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Modelling of Non-Equilibrium Heavy Oil-Solvent Behaviour

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Modelling of Non-Equilibrium Heavy Oil-Solvent Behaviour

by

Nan Tai

A THESIS

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Abstract

A multi-component kinetic model is proposed to simulate non-equilibrium solvent exsolution and back dissolution processes in the heavy oil bulk environment. The model consists of micro bubbles, which inherit physical properties from the solution gas and is treated as a gas-like liquid, to simulate foamy oil behavior during volume expansion processes. Free gas is considered as being able to transfer directly to solution gas to simulate the hysteresis which happens in the dissolution process when volume pressure increases. The kinetic model comprises three pseudo-chemical reactions with seven parameters which were calibrated against experimental data. The model was validated by using a thermal reservoir simulator and the results were capable of predicting the oil-gas system volume changes for two different solvent-heavy oil systems accurately under various pressure variation rates at both 15 and 75°C. Four reaction orders and three reaction frequency factors were tuned and it indicated that in a solvent-heavy oil system with solvent CH₄ or C₂H₆: (1) stronger foamy oil behavior exists with solvent of C₂H₆ instead of CH₄ during pressure depletion processes for heavy oil with the similar solvent concentration; (2) for both solvents, micro bubble release rates are larger at higher temperature and the rates tend to increase with pressure decline regardless of temperature; and (3) in the solvent dissolution process, for both CH₄ and C₂H₆, relatively high pressure and temperature are both significant elements for promoting solvent dissolution back into heavy oil.

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List of Symbols, Abbreviations and Nomenclature

Symbols

V_{ini}	Initial volume
V_t	Total volume
P_b	Thermodynamic bubble point pressure
R	Universal gas constant
Z	Compressibility factor

Abbreviations

API	American Petroleum Institute
CSS	Cyclic Steam Stimulation
SAGD	Steam-Assisted Gravity Drainage
CHOPS	Cold Heavy Oil Production with Sand
OOIP	Original Oil In Place
EOR	Enhanced Oil Recovery
CSI	Cyclic Solvent Injection
GOR	Gas-oil Ratio
PCPs	Progressive Cavity Pumps
IN	Instantaneous Nucleation
PN	Progressive Nucleation
PDE	Partial Differential Equation
DPDVA	Dynamic Pendant Drop Volume Analysis
DVA	Dynamic Volume Analysis
CCE	Constant Composition Expansion
PVT	Pressure-volume-temperature
CCEC	Constant Composition Expansion and Compression
GC	Gas Chromatography

Nomenclature

SG_{oil}	Solution gas dissolved in the oil phase
$MB_{SG, oil}$	solution-gas micro bubbles hosted in the oil phase
$FG_{SG, gas}$	Solution gas as a connected free gas in the gas phase
C_{SGoil}	Actual dissolved gas concentration in the unit volume of the oil phase
C^*_{SGoil}	Equilibrium dissolved gas concentration
$C_{MBSG, oil}$	Micro bubble concentration in the unit volume of the oil phase
$C_{FGSG, gas}$	Free gas concentration in the unit volume of the gas phase
$R_{I(MBSG, oil)}$	Micro bubble formation rate, $\frac{\text{mole}}{\text{cm}^3 \text{min}}$

$R_{2(FGSG, gas)}$

$R_{3(SGoil)}$

$k_1, k_2 \text{ and } k_3$

$m_1, m_2, m_3 \text{ and } n_3$

K

Free gas formation rate, $\frac{\text{mole}}{\text{cm}^3 \text{min}}$

Solution gas formation rate, $\frac{\text{mole}}{\text{cm}^3 \text{min}}$

Reaction frequency factor

Order of reaction rate

Phase equilibrium constant

Chapter One: Introduction

1.1 Western Canadian Heavy Oil

In recent years, heavy oil has increasingly become an attractive target for oil production due to its vast resource volume discovered globally. It is estimated that there are approximately 5.5 trillion barrels of heavy oil worldwide, which accounts for around 53% of the world's oil reserves (Istchenko 2012).

In Canada, heavy oil and bitumen resources are mainly located in the western provinces of Alberta and Saskatchewan, as shown in Figure 1-1. From the API gravity, a system introduced by the American Petroleum Institute (API) in 1921 (Huc, 2010), these resources can be subdivided into oil sands (bitumen) ($\text{API} < 10^\circ$) and heavy oils ($10^\circ \leq \text{API} < 20^\circ$). The oil sands in Western Canada are estimated to have a resource volume size of 1.7 trillion barrels with covering an area around 141,000 km² (Istchenko 2012). In addition, approximately 10% of them can be economically recovered with current technology. Heavy oil is mainly located near the border of Alberta and Saskatchewan with about 1.3 billion barrels of reserves. Compared with oil sands, heavy oil reserves are attractive due to their lower recovery expenses as well as energy consumption. Therefore, it is critical to effectively develop innovative techniques for recovering heavy oil reservoirs in Canada considering both economic and environmental benefits.

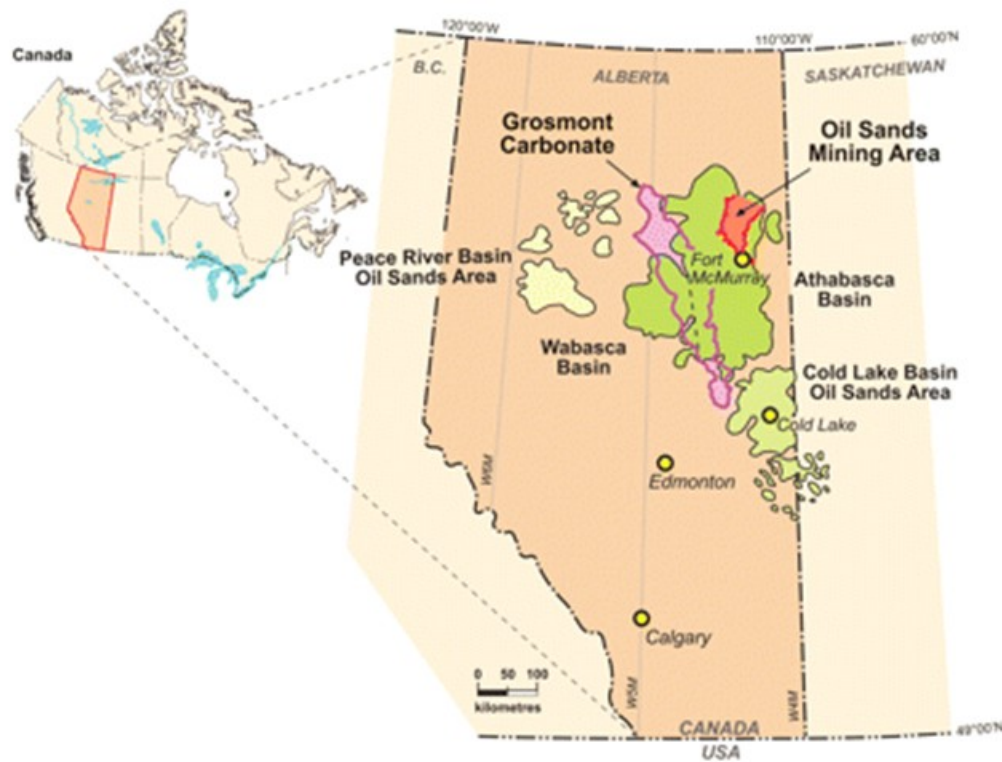


Figure 1-1: Heavy oil and oil sands deposits in Canada (Peacock, 2010).

1.2 Recovery Processes

Heavy oil and bitumen are recovered by several techniques. Surface mining techniques are generally applied for Athabasca deposits that are at surface or less than about 70 m below the surface as is the case in Ft. McMurray, Alberta. These deposits account nearly 20% of known bitumen deposits in Western Canada (Istchenko 2012). For the other 80%, in-situ methods are required. Due to the high viscosity of bitumen, a viscosity reduction of the oil is needed to improve its mobility to be sufficient for production to surface. Generally, increasing temperature will reduce bitumen viscosity dramatically, as shown

in Figure 1-2. Currently, two commercial techniques that are utilized to recovery oil sands reservoirs are both thermal using steam injection to enhance bitumen mobilization within the oil sands deposits: 1. Cyclic Steam Stimulation (CSS) and 2. Steam-Assisted Gravity Drainage (SAGD).

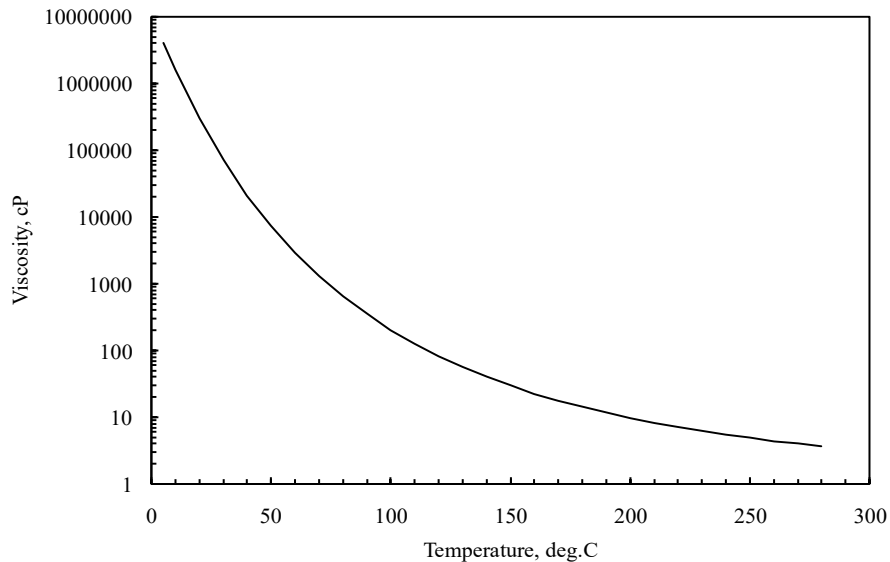


Figure 1-2: Effect of temperature on viscosity of Athabasca bitumen (Mehrotra and Svrcek, 1986).

For heavy oil reservoirs, oil is sufficiently mobile to be produced under cold production at reservoir conditions. The key requirement for cold production is that the oil has low enough viscosity so that solution gas drive within the reservoir can establish and maintain sufficient production for the process to be economic (Istchenko 2012). The solution gas drive takes the form of foamy oil flow. Without injection, cold production can be conducted with or without sand production. Cold production is a single well recovery process that can be applied with vertical, deviated, horizontal or multi-lateral wells. In Western Canada, for cold production without sand, horizontal wells are mostly used

(Dusseault, 2001). For Cold Heavy Oil production with Sand (CHOPS), vertical or deviated wells are applied in most cases.

The dominant mechanism in cold production with or without sand for heavy oil is solution gas drive, which occurs in the form of foamy oil flow. The recovery factors for heavy oil reservoirs undergoing cold production have recovery factors ranging from 5-15% of the original oil in place (OOIP) (Maini, 2001). Most of the heavy oil remains underground indicates further recovery steps need to be taken. In Western Canada, in most cases, water flooding and polymer flooding have been the most widely applied methods to increase further heavy oil recovery after primary production, since they are simple to implement and have relatively low operation cost (Miller 2005; Asghari and Nakutuyy, 2008). However, due to the huge viscosity difference between heavy oil and water as well as the extremely high conductivity of the wormholes in the reservoirs, flooding processes may suffer with respect to water bypassing and the incremental oil recovery factors are not much larger than cold production.

Despite water-based injection methods, many other different Enhanced Oil Recovery (EOR) techniques can be developed for heavy oil reservoirs. Thermal methods such as SAGD, CSS, Steam Flooding and hot water flooding, have been widely applied through heat conduction to reduce heavy oil viscosity to increase recovery factors. However, in Western Canada, up to 80% of the heavy oil resources are contained in reservoirs with thickness less than 5m (Adam, 1982). Although thermal methods are the most effective techniques to enhance heavy oil mobility, thin pay zones make thermal techniques less

economical and practical due to heat loss through the overburden and understrata of the reservoirs. Since both water-based injection and thermal methods are not reliable in the further heavy oil recovering processes, solvent-based injection methods such as solvent flooding and Cyclic Solvent Injection (CSI) may have potential. Solvent can be injected under reservoir pressure and temperature to contact the oil phase diluting it to lower its viscosity and raising the pressure within the reservoir enabling production. Solvent-based injection techniques apply mass transfer mechanism to reduce oil viscosity and enhance oil mobility. In these EOR methods, gas-oil thermodynamic interactions are widely involved and need to be deeply understand for designing the best injection and production schemes.

1.3 Non-Equilibrium Behaviour of Solvent-Heavy oil Systems

Due to the high viscosity of heavy oil, during solution gas, complex behaviour occurs due to steric factors associated by pore size distribution and the dynamics of bubble formation and growth, bubble cleavage, foamy oil flow, and dissolved gas transport within the oil phase. The solution gas drive yields higher oil production rate, a low gas-oil ratio (GOR), a slow pressure depletion rate and higher-than-expected oil recovery factors (Maini, 2001). In low viscosity systems, solution gas drive tends to de-pressure the reservoir rapidly due to the aggregation of the gas phase into a connected gas volume with gas saturation exceeding the critical gas saturation. The abnormal performance of heavy oil reservoirs under foamy oil solution gas drive during cold production and solvent injection processes are opposite to the typical characteristics of conventional solution gas drive. In

heavy oil reservoirs, unlike conventional solution gas drive in light oil reserves, the solution gas tends to be entrapped in the oil phase as small bubbles when pressure dropped below the bubble point pressure, delaying the formation of a continuous gas phase. The trapped solution gas bubbles in the oil phase will help maintain the pressure of the reservoir to establish a longer period of pressure differential between the reservoir and the production well, leading to longer drive force endurance for the foamy oil production (Wang, 2020). In the solvent-heavy oil systems, the gas bubble trapping and the delay of the pressure depletion rate could be attributed to the non-equilibrium solvent ex-solution behaviour. Additionally, compared with solvent-light oil systems, the dissolution process for solvent in heavy oil consume a much longer time mainly based on the high viscosity of heavy oil. The non-equilibrium solvent dissolution behaviour should also be deeply investigated to design the best injection schemes, aiming to enhance the solvent mass transfer efficiency in industry.

1.4 Research Questions

Despite many experiments and reservoir simulation studies on non-equilibrium solvent ex-solution and dissolution behaviour in heavy oil, there is a lack of unified numerical model which can simulate both solvent ex-solution and dissolution processes under various pressure and temperature conditions. The research questions that are answered in the research conducted and reported in this thesis are as follows:

1. What are the major characteristics of non-equilibrium solvent ex-solution and dissolution behavior in a heavy oil system based on the real experimental data?

2. How does the model being built to simulate both solvent non-equilibrium ex-solution and dissolution behavior in heavy oil?
3. What are the parameters in the model for history-matching the experimental data under various pressure and temperature conditions?
4. What are the model parameters differences between two different solvents?
5. What are the underlying mechanisms for parameters differences between two different solvents ex-solving and dissolving in a heavy oil system?
6. What reactions in the model need to be further developed to enhance the history matching accuracy, based on the modeling results.

1.5 Organization of Thesis

This thesis consists of six chapters as outlined below:

Chapter 1 introduces the general background of the Western Canadian heavy oil and its recovery processes. Non-equilibrium behaviour of solvent -heavy oil systems are described. Research questions and thesis organization are also stated.

Chapter 2 presents a literature review about basic information of cold heavy oil, cold production and its challenges. Next, foamy oil and its mechanisms are introduced, followed by a detailed review of previous work related to numerical simulation on diffusion coefficient determination and foamy oil phenomenon. Thesis objectives are also included.

Chapter 3 presents an overview of experiment details, including materials, setups, procedures and experimental results for model validation. Next, the non-equilibrium kinetic model and the reservoir simulation model are established and described.

Chapter 4 presents the procedures of modeling study of CH_4 non-equilibrium exsolution and dissolution in heavy oil. Component properties and K-values are obtained first, followed by tuning model parameters to history match the experiment data. Also, parameter variations are analyzed with respect to temperature and pressure.

Chapter 5 presents the procedures of modeling study of C_2H_6 non-equilibrium exsolution and dissolution in heavy oil. Like last chapter, component properties and K-values are obtained first, followed by tuning model parameters to history match the experiment data. In addition, parameter variations are analyzed and compared with previous CH_4 case.

Chapter 6 lists the overall conclusions from the research conducted and provides recommendations for future research.

Chapter Two: Literature Review

In this chapter, previous studies on solvent ex-solution and dissolution process in heavy oil were presented and discussed. First, cold heavy oil and its production are discussed. Next, fundamental information as well as generation mechanisms of foamy oil are described. Last, past research work related to numerical simulation on non-equilibrium solvent dissolution and ex-solution process was discussed.

2.1 Introduction

2.1.1 Cold Heavy Oil

Conventional heavy oil is found along the Alberta-Saskatchewan border (Lloydminster), which is known as the “Heavy Oil Belt” deposit. The area contains approximate 1.3 billion barrels of reserves for major exploitation and development due to its considerably lower oil viscosity as compared to the main oil sand reservoirs (NEB, 2017). In the Heavy Oil Belt and certain areas of Cold Lake and Wabasca deposits, as shown in Figure 2-1, most reservoirs are characterized for being shallow (800-1000 m) with high permeabilities ranging from 1-5 Darcy. In addition, the effective porosity of these reservoirs is from 26-32% with average liquid saturation of 75% (Dusseault, 2001). In terms of fluid properties, heavy oil viscosity in these reservoirs generally ranges between 1,000 to 10,000 mPa·s with a gravity of 10° to 20° API.

