85	63.15
	3		1.4	10.32	1.10	4.45	49.05	45.92	54.08
	4		1.2	8.41	0.93	6.36	50.16	53.43	46.57

Note: Standard uncertainties u are u(T) = 0.288 K, u(P) = 0.003 MPa, and the combined expanded uncertainties U are U(μ) = 0.55 U(ρ) = 0.44 (level of confidence = 0.95)

Table 5-8: Experimental K-value, density, and viscosity data of methane/n-heptane/bitumen system (using 15, 50, 35 mole% of methane, n-heptane, and bitumen as our feed).

				Phase Composition (mol%)					
				K-value		Liquid		Gas	
T (°C)	P (MPa)	ρs (kg/m^3)	Viscosity	C1	n-C7	C1	n-C7	C1	n-C7
70	1	875.4	17.4	30.02	0.07	3.20	54.54	96.20	3.80
	2	870.6	15.1	14.98	0.04	6.53	53.49	97.78	2.22
	3	870.2	13.9	10.38	0.03	9.47	51.73	98.31	1.69
110	1	861.6	5.7	31.06	0.26	2.78	52.81	86.19	13.81
	2	858.0	5.3	15.61	0.12	5.97	54.12	93.26	6.74
	3	854.2	4.8	10.49	0.09	9.06	54.05	95.11	4.89
	4	849.3	4.6	8.59	0.08	11.14	51.04	95.68	4.32
150	1	838.4	2.9	30.83	0.54	2.25	56.45	69.36	30.64
	2	831.7	2.6	16.12	0.30	5.16	55.23	83.19	16.81
	3	828.2	2.4	10.78	0.23	8.16	53.37	87.96	12.04
	4	824.6	2.3	8.64	0.20	10.40	51.86	89.88	10.12
190	1	824.3	2.1	31.05	1.05	1.57	48.68	48.69	51.31
	2	808.4	1.6	16.01	0.60	4.15	55.69	66.48	33.52
	3	801.7	1.5	11.04	0.47	6.76	54.31	74.62	25.38
	4	797.5	1.4	8.38	0.36	9.61	54.12	80.57	19.43
230	1		1.6	28.94	1.78	1.16	37.43	33.46	66.54
	2		1.2	15.81	1.00	3.15	50.16	49.79	50.21
	3		1.1	11.27	0.75	5.38	52.44	60.62	39.38
	4		1	8.58	0.61	7.92	52.75	67.96	32.04

Note: Standard uncertainties u are u(T) = 0.288 K, u(P) = 0.003 MPa, and the combined expanded uncertainties U are U(μ) = 0.55 U(ρ) = 0.44 (level of confidence = 0.95)

Table 5-9: Experimental K-value, density, and viscosity data of methane/propane, n-butane, n-pentane/bitumen system (using 10, 15, 20, 15, 40 mole% of methane, propane, n-butane, n-pentane, and bitumen as our feed).

				Phase Composition (mol%)											
				K-value				Liquid				Gas			
T (°C)	P (MPa)	ρs (kg/m^3)	Viscosity	C1	C3	nC4	nC5	C1	C3	nC4	nC5	C1	C3	nC4	nC5
70	1	918.2	52.3	28.57	2.57	0.99	0.41	1.47	11.91	20.78	16.98	41.92	30.59	20.59	6.90
	2	907.1	36.3	16.78	1.59	0.62	0.26	3.62	14.00	20.88	15.95	60.69	22.21	12.98	4.12
	3	901.1	30	10.64	1.12	0.46	0.19	6.65	14.95	20.84	15.39	70.79	16.71	9.50	3.00
110	1	910.4	24.1	31.59	4.03	1.85	0.91	0.82	7.50	16.04	15.58	25.81	30.26	29.70	14.23
	2	888.5	13.4	16.08	2.38	1.13	0.57	2.52	11.88	19.57	15.91	40.45	28.33	22.14	9.08
	3	877.3	10.1	11.16	1.78	0.86	0.45	4.52	13.91	20.56	15.63	50.49	24.72	17.76	7.03
	4	872.4	9.0	8.86	1.48	0.73	0.39	6.55	14.38	20.23	15.11	58.00	21.32	14.85	5.84
150	1	901.8	12.6	29.22	5.52	2.87	1.60	0.69	5.08	11.35	12.06	20.13	28.05	32.55	19.27
	2	879.5	7.4	15.83	3.35	1.75	0.99	1.68	8.74	16.71	15.02	26.60	29.28	29.18	14.94
	3	863.9	5.3	10.71	2.36	1.31	0.78	3.26	11.92	19.14	15.34	34.89	28.19	25.00	11.92
	4	854.7	4.4	8.60	1.98	1.11	0.67	4.76	13.39	20.05	15.48	40.94	26.46	22.27	10.33
190	1	887.1	7.3	30.95	7.74	4.43	2.69	0.57	3.45	7.56	8.25	17.63	26.68	33.51	22.18
	2	867.8	5.0	16.00	4.13	2.45	1.56	1.32	6.75	13.03	12.26	21.10	27.91	31.90	19.09
	3	852.8	3.8	10.77	2.98	1.81	1.17	2.34	9.51	16.48	14.19	25.24	28.34	29.83	16.60

	4	840.6	3.1	8.20	2.37	1.47	0.97	3.66	11.73	18.66	15.10	30.05	27.82	27.48	14.65
230	1		4.6	33.59	9.59	5.91	3.88	0.50	2.71	5.69	6.04	16.89	26.00	33.67	23.44
	2		3.5	16.23	4.94	3.13	2.10	1.17	5.44	10.49	10.13	18.98	26.89	32.80	21.32
	3		2.9	10.85	3.54	2.30	1.59	1.98	7.75	13.75	12.25	21.52	27.44	31.60	19.44
	4		2.4	8.43	2.83	1.87	1.31	2.93	9.74	16.09	13.49	24.75	27.53	30.02	17.71

Note: Standard uncertainties u are u(T) = 0.288 K, u(P) = 0.003 MPa, and the combined expanded uncertainties U are U(μ) = 0.55 U(ρ) = 0.44 (level of confidence = 0.95)

5.4.1 Phase behavior modeling

The collected experimental PVT data of solvent and bitumen were modeled using PR-EoS[94] in CMG WinProp[95]. Liquid phase density and viscosity were modeled were also modeled by using the experimental data.

The binary interaction coefficient (BIC) between hydrocarbons were turned to model the solubility data. The exponent (n) in the following equation will was adjusted to calculate the BIC:

$$d_{ij} = 1 - \left(\frac{2\sqrt{V_{ci}^{1/3} V_{cj}^{1/3}}}{V_{ci}^{1/3} + V_{cj}^{1/3}} \right)^{n} \qquad 5\text{-}2$$

where V_c is critical volume of the component. The tuned parameters for each solvent bitumen system are reported in the next section.

In the first step to model the phase behaviour of the system, critical properties of the bitumen were tuned. Then, T_c and P_c of the bitumen were found by using regression to match density data of the dead bitumen. Table 5-10 shows properties of bitumen were used in the PR-EoS to model the phase behaviour of various Methane / bitumen / solvent(s) systems.

Table 5-10: Molecular weight, specific gravidity, acentric factor, and critical properties of the Athabasca bitumen sample.

Component	MW (g/mole)	P_c (MPa)	T_c(K)	ω	SG
Bitumen	523	0.997	783.99	1.19	1.004

The exponent (n) of the binary interaction parameter in Equation 5-2 was tuned to match the experimental K-values. Table 3-1 summarized the values of *n* for each system as well as their average absolute relative deviation (AARD).

Table 5-11: Exponent (n) and AARD for K-values for methane/solvent(s)/bitumen system.

System	n	AARD %					
		C1	**C3**	**nC4**	**nC5**	**nC6**	**nC7**
C1/C3-nC4-nC5/Bitumen	0.23534	6.17	5.69	4.30	3.83	n/a	n/a
C1/nC5/Bitumen	0.37352	5.13	n/a	n/a	5.34	n/a	n/a
C1/nC6/Bitumen	0.92689	4.25	n/a	n/a	n/a	3.33	n/a
C1/nC7/Bitumen	1.2108	2.70	n/a	n/a	n/a	n/a	3.65

Figure 5-4 to Figure 5-9 show the comparison between experimental and calculated k-values of methane, propane, n-butane, n-pentane, n-hexane, and n-heptane data. The results show that methane K-values is not sensitive to temperature. However, other K-values are decreasing by pressure and increasing by temperature.

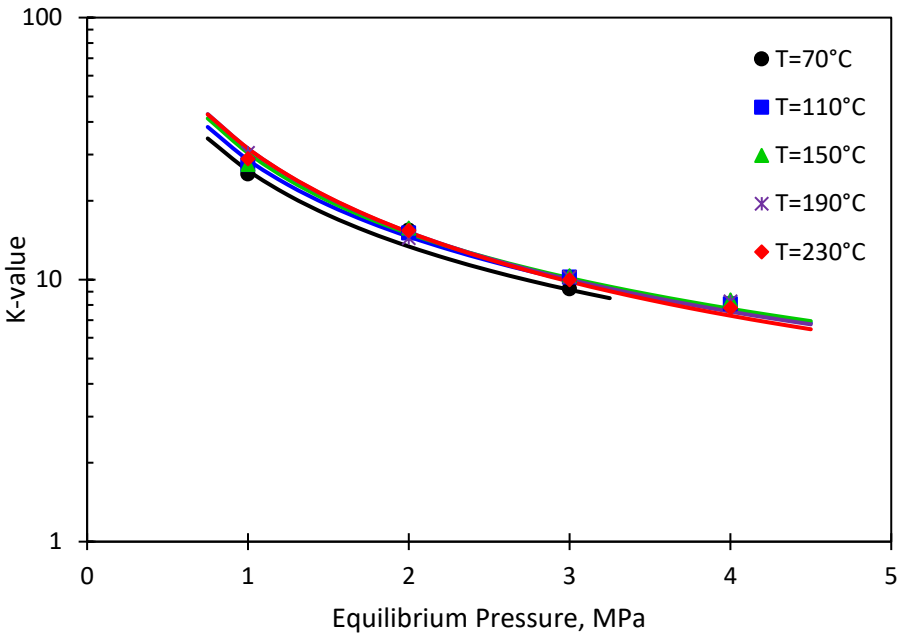


Figure 5-4: Measured K-value of methane in MacKay River bitumen as a function of pressure versus predicted K-value; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