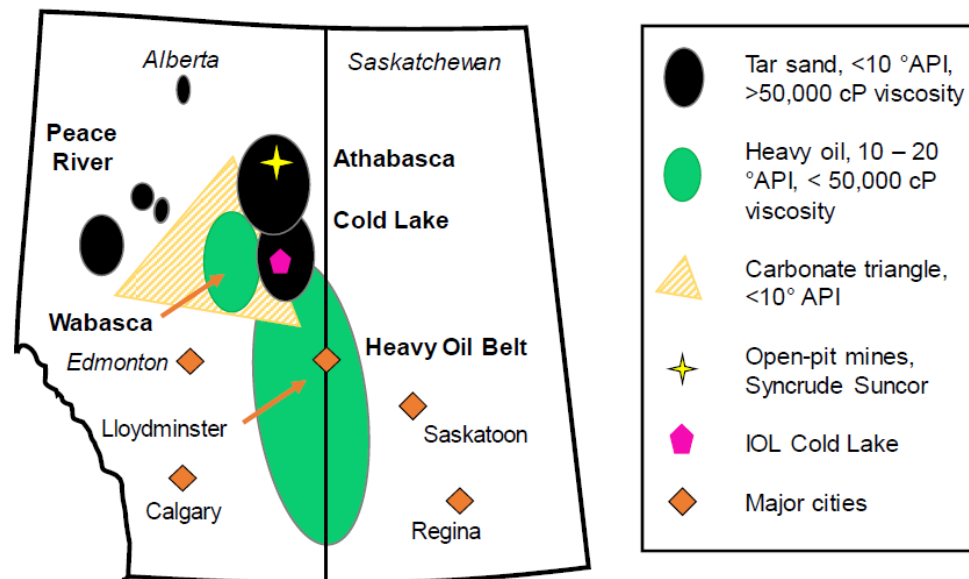


Figure 2-1: Heavy oil regions and oil sands in Alberta-Saskatchewan (Plata Sanchez, 2019).

2.1.2 Cold Heavy Oil Recovery Processes

In Western Canada, heavy oil deposits are generally recovered by primary or cold production with two different methods: (1) Cold Heavy Oil Production Without Sand and (2) Cold Heavy Oil Production Without Sand (CHOPS). In the first technique, reservoir fluids are produced without sand by applying sand exclusion devices during the completion of the wellbores. However, in CHOPS process, the sand is produced along with fluids by implementing Progressive Cavity Pumps (PCPs) and separated from oil at the surface. Through applying the CHOPS approach, foamy oil flows generally happen and the production rates have 10 to 20 times greater than the expected value, with increments from 10% to 15% in recovery factors (Maini, 1999). The CHOPS method has

been applied for the past 15 -20 years in Alberta and Saskatchewan mainly because its relatively easy to implement and economic success.

2.1.3 Challenges faced by CHOPS

At the end of the CHOPS process, oil production declines dramatically with increasing water cut. The reservoir energy is almost depleted and around 85-90% of heavy oil remains underground. The low efficiency of CHOPS will bring potential economic loss, leaving inactive CHOPS wells and a large amount of infrastructure for further EOR process. Besides, due to massive sand production, high permeability network of flow paths know as “wormholes” are extended along the reservoirs (Dusseault, 2001). To recover the remaining oil, there is the need to develop a recover method which can re-pressurize the reservoir as well as mobilizing oil along with wormholes towards wellbore. Therefore, different types of EOR techniques are studied to further enhance heavy oil reservoirs.

2.2 Bubble-Scale Non-Equilibrium Solvent Ex-Solution Behavior

2.2.1 Foamy Oil Definition

By changing the intensive parameters such as temperature and pressure in conventional gas-light oil system, thermodynamic equilibrium can be easily reached. However, in a gas-heavy oil system, thermodynamic equilibrium is usually difficult to achieve within a

short period of time mainly due to the high viscosity of the liquid phase. When the pressure drops below the bubble point pressure, the solution gas trapped in the heavy oil phase ex-solves as small bubbles (Sheng et al., 1999). Due to the high viscosity of the heavy oil, the bubbles tend to stay separated delaying the formation of a continuous gas phase. It happens in many Canadian and Venezuelan heavy oil reservoirs, resulting in an unusual “oil/gas combination” production fluid at wellheads. The concept of “foamy oil” was then proposed to describe this phenomenon and it has been widely used in both research and industry.

2.2.2 Foamy Oil Generation Mechanisms

Since dissolved gas will not escape as freely as in a light oil system, the deviation from phase equilibrium will induce non-equilibrium phase behavior. The most significant characteristic of solvent injection in heavy oil is the existence of non-equilibrium foamy oil flow. Therefore, a better understanding of how foamy oil evolves is significant to guide the design of a solvent injection scheme.

In general, foamy oil generation can be divided into four steps: bubble nucleation, bubble growth, coalescence and break up, as shown in Figure 2-2. Bubble nucleation is the first step for gas bubbles formation. In the pressure depletion process, gas begins to escape from heavy oil and bubbles tend to nucleate as the formation becomes supersaturated. Foamy oil bubbles are generally formed at this point. There are two principal models for bubble nucleation process: instantaneous nucleation (IN) (Mastmann et al., 2001) and

progressive nucleation (PN) (Shi et al., 2016). The instantaneous nucleation model assumes that all the bubble nuclei are formed at the same time. In addition, the bubbles grow on the nucleus and do not originate from pre-existing bubbles trapped in the pores. In this model, it is assumed that bubble nucleation starts at supersaturation period and depends on the pressure depletion rate in the pore space. For progressive nucleation, new bubble nucleus is released from the sites on pore walls with poor liquid wetting characteristics. These bubbles grow continuously from pre-existing trapped bubbles and a nucleated gas phase in the pore space. About these two bubble nucleation processes, some argued that IN model was not realistic since pressure needs time to expand and influence the phase equilibrium at various locations in the reservoir. While some insisted that PN model cannot verify what the experiments showed based on the mathematical model derived from the experiments (Wang 2020). The bubble nucleation process has not been determined until today due to the lack of apparatus which can visualize many tiny micro-scales simultaneously. Thus, many numerical models covered the usage of both IN and PN to make assumptions (Wang 2020).

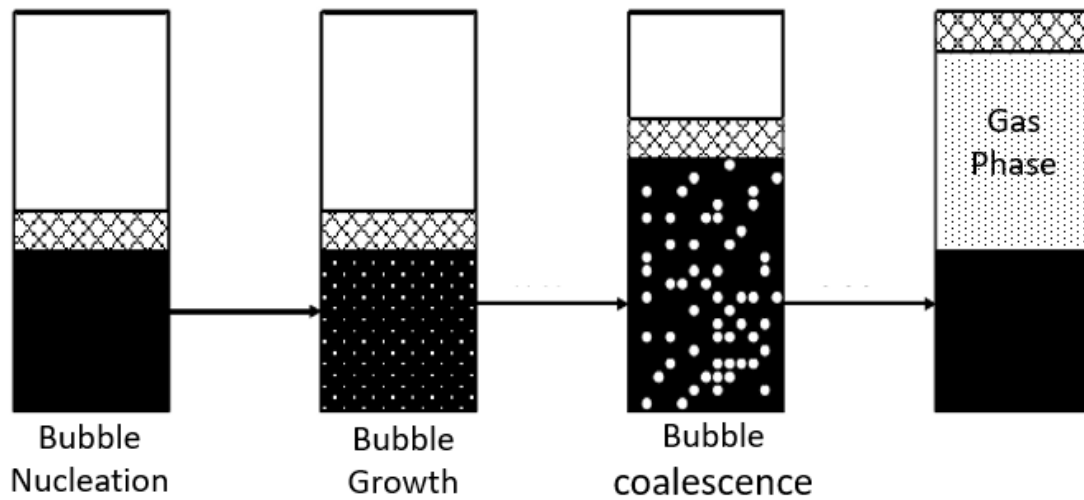


Figure 2-2: The process of gas bubbles nucleation, growth and break up to a free gas phase (Wang 2019)

After nucleation, bubbles will grow at a specific rate which involves many physical influential factors. Generally, bubble growth is dominated by mainly three influential factors: mass transfer, heat transfer and momentum transfer (Wang 2020). Mass transfer contains many aspects, such as mass diffusion and dispersion, also compositional change on the component-interface based on evaporation and condensation. Heat transfer involves energy/heat supply to break the phase equilibrium and lead to a phase change at the component interface. As for momentum transfer, hydrodynamic forces are the dominated factors of the system. Pressure gradient, capillary pressure as well as viscous force is significant to control the bubble growth in porous media. While in bulk phase, liquid inertia plays an important role. In addition, there are many factors affecting bubble growth, including temperature, heavy oil viscosity, solvent types and pressure depletion rates.

In general, bubbles will coalesce into a continuous gas phase when gas saturation increases to approximate 12% to 15% (Wang 2019). Kraus et al. (1993) proposed a concept of pseudo-bubble point to describe the critical status of foamy oil before bubbles collapse. It was assumed that the gas-oil ratio remains constant between the bubble point pressure and the pseudo-bubble point pressure. Through applying this concept, they found the simulation results matched three of the anomalous production behaviour for foamy oil reservoirs: (1) natural pressure maintenance; (2) high oil recovery, and (3) low producing gas-oil ratio.

2.3 Numerical Studies on Non-Equilibrium Solvent Dissolution and Ex-solution Behavior

2.3.1 Numerical Simulation on Diffusion Coefficient Determination

To determine diffusion coefficient numerically, most modeling techniques apply diffusion equations to solve lab-/field-scale problems. These models are normally presented as partial differential equation (PDE) with boundary conditions (e.g., equilibrium, quasi-equilibrium, non-equilibrium). Although these simulation methods are straightforward, their application may be limited since multi-physics is difficult to consider and boundary conditions are not always uniform.

Yang and Gu (2005) applied a mass-transfer model to describe the diffusion process of the gas into pendant heavy oil drop. The model was developed based on the experimental

study of dynamic pendant drop volume analysis (DPDVA) and it was solved by applying finite element method. The volume of dynamic pendant oil drop was calculated based on the solvent concentration distribution in the oil drop. Next, the gas diffusion coefficient was determined by matching the volume change of the pendant oil drop.

Tharanivasan (2006) determined the diffusion coefficient of methane, propane and CO₂ oil system by applying the pressure decay method under reservoir pressure and temperature conditions. Three types of boundary conditions including equilibrium, quasi-equilibrium and non-equilibrium conditions were applied at the heavy oil-solvent interface, respectively. The diffusion coefficient was determined by matching the experimental measured pressures. It was found that different solvent-heavy oil system should apply various boundary conditions to better describe the mass transfer during solvent dissolution processes.

Li and Yang (2016) determined the diffusion coefficient of various types of solvent-heavy oil system based on the pressure decay method. A 1D-diffusion model was developed to describe the solvent diffusion process. The composition analysis of the solvent-heavy oil system was conducted at the beginning and the end of experiments. Thus, the individual molecular-diffusion coefficient for each component was determined by matching the experimental composition change in the system. In addition, it was found that the diffusion coefficient of solvent, such as C₃H₈ and n-C₄H₁₀ was significantly larger than that of CO₂ in heavy oil.

Zheng and Yang (2017) determined the diffusion coefficient of alkane solvents and CO₂ in heavy oil by using dynamic volume analysis (DVA). To describe the solvent diffusion process, a 2D heat-and-mass-transfer model was developed and solved by the alternating-direction-implicit algorithm. The volume change of liquid phase was monitored during experiments, whereas the composition of solvent mixture was measured at the beginning and the end of the diffusion tests. Therefore, the individual diffusion coefficients were determined by matching the system volume change as well as experimental composition variation is the solvent-oil mixture. They concluded that alkane solvents not only diffuse faster than CO₂ in heavy oil, but also significantly enhanced swelling effect of heavy oil.

Zhou et al. (2020) conducted diffusion experiments in a CO₂-heavy oil system under both bulk phase and porous media. Pressures were monitored in two experiments were compared after diffusion process. Considering non-equilibrium boundary condition at the gas-liquid phase interface, a 1D-diffusion model was developed to describe CO₂ diffusion process at both experiments by history-matching pressure decay curves.

Wang et al. (2020) utilized pressure decay methods to study CO₂ dissolution process in heavy oil with a high-pressure visual cell. Pressure decay curves and oil swelling factor curves were obtained and served as matching targets. To get more accurate modeling results, a MATLAB-controlled reservoir simulator was developed for numerical validation. The model was able to dynamically update the value of the diffusion coefficient at various stage of time to simulate Darcy-scale pressure decay behavior. In

this study, CO₂ diffusion coefficient in oil was obtained by history matching the pressure decay curves, and the coefficient value increased dramatically with increasing pressure.

2.3.2 Numerical Simulation on Foamy Oil Phenomenon

Two types of non-equilibrium processes are believed to exist under solution gas drive in heavy oil reservoirs. The first type of process focuses on gas evolution which potentially leads to supersaturation of the oil phase, while the second process describes the fluid distribution in porous media. Both non-equilibrium processes are important and need to be well understood to model cold heavy oil production process. In simulating solution gas drive in heavy oil reservoirs, kinetic models are widely utilized to simulate the non-equilibrium processes during the bubble formation, dispersion and release processes.

A number of kinetic models have been proposed in the literature to simulate foamy oil behavior. These models can be divided into two categories. In the first category, the effect of porous media is considered, and both non-equilibrium processes are simulated simultaneously. The models simulate dynamic behavior of foamy oil flow mainly by history matching the oil production behavior of pressure depletion tests. Luigi et al. (1998) studied the sensitivity of the frequency factors and activation energy of the foamy oil pseudo chemical reaction in CMG STARS foamy oil module. Non-equilibrium reaction model was utilized to simulate foamy oil behavior for well SDZ-182 in Orinoco belt in Venezuela. Two pseudo chemical reactions were developed representing gas bubble nucleation and dispersed gas transferring to free gas, respectively. It was found that the

modification of the frequency factors and the activation energy of the first reaction had much less sensitivity to the results than that of the second reaction, due to the much slower time duration for the first reaction.

Bayon et al. (2002) compared two different kinetic models for foamy oil flow under reservoir conditions on a sand pack model. The first model considered gas bubbles flowing in the oil phase whereas the second model handled two types of gas bubbles: with small bubbles flowing with oil phase and large bubbles trapped in the porous media without flowing. The performance of both models was compared through history matching oil and gas production, in-situ gas saturation profiles, critical gas saturation etc. The results revealed that both models can predict production behavior properly. Compared with the first model mainly applying relative permeability as adjustable parameters, the second model involved more tunable parameters, including a set of reaction frequency factors and reaction orders as well as the relative permeability curves.

Chen and Maini (2005) conducted a set of numerical simulations of foamy oil depletion experiments applying both CMG IMEX and CMG STARS foamy oil module in a porous media. Both modeling results indicated that tuning relative permeabilities of gas and oil was critical on production behavior. Besides, the distribution of pressure, oil, dissolved gas and free gas along the porous media were significantly influenced by depletion rates. By comparing the results between two modeling techniques, it was concluded that foamy oil modules in CMG STARS could better match the production data in the porous media, and up-scaling simulation for a real reservoir should be further studied.

Uddin (2005) performed numerical simulation to study gas ex-solution in hand transport process in heavy live oil reservoir by applying CMG STARS foamy oil module. A five-component kinetic model consisting of four reactions was built to represent bubble nucleation, growth and release in the porous media. The bubble nucleation was presented by dissolved gas to dispersed gas, and the bubble growth process was symbolized by dispersed gas to free gas. In this study, eight sets of constant withdrawal rate tests and four pressure depletion tests were history matched. By tuning the four transfer coefficients in the reactions, both oil and gas production behaviors were accurately predicted under pressure depletion experiments.

Ivory et al. (2010) applied CMG STARS foamy oil module to represent the physical behavior of the cyclic solvent injection (CSI) experimental results. CSI as a follow-up technique after primary production, which involved a large amount of foamy oil generation, was proved to be efficiently in thin heavy oil reservoirs experimentally. The model contained non-equilibrium rate equations which simulated the delay time for solvent reaching its equilibrium concentration either by dissolving or ex-solving into and out of the oil phase under specific pressure and temperature. Besides the kinetic frequency factors, reduced gas-phase permeability resulting from gas ex-solution were also included. It was found that significant oil swelling by solvent dissolution would reduce solvent injectivity and the penetration of solvent into a heavy oil reservoir. In addition, low oil and gas-phase relative permeabilities were required to match the experimental oil and gas production data. The final oil rate was highly dependent on the

efficiency of solvent dissolving in the oil during injection and ex-solving from oil during production.

Shen (2015) created a five-component dynamic model to describe the kinetic behavior of foamy oil flow in porous media by applying CMG STARS foamy oil module. The model applied four reactions to represent gas phase formation and matched oil production behavior of core pressure depletion tests. Instead of adjusting the relative permeability curves, a much higher viscosity was assigned to the dispersed gas component to simulate the low mobility of the gas phase during foamy oil flow.

More recent, Lu et al. (2019, 2020) developed a four-component non-equilibrium kinetic model to characterize foamy oil behavior in heavy oil/methane and heavy oil/propane system in sand packs. The model applied two reactions to simulate the processes of dispersed gas bubbles nucleation and release under various pressure depletion rates. Both pressure distribution and production data were well matched by tuning K-values, relative permeability curves, and two reaction frequency factors. In addition, It was found in this study that higher pressure depletion rate would cause stronger foamy oil flow. However, the exceed pressure decrease rate could shorten foamy oil lifetime.