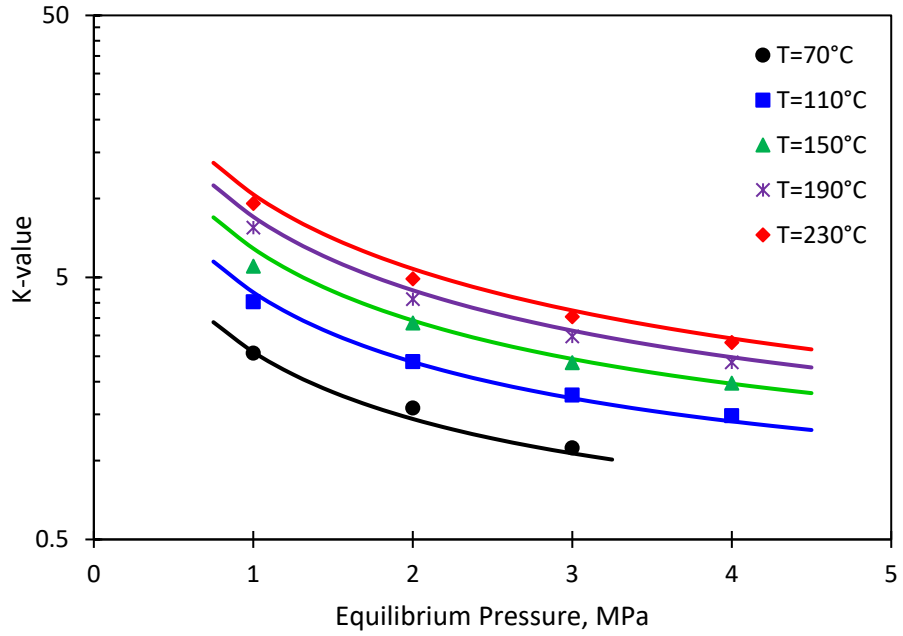


Figure 5-5: Measured K-value of propane in MacKay River bitumen as a function of pressure versus predicted K-value; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

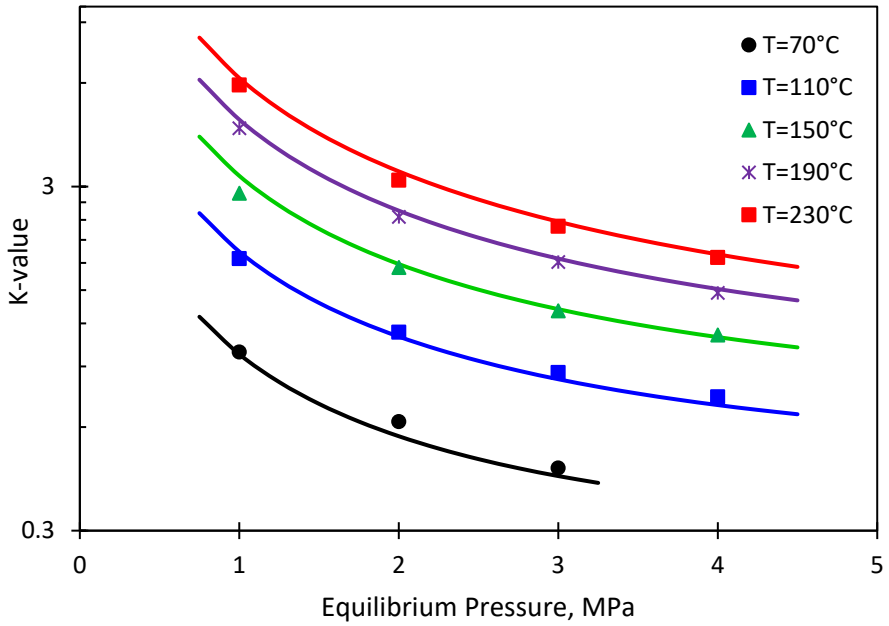


Figure 5-6: Measured K-value of n-butane in MacKay River bitumen as a function of pressure versus predicted K-value; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

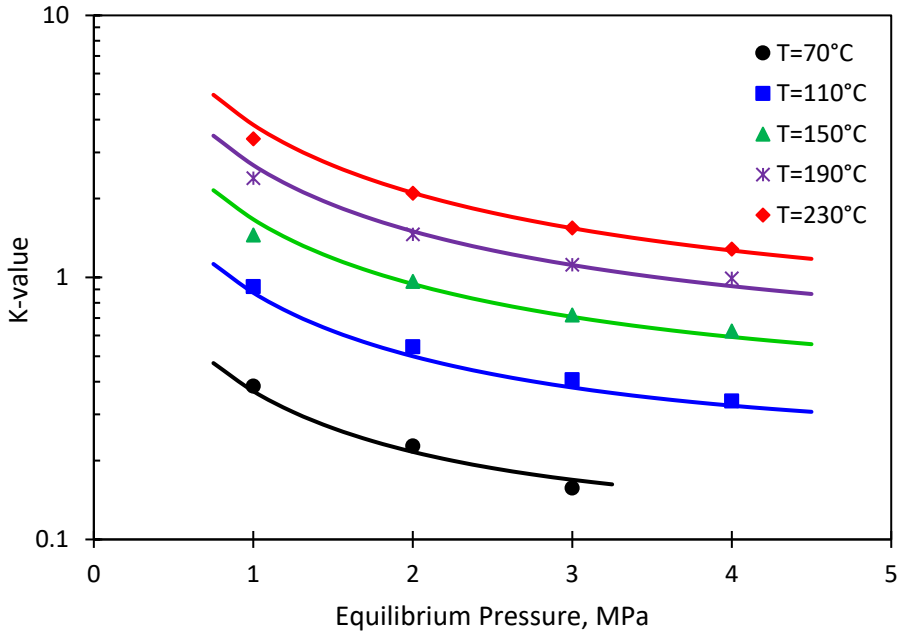


Figure 5-7: Measured K-value of n-pentane in MacKay River bitumen as a function of pressure versus predicted K-value; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

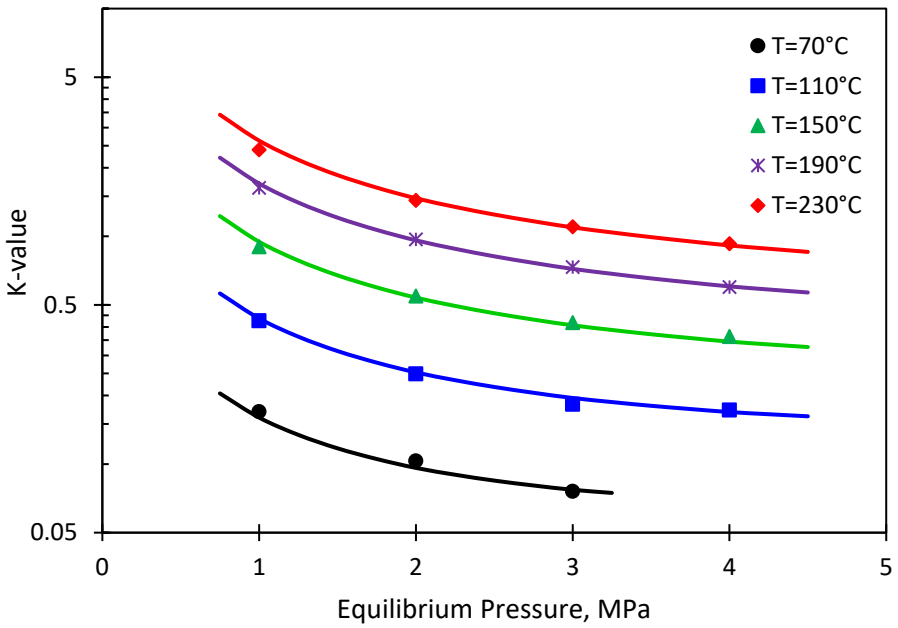


Figure 5-8: Measured K-value of n-hexane in MacKay River bitumen as a function of pressure versus predicted K-value; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

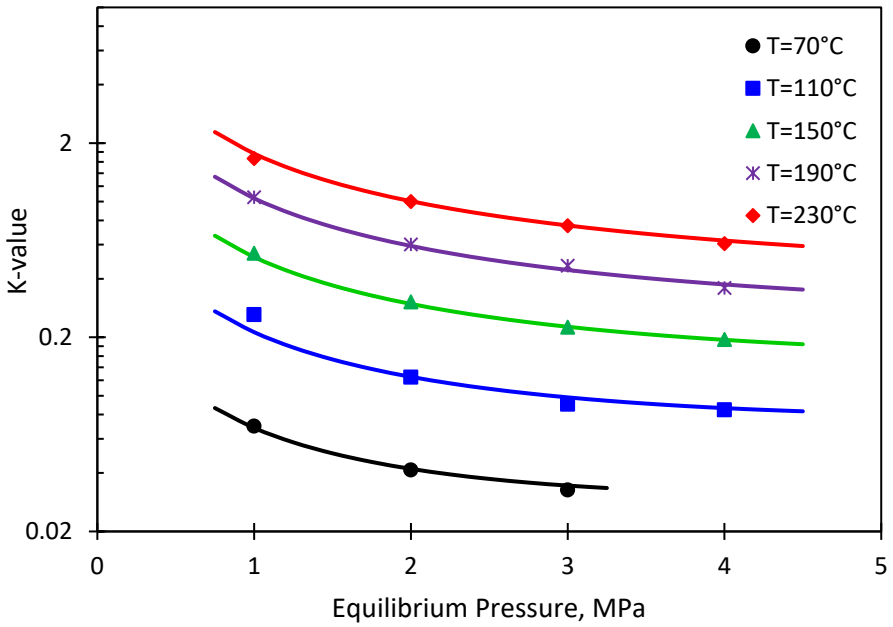


Figure 5-9: Measured K-value of n-heptane in MacKay River bitumen as a function of pressure versus predicted K-value; ♦, ■, ×, ▲, •, experiment data, ─, predicted solubility.

Figure 5-10 and Figure 5-11 show the comparison between experimental and calculated k-values of methane and n-pentane data. In the k-value calculation process, we only applied the data from C_1/nC_5/bitumen (High GOR) system and the deviation between calculated and measured data for various system is within acceptable range.

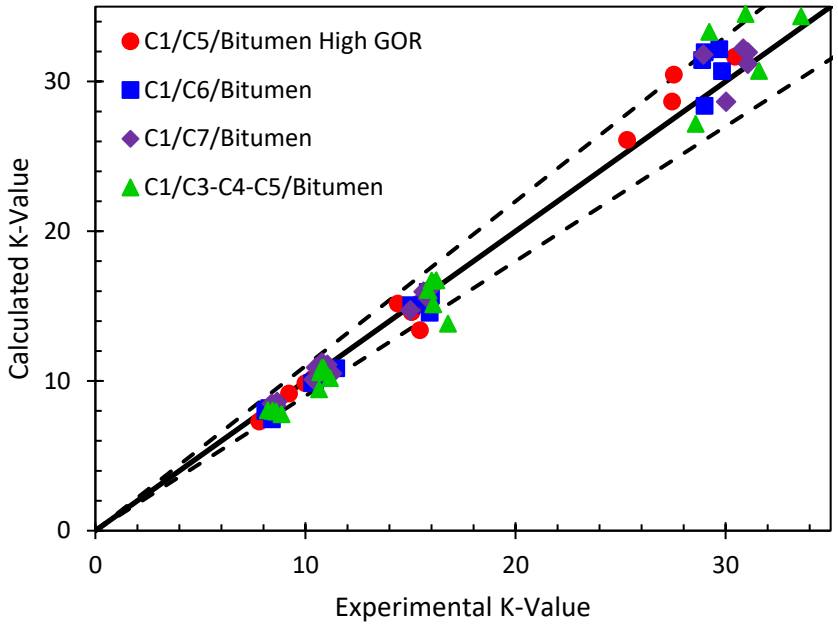


Figure 5-10: Measured K-values of methane vs calculated K-values.

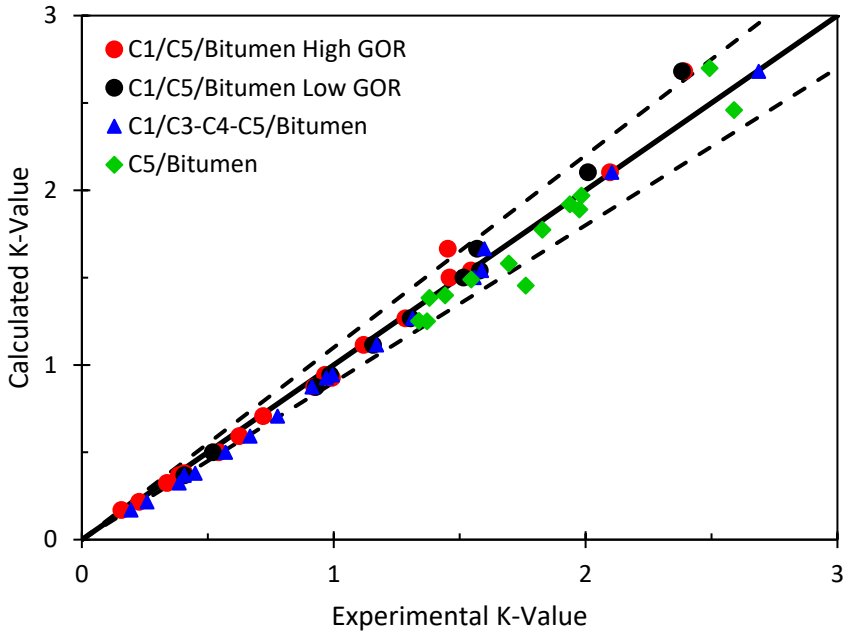


Figure 5-11: Measured K-values of n-pentane vs calculated K-values.

Figure 5-12 shows the comparison between K-values of methane for methane/solvent(s)/bitumen and methane/bitumen systems. Likewise, K-values of n-pentane for various PVT systems were compared and the results are presented in Figure 5-13. The results show variation of methane and n-pentane K-values between various systems are within the experimental error which means for the modeling and reservoir simulation purposes, we can use the K-values for any of these systems.

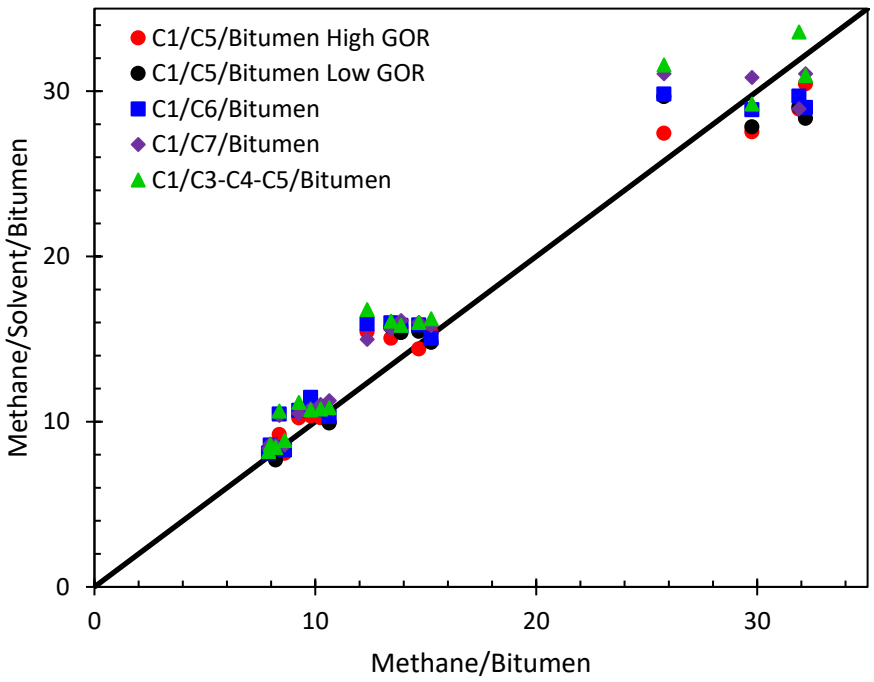


Figure 5-12: Measured K-values of methane for C1/Solvent(s)/Bitumen vs measured K-values of methane of C1/Bitumen system.

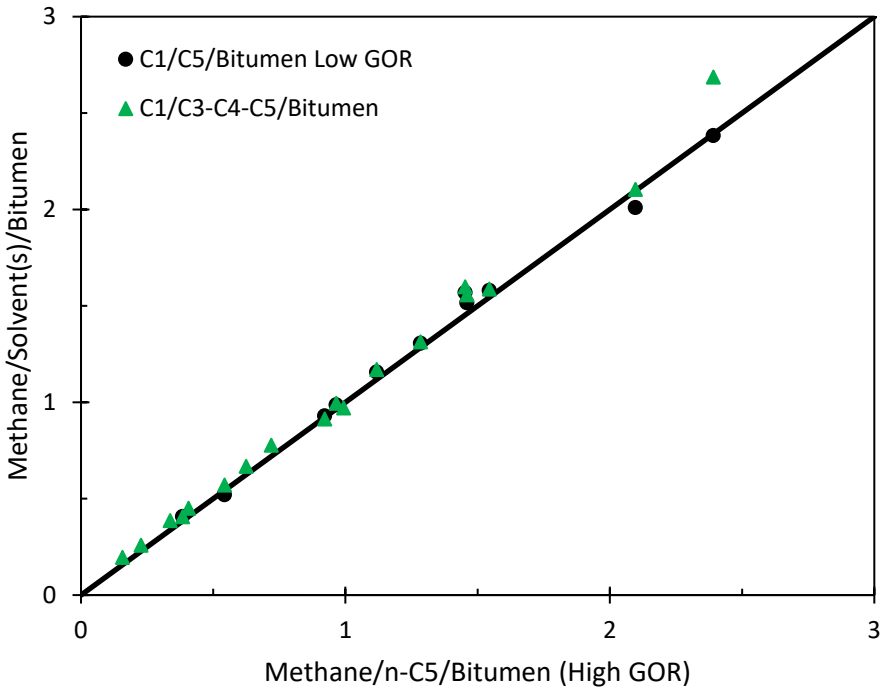


Figure 5-13: Comparison of measured K-values of n-pentane for various C1/Solvent(s)/Bitumen system

5.4.2 Density modeling

Linear temperature-dependent volume shift method was used to model the density of the bitumen with solvent system[96].

$$S_i = S_{0i} + S_{1i}\left(T - T_{ref}\right) \quad 5\text{-}3$$

$$S_{0i} = \frac{MW_i}{\rho_i} - V_i^L \quad 5\text{-}4$$

where T is absolute temperature in Kelvin, V_i^L is the molar volume ρ_i is the density, S_{1i} is the Peneloux parameters. To match the liquid density, one or both coefficients (S_{0i} , S_{1i}) can be used in the regression.

Volume shift coefficients (S_{0i} , S_{1i}) of each component were tuned and the experimental liquid phase densities were matched. Table 5-12 summarized the values of S_{0i} , S_{1i} for each system as well as their average absolute relative deviation (AARD). The density of liquid phase was matched whit AARD of less than 1% for all the systems.

Table 5-12: exponent (n) and AARD for density for methane/solvent(s)/bitumen system.