Although the first category kinetic model is capable of accurately predicting production behavior along with pressure distribution within reservoirs, the fluid properties are not well predicted at each reservoir location since the flow mechanisms cover the gas evolution mechanisms when both non-equilibrium processes are simulated

simultaneously. Therefore, these kinetic models cannot predict fluid properties properly since gas evolution process is not well analyzed. In addition, the mutual influence and sensitivity of tuning various parameters including kinetic frequency factors, relative permeability curves, diffusion and dispersion coefficients, are not clear enough. To concentrate on the non-equilibrium gas evolution processes in a closed thermodynamic system, the second category of kinetic models which based on bulk volume phase modeling are recently introduced. Oskouei et al. (2017) proposed a five-component kinetic model for gas ex-solution from heavy oil in a PVT cell under three pressure depletion rates. Four reactions were applied and gas evolution processes were assumed to start with microbubbles formation. In this model, the microbubbles either grow to become dispersed bubbles in the oil phase or form a free gas phase with the evolution paths determined by the pressure depletion rate. Oskouei et al.'s model is capable of simulating both equilibrium and nonequilibrium behaviors simultaneously. The oil formation volume factors and the oil phase viscosity were accurately predicted under various pressure depletion rates by tuning reaction orders and frequency factors.

Zhou et al. (2020) developed a four-component kinetic reaction rate model to history-match foamy oil stability during constant composition expansion (CCE) processes with different pressure depletion rates in a pressure-volume-temperature (PVT) cell. The model consisted of two reactions to control the transfer of solution gas to dispersed gas and dispersed gas to free gas, respectively. Both foamy oil volume and gas-liquid system volume were well matched by tuning two reaction rate constants (k_1 and k_2). The relationship between the reaction rate constants and pressure depletion rates, along with

the sensitivity of the two reaction rate constants were investigated. Both parameters were found to be in the order of magnitude at 10^{-3} min^{-1} .

Wang et al. (2020) also developed a four-component kinetic model to predict foamy oil behaviors in CO_2 ex-solution experiments in a PVT cell. Two reaction frequency factors, which indicated the multi-component inter-phase mass transfer, were tuned to obtain a good match of the simulated foamy oil volume with experiment results. And a MATLAB-controlled reservoir simulator was developed for model validation. The results suggested that higher initial gas-to-oil ratio (GOR), pressure depletion rate and pressure drawdown as well as for solvent-oil contact time, were found to increase the foamy oil stability. Also, Wang et al. predicted the volume change of oil phase during gas dissolution experiments by tuning the diffusion coefficient achieving a simulated oil volume precisely matched to the experimental results. However, they did not combine their dissolution model with their gas ex-solution model limiting the application of the model.

The aforementioned second category of kinetic models mainly focus on the effects of pressure depletion rates when simulating the foamy oil behavior. However, limited study has been done so far to investigate the influence of temperature on the kinetic models during non-equilibrium foamy oil evolution. Even fewer efforts have been made on modeling the dissolution of gas back to the heavy oil phase under various pressure increase rates by utilizing kinetic models.

2.4 Research Objectives: What is missing in the literature?

This research aims to fill the knowledge gaps on robust and general models for non-equilibrium foamy oil dynamics in heavy oil systems. The research documented in this thesis is on the development of a robust second category kinetic model aiming to simulate both solvent ex-solution and dissolution processes in heavy oil under various temperature and pressure depletion rates. The model applies a non-equilibrium mass transfer approach with pseudo-chemical reactions which are able to represent both solution gas ex-solution and back dissolution processes. For model validation, a set of laboratory data from a Constant Composition Expansion and Compression (CCEC) experiment will be introduced and the model should be able to history-match the experimental results. The reaction orders and frequency factors in the pseudo-chemical reactions will be designed as adjustable parameters. Through analyzing the sensitivity of these parameters with respect to pressure and temperature, another goal of this study is to be able to understand the regularities of different solvents ex-solution and dissolution behavior in heavy oil on the conditions of various temperature and pressure depletion rates.

Chapter Three: Overview of Experiments and Modelling Methodology

This chapter describes experiments for model validation and establishing the non-equilibrium kinetic model. First, a series of previous laboratory experiments were introduced in detail. Second, a non-equilibrium model with pseudo-chemical reactions is proposed aiming to simulate both gas ex-solution and dissolution processes in the static heavy oil phase. Next, a reservoir simulation model is described for tuning the parameters in the pseudo-chemical reactions of the non-equilibrium model.

3.1 Experimental Data

Experimental data from the literature and collaborative research from the University of Regina (Professor Na Jia) were used to validate the proposed model. Dong et al. studied the CH_4 ex-solution and dissolution process for dead heavy oil obtained from the Sparky formation, Lloydminster area (Dong et al. 2020). Same oil sample was used by Lu in University of Regina to study the C_2H_6 ex-solution and dissolution process in his PhD thesis. To finish the study, both of them utilized constant composition expansion and compression (CCEC) tests to measure and analyze the live oil expansion and compression under different temperatures and pressures conditions through a PVT apparatus. The live oil samples were first prepared through recombining dead oil with various concentration of CH_4 or C_2H_6 , followed by measuring the density and viscosity by experiments. CCEC tests were conducted applying various live oil samples in a PVT cell through three different constant volume change rates (“fast rate”, $1.5 \text{ cm}^3/\text{min}$;

“moderate rate”, $0.015 \text{ cm}^3/\text{min}$; and “slow rate”, $0.0003 \text{ cm}^3/\text{min}$) at 75°C and 15°C . The PVT cell volume expanded until it reached the cell maximum during expansion stage. Next, the oil and gas were compressed back to the initial pressure following the same rates as the expansion process. The total system volume was monitored and recorded during the whole process. Finally, P-V diagrams were plotted according to the CCEC tests results to make comparisons among different cases. The details of the experimental apparatus, procedures and results are described below. In this study, we assume the experimental data is accurate and all the simulation procedures are based on these results.

3.1.1 Materials

The stock tank oil sample utilized in this study has a molecular weight of 540 g/mol , which was measured by Saskatchewan Research Council and Maxxam Analytics. The oil came from the Sparky formation, Lloydminster area. The AgilentTM 6890N Gas Chromatography (GC) was applied to analyze the composition of the crude oil sample based on ASTM D6352 method, and the oil composition is presented in Table 3-1. The water content of the stock tank oil is less than $0.1 \text{ wt}\%$. There are two live oil samples which were synthesized by recombining CH_4 and C_2H_6 with stock tank oil, respectively. Sample No.1 was the combination of $11.4 \text{ mol}\% \text{ CH}_4$ and $88.6 \text{ mol}\% \text{ STO}$ (measured gas-oil ratio (GOR) was $8.63 \text{ cm}^3/\text{cm}^3$). Sample No.2 was the combination of $16.5 \text{ mol}\% \text{ C}_2\text{H}_6$ and $83.5 \text{ mol}\% \text{ STO}$.

Table 3-1: Compositional analysis of stock tank oil (Dong et al., 2020).

Carbon number	mol%	Carbon number	mol%	Carbon number	mol%
C8	0.89	C17	4.00	C26	1.82
C9	3.44	C18	3.64	C27	1.88
C10	3.05	C19	3.45	C28	1.84
C11	3.61	C20	3.11	C29	1.56
C12	4.14	C21	2.81	C30	1.47
C13	4.47	C22	2.59	C31+	31.95
C14	4.82	C23	2.43		
C15	4.75	C24	2.13		
C16	4.16	C25	1.99	Total	100.00

3.1.2 CCEC Experiments Setup

The CCEC tests were performed in mercury-free DBR PVT system (PVT-015-100-200-316-155, Schlumberger), the primary part of this equipment is the visual and high-pressure PVT cell. Figure 3-1 presents the schematic of the PVT system. The core part of the PVT system is a glass tube with an inner diameter of 3.177 cm and total height of 20.320 cm, which is contained in a stainless cell with a floating flat piston fitted inside. The maximum operating pressure and temperature of the PVT system is 69,000 kPa and 200°C, respectively.

During the experiments, the required temperature was kept stable by PVT cell thermal control system with the accuracy of 0.1°C. A high-pressure syringe pump (500 HP, ISCO Inc., USA) was applied to inject the live oil into the PVT cell via a transfer cylinder. The piston positions, which represent total volume of the fluids inside the PVT cell, were

monitored and recorded by the high precision cathetometer which has an uncertainty of ± 0.001 cm. The pressure gauge has the accuracy of 1 kPa.

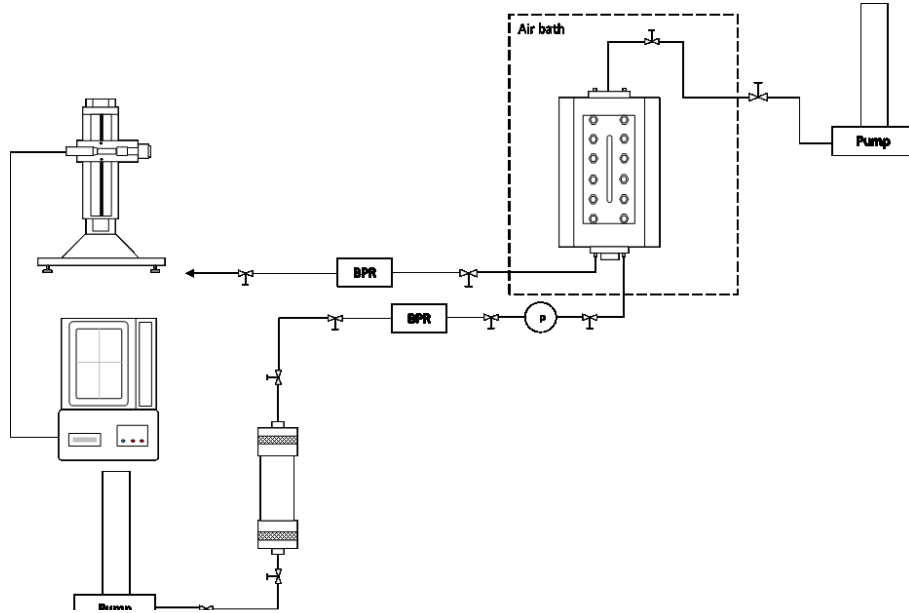


Figure 3-1: Schematic diagram of PVT setup (Dong et al., 2020).

3.1.3 Experimental Procedures

3.1.3.1 Density and Viscosity Measurement

To prepare the live oil samples, two cylinders were utilized to contain calculated amount of dead oil sample and pure gas separately for combination. The system pressure was maintained above the bubble point pressure of the live oil when combining the fluids back and forth between two cylinders, aiming to obtain an equilibrium mixture. After the live oil samples were prepared, a stainless fluid sampler with the known volume of live

oil (54.13 cc) is utilized for the density measurement. The temperature of the sampler was maintained at room temperature and the pressure was controlled by the syringe pump. As for the viscosity measurement, the capillary tube with length of 6 m and inner diameter of 0.0016 m was applied. The upstream flow rate kept stable during the measurement. Besides, the fluid flow rate and pressure were controlled by the syringe pump, while the system temperature was controlled by the air bath.

3.1.3.2 CCEC Experiments Procedures

The CCEC experiments were carried out for two live oil samples with various constant volume change rates under isothermal conditions (i.e., 75°C and 15°C). The brief procedure of one of the CCEC tests is described as follows: The live oil sample is contained within the transfer cylinder and prepared to be introduced into the PVT cell. All the tubing lines and PVT cell have been vacuumed first and flushed with live oil sample to minimize the air contamination and dead volume on the measurement of saturation pressure. Next, the oil sample was injected into the PVT from the bottom of the cell at room temperature. The inlet and outlet valves of the PVT cell were closed until the specific amount of live oil sample was injected. The content within the PVT cell has been stabilized for at least 24 hours to ensure the live oil sample reached equilibrium at the required test temperature, and the initial position of the loaded oil sample has been recorded. The pressure depletion tests started until the cell reached its maximum volume. Next, the oil and gas were compressed back to the initial pressure by applying the same

rates as the expansion process. Table 3-2 summarizes the CCEC experiments designs in this study.

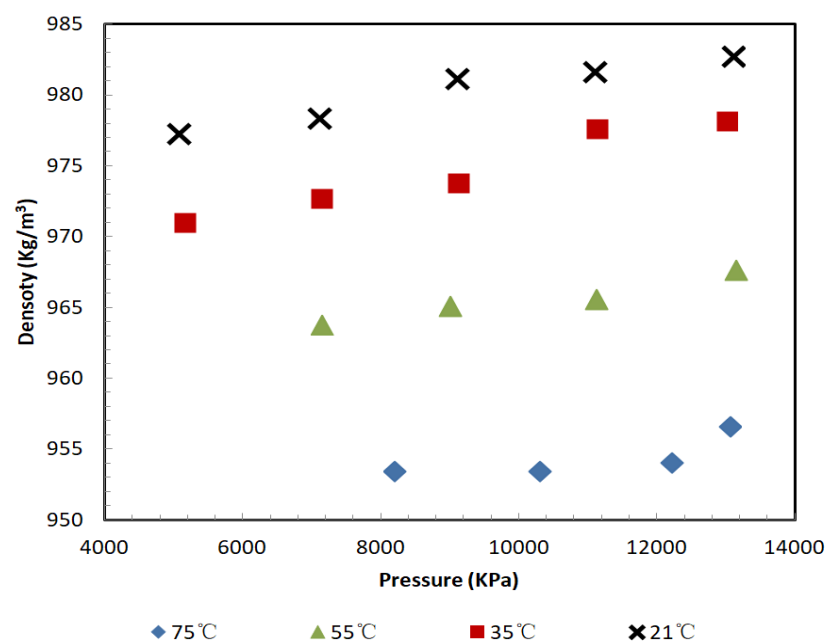
Table 3-2: Summary of CCEC experiments designs.

Experiment	Live oil sample	Temperature (°C)	Initial pressure (KPa)	Volume expansion rate (cm ³ /min)
1	Sample No.1 (11.4% CH ₄ +88.6% STO)	15	13103	1.5
2		15	11831	0.015
3		15	3038	0.0003
4		75	13177	1.5
5		75	13129	0.15
6		75	6611	0.0003
7	Sample No.2 (16.5% C ₂ H ₆ +83.5% STO)	15	11501	1.5
8		15	11925	0.015
9		15	1131	0.0003
10		75	11961	1.5
11		75	11954	0.015
12		75	6113	0.0003

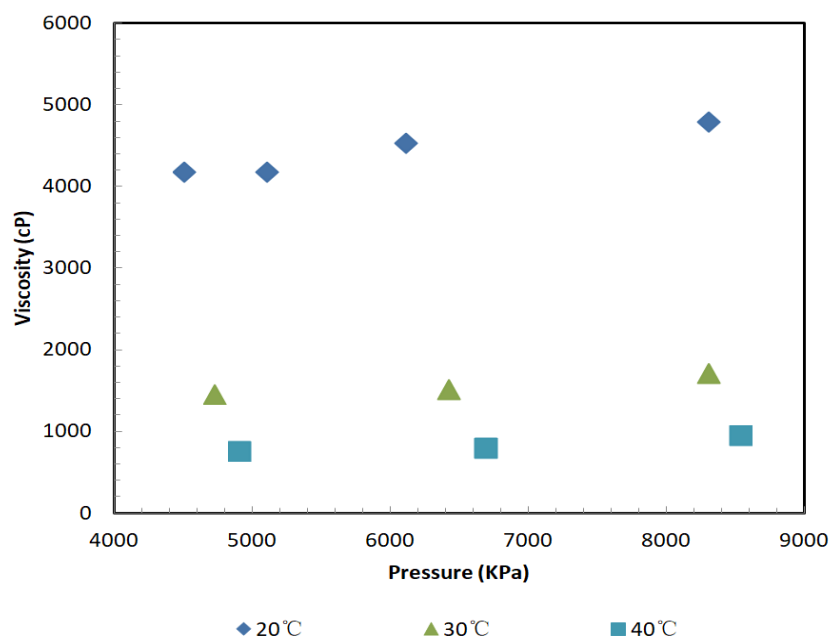
3.1.4 Experimental Results

3.1.4.1 Density and Viscosity Measurement Results

Density and viscosity have been measured for live oil samples at various temperatures and pressures, as shown in Figure 3-2 and 3-3. It can be seen from figures that increasing temperature and reducing pressure could decrease both density and viscosity of the live oil, and these experimental results match the general understanding.

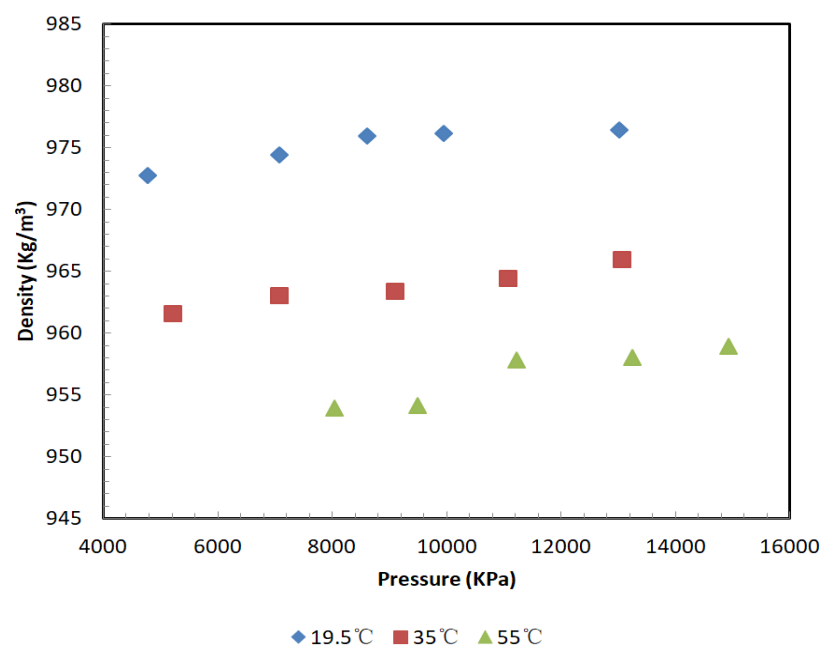


(a)

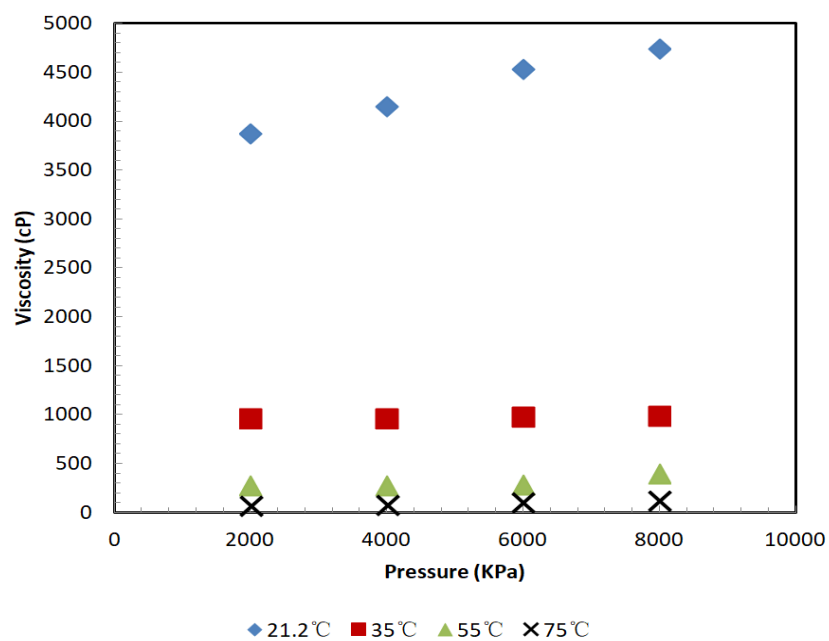


(b)

Figure 3-2: Experimentally measured (a) density; (b) viscosity of live oil sample No.1.