System		Component							AARD
		Bitumen	C1	C3	nC4	nC5	nC6	nC7	
C_1/C_3-nC_4-nC_5/Bitumen	S_0	9.50E-02	0	0	0	0	n/a	n/a	0.63%
	S_1	7.04E-02	0	0	0	0	n/a	n/a	
C_1/nC_5/Bitumen	S_0	2.38E-01	0	n/a	n/a	0	n/a	n/a	0.54%
	S_1	-2.85E-04	0	n/a	n/a	0	n/a	n/a	
C_1/nC_6/Bitumen	S_0	1.38E-01	0	n/a	n/a	n/a	0	n/a	0.34%
	S_1	-3.63E-04	0	n/a	n/a	n/a	0	n/a	
C_1/nC_7/Bitumen	S_0	1.14E-01	0	n/a	n/a	n/a	n/a	0	0.52%
	S_1	-3.59E-04	0	n/a	n/a	n/a	n/a	0	

Figure 5-14 to Figure 5-17 show the comparison between experimental and calculated density of liquid phase for methane/ solvent(s)/bitumen system.

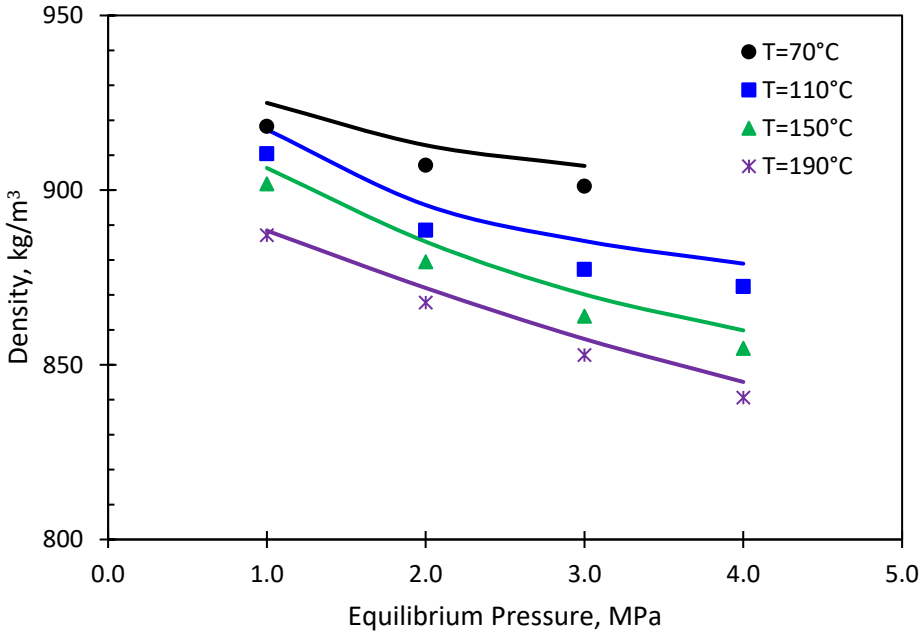


Figure 5-14: Measured density of liquid phase of C1/ C3, -nC4, -nC5/Bitumen as a function of pressure versus predicted density; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

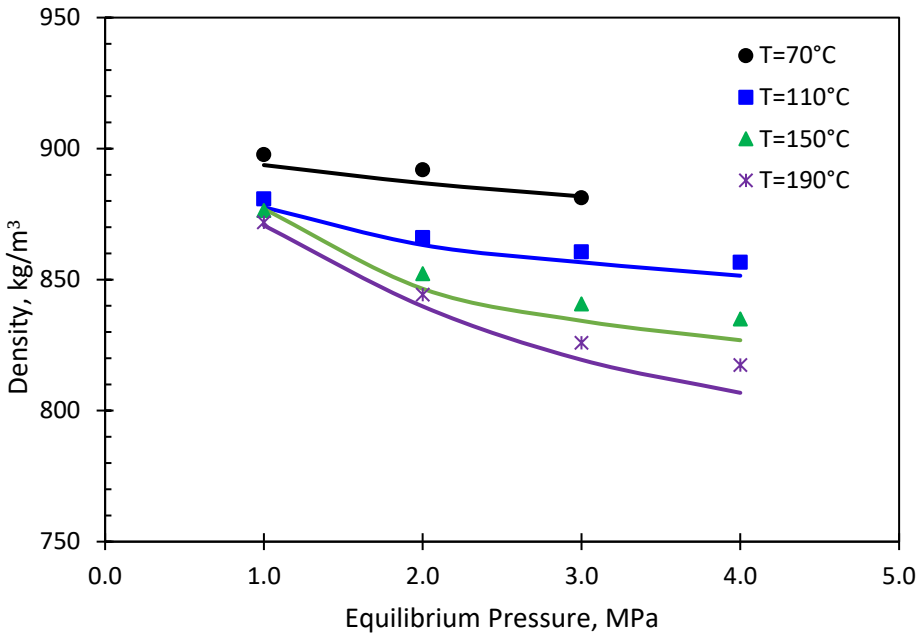


Figure 5-15: Measured density of liquid phase of C1/ nC5/Bitumen as a function of pressure versus predicted density; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

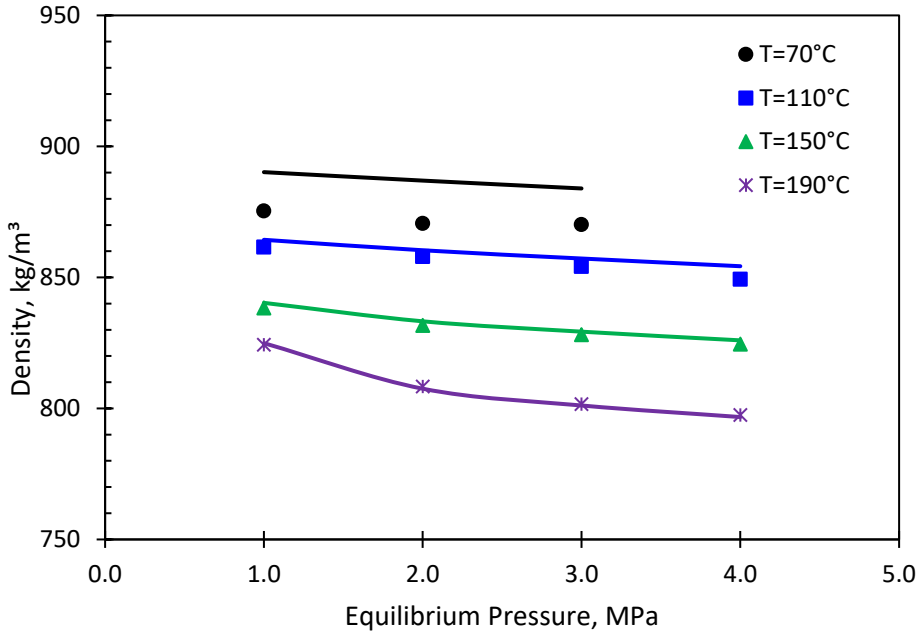


Figure 5-16: Measured density of liquid phase of C1/nC6/Bitumen as a function of pressure versus predicted density; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

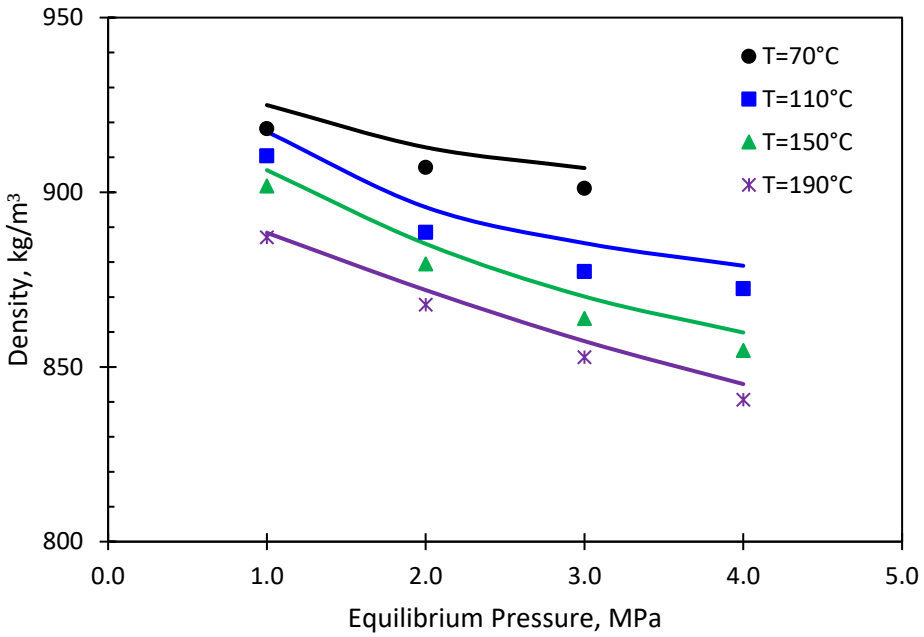


Figure 5-17: Measured density of liquid phase of C1/nC7/Bitumen as a function of pressure versus predicted density; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

5.4.3 Viscosity modeling

The following mixing rule implemented to calculate the viscosity of the mixture.

$$\ln \mu = \sum_{i=1}^{N} x_i \ln \mu_i \qquad 5\text{-}5$$

where μ is the dynamic viscosity, N is the number of components in the mixture, x_i and μ_i are the mole fraction and liquid viscosity. The viscosity of the bitumen was measured and reported in Table 2-1. For the methane and solvent(s) dissolved in the bitumen, an effective viscosity is a function of the temperature and pressure was assumed [93].

$$\mu_s = C_1 + C_2 T + C_3 T^2 + (C_4 + C_5 T)P \qquad 5\text{-}6$$

where C_1 to C_5 are the fitting parameters and were tuned using experimental viscosity data for live bitumen – solvent systems. T and P are temperature (K) and pressure (MPa), respectively. Table 5-13 summarized fitting parameters for methane, propane, n-butane, n-pentane, n-hexane, and n-heptane.

Table 5-13: Required parameters to calculate the effective viscosity of solvents.

Solvent	Model Parameters				
	C_1	C_2	C_3	C_4	C_5
Methane	5.78E+01	-1.58E-01	8.34E-05	-9.94E+00	2.15E-02
Propane	3.43E+00	-3.11E-03	-2.36E-06	-8.86E-02	-1.03E-04
n-Butane	1.52E+00	4.31E-04	-3.43E-07	-1.12E-01	1.56E-04
n-Pentane	6.58E-01	-6.68E-05	4.62E-09	2.42E-02	-7.81E-05
n-Hexane	6.69E-01	-3.02E-04	-7.63E-08	-2.07E-02	-5.44E-05
n-Heptane	5.45E-01	-2.81E-04	-1.68E-07	-1.53E-07	-3.45E-05

Experimental viscosity data and proposed calculated viscosity using effective viscosity of solvent were compared. AARD between measured and calculated viscosities are summarized in Table 5-14.

Table 5-14: AARD between experimental and calculated viscosity data.

System	AARD
C1/Bitumen	6.5%
C3/Bitumen	8.5%
C1/C3-nC4-nC5/Bitumen	10.7%
C1/nC5/Bitumen	13.0%
C1/nC6/Bitumen	7.7%
C1/nC7/Bitumen	8.1%

Figure 5-18 to Figure 5-21 show comparison of measured and calculated viscosities of methane/solvent(s)/bitumen systems. The results show a good agreement, and the deviation of calculated and measured viscosities increases at lower temperature.

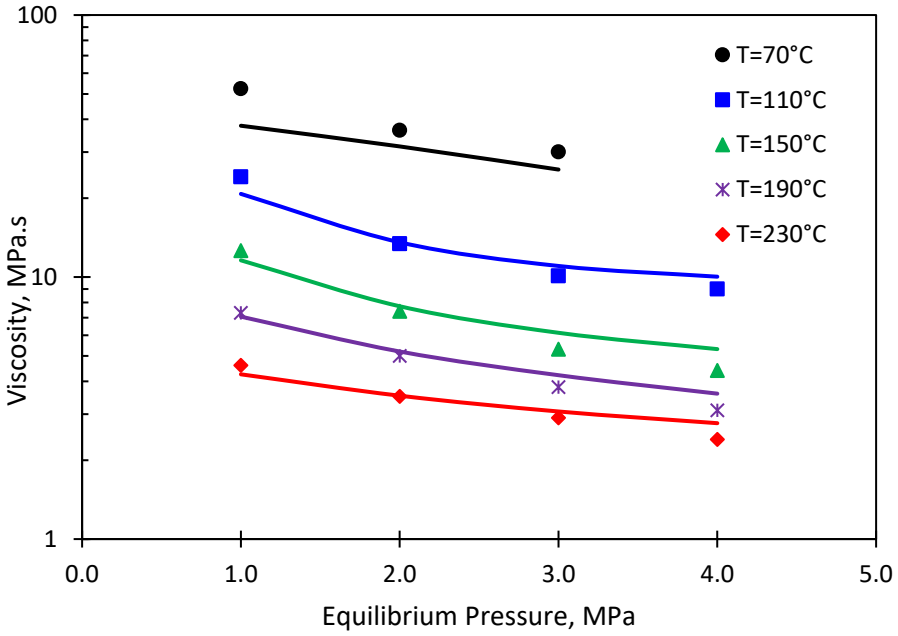


Figure 5-18: Measured viscosity of liquid phase of C1/ C3-nC4-nC5/Bitumen as a function of pressure versus predicted viscosity; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

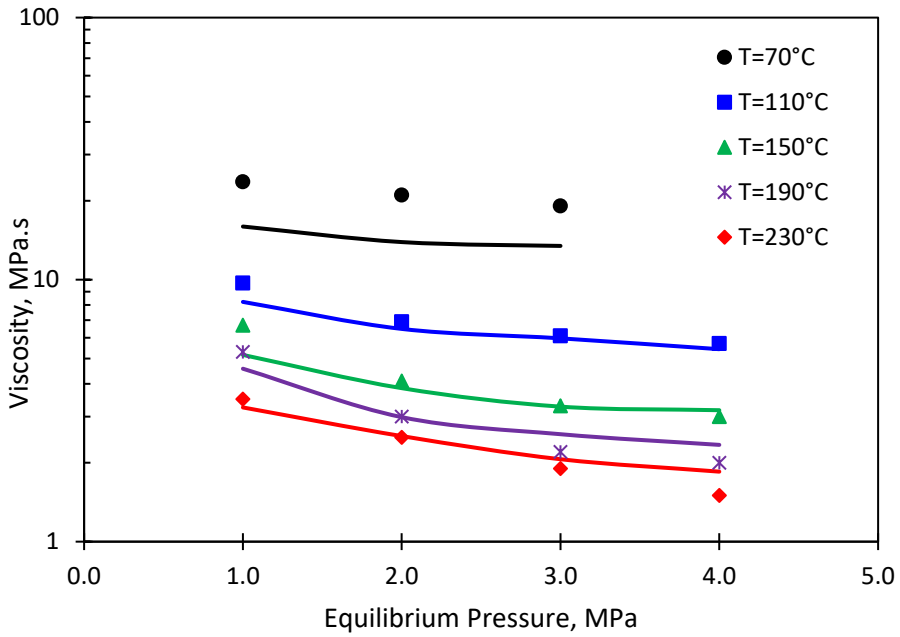


Figure 5-19: Measured viscosity of liquid phase of C1/nC5/Bitumen as a function of pressure versus predicted viscosity; ♦, ■, ▲, •, experiment data, —, predicted solubility.

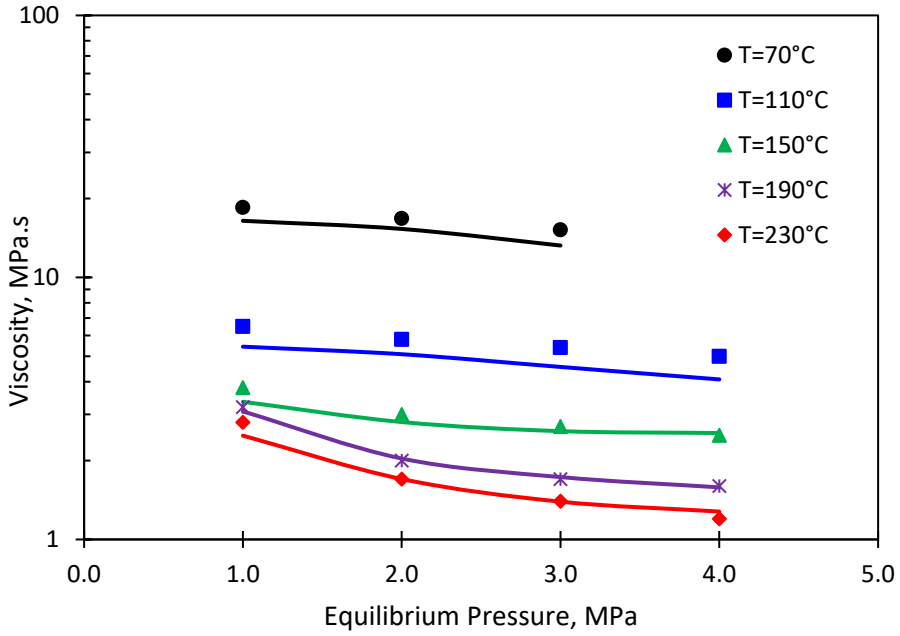


Figure 5-20: Measured viscosity of liquid phase of C1/nC6/Bitumen as a function of pressure versus predicted viscosity; ♦, ■, ▲, •, experiment data, —, predicted solubility.

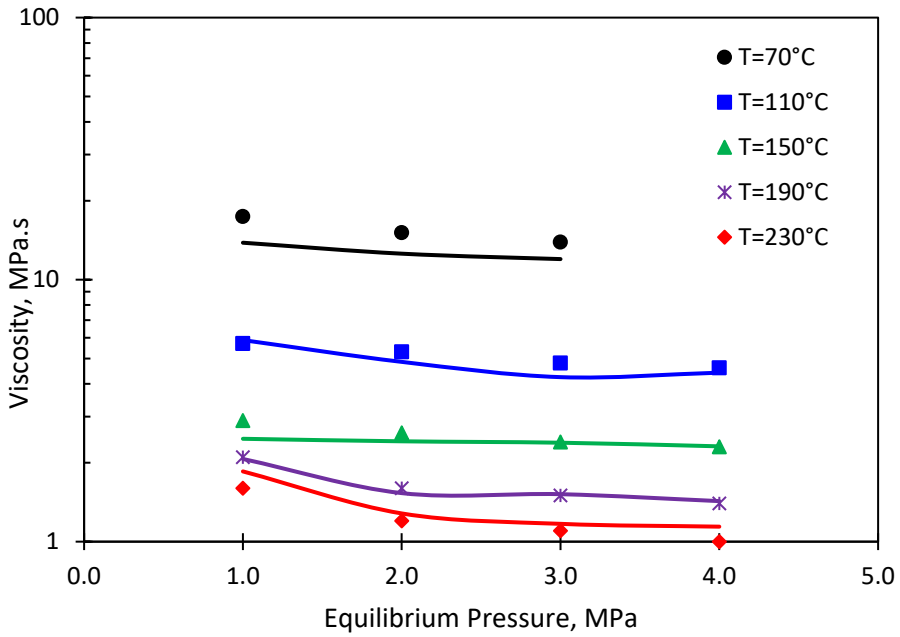


Figure 5-21: Measured viscosity of liquid phase of C1/nC7/Bitumen as a function of pressure versus predicted viscosity; ♦, ■, ▲, •, experiment data, ─, predicted solubility.