(a)

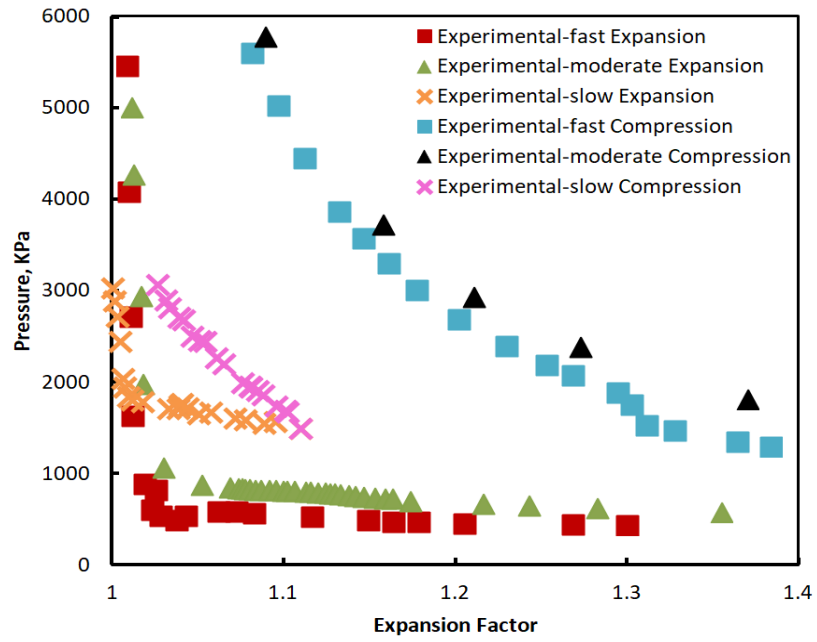


(b)

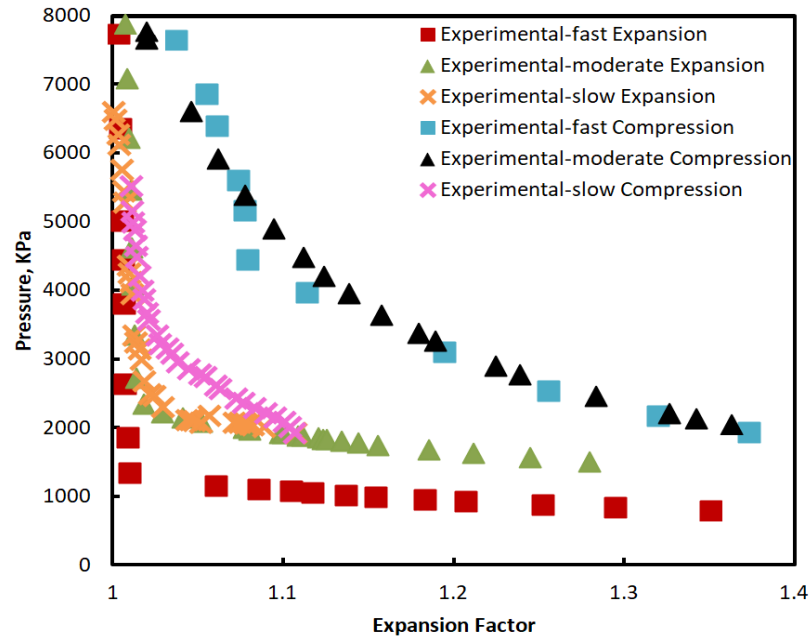
Figure 3-3: Experimentally measured (a) density; (b) viscosity of live oil sample No.2.

3.1.4.2 CCEC Tests Results

For each CCEC test, it started with volume expansion stage with an initial pressure higher than expected bubble point pressure of the live oil sample. Considering both the maximum volume of the PVT cell and time restriction of the experiment duration, the fast pressure depletion rate was set to $1.5 \text{ cm}^3/\text{min}$, the moderate rate was set to $0.015 \text{ cm}^3/\text{min}$, and the slow rate was chosen to be $0.0003 \text{ cm}^3/\text{min}$. As the PVT cell reached its maximum volume, the gas and oil were subjected to the compression process following the same rates as expansion stage. During the whole process, the total volume of the mixture (V_t) and corresponding pressures were recorded. The initial volume (V_{ini}) at the highest volume was considered as the basic pressure to calculate expansion factor (V_t/V_{ini}). Figure 3-4 and 3-5 shows the relationship between system pressure and expansion factor during CCEC tests for live oil sample No.1 and No.2, respectively. It can be observed from both figures that during expansion process, there exists a sharp pressure decrease rate during the early period indicating single liquid phase region. A free gas phase then started to form and the slope changed. For both live oil samples, faster pressure depletion rates result in a stronger foamy oil behavior, delaying the formation of free gas phase. A different path was followed for compression stage, which indicates resistance existing during gas back dissolving into oil phase. The thermodynamic bubble point pressures (P_b) for both oil samples were determined based on data from slow expansion processes and they are summarized in Table 3-3.

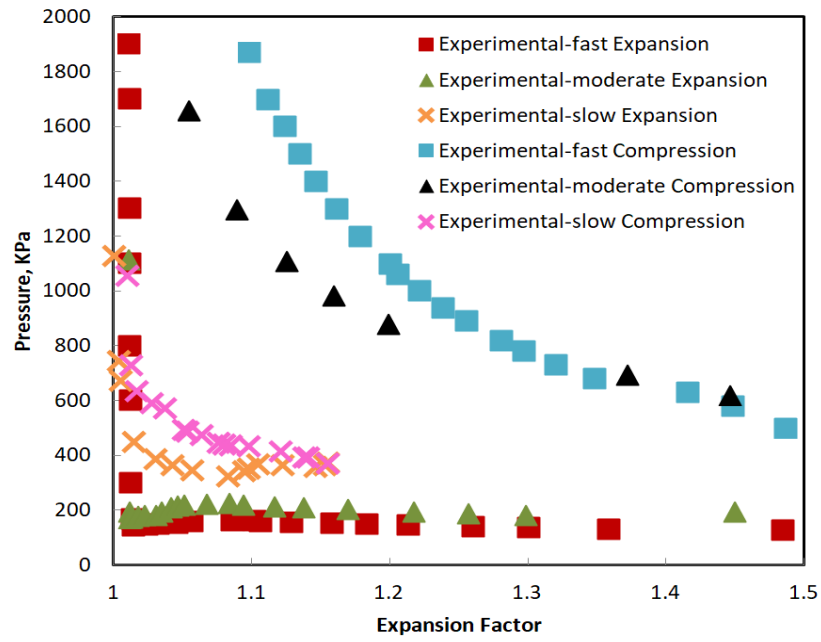


(a)

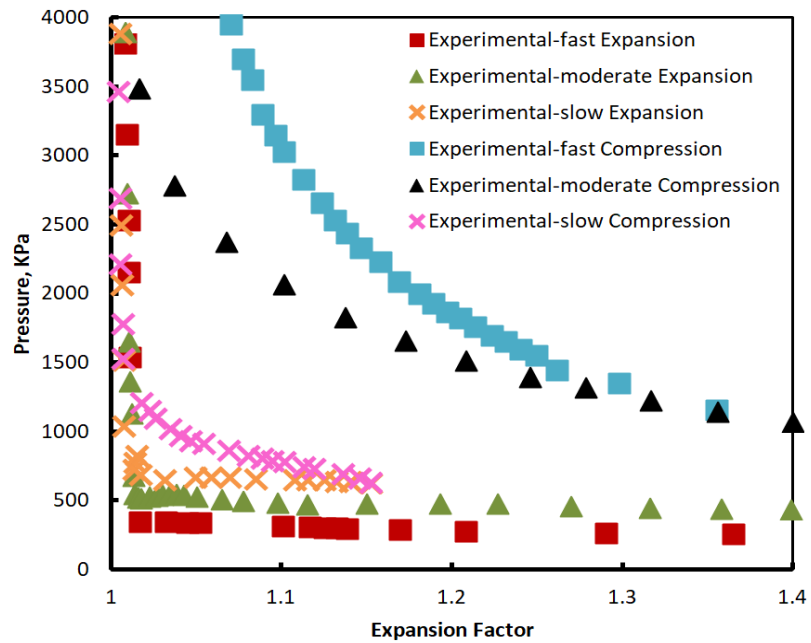


(b)

Figure 3-4: Variation of volume expansion factor change and pressure at (a) $T=15^{\circ}\text{C}$ and (b) $T=75^{\circ}\text{C}$ with different depletion rates of live oil sample No.1



(a)



(b)

Figure 3-5: Variation of volume expansion factor change and pressure at (a) $T=15^{\circ}\text{C}$ and (b) $T=75^{\circ}\text{C}$ with different depletion rates of live oil sample No.2.

Table 3-3: Calculated bubble point pressure (P_b) for both oil samples.

Live oil sample	Temperature ($^{\circ}\text{C}$)	P_b (KPa)
Sample No.1	15	1900
(11.4% CH_4 +88.6% STO)	75	2700
Sample No.2	15	470
(16.5% C_2H_6 +83.5% STO)	75	860

3.2 Non-equilibrium Model Description

The proposed model is a non-equilibrium kinetic model, which involves three pseudo-chemical reactions with four pseudo components. The model applies mass transfer approach, concentrating on micro bubble formation and release during the pressure depletion period, as well as free gas dissolving back to the oil phase to form solution gas when the pressure increases. The model assumes three steps to simulate processes in the heavy oil-gas system.

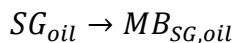
3.2.1 Step 1: Bubble Nucleation and Growth

Because of high viscosity of heavy oil, the liberated gas tends to be trapped in the oil phase in the form of tiny bubbles that remain separated when the pressure drops below the P_b . In the pressure depletion processes, it is generally believed that gas ex-solution starts from bubble nucleation in the oil phase. When the pressure decreases to the P_b and potentially below it, solution gas tends to ex-solve from the heavy oil by nucleating a number of micro bubbles and the system is supersaturated. The nucleation process is strictly controlled by the supersaturation pressure and the initiated very small micro

bubbles have nearly no influence on the oil phase volume. After nucleation, with more gas molecular diffusion and exsolution, the micro bubbles grow. Unlike the behaviour in porous media, bubble growth in a bulk environment is mainly driven by gas solubility due to the lack of influence from capillary characteristics (Oskouei et al., 2017). The following assumptions are applied to describe bubble nucleation and growth in the bulk volume (Shi et al., 2016; Oskouei et al., 2017; Zhou et al., 2020):

- (1) The nucleated micro bubbles inherit the properties of the solution gas, leading to limited influence on the heavy oil phase (phase volume etc.).
- (2) To simulate the evolving processes after nucleation, the micro bubbles are treated as gas-like density liquid according to the non-ideal gas law: $PV=ZRT$ (R is the universal gas constant and Z is the compressibility factor). The collective volume of dispersed gas is considered the same as that of free gas at the same pressure and temperature.
- (3) The Laplace pressure arising from interfacial tension in the micro bubbles is negligible and as such, the capillary pressure between the heavy oil and micro bubbles in the oil phase is ignored.
- (4) The entrained gas is at the same pressure as the heavy oil phase in foamy oil.
- (5) The foamy oil contains micro bubbles, solution gas and dead heavy oil.

The following pseudo-chemical reaction describes micro bubbles formation in heavy oil phase through non-equilibrium mass transfer:



where SG_{oil} is the solution gas dissolved in the oil phase and $MB_{SG,oil}$ is the solution-gas micro bubbles hosted in the oil phase. The driving force for the formation of micro bubbles can be defined as the difference between actual concentration and equilibrium concentration of the solution gas in oil phase as follows:

$$R_{1(MB_{SG,oil})} = k_1 (C_{SG_{oil}} - C_{SG_{oil}}^*)^{m_1} \quad 2$$

3.2.2 Step 2: Free Gas Phase Formation

In the heavy oil phase, generally the accumulated bubbles in the oil phase tend to collapse when pressure drops to the P_{pb} , releasing gas to form a continuous free gas phase (Kraus et al., 1997). It is a complicated process and depends on the stability of generated foam. In a bulk environment, previous studies have found that the stability of foamy oil increases at higher pressure depletion rates, higher initial GOR, higher oil viscosity, and lower temperature (Modaresghazani et al., 2019; Wang et al., 2020; Zhou et al., 2020). The following pseudo-chemical reaction describes free gas liberation process:



where $FG_{SG,gas}$ is the solution gas as a connected free gas in the gas phase. It is believed that the free gas formation rate is positively correlated with the micro bubble concentration in heavy oil phase, which gives rise a rate law of the form:

$$R_{2(FG_{SG,gas})} = k_2 (C_{MB_{SG,oil}})^{m_2} \quad 4$$

3.2.3 Step 3: Free Gas Back Dissolution

Both Dong et al. and Modaresghazani et al. observed experimentally that there exists a resistance against free gas dissolution back to the heavy oil in the bulk environment (Modaresghazani et al., 2019; Dong et al., 2020). During dissolution processes, mass transfer is mainly controlled by molecular diffusion. To model this hysteretic phenomena, the observations suggest that solution-gas free gas will turn to dissolved solution gas in the oil phase directly instead of forming bubbles when then subsequently dissolve back into the oil phase. This is reasonable since bubbles only appear in the saturated solution and the heavy oil phase is far from reaching saturation at the back dissolution stage. Furthermore, when the pressure is high enough, the net mass transfer of solution gas molecules is to the oil phase. The pseudo-chemical reaction of solution gas dissolving back to oil phase is described as:



Thus, the solution gas back dissolution rate can be defined as the function of both free gas and solution gas concentrations as follows:

$$R_{3(SG_{oil})} = k_3 (C_{SG_{oil}}^* - C_{SG_{oil}})^{m_3} (C_{FG_{SG,gas}})^{n_3} \quad 6$$

3.2.4 Model Summary

The four-component kinetic model contains three pseudo-chemical reactions, with two reactions representing the gas ex-solution process and one describing the free gas back dissolution process. Table 3-4 lists the components' reference phase in the model and it should be emphasized that the micro bubble ($MB_{SG,oil}$) is considered as a gas-like liquid (hosted in the oil phase). The physical properties are set for each component based on the reference phase. In the current model, solution gas, micro bubble, and free gas share the same critical properties and molecular weight. The micro bubble pseudo-component inherits the critical physical properties from solution gas to model the nucleation process. Besides, solution gas and micro bubble do not have volatility and they only exist in the reference phase.

Table 3-4: Pseudo components and reference phases.

Pseudo Component	Phase		
	Aqueous	Oleic	Gas
SG_{oil}		*	
$MB_{SG,oil}$		*	
$FG_{SG,gas}$			*
<i>Heavy Oil</i>		*	

3.3 Non-equilibrium Reservoir Simulation Model

A two-dimensional thermal reactive reservoir simulation model was constructed for tuning the parameters ($k_1, k_2, k_3, m_1, m_2, m_3, n_3$) of the three pseudo-chemical reactions in the kinetic model. Figure 3-1 shows the layout of the simulation model, which is similar to that of Oskouei et al.'s model with additional injectors which as used to raise the pressure to model the gas dissolution process (Oskouei et al., 2017). The layers in the model are colored with blue, green, and red representing fast ($1.5 \text{ cm}^3/\text{min}$), moderate ($0.015 \text{ cm}^3/\text{min}$), and slow ($0.0003 \text{ cm}^3/\text{min}$) expansion and compression rates, respectively. Thus, the model consists of three submodels. Two null blocks were applied to isolate each submodel from each other. Each layer was split further into two blocks. The left side one was saturated with oil, water, and free gas, whereas the right side block was full of water only. The left blocks were like PVT cells since oil and gas was set to be immobile in the grid blocks by adjusting the relative permeability curves, which are presented in Table 3-5. To simulate both pressure depletion and increase processes, water was withdrawn or injected like a piston controlling the pressure variations in the blocks through producers and injectors. Water was set to be non-volatile and incompressible. The model size, initial properties (pressure, temperature, oil volume), and well operation constraints were set to follow the experimental conditions.

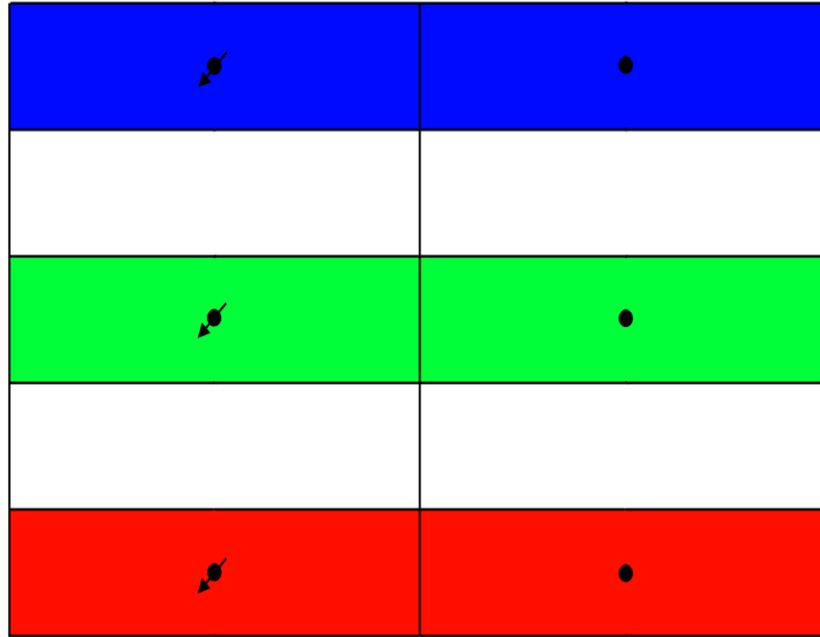


Figure 3-6: A layout of the simulation model. The injectors and producers are located in the left and right blocks, respectively.

Table 3-5: Relative permeability data of the simulation model.

Water-Oil Relative permeability Table			Liquid-Gas Relative Permeability Table		
Sw	Krw	Krow	SI	Krg	Krog
0.00	0.00	1.00	0.00	1.00	0.00
0.03	1.00	0.00	0.03	0.00	1.00
1.00	1.00	0.00	1.00	0.00	1.00

3.4 Summary

In this chapter, a non-equilibrium kinetic model is developed with three pseudo-chemical reactions aiming to simulate the gas-liquid system volume variation during the CCEC

processes in the static heavy oil. A reservoir simulation model is then created to validate the kinetic model by numerically imitating the CCEC experiments. Through running the kinetic model in the reservoir simulation model, parameters $(k_1, k_2, k_3, m_1, m_2, m_3, n_3)$ from the pseudo-chemical reactions will be tuned to history-match the experimental results.

Chapter Four: Modeling Study of CH₄ Non-Equilibrium Ex-solution and Dissolution in a Static Heavy Oil System

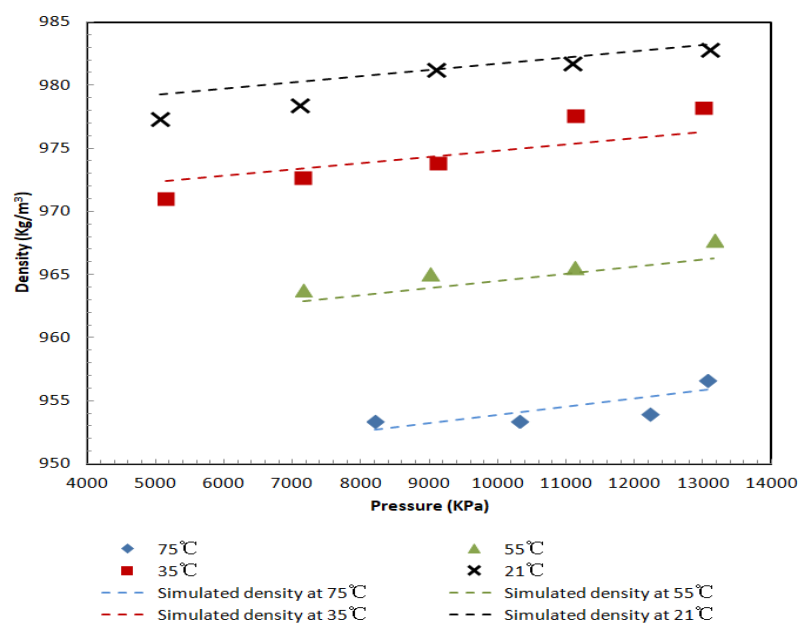
In this chapter, parameters of the non-equilibrium kinetic model are tuned to match the experimental data of the oil-gas system expansion factors presented in Figure 3-4. First, the basic properties of the model components and K-values are obtained through PVT phase behavior modeling. Then, the kinetic model is validated by the reservoir simulation model and the parameters are confirmed. Finally, by analyzing the parameters, the influence of pressure and temperature on CH₄ ex-solution and dissolution in heavy oil can be well understood.

4.1 Component Properties and K-values

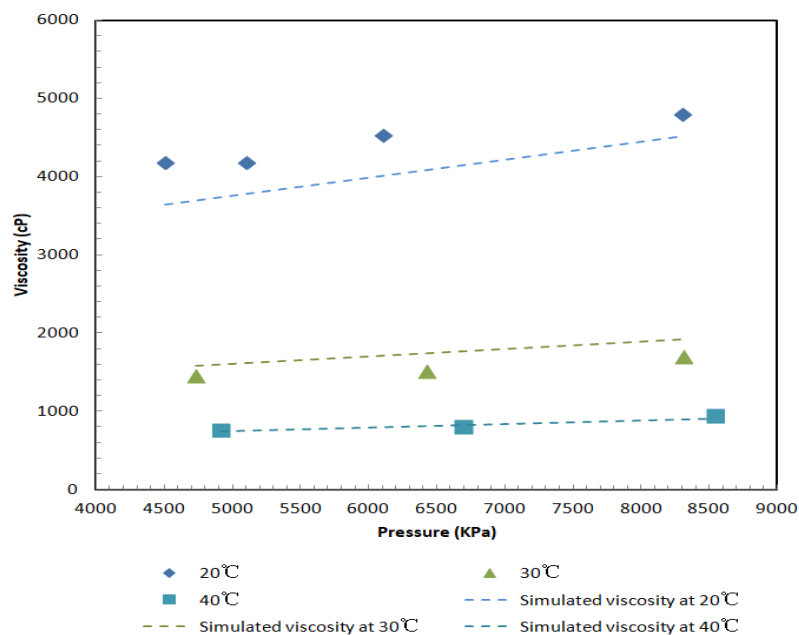
The basic properties of the model components such as molecular weight, mass density, compressibility factor, critical pressure and temperature are determined for the following modeling procedures. The molecular weight and critical pressure and temperature of the solution gas (as dissolved gas, micro bubble, or free gas) were taken to be that of methane (as was used in the experiments). The densities, viscosities, and compressibilities were obtained from the thermodynamic equilibrium package CMG WinProp (CMG WinProp 2019) by history-matching both density and viscosity of the live oil versus pressure and temperature. In WinProp, the Peng-Robinson equation of state (1978) (Robinson and Peng, 1978) was selected for overall tuning and the mixture was defined by two pseudo components: heavy oil and methane.

For the heavy oil pseudo component, the molecular weight was set to be 539.9 g/mol and the Twu correlations were used to calculate the critical properties (Twu, 1984). A linearly temperature dependent volume shift and modified Pederson (1987) model was applied for density and viscosity tuning, respectively (Pederson and Fredenslund, 1987). Moreover, the thermodynamic bubble point pressure (P_b) was tuned to match the experimental results at both 15 and 75°C by adjusting the heavy oil critical temperature and pressure, volume shift coefficient, and the interaction coefficient between heavy oil and methane.

Figure 4-1 compares the tuning results of the experimental data related to density and viscosity. The matching results are good in general, though the deviation is relatively large for viscosity at lower temperature indicating the effect of strong foamy oil behavior (Dong et al., 2020). As for the P_b , the tuning results are 1899.9 and 2689.0 kPa for 15 and 75°C, respectively. The results are close to the experimental results (Table 3-3) for further modeling. It should be mentioned that the micro bubbles inherit the solution gas properties when they are beginning to form when pressure drops below P_b . Therefore, the properties (including density) of micro bubbles were set to be equal to the solution gas at P_b for both temperatures. The basic properties of the model components are listed in Table 4-1.



(a)



(b)

Figure 4-1: Comparison between simulation and experimental measured (a) density and (b) viscosity of the live oil sample.

Equilibrium K-values is defined as vapor mole fraction y_i to the liquid mole fraction x_i , of a component i in a mixture ($K_i=y_i/x_i$) at a given pressure and temperature. It defines the partitioning of the solution gas between the gas and oil phases at equilibrium. In this case, the K-values were calculated by WinProp after tuning the components properties and the output K-values were applied to model equilibrium behaviour in the kinetic model. Figure 4-2 presents the variation of calculated solution gas K-values verse pressure at both 15 and 75°C.

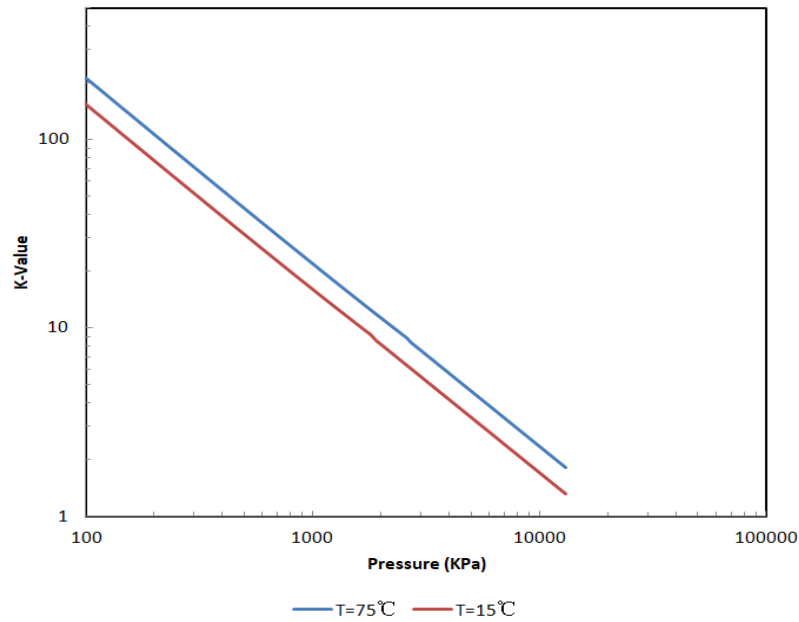


Figure 4-2: Calculated K-values for solution gas at various pressure at both 15°C and 75°C.

Table 4-1: Pseudo-components properties at (a) 15°C, 1899.9 KPa and (b) 75°C, 2689.0 KPa.

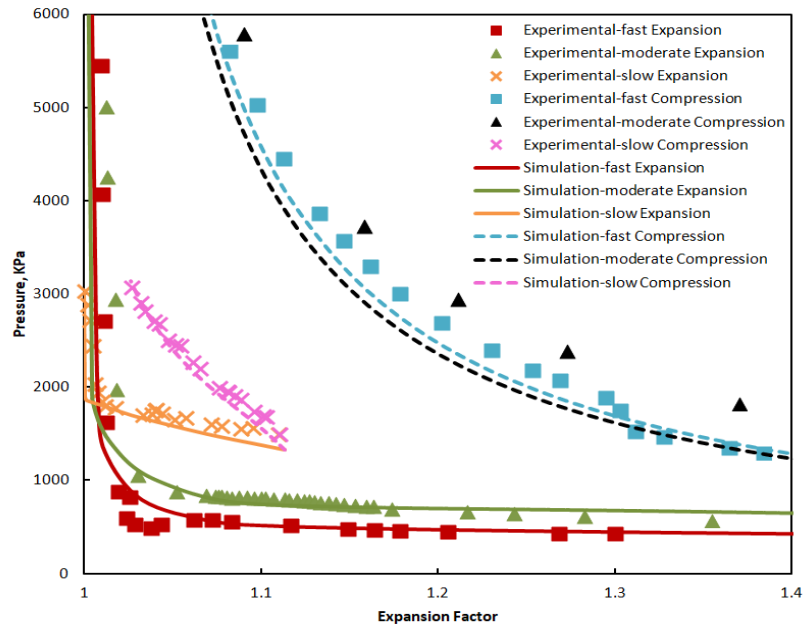
(a) 15°C, 1899.9 KPa					
Pseudo Component	MW (g/mol)	ρ (kg/m ³)	C_p (KPa ⁻¹)	T_c (°C)	P_c (KPa)
SG_{oil}	16.0	0.316	6.001×10^{-6}	-82.55	4600.15
$MB_{SG,oil}$	16.0	0.316	-	-82.55	4600.15
$FG_{SG,gas}$	16.0	-	-	-82.55	4600.15
Heavy Oil	539.9	0.988	4.335×10^{-7}	471.5	1109.93

(b) 75°C, 2689.0 KPa					
Pseudo Component	MW (g/mol)	ρ (kg/m ³)	C_p (KPa ⁻¹)	T_c (°C)	P_c (KPa)
SG_{oil}	16.0	0.252	9.381×10^{-6}	-82.55	4600.15
$MB_{SG,oil}$	16.0	0.252	-	-82.55	4600.15
$FG_{SG,gas}$	16.0	-	-	-82.55	4600.15
Heavy Oil	539.9	0.959	7.294×10^{-7}	471.5	1109.93

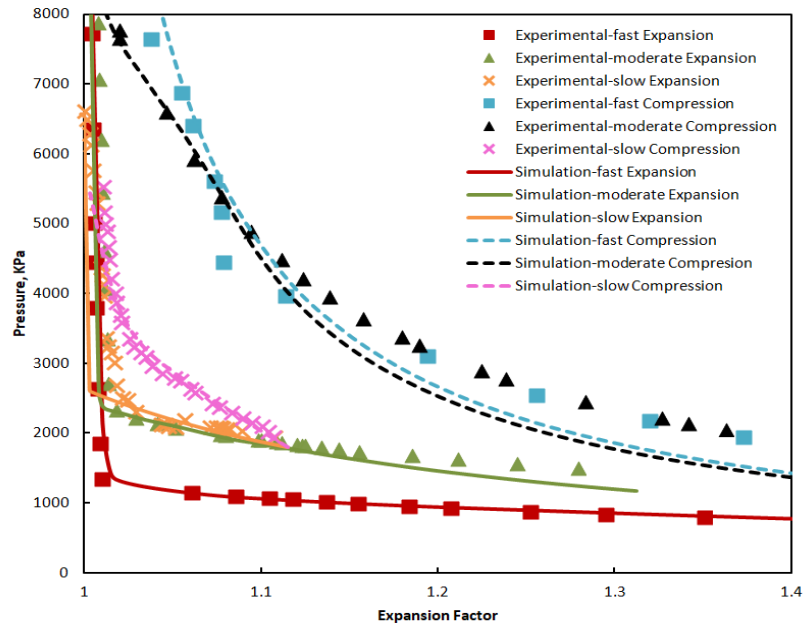
4.2 Non-Equilibrium Kinetic Modeling Results

The parameters ($k_1, k_2, k_3, m_1, m_2, m_3, n_3$) were tuned so that the model results matched the experimental data of the oil-gas system expansion factors presented in Figure 3-4. In the model, the calculated K-values were applied to determine the equilibrium concentration of solution gas in Reactions 2 and 6 of Chapter 3. The activation energies for all reactions were set to be equal to zero since the experiments were conducted at isothermal conditions. In the model, the micro bubbles began to emerge from a small fraction of the solution gas when the pressure declines below the saturation pressure. Micro bubbles start to grow and accumulate as the pressure continues to decline and collapse of the micro bubbles to free gas phase occurs when P_{pb} is reached. When the pressure increases from a low level, free gas begins to back dissolve into the oil phase. A comparison of the experimental and model results are presented in Figure 4-3. The results

show that the model produces profiles that agree with the experimental data at both temperatures. However, as shown in red circles of Figure 4-4, the model cannot predict the rebound pressure during pressure depletion processes at both temperatures. Table 4-2 summarizes the maximum absolute values for the model deviation from measured expansion factors for each case without considering the rebound pressure behavior. In the expansion stage, the maximum absolute deviations were less than 6% and most of them were found after the free gas phase has been formed. Similar observations were made by Zhou et al. and this phenomenon is mainly due to the volume variation mechanism was changed at the middle of the expansion processes. Before free gas was released, the system volume variation was mainly determined by single process (micro bubbles formation and growth). However, when free gas phase is formed, there were two processes (micro bubbles formation and growth, micro bubbles transform to free gas phase) involved resulting in the larger deviation of the calculated system volume (Zhou et al. 2020). Compared with the expansion stage, the simulation results of the compression processes have relatively larger deviations. As shown in Table 4-2, half of the cases in compression stages have maximum absolute deviation greater than 6%, though all the figures are less than 9%. This may be because during the expansion stages, two processes of the oil-gas system volume change are described by two reactions. However, only one reaction is applied to describe the two processes of system volume change occurring in the compression stages (free gas shrinkage and free gas transforms to solution gas), which results in the calculated volume of oil-gas system being less matched with the laboratory results.