5.5 Summary and conclusion

There is a requirement to improve current bitumen recovery processes as oil producer companies need to reduce their GHG and energy consumptions. Using solvent, as an additive to steam or in solvent dominant bitumen recoveries, has shown promises to reduce the GHG emission and production cost. K-value, viscosity and density of the bitumen/solvent systems are one of the key properties to design and optimize solvent-aided thermal recoveries. Current available data are focusing on pure lighter solvent/bitumen system. Multicomponent solvents such as naphtha, condensate and LPG are among the proposed solvents for the solvent-aided thermal processes and very limited data available for these types of these multicomponent solvents.

Following are the main contributions and conclusion of this work:

A systematic approach to compare the effect of presence methane and other solvents on their K-values was presented.

A new set of K-value, density, and viscosity data for n-alkane and bitumen at temperatures from 70-230°C and pressures from 1-4 MPa was presented, which is necessary for the simulation and optimization of solvent aided thermal recovery of bitumen.

A fluid model was generated based on the experimental PVT data using WinProp with acceptable accuracy.

CHAPTER SIX:

6 Conclusions and Recommendations

This study presented experimental and modelling results for DME and various hydrocarbon solvents (C_1 to n-C_7) with MacKay River bitumen. The effect of the existence of methane on the K-values of other hydrocarbon solvents is studied in this chapter. The K-value, density, and viscosity of methane / solvent (n-C_5, n-C_6, n-C_7, and n-C_5+n-C_6+n-C_7) / bitumen are measured and modeled. The K-values of methane, propane, n-C_5, and n-C_6 were compared in live and dead bitumen systems.

6.1 Conclusions

6.1.1 Methane-, Ethane-, Propane- and Butane- Bitumen Systems at High Temperatures

Solubilities of gaseous solvents, including methane, ethane, propane, and n-butane in Athabasca bitumen at high temperatures up to 260°C were measured, and the Peng-Robinson EoS was employed to model the solubility data. It was found that the solubility of methane in bitumen varies slightly with the temperature at the experimental condition. However, pressure can highly affect the methane solubility in bitumen. The results showed that the effect of temperature is more evident on the solubility of ethane, propane and n-butane in bitumen compared to the solubility of methane.

It was found that the solubility of heavier solvents in bitumen decreases significantly at high temperatures. This is particularly more evident at higher pressures.

6.1.2 Experimental Phase Behavior Data of DME-Bitumen System

As a potential alternative to low boiling point hydrocarbons such as propane and butane, DME was suggested as a solvent in ES-SAGD processes. The vapor-liquid equilibrium data for DME/ bitumen at various temperatures and pressure ranges were measured. The measured data, including solubility, density, and viscosity, were compared to propane/bitumen and butane/bitumen systems. The measured DME solubility is more than propane and less than butane. The same trends were observed for density and viscosity measurements. The results show that DME, with higher solubility and viscosity reduction compared to propane, has the potential to be considered as an alternative to hydrocarbons in solvent-aided processes.

6.1.3 Co-injection of Steam and DME in 2D Sand-Pack

Co-injection of DME as a solvent with steam was evaluated in bitumen recovery processes. To investigate the performance of DME, a series of experiments were conducted using a 2D sand-pack saturated with Athabasca bitumen. Co-injection of steam with DME was compared with steam and steam/butane injections. Experimental results revealed that using butane and DME as additives to steam will improve the bitumen recovery. DME showed a performance close to butane.

6.1.4 Experimental Phase Behavior Data of Methane-Solvent(s)-Bitumen Systems

The effect of the existence of methane on the K-values of other hydrocarbon solvents in bitumen was studied. The comprehensive phase behaviour data set of methane, propane, butane and n-C_5 / bitumen and methane / solvent (n-C_5, n-C_6, n-C_7, and n-C_3+n-C_4+n-C_5) / bitumen systems

including solvent K-value, density, and viscosity at temperatures up to 230 °C and pressures up to 4 MPa were generated. The results show the variation of methane and n-pentane K-values between various systems are within the experimental error, which means for the modeling and reservoir simulation purposes, we can use the K-values for any of these systems.

6.2 Recommendations

This study presented experimental measurement and modeling results of vapor-liquid equilibrium (VLE) of solvents with bitumen and methane-bitumen mixtures. Extension of this work with other solution gas, such as CO_2, is recommended. It is also recommended to conduct experiments with higher concentrations of solvent to evaluate the vapor-liquid-liquid equilibrium (VLLE) of live bitumen and solvent system.

Water is an essential part of in-situ thermal recovery processes. Some water already exists in the reservoir as residual water saturation, affecting the solvent/bitumen equilibrium properties. Therefore, we recommend further phase behavior experiments on water-solvent-live bitumen equilibrium systems.

7 References

1. James, L. A., Rezaei, N. & Chatzis, I. VAPEX, warm VAPEX and hybrid VAPEX - The state of enhanced oil recovery for in situ heavy oils in Canada. *Journal of Canadian Petroleum Technology* **47**, 12–18 (2008).

2. Sadeghi, A. *et al.* Numerical modeling of electromagnetic-based thermal recovery techniques combined with solvent injection. *Int J Heat Mass Transf* **151**, 119393 (2020).

3. Sadeghi, A., Hassanzadeh, H. & Harding, T. G. A comparative study of oil sands preheating using electromagnetic waves, electrical heaters and steam circulation. *Int J Heat Mass Transf* **111**, 908–916 (2017).

4. Nasr, T. N., Beaulieu, G., Golbeck, H. & Heck, G. Novel expanding solvent-SAGD process "ES-SAGD". *Canadian International Petroleum Conference 2002, CIPC 2002* **42**, (2002).

5. Kar, T. *et al.* Mobilization of Trapped Residual Oil via Secondary SAGD with Propane. in *SPE Western Regional Meeting* (Society of Petroleum Engineers, 2017).

6. Hascakir, B. How to select the right solvent for solvent-aided steam injection processes. *J Pet Sci Eng* **146**, 746–751 (2016).

7. Nourozieh, H., Kariznovi, M. & Abedi, J. Measurement and Modeling of Solubility and Saturated-Liquid Density and Viscosity for Methane/Athabasca-Bitumen Mixtures. *SPE Journal* **21**, 180–189 (2016).

8. Govind, P. A., Das, S. & Company, C. Expanding Solvent SAGD in Heavy Oil Reservoirs. in *International Thermal Operations and Heavy Oil Symposium* (Society of Petroleum Engineers).

9. Ardali, M., Mamora, D. D. & Barrufet, M. A Comparative Simulation Study of Addition of Solvents to Steam in SAGD Process. in *Canadian Unconventional Resources and International Petroleum Conference* (Society of Petroleum Engineers). doi:10.2118/138170-MS.

10. Sheng, K., Okuno, R. & Wang, M. Water-Soluble Solvent as an Additive to Steam for Improved SAGD. in *SPE Canada Heavy Oil Technical Conference* (Society of Petroleum Engineers). doi:10.2118/184983-MS.

11. Zare, A., Abdulhameed, F. M., Hesland, B. & Hamouda, A. A. Enhanced heavy oil recovery (SAGD), coinjection of steam and solvent, reduction of CEOR and CSOR. *Pet Sci Technol* **35**, 570–577 (2017).

12. Mehrotra, A. K. & Svrcek, W. Y. Properties of cold lake bitumen saturated with pure gases and gas mixtures. *Can J Chem Eng* **66**, 656–665 (1988).

13. Fu, C. T. *et al*. Vapour-Liquid Equilibrium Properties for Gas-Cold Lake Bitumen. in *Annual Technical Meeting* (Petroleum Society of Canada).

14. Kariznovi, M., Nourozieh, H. & Abedi, J. Phase Behavior and Viscosity Measurements of Heavy Crude Oil With Methane and Ethane at High-Temperature Conditions. in *SPE Western Regional Meeting* (Society of Petroleum Engineers This). doi:10.2118/152321-MS.

15. Badamchi-Zadeh, A., Yarranton, H. W., Svrcek, W. Y. & Maini, B. B. Phase behaviour and physical property measurements for VAPEX solvents: Part I. Propane and athabasca bitumen. *Journal of Canadian Petroleum Technology* **48**, 54–61 (2009).

16. Jossy, C., Frauenfeld, T. & Rajan, V. Partitioning of bitumen-solvent systems into multiple liquid phases. *Journal of Canadian Petroleum Technology* **48**, 16–20 (2009).

17. Frauenfeld, T., Gerald, K. & Zhou, S. PVT and Viscosity Measurements for Lloydminster-Aberfeldy and Cold Lake Blended Oil Systems. in *nternational Thermal Operations and Heavy Oil Symposium and International Horizontal Well Technology Conference* (Society of Petroleum Engineers). doi:10.2118/79018-MS.

18. Nourozieh, H., Kariznovi, M. & Abedi, J. Experimental and modeling studies of phase behavior for propane/Athabasca bitumen mixtures. *Fluid Phase Equilib* **397**, 37–43 (2015).

19. Han, B., Yang, G., Ke, J., Mao, C. & Yan, H. Phase equilibria of supercritical propane–Fengcheng bitumen system and the density and viscosity of the liquid phase. *Fluid Phase Equilib* **143**, 205–211 (1998).

20. Zirrahi, M., Hassanzadeh, H. & Abedi, J. Experimental and modelling studies of MacKay River bitumen and light n-alkane binaries. *Can J Chem Eng* **95**, 1417–1427 (2017).

21. Haddadnia, A., Azinfar, B., Zirrahi, M., Hassanzadeh, H. & Abedi, J. Thermophysical properties of dimethyl ether/Athabasca bitumen system. *Canadian Journal of Chemical Engineering* **96**, 597–604 (2018).

22. Zirrahi, M., Hassanzadeh, H. & Abedi, J. Experimental and modeling studies of MacKay River bitumen and water. *J Pet Sci Eng* **151**, 305–310 (2017).

23. Zirrahi, M., Azinfar, B., Hassanzadeh, H. & Abedi, J. Measuring and Modeling the Solubility and Density for CO2-Toluene and C2H6-Toluene Systems. *J Chem Eng Data* **60**, 1592–1599 (2015).