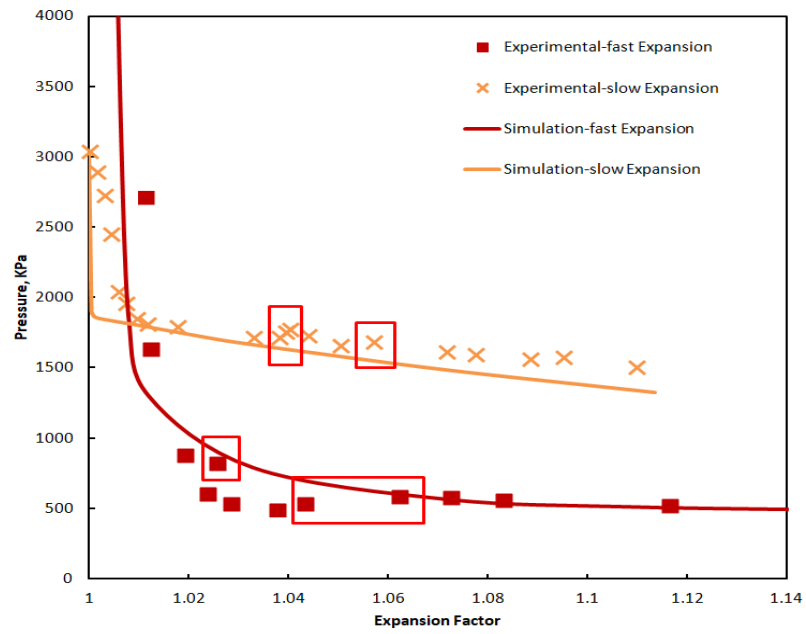


(a)

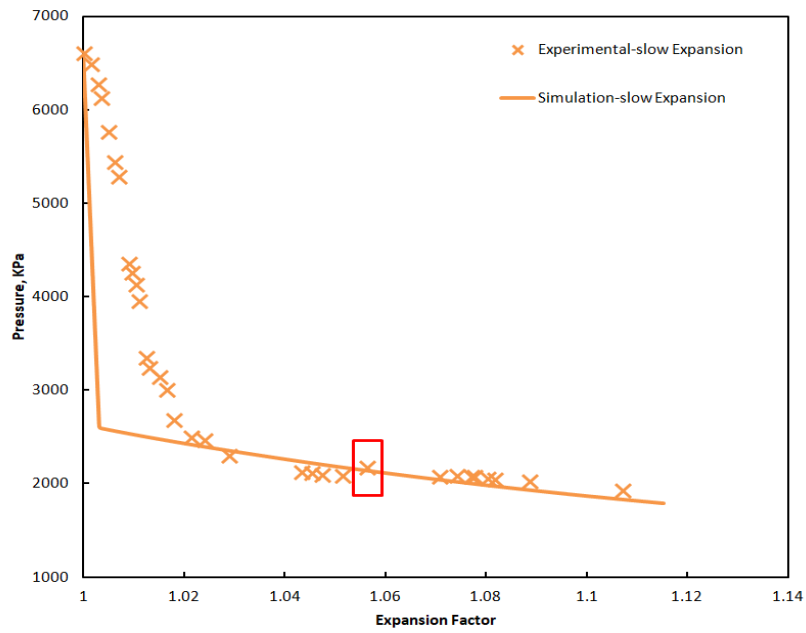


(b)

Figure 4-3: The measured and simulated volume expansion factors at (a) 15°C and (b) 75°C.



(a)



(b)

Figure 4-4: The comparison of modeling results verse rebound pressure behavior at (a) 15°C and (b) 75°C.

Table 4-2: Summary of the maximum model deviation from experimental data of different cases.

Experimental cases (temperature and rate)		Pressure values (kPa) at the maximum deviation points	Maximum absolute deviation
Expansion at 15°C	Fast	603.325	3.53%
	Moderate	577.325	4.60%
	Slow	1571.325	3.91%
Expansion at 75°C	Fast	1341.325	0.99%
	Moderate	1503.325	5.93%
	Slow	2686.325	1.44%
Compression at 15°C	Fast	1885.325	1.94%
	Moderate	1817.325	8.03%
	Slow	1679.325	0.85%
Compression at 75°C	Fast	1937.325	6.85%
	Moderate	2058.325	7.38%
	Slow	5528.325	0.94%

4.3 Kinetic Model Parameters

4.3.1 Reaction Orders

Four reaction orders (m_1, m_2, m_3, n_3) were tuned to achieve the match of the model results to the experimental data. In many studies, the reaction orders are independent of the concentration of the components and are normally set as first order (equal to 1) for the reacting component (CMG, 2019). In this study, the reaction orders are set differently for various reactions, which are listed in Table 4-3. However, they have the same value at both 15 and 75°C. The reaction order n_3 was more than 10,000 times smaller than m_i ($i=1, 2, 3$) in the model, which reveals the extent of resistance against the free gas dissolving back into the heavy oil phase.

Table 4-3: Reaction orders for gas ex-solution and dissolution kinetic model at both 15°C and 75°C.

i	m_i	n_i
1	1.3	-
2	1.15	-
3	1	0.0001

4.3.2 Reaction Frequency Factors

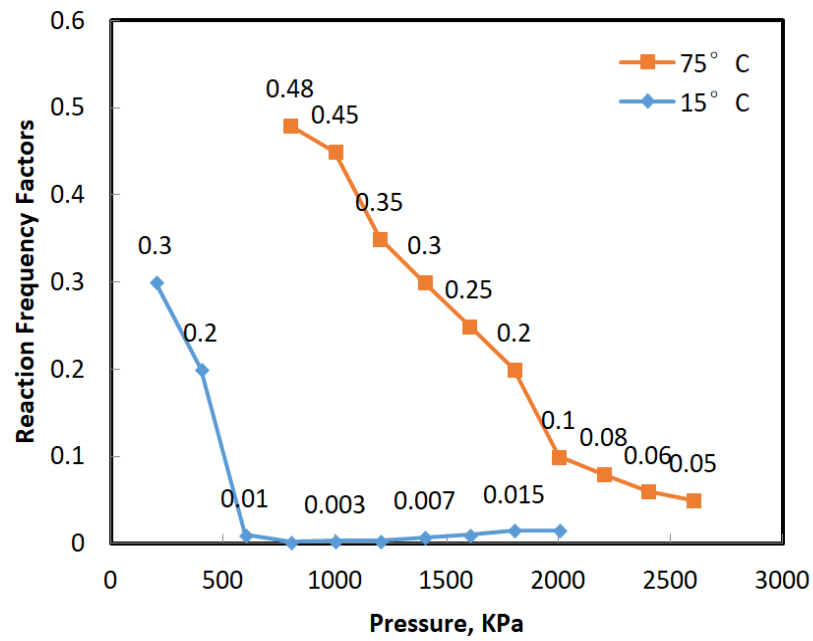
To simulate the oil-gas system volume changes during the expansion processes, the reaction frequency factors were set to be dependent on both pressure and temperature. The results are presented in Table 4-4 and Figure 4-5(a). From Table 4-4, it is found that k_1 , representing the micro bubbles formation rate, was the same at the two temperatures. This is due to the limited influence of temperature on the tendency of solution gas exsolving from the oil phase when the pressure drops below P_b . Although the micro bubble formation rates were identical, its collapse rates were strongly dependent on temperature. From Figure 4-5(a), at each pressure, k_2 is much higher at 75°C compared with 15°C, indicating that the micro bubbles release rates increase dramatically with rising temperature. This is because the foam stability in bulk decreases as the oil viscosity drops (Sheng et al., 1997). The oil viscosity at 75°C is much lower than it at 15°C, leading to the stability of the generated bubbles becoming weaker and the gas trapped in the bubbles easier to form a connected free gas phase. Furthermore, the overall trend of k_2 was that it increased with the decrease of pressure at both temperatures, showing the micro bubble collapse speeds increase with the decline of pressure. At 15°C, k_2 slightly

decreases initially, followed by drastic increase from 0.002 to 0.3 during the pressure depletion process. At 75°C, k_2 increased from 0.05 to 0.48 gradually as the pressure dropped from 2,600 to 800 kPa. This may be attributed to a longer time period which is needed to reach the lower pressure conditions and that the micro bubbles will accumulate more in the oil phase, which are likely to collapse to form a connected free gas phase.

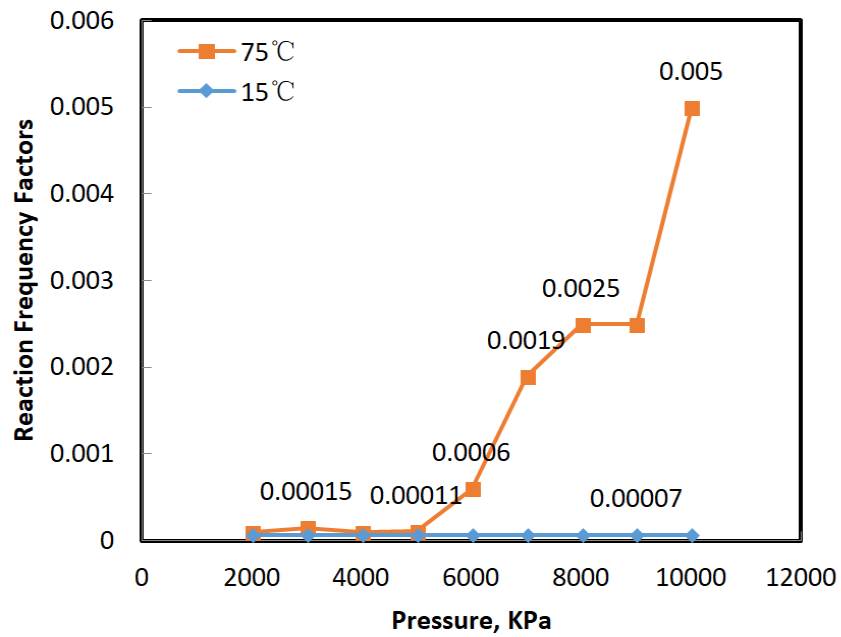
Based on the results of k_1 and k_2 , the model presents: (1) at bulk environment, stronger foamy oil phenomenon at lower temperature is mainly determined by having relatively higher oil phase viscosity, which restricts the micro bubbles collapse rates (k_2). Temperature has limited impact on micro bubbles generation speeds (k_1). (2) Free gas formation rates (k_2) are dependent on pressure and this tendency grows with decreasing pressure, which is similar to the results found by (Oskouei et al., 2017). (3) Unlike previous studies (Wang et al., 2020; Zhou et al., 2020), both k_1 and k_2 are independent on pressure depletion rates, meaning that once the parameters are tuned, the model has the potential to model foamy oil behavior without considering the rate of pressure change.

Table 4-4: Reaction frequency factors of Reaction 1 at 15°C and 75°C.

Temperature (°C)	15	75
Reaction Frequency Factors (k_1) (lab units)	75	75



(a)



(b)

Figure 4-5: Reaction frequency factors of reaction (a) 3 (k_2) and (b) 5 (k_3) at 15°C and 75°C.

In the compression stages, the only reaction frequency factor (k_3) was also set to be dependent on temperature and pressure. As is shown in Figure 4-5(b) and Appendix, the value of k_3 was equal to 0.00007 at 15°C regardless of pressure. At 75°C, the minimum value for was equal to 0.0001 and it increased dramatically to 0.005 when the pressure reached 10,000 kPa, which indicates the resistance for solution gas back dissolution is lower at 75°C compared with 15°C. This result is reasonable since the oil viscosity at 75°C is much lower than that at 15°C, making the gas easier to dissolve back into the oil phase when the pressure rises. However, it seems the influence from temperature was not that evident at lower pressure since k_3 remained about the same for both temperatures when the pressure was below 5,000 kPa. This phenomenon indicates that in the bulk environment, increasing both temperature and pressure together is the most efficient way to accelerate gas dissolution speeds. When both temperature and pressure are relatively low, increasing single parameter (temperature or pressure) may have limited influence on promoting gas dissolution speeds. Based on the results in Figure 4-5(b), it can also be concluded that to promote gas dissolution rates, rising pressure is efficient only when temperature is relatively high.

4.4 Summary

In this chapter, the non-equilibrium kinetic model was validated to describe both CH₄ ex-solution and dissolution processes in the bulk environment of heavy oil. The model was tuned against experimental data via four reaction orders (m_1, m_2, m_3, n_3), as well as three reaction frequency factors (k_1, k_2, k_3). The model results match experimental data and the

parameters are analyzed for better understanding the processes of CH₄ ex-solution and dissolution in heavy oil.

Chapter Five: Modeling Study of C₂H₆ Non-Equilibrium Ex-solution and Dissolution in a Static Heavy Oil System

In this chapter, parameters of the non-equilibrium kinetic model are tuned to match the experimental data of the oil-gas system expansion factors presented in Figure 3-5. Similar to the previous CH₄ modeling cases, the basic properties of the model components and K-values are obtained first through PVT phase behavior modeling. Next, the kinetic model is validated by the reservoir simulation model to confirm the model parameters. Finally, by analyzing the parameters, the influence of pressure and temperature on C₂H₆ ex-solution and dissolution in heavy oil can be well understood. In addition, by comparing the parameters with CH₄ modeling cases, we can understand the different behavior of C₂H₆ ex-solution and dissolution in heavy oil phase.

5.1 Component Properties and K-values

Similar to the previous CH₄ modeling procedures, the basic properties of the model components are determined first for the following modeling procedures. In this study, same type of dead oil sample was utilized for recombining with either CH₄ or C₂H₆ for live oil samples preparation. Therefore, the dead oil properties were supposed to be same for both modeling cases. In WinProp, the Peng-Robinson equation of state (1978) (Robinson and Peng, 1978) was selected for density, viscosity and P_b tuning and the mixture was defined by two pseudo components: heavy oil and ethane. Since the pseudo component “heavy oil” had the same properties as the previous CH₄ modeling work,

density was calculated instead of being tuned in C_2H_6 live oil sample. Figure 5-1(a) compares the calculated results of the experimental data related to density. Although the calculated results do not match with the experimental results perfectly, the average deviations are less than 1% at all three temperatures and it is good enough for the following modeling work. As for the viscosity tuning, the Modified Pederson (1987) (Pederson and Fredenslund, 1987) correlation was applied to focus on calculating the mixture viscosity. Correlation parameters were re-tuned from CH_4 modeling case since the mixture components were changed.

Figure 5-1(b) represents the tuned viscosity verse experimental data at various pressure and temperature. The matching results are good in general, though the deviation is relatively large for viscosity at lower temperature indicating the effect of strong foamy oil behavior. Moreover, since the dead oil properties were set to be same for both modeling cases, P_b was tuned to match the experimental results at both 15 and 75°C by only adjusting the interaction coefficient between heavy oil and ethane. The tuning results of P_b are 425.6 and 975.6 KPa for 15 and 75°C, respectively. According to Table 3-3, the tuning P_b is close to the experimental results at 15°C, but has approximate 13% deviations at 75°C. This is because the critical temperature and pressure of heavy oil applied in the tuning processes were obtained from previous CH_4 modeling work, which may not be accurate enough for C_2H_6 live oil sample. However, to keep consistency of the modeling work, we decided to keep the heavy oil critical temperature and pressure as same as previous CH_4 modeling work instead of adjusting them. In this modeling case,

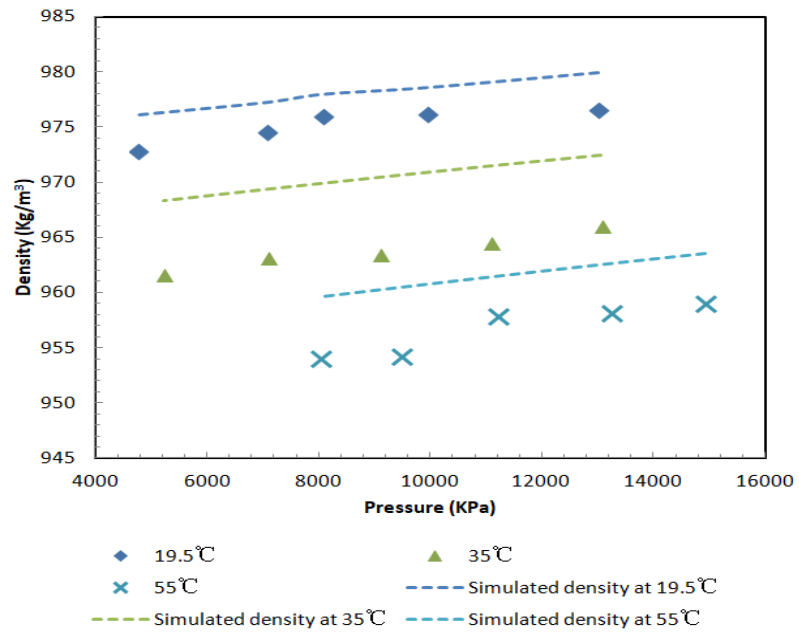
micro bubbles still inherit the properties of solution gas when pressure declines below P_b . Therefore, the properties of micro bubbles were set to be equal to the solution gas at P_b for both temperatures. The basic properties of the model components are listed in Table 5-1.

Similar to the CH_4 modeling case, equilibrium K-values were calculated by EOS after tuning the components properties and the output K-values were applied to model equilibrium behavior in the kinetic model. Figure 5-2 presents the variation of calculated K-values for dissolved C_2H_6 in live oil samples verse pressure at both 15 and 75°C.

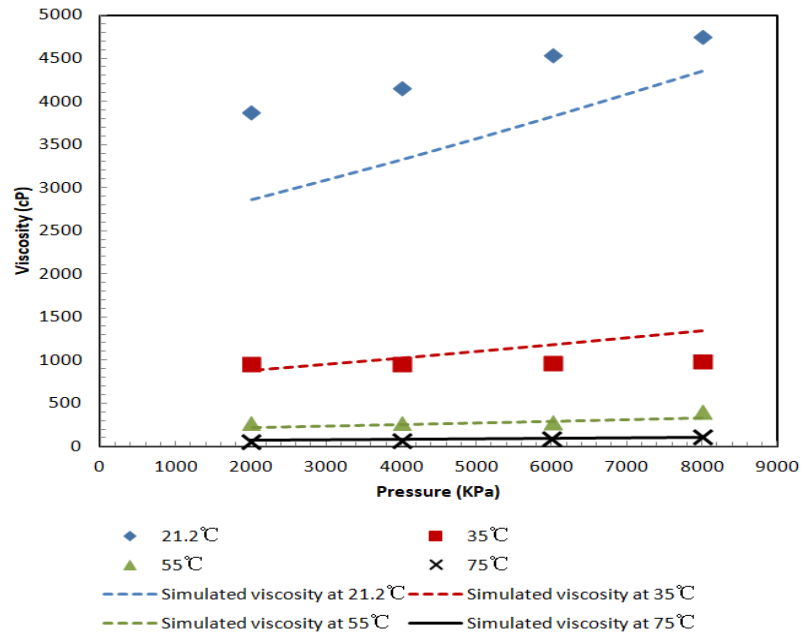
Table 5-1: Pseudo-components properties at (a) 15°C, 425.6 KPa and (b) 75°C, 975.6 KPa.

(a) 15°C, 425.6 KPa					
Pseudo Component	MW (g/mol)	ρ (kg/m ³)	C_p (KPa ⁻¹)	T_c (°C)	P_c (KPa)
SG_{oil}	30.1	0.467	4.585×10^{-6}	32.25	4883.87
$MB_{SG,oil}$	30.1	0.467	-	32.25	4883.87
$FG_{SG,gas}$	30.1	-	-	32.25	4883.87
Heavy Oil	539.9	0.988	4.483×10^{-7}	471.5	1109.93

(b) 75°C, 975.6 KPa					
Pseudo Component	MW (g/mol)	ρ (kg/m ³)	C_p (KPa ⁻¹)	T_c (°C)	P_c (KPa)
SG_{oil}	30.1	0.394	7.652×10^{-6}	32.25	4883.87
$MB_{SG,oil}$	30.1	0.394	-	32.25	4883.87
$FG_{SG,gas}$	30.1	-	-	32.25	4883.87
Heavy Oil	539.9	0.958	7.663×10^{-7}	471.5	1109.93



(a)



(b)

Figure 5-1: Comparison between simulation and experimental measured (a) density and (b) viscosity of the live oil sample.

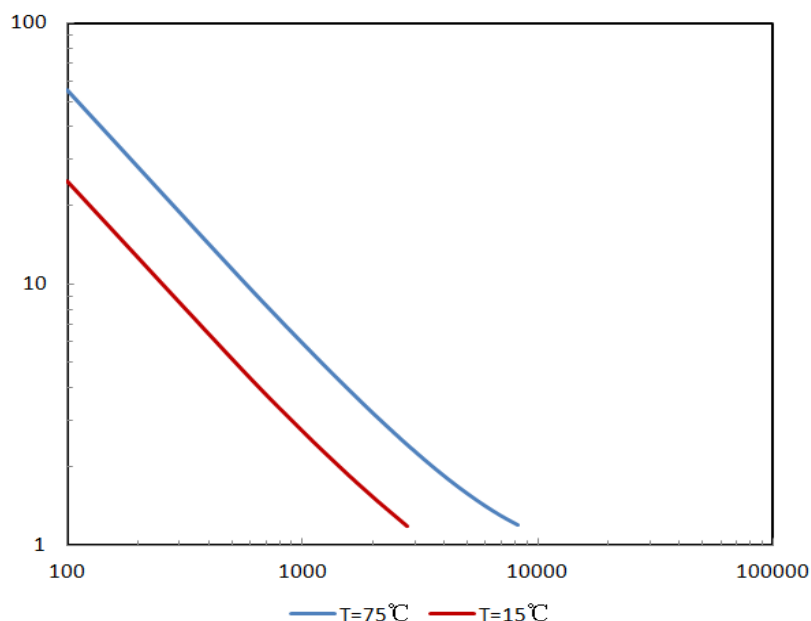


Figure 5-2: Calculated K-values for solution gas at various pressure at both 15°C and 75°C.

5.2 Non-Equilibrium Kinetic Modeling Results

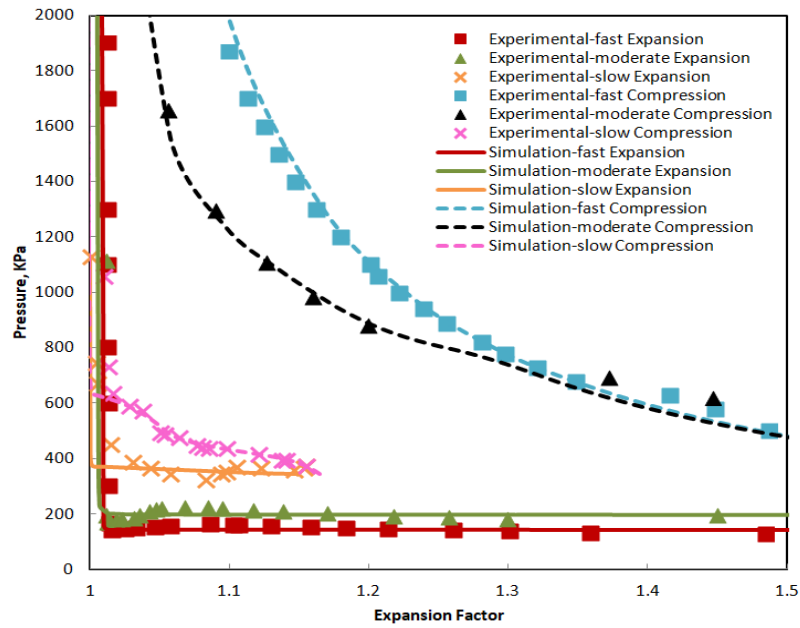
The parameters ($k_1, k_2, k_3, m_1, m_2, m_3, n_3$) were tuned so that the model results matched the experimental data of the oil-gas system expansion factors presented in Figure 3-5. Similar to the previous CH₄ modeling work, the calculated K-values were applied to determine the equilibrium concentration of solution gas in Reactions 2 and 6 of Chapter 3. The activation energies for all reactions were set to be equal to zero since the experiments were conducted at isothermal conditions. A comparison of the experimental and model results are presented in Figure 5-3. The model results show that the model produces profiles that agree with the experimental data at both temperatures. However, as shown in red circles in Figure 5-4, the modeling curves are smooth in general, which cannot predict

the rebound pressure behavior during pressure depletion processes at both temperatures. Similar phenomenon happened in Chapter 4 and it is more frequently occurred at slower pressure depletion rates. This is because during slower pressure depletion processes, the amount of gas exsolved out of the oil phase is larger than that in a faster expansion process, which indicates a higher concentration difference between liquid mixture and gas bubbles, resulting in a stronger mass transfer process between liquid mixture and micro bubbles as well as higher micro bubble growth rate. Furthermore, higher bubble growth rate will make the gas bubbles much easier to collapse. During pressure depletion processes, more fragile bubbles tend to release a large amount of gas in a short period of time compared with stable bubbles, resulting in system pressure rebound. However, in this model, micro bubbles growth speeds are strictly controlled by the non-ideal gas law: $PV=ZRT$ and it cannot increase dramatically either when free gas phase starts forming or with large amount of gas exsolved out of the oil phase. Therefore, this model cannot predict the rebound pressure behavior happened in pressure depletion processes.

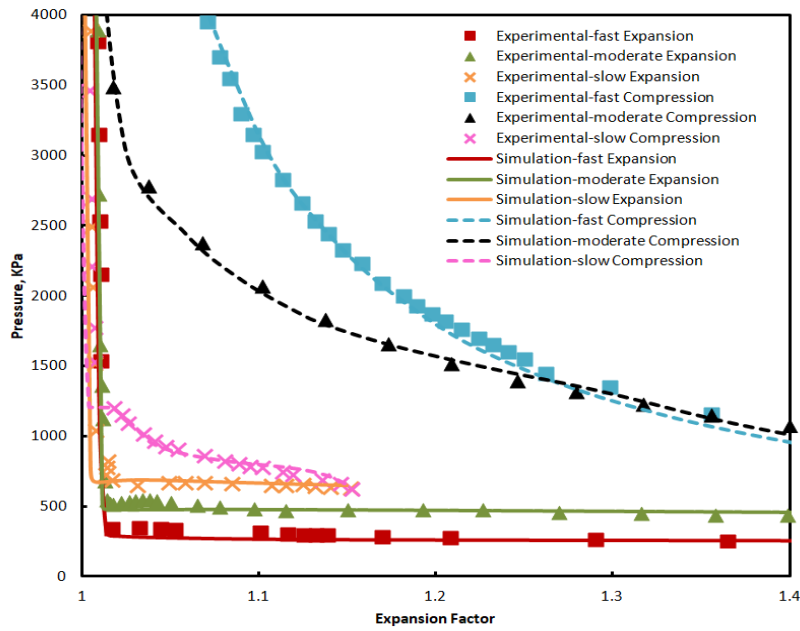
Table 5-2 summarizes the maximum absolute values for the model deviation from measured expansion factors for each case without considering the rebound pressure behavior. Unlike previous CH_4 modeling case, the simulation results of the pressure depletion stages have relatively larger deviations compared with the pressure increase processes in C_2H_6 modeling case. The maximum absolute deviations of pressure depletion stages were larger than 10% for most volume expansion rates at both temperatures, while they were less than 6% for volume compression stages. The reason is that compared with the volume expansion stage in CH_4 modeling case, rebound pressure

behavior was more drastic in C_2H_6 live oil samples at both temperatures, leading to relatively high fluctuation in pressure variations when system volume increases and higher deviations in history-matching the expansion factors at different pressure.

As shown in Table 5-2, in the volume expansion stage, most of the maximum absolute deviations were found after the free gas phase has been formed and the reason has been described in Chapter 4.2, which is similar to the CH_4 modeling case. Compared Table 5-2 with Table 4-2, the maximum simulation deviations of the compression stage is similar for both modeling cases. For C_2H_6 modeling case, the main reason caused modeling deviations during volume increase stages is still the number of pseudo-chemical reactions. One reaction may not be accurate enough to describe the two processes of system volume change occurring in the compression stages (free gas shrinkage and free gas transforms to solution gas).

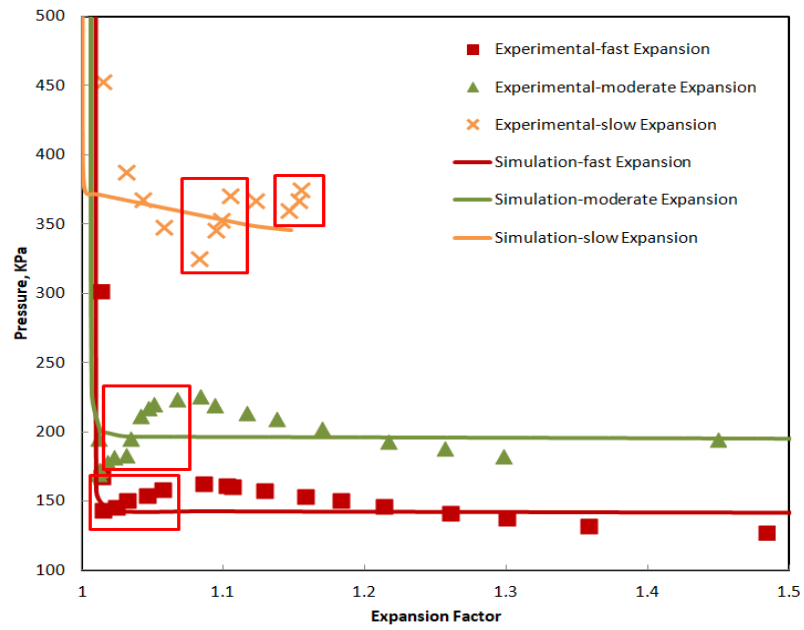


(a)

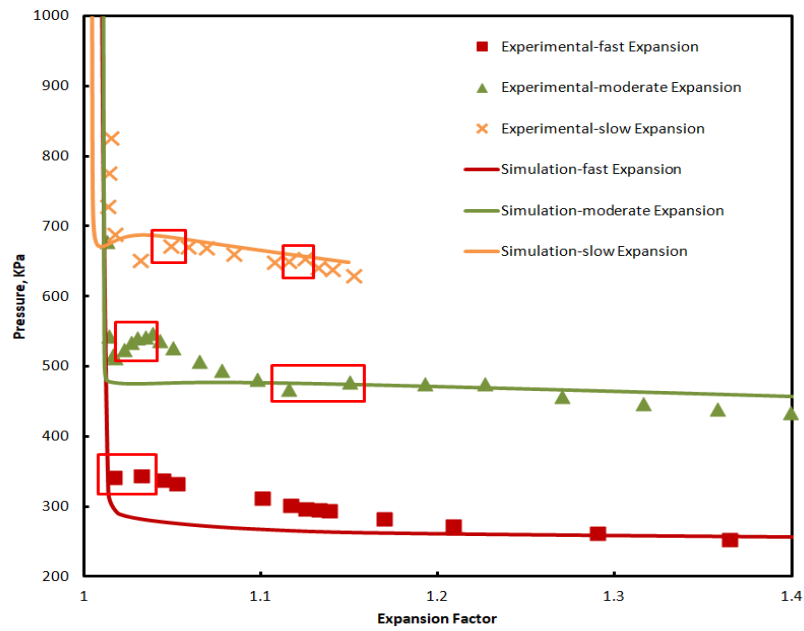


(b)

Figure 5-3: The measured and simulated volume expansion factors at (a) 15°C and (b) 75°C.



(a)



(b)

Figure 5-4: The measured and simulated volume expansion factors at (a) 15°C and (b) 75°C.

Table 5-2: Summary of the maximum model deviation from experimental data of different cases.

Experimental cases (temperature and rate)		Pressure values (kPa) at the maximum deviation points	Maximum absolute deviation
Expansion at 15°C	Fast	146.325	15.9%
	Moderate	202.325	13.5%
	Slow	367	7.9%
Expansion at 75°C	Fast	283.325	11.2%
	Moderate	439.325	16.5%
	Slow	651.325	10.5%
Compression at 15°C	Fast	631.325	3.2%
	Moderate	621.325	5.3%
	Slow	638	1.5%
Compression at 75°C	Fast	1161.325	2.4%
	Moderate	1397.325	1.5%
	Slow	732.325	1.3%

5.3 Kinetic Model Parameters

5.3.1 Reaction Orders

Four reaction orders (m_1, m_2, m_3, n_3) were tuned to achieve the match of the model results to the experimental data. In current modeling case, the reaction orders are set differently for various reactions, which are listed in Table 5-3. However, they have the same value at both 15 and 75°C. The reaction order n_3 was more than 20 times smaller than m_i ($i=1, 2, 3$) in the model, which reveals the extent of resistance against C_2H_6 dissolving back into the heavy oil phase. Compared Table 5-3 with Table 4-3, m_i was set to be equal at both modeling cases, which indicates reaction orders have limited impact on different oil samples volume expansion factors during gas ex-solution processes. Since

the reaction orders were set the same at both modeling cases for gas ex-solution processes, comparing the reaction frequency factors in the following section is a more direct and reliable way to understand the differences of gas ex-solution behavior between two modeling cases. In addition, compared with n_3 between two modeling cases, C_2H_6 was much easier to dissolve back to heavy oil phase when pressure increases.

Table 5-3: Reaction orders for gas ex-solution and dissolution kinetic model at both 15°C and 75°C.

i	m_i	n_i
1	1.3	-
2	1.15	-
3	1	0.05

5.3.2 Reaction Frequency Factors

To simulate the oil-gas system volume changes during the expansion processes, the reaction frequency factors were set to be dependent on both pressure and temperature. The results are presented in Figure 5-5. From Figure 5-5(a), it is found that k_1 , representing the micro bubbles formation rate, increased with decreasing of pressure at both temperatures. At 15°C, k_1 slightly fluctuated initially, followed by drastic increase from 1 to 75 within a short pressure range during the pressure depletion processes. Similar variation tendency of k_1 was found at 75°C, k_1 increased from 0.01 to 0.08 as the pressure dropped from 1,000 to 600 kPa, followed by drastic increase to 75 at 200 KPa. At 75°C, k_1 reached higher value at each pressure when pressure dropped below 500 KPa, indicating when pressure decreases below a certain degree, micro bubbles formation rate

is accelerated with temperature increase. However, the maximum values of k_1 are the same (75) for both temperatures during pressure depletion processes, indicating the influence of temperature on k_1 is not that evident when the pressure drops below P_b . This phenomenon is similar to the CH_4 modeling case, though k_1 in Chapter 4 is exactly identical (75) regardless of temperature and pressure. Moreover, with the same reaction orders of two pressure depletion cases, by comparing k_1 values of two modeling cases, it can be found that in heavy oil with the same GOR level, micro bubbles formation or bubble nucleation is much harder for dissolved C_2H_6 compared with CH_4 at both temperatures.