24. Riazi, M. R. & Al-Sahhaf, T. A. Physical properties of heavy petroleum fractions and crude oils. *Fluid Phase Equilib* **117**, 217–224 (1996).

25. Peng, D. Y. & Robinson, D. B. A New Two-Constant Equation of State. *Industrial and Engineering Chemistry Fundamentals* **15**, 59–64 (1976).

26. Nourozieh, H., Kariznovi, M. & Abedi, J. Solubility of n-Butane in Athabasca Bitumen and Saturated Densities and Viscosities at Temperatures Up to 200 º C. *SPE Journal* **22**, 94–102 (2017).

27. Boleslaw L. Ignasiak & Keijiro Yamaoka. In-situ recovery of bitumen or heavy oil by injection of di-methyl ether. (2009).

28. Nasr, T. N. & Ayodele, O. R. New Hybrid Steam-Solvent Processes for the Recovery of Heavy Oil and Bitumen. *12th Abu Dhabi International Petroleum Exhibition and Conference, ADIPEC 2006: Meeting the Increasing Oil and Gas Demand Through Innovation* **2**, 791–807 (2006).

29. Nourozieh, H., Kariznovi, M. & Abedi, J. Experimental and modeling studies of phase behavior for propane/Athabasca bitumen mixtures. *Fluid Phase Equilib* **397**, 37–43 (2015).

30. Orr, B. ES-SAGD; Past, Present and Future. *SPE Annual Technical Conference and Exhibition* **7**, 4756–4771 (2009).

31. Diedro, F., Bryan, J., Kryuchkov, S. & Kantzas, A. Evaluation of Diffusion of Light Hydrocarbon Solvents in Bitumen. *Society of Petroleum Engineers - SPE Canada Heavy Oil Technical Conference 2015, CHOC 2015* 307–328 (2015) doi:10.2118/174424-MS.

32. Arcoumanis, C., Bae, C., Crookes, R. & Kinoshita, E. The potential of di-methyl ether (DME) as an alternative fuel for compression-ignition engines: A review. *Fuel* **87**, 1014–1030 (2008).

33. Larson, E. D. & Yang, H. Dimethyl ether (DME) from coal as a household cooking fuel in China. *Energy for Sustainable Development* **8**, 115–126 (2004).

34. de Mestier du Bourg, H. & Rondenay, J.-F. DME - A New Fuel - Perspectives And Challenges. *Offshore Mediterranean Conference and Exhibition* (2007).

35. Ohno, Y., Inoue, N., Okuyama, K. & Yajima, T. New Clean Fuel DME. *International Petroleum Technology Conference Proceedings* 475–479 (2005) doi:10.2523/IPTC-10325-MS.

36. Lee, S., Oh, S., Choi, Y. & Kang, K. Effect of n-Butane and propane on performance and emission characteristics of an SI engine operated with DME-blended LPG fuel. *Fuel* **90**, 1674–1680 (2011).

37. te Riele, P. *et al.* Implementing a Water Soluble Solvent Based Enhanced Oil Recovery Technology - Aspects of Field Development Planning. *Society of Petroleum Engineers* -

SPE EOR Conference at Oil and Gas West Asia, OGWA 2016 21–23 (2016) doi:10.2118/179849-MS.

38. Tapantosh Chakrabarty. Diluting agent for diluting viscous oil. (2012).

39. Azinfar, B., Haddadnia, A., Zirrahi, M., Hassanzadeh, H. & Abedi, J. Effect of asphaltene on phase behavior and thermophysical properties of solvent/bitumen systems. *J Chem Eng Data* **62**, 547–557 (2017).

40. Donald B. Robinson & Peng Ding-Yu. The characterization of the heptanes and heavier fractions for the GPA Peng-Robinson programs. *Gas processors association* (1978).

41. Computer Modeling Group. WinProp User's Guide. Preprint at (2013).

42. Péneloux, A., Rauzy, E. & Fréze, R. A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilib* **8**, 7–23 (1982).

43. Pedersen, K. S., Milter, J. & Sørensen, H. Cubic Equations of State Applied to HT/HP and Highly Aromatic Fluids. *SPE Journal* **9**, 186–192 (2004).

44. Pedersen, K. S., Fredenslund, A., Christensen, P. L. & Thomassen, P. Viscosity of crude oils. *Chem Eng Sci* **39**, 1011–1016 (1984).

45. Wu, J., Liu, Z., Pan, J. & Zhao, X. Vapor pressure measurements of dimethyl ether from (233 to 399) K. *J Chem Eng Data* **49**, 32–34 (2004).

46. Nourozieh, H., Kariznovi, M. & Abedi, J. Density and Viscosity of Athabasca Bitumen Samples at Temperatures Up to 200°C and Pressures Up to 10 MPa. *SPE Reservoir Evaluation & Engineering* **18**, 375–386 (2015).

47. Twu, C. H. An internally consistent correlation for predicting the critical properties and molecular weights of petroleum and coal-tar liquids. *Fluid Phase Equilib* **16**, 137–150 (1984).

48. Lee, B. I. & Kesler, M. G. A generalized thermodynamic correlation based on three-parameter corresponding states. *AIChE Journal* **21**, 510–527 (1975).

49. Natural Resources Canada. Crude oil facts. *http://www.nrcan.gc.ca* (2017).

50. Al-Bahlani, A. M. & Babadagli, T. SAGD laboratory experimental and numerical simulation studies: A review of current status and future issues. *J Pet Sci Eng* **68**, 135–150 (2009).

51. Sheng, K., Okuno, R. & Wang, M. Water-Soluble Solvent as an Additive to Steam for Improved SAGD. *Society of Petroleum Engineers - SPE Canada Heavy Oil Technical Conference 2017* 215–239 (2017) doi:10.2118/184983-MS.

52. Haddadnia, A., Azinfar, B., Zirrahi, M., Hassanzadeh, H. & Abedi, J. Thermophysical properties of dimethyl ether/Athabasca bitumen system. *Can J Chem Eng* **96**, 597–604 (2018).

53. Baek, K. H., Sheng, K., Argüelles-Vivas, F. J. & Okuno, R. Comparative Study of Oil-Dilution Capability of Dimethyl Ether and Hexane as Steam Additives for Steam-Assisted Gravity Drainage. *SPE Reservoir Evaluation & Engineering* **22**, 1030–1048 (2019).

54. Colin L. Young & Peter GT Fogg. *Ammonia, Amines, Phosphine, Arsine, Stibine, Silane, Germane and Stannane in Organic Solvents: Ammonia, Amines, Phosphine and Arsine in Organic Solvents*. vol. 21 (Elsevier, 2013).

55. International DME Association. *https://www.aboutdme.org* (2017).

56. NIST Chemistry Webbook. *https://www.nist.gov* (2017).

57. Wu, J. & Yin, J. Vapor pressure measurements of dimethyl ether from (213 to 393) K. *J Chem Eng Data* **53**, 2247–2249 (2008).

58. Al-Murayri, M. T., Maini, B. B., Harding, T. G. & Oskouei, J. Cracked Naphtha Coinjection in Steam-Assisted Gravity Drainage. (2016) doi:10.1021/acs.energyfuels.5b02773.

59. Rabiei Faradonbeh, M., Hassanzadeh, H. & Harding, T. Numerical simulations of bitumen recovery using solvent and water assisted electrical heating. *Fuel* **186**, 68–81 (2016).

60. Nenniger, J. E. & Dunn, S. G. How Fast is Solvent Based Gravity Drainage? *Canadian International Petroleum Conference 2008* 17–19 (2008) doi:10.2118/2008-139.

61. Bamzad, S. *et al.* Measurements and Correlations of Thermophysical Properties for Multicomponent Solvent/Live Bitumen Mixtures. *J Chem Eng Data* (2022) doi:10.1021/ACS.JCED.2C00316.

62. Kar, T. *et al.* Mobilization of Trapped Residual Oil via Secondary SAGD with Propane. in *SPE Western Regional Meeting* (Society of Petroleum Engineers, 2017). doi:10.2118/185684-MS.

63. Souraki, Y., Ashrafi, M. & Torsaeter, O. Experimental Investigation and Comparison of Thermal Processes: SAGD, ES-SAGD and SAS. *International Journal of Engineering Trends and Technology* **31**, 2231–5381 (2016).

64. Hascakir, B. How to select the right solvent for solvent-aided steam injection processes. *J Pet Sci Eng* **146**, 746–751 (2016).

65. Nourozieh, H., Kariznovi, M. & Abedi, J. Measurement and Modeling of Solubility and Saturated-Liquid Density and Viscosity for Methane/Athabasca-Bitumen Mixtures. *SPE Journal* **21**, 180–189 (2016).

66. Mohammadzadeh, O., Rezaei, N. & Chatzis, I. Pore-Scale Performance Evaluation and Mechanistic Studies of the Solvent-Aided SAGD (SA-SAGD) Process Using Visualization Experiments. *Transp Porous Media* **108**, 437–480 (2015).

67. Govind, P. A., Das, S. K., Srinivasan, S. & Wheeler, T. J. Expanding Solvent SAGD in Heavy Oil Reservoirs. in *International Thermal Operations and Heavy Oil Symposium* (Society of Petroleum Engineers, 2008). doi:10.2118/117571-MS.

68. Ardali, M., Mamora, D. D. & Barrufet, M. A Comparative Simulation Study of Addition of Solvents to Steam in SAGD Process. in *Canadian Unconventional Resources and International Petroleum Conference* (Society of Petroleum Engineers, 2010). doi:10.2118/138170-MS.

69. Sheng, K., Okuno, R. & Wang, M. Water-Soluble Solvent as an Additive to Steam for Improved SAGD. in *SPE Canada Heavy Oil Technical Conference* (Society of Petroleum Engineers, 2017). doi:10.2118/184983-MS.

70. Zare, A., Abdulhameed, F. M., Hesland, B. & Hamouda, A. A. Enhanced heavy oil recovery (SAGD), coinjection of steam and solvent, reduction of CEOR and CSOR. *Pet Sci Technol* **35**, 570–577 (2017).

71. Sabet, N., Hassanzadeh, H. & Abedi, J. Selection of efficient solvent in solvent-aided thermal recovery of bitumen. *Chem Eng Sci* **161**, 198–205 (2017).

72. Mehrotra, A. K. & Svrcek, W. Y. Properties of Cold Lake bitumen saturated with pure gases and gas mixtures. *Canadian Journal of Chemical Engineering* **66**, 656–665 (1988).

73. Fu, C.-T., Puttangunla, R. & Vilcsak, G. Vapour-Liquid Equilibrium Properties For Gas - Cold Lake Bitumen. in *Annual Technical Meeting* (Petroleum Society of Canada, 1986). doi:10.2118/86-37-05.

74. Kariznovi, M., Nourozieh, H. & Abedi, J. Phase Behavior and Viscosity Measurements of Heavy Crude Oil With Methane and Ethane at High-Temperature Conditions. in *SPE Western Regional Meeting* (Society of Petroleum Engineers, 2012). doi:10.2118/152321-MS.

75. Badamchi-Zadeh, A., Yarranton, H. W., Svrcek, W. Y. & Maini, B. B. Phase Behaviour and Physical Property Measurements for VAPEX Solvents: Part I. Propane and Athabasca Bitumen. *Journal of Canadian Petroleum Technology* **48**, 54–61 (2009).

76. Jossy, C., Frauenfeld, T. & Rajan, V. Partitioning of Bitumen-Solvent Systems Into Multiple Liquid Phases. *Journal of Canadian Petroleum Technology* **48**, 16–20 (2009).

77. Frauenfeld, T. W. J., Kissel, G. A. & Shibing Zhou, W. PVT and Viscosity Measurements for Lloydminster-Aberfeldy and Cold Lake Blended Oil Systems. in *Canadian International Petroleum Conference* (Petroleum Society of Canada, 2002). doi:10.2118/2002-110.

78. Nourozieh, H., Kariznovi, M. & Abedi, J. Experimental and modeling studies of phase behavior for propane/Athabasca bitumen mixtures. *Fluid Phase Equilib* **397**, 37–43 (2015).

79. Han, B., Yang, G., Ke, J., Mao, C. & Yan, H. Phase equilibria of supercritical propane–Fengcheng bitumen system and the density and viscosity of the liquid phase. *Fluid Phase Equilib* **143**, 205–211 (1998).

80. Zirrahi, M., Hassanzadeh, H. & Abedi, J. Experimental and modelling studies of MacKay River bitumen and light *n* -alkane binaries. *Can J Chem Eng* **95**, 1417–1427 (2017).

81. Haddadnia, A., Azinfar, B., Zirrahi, M., Hassanzadeh, H. & Abedi, J. Thermophysical properties of dimethyl ether/Athabasca bitumen system. *Can J Chem Eng* **96**, 597–604 (2018).

82. Gao, J., Okuno, R. & Li, H. A. A Phase-Behavior Study for n-Hexane/Bitumen and n-Octane/Bitumen Mixtures. *SPE Journal* **23**, 128–144 (2018).

83. Johnston, K. A., Schoeggl, F. F., Satyro, M. A., Taylor, S. D. & Yarranton, H. W. Phase behavior of bitumen and n-pentane. *Fluid Phase Equilib* **442**, 1–19 (2017).

84. Kariznovi, M., Nourozieh, H. & Abedi, J. Volumetric Properties of Athabasca Bitumen + n-Hexane Mixtures. *Energy & Fuels* **28**, 7418–7425 (2014).

85. Nourozieh, H., Kariznovi, M. & Abedi, J. Measurement and Prediction of Density for the Mixture of Athabasca Bitumen and Pentane at Temperatures up to 200 °C. *Energy & Fuels* **28**, 2874–2885 (2014).

86. Nourozieh, H., Kariznovi, M. & Abedi, J. Viscosity measurement and modeling for mixtures of Athabasca bitumen/hexane. *J Pet Sci Eng* **129**, 159–167 (2015).

87. Haddadnia, A., Zirrahi, M., Hassanzadeh, H. & Abedi, J. Thermo-physical properties of n-pentane/bitumen and n-hexane/bitumen mixture systems. *Can J Chem Eng* **96**, 339–351 (2018).

88. Sadeghi Yamchi, H., Zirrahi, M., Hassanzadeh, H. & Abedi, J. Measurements and modeling of liquid-liquid equilibrium of Propane + n-Butane + Bitumen system. *Fuel* **293**, 120353 (2021).

89. Sadeghi Yamchi, H., Zirrahi, M., Hassanzadeh, H. & Abedi, J. Measurements and NRTL modeling of liquid-liquid equilibrium of dimethyl ether/bitumen. *Fluid Phase Equilib* **512**, 112549 (2020).

90. Bamzad, S. *et al*. Experimental measurement and thermodynamic modeling of vapor-liquid equilibrium data of C1/bitumen, CO2/bitumen, C1/ CO2/bitumen, C1/diluent/bitumen, and C1/ CO2/diluent/bitumen systems. *Ind Eng Chem Res* (2023).

91. Azinfar, B., Zirrahi, M., Hassanzadeh, H. & Abedi, J. Characterization of heavy crude oils and residues using combined Gel Permeation Chromatography and simulated distillation. *Fuel* **233**, 885–893 (2018).

92. Azinfar, B., Haddadnia, A., Zirrahi, M., Hassanzadeh, H. & Abedi, J. A thermodynamic model to predict propane solubility in bitumen and heavy oil based on experimental fractionation and characterization. *J Pet Sci Eng* **168**, 156–177 (2018).

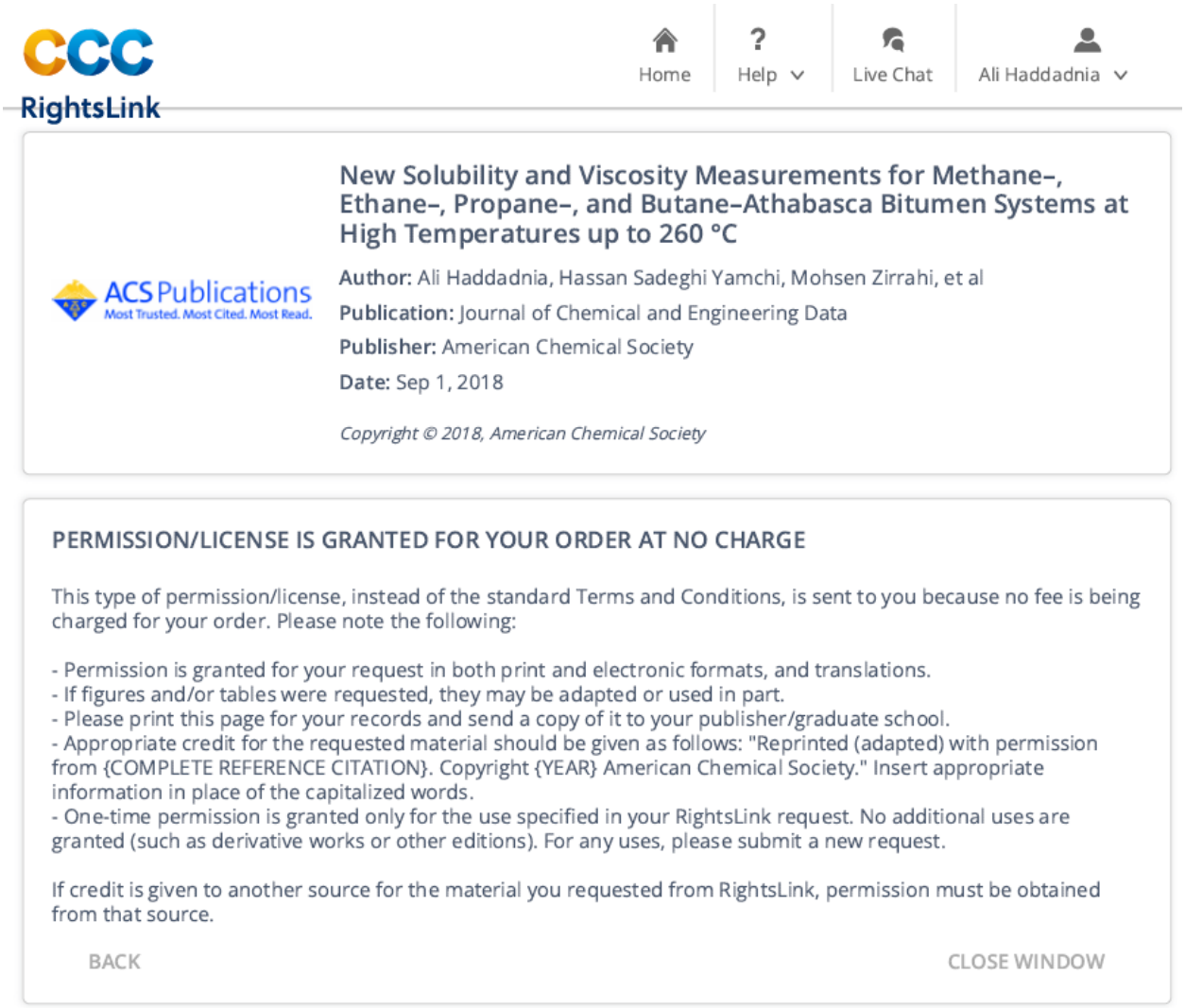
93. Zirrahi, M., Hassanzadeh, H. & Abedi, J. Experimental and modelling studies of MacKay River bitumen and light n-alkane binaries. *Can J Chem Eng* **95**, 1417–1427 (2017).

94. Peng, D.-Y. & Robinson, D. B. A New Two-Constant Equation of State. *Industrial & Engineering Chemistry Fundamentals* **15**, 59–64 (1976).

95. Computer Modeling Group. CMG User's Guide. Preprint at (2022).

96. Péneloux, A., Rauzy, E. & Fréze, R. A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilib* **8**, 7–23 (1982).

8 Appendix



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