According to Figure 5-5(b), the overall trend of k_2 was that it increased with the decrease of pressure at both temperatures, which was similar to k_1 . This is because micro bubbles formation speeds increase with the decrease of pressure, indicating more micro bubbles will be accumulated in the oil phase at lower pressure conditions and they tend to collapse to form a free gas phase. At 15°C , k_2 kept relatively stable at 0.00007 from 550 to 200 KPa, followed by dramatic increase to 0.35 at 100 KPa. At 75°C , k_2 increased from 0.0001 to 0.005 as pressure dropped from 1,000 to 400 KPa, followed by drastic increase to 0.5 at 100 KPa. Similar to k_1 , k_2 of 75°C reached higher value at each pressure when pressure is below 400 KPa, which indicates micro bubbles are more likely to collapse at higher temperature when pressure decreases below a certain degree. This is because the oil viscosity at 75°C is much lower than it at 15°C , leading to the stability of the generated bubbles becoming weaker and the gas trapped in the bubbles easier to form

a connected free gas phase. Although k_2 of 75°C is higher than that of 15°C, this phenomenon is not that obvious compared with previous CH₄ modeling case with k_2 of 75°C is extremely higher than that of 15°C at each pressure (Figure 4-5 (a)), indicating temperature has not evident influence on free gas formation process in current case. In addition, by comparing k_2 between two modeling case, it can be found that at 15°C, free gas release rate is slightly smaller for C₂H₆ modeling case. However, at 75°C, free gas release process is much harder for heavy oil with dissolved C₂H₆ compared with CH₄. This phenomenon indicates that gas tends to be trapped in the oil phase for heavy oil sample with dissolved C₂H₆ during pressure depletion processes

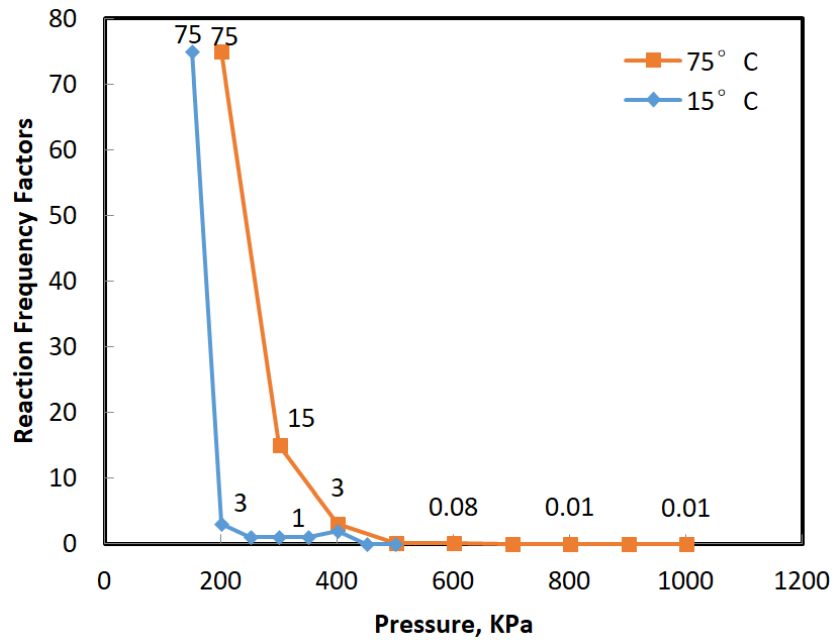
Based on the results of k_1 and k_2 , in C₂H₆ modeling case: (1) Both micro bubbles generation speeds (k_1) and free gas formation rates (k_2) are dependent on pressure and they increase with the decrease of pressure. (2) Higher temperature can slightly promote both micro bubbles generation speeds (k_1) and free gas formation rates (k_2). However, compared with CH₄ modeling case, currently the temperature influence is not that evident on free gas formation process. (3) By comparing two modeling case, micro bubbles formation rates (k_1) are much smaller at both temperatures in C₂H₆ modeling case, indicating C₂H₆ is harder to nucleate as micro bubbles in heavy oil during pressure depletion processes. In addition, free gas formation rates (k_2) are also smaller in C₂H₆ modeling case, especially at 75°C. These circumstances indicate that for heavy oil with the similar solvent concentration, stronger foamy oil behavior exists with solution gas of C₂H₆ instead of CH₄ during pressure depletion processes.

In the compression stages, the only reaction frequency factor (k_3) was also set to be dependent on temperature and pressure. As shown in Figure 5-5 (c), at 15°C, k_3 fluctuated from 400 to 2,000 KPa, followed by keeping stable at 0.00005 as pressure kept increasing. At 75°C, k_3 started from 0.0001 at 600 KPa and it kept relatively stable at around 0.0005 from 1,400 to 3,400 KPa. Next, k_3 increased from 0.0006 to 0.006 as pressure increasing to 5,800 KPa. The different variation tendencies of k_3 at two temperatures indicate the resistance for solution gas back dissolution is lower at 75°C compared with 15°C. This phenomenon is similar to previous CH₄ modeling case since the oil viscosity at 75°C is much lower than that at 15°C, leading to the gas easier to dissolve back into the oil phase when the pressure increases. Although k_3 at 75°C was higher than that of 15°C in the C₂H₆ modeling case, k_3 at 75°C kept relatively low values when pressure was below 3,400 KPa. This situation indicates increasing both temperature and pressure together is the most efficient way to accelerate C₂H₆ dissolution speeds, which is similar to the CH₄ modeling case. In addition, based on Figure 5-5 (c), to promote C₂H₆ dissolution rates, increasing pressure is efficient only when temperature is relatively high.

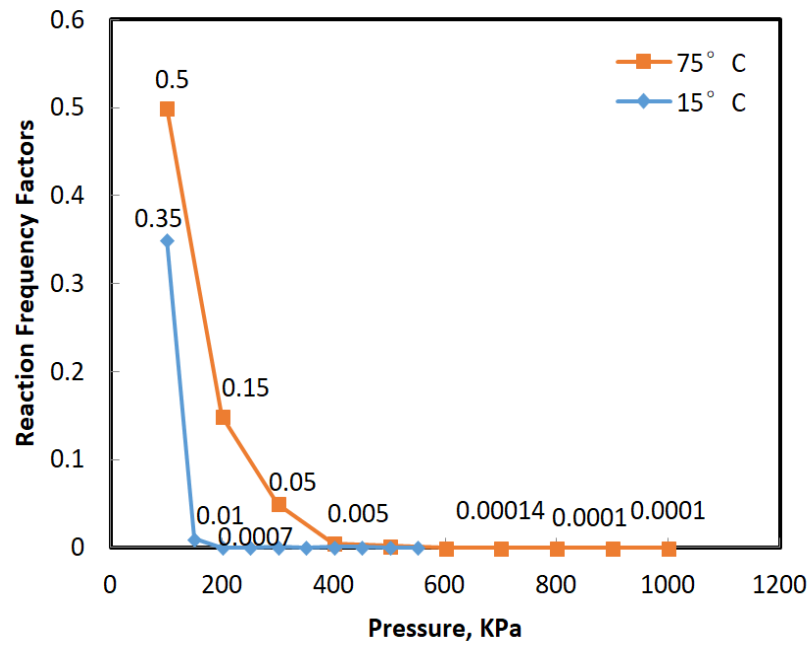
5.4 Summary

In this chapter, the non-equilibrium kinetic model was validated to describe both C₂H₆ ex-solution and dissolution processes in the bulk environment of heavy oil. The model

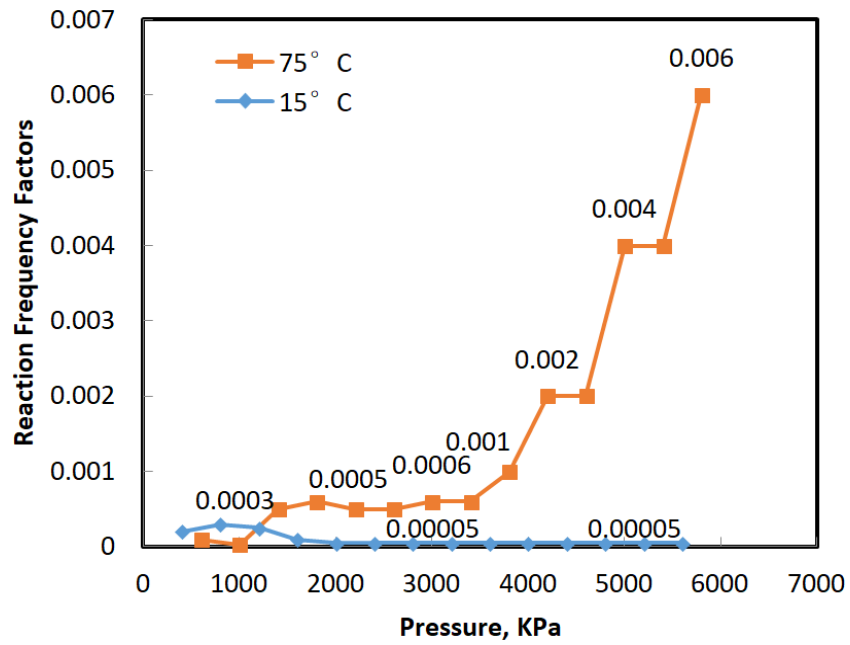
was tuned against experimental data via four reaction orders (m_1, m_2, m_3, n_3), as well as three reaction frequency factors (k_1, k_2, k_3). The model results match experimental data and the parameters are analyzed for better understanding the processes of C_2H_6 ex-solution and dissolution in heavy oil. In addition, by comparing the parameters with previous CH_4 modeling cases, the different behavior of C_2H_6 ex-solution and dissolution in heavy oil phase is well understood.



(a)



(b)



(c)

Figure 5-5: Reaction frequency factors of reaction (a) 1 (k_1), (b) 3 (k_2) and (c) 5 (k_3) at 15°C and 75°C.

Chapter Six: Conclusions and Recommendations

In the research documented in this thesis, a four pseudo-component kinetic model was proposed to describe both non-equilibrium solvent ex-solution and dissolution processes in bulk environment for heavy oil at both 15°C and 75°C. The model applies a mass transfer approach, concentrating on micro bubble formation and release during the pressure depletion period, as well as free gas dissolving back to the oil phase to form solution gas when the pressure increases. The model was tuned against experimental data via four reaction orders (m_1, m_2, m_3, n_3), as well as three reaction frequency factors (k_1, k_2, k_3). Two solvents (CH_4 and C_2H_6) were evaluated for model validation and the parameter variations for each solvent case was deeply analyzed. Several conclusions and recommendations can be made from the results.

6.1 Conclusions

1. The developed kinetic model can describe the heavy oil system volume change with different pressure variation rates simultaneously. In the CH_4 case, the maximum absolute deviations were less than 6% and 9% for expansion and compression steps, respectively. Relatively higher deviations were found for the compression process indicates more pseudo-chemical reactions may be needed to describe gas dissolution processes in heavy oil.
2. In the C_2H_6 case, the maximum absolute deviations were larger than 10% for most

volume expansion processes, while they were less than 6% for volume compression stages. Compared with the CH₄ modeling case, relatively higher modeling deviations for C₂H₆ in volume expansion process is the rebound pressure behavior was more drastic in C₂H₆ live oil samples at both temperatures, leading to relatively high fluctuation in pressure variations when system volume increases and higher deviations in history-matching the expansion factors at different pressures.

3. In the CH₄ case, the reaction order for dissolution of solvent back into the oil phase (n_3) was found to be more than 10,000 times smaller than the reaction orders for the formation of micro bubble (m_1) and free gas (m_2) at both 15°C and 75°C, indicating the resistance against the solvent dissolving back into the heavy oil can be described by the reaction orders of the model.
4. In the C₂H₆ case, the reaction orders for the formation of micro bubble (m_1) and free gas (m_2) are the same compared with the CH₄ case, which indicates reaction orders have limited impact on different solvent-heavy oil system volume expansion factors during gas ex-solution processes. In the C₂H₆ case, the reaction order for solvent back dissolution (n_3) was more than 20 times smaller than m_i ($i=1, 2, 3$) in the model, which reveals the extent of resistance against C₂H₆ dissolving back into the heavy oil phase. However, compared with n_3 between two modeling cases, C₂H₆ was much easier to dissolve back to heavy oil phase when pressure increases.
5. In the CH₄ case, during the expansion stage, both pressure and temperature had

limited influence on micro bubble formation rate (k_1). However, higher temperature reduces the oil phase viscosity, therefore increasing the micro bubble release rate (k_2) weakening the foamy oil behavior. Besides, the overall trend of k_2 is that it rises with decreasing pressure regardless of temperature.

6. In the C_2H_6 case, micro bubble formation rate (k_1) was sensitive to the pressure, indicating bubble nucleation process was accelerated under lower pressure condition. In addition, with the same reaction orders of two pressure depletion cases, by comparing k_1 values of two modeling cases, it can be found that in heavy oil with the similar solvent concentration, bubble nucleation is much harder for dissolved C_2H_6 compared with CH_4 at both temperatures.
7. Similar to the CH_4 case, free gas formation rates (k_2) are dependent on pressure and they increase with the decrease of pressure in the C_2H_6 case. By comparing k_1 as well as k_2 between two cases, it can be concluded that for heavy oil with the similar solvent concentration level, stronger foamy oil behavior exists with solvent of C_2H_6 instead of CH_4 during pressure depletion processes.
8. In both CH_4 and C_2H_6 case, to accelerate solvent dissolution rates in heavy oil, rising pressure is effective only when the temperature is relatively high and increasing temperature is more efficient at higher pressure conditions. Therefore, increasing both temperature and pressure together is the most efficient way to promote solvent dissolution back into the heavy oil.

6.2 Recommendations

1. Investigate the concentration influence on solvent ex-solution and dissolution behaviour in heavy oil, modeling study of same solvent with different concentrations in heavy oil should be conducted in future.
2. Modify the pseudo-reactions aiming to improve the prediction of the solvent dissolution process.
3. The parameters in the model can be further studied by cutting-edge techniques, i.e., Artificial Intelligence and Machine Learning, to derive further understanding of the model and physics as well as to improve the history matching results for further application in industry.

References

- Adams, D. M. (1982). Experiences with waterflooding Lloydminster heavy-oil reservoirs. *Journal of Petroleum Technology*, 34(08), 1643-1650.
- Arora, P., & Kovscek, A. R. (2003). A mechanistic modeling and experimental study of solution gas drive. *Transport in porous media*, 51(3), 237-265.
- Asghari, K., & Nakutnyy, P. (2008, June). Experimental results of polymer flooding of heavy oil reservoirs. In Canadian international petroleum conference. OnePetro.
- Bayon, Y. M., Cordelier, P. R., Coates, R. M., Lillico, D. A., & Sawatzky, R. P. (2002, November). Application and comparison of two models of foamy oil behavior of long core depletion experiments. In SPE International Thermal Operations and Heavy Oil Symposium and International Horizontal Well Technology Conference. OnePetro.
- Chen, J. Z., & Maini, B. (2005, June). Numerical simulation of foamy oil depletion tests. In Canadian International Petroleum Conference. OnePetro.
- CMG-STARSTM User Manual, version 2019.

Dong, X., Xi, Z., Badamchi Zadeh, A., Jia, N., & Gates, I. D. (2020, September). A Novel Experimental Method CCEC and Modelling of Methane Dissolution and Exsolution in Heavy Oil. In SPE Canada Heavy Oil Conference. Society of Petroleum Engineers.

Dusseault, M. B. (2001, June). Comparing Venezuelan and Canadian heavy oil and tar sands. In Canadian international petroleum conference. OnePetro.

Huc, A. Y. (2010). Heavy crude oils: from geology to upgrading: an overview.

Istchenko, C. (2012). A new fundamental model for cold heavy oil production with sand (Master's thesis, Graduate Studies).

Ivory, J., Chang, J., Coates, R., & Forshner, K. (2010). Investigation of cyclic solvent injection process for heavy oil recovery. Journal of Canadian Petroleum Technology, 49(09), 22-33.

Kraus, W. P., McCaffrey, W. J., & Boyd, G. W. (1993, May). Pseudo-bubble point model for foamy oils. In Annual Technical Meeting. OnePetro.

Li, H., & Yang, D. (2016). Determination of individual diffusion coefficients of solvent/CO₂ mixture in heavy oil with pressure-decay method. SPE Journal, 21(01), 131-143.

- Lu, X., Zhou, X., Luo, J., Zeng, F., & Peng, X. (2019). Characterization of foamy oil and gas/oil two-phase flow in porous media for a heavy oil/methane system. *Journal of Energy Resources Technology*, 141(3).
- Lu, X., Peng, X., Lin, Z., Zhou, X., & Zeng, F. (2020). Numerical simulation study on characterization of foamy oil behavior in heavy oil/propane system. *Fuel*, 262, 116559.
- Luigi, A., Saputelli, B., Carlas, M., Canache, P., & Lopez, E. (1998). Application of a non-equilibrium reaction model for describing horizontal well performance in foamy oil.
- Maini, B. B. (1999, January). Foamy oil flow in primary production of heavy oil under solution gas drive. In *SPE Annual Technical Conference and Exhibition*. Society of Petroleum Engineers.
- Maini, B. B. (2001). Foamy-oil flow. *Journal of Petroleum Technology*, 53(10), 54-64.
- Mastmann, M., Moustakis, M. L., & Bennion, D. B. (2001, March). Predicting foamy oil recovery. In *SPE Western Regional Meeting*. OnePetro.

- Mehrotra, A. K., & Svrcek, W. Y. (1986). Viscosity of compressed Athabasca bitumen. *The Canadian Journal of Chemical Engineering*, 64(5), 844-847.
- Miller, K. A. (2005, June). State of the art of western Canadian heavy oil water flood technology. In Canadian International Petroleum Conference. OnePetro.
- Modaresghazani, J., Moore, R. G., Mehta, S. A., Anderson, M., & Badamchi-Zadeh, A. (2019). A novel method (CCE&C) to study transient phase behaviour in heavy oil and ethane. *Fuel*, 257, 115946.
- National Energy Board. (2017). Energy Futures 2017 Supplement: Oil Sands. Retrieved from: <https://www.neb-one.gc.ca/nrg/ntgrtd/ft/2017lsnds/>
- Oskouei, S. J. P., Zadeh, A. B., & Gates, I. D. (2017). A new kinetic model for non-equilibrium dissolved gas ex-solution from static heavy oil. *Fuel*, 204, 12-22.
- Peacock, M. J. (2010, January). Athabasca oil sands: reservoir characterization and its impact on thermal and mining opportunities. In Geological Society, London, Petroleum Geology Conference series (Vol. 7, No. 1, pp. 1141-1150). Geological Society of London.

- Pedersen, K. S., & Fredenslund, A. A. G. E. (1987). An improved corresponding states model for the prediction of oil and gas viscosities and thermal conductivities. *Chemical Engineering Science*, 42(1), 182-186.
- Plata Sanchez, M. A. (2019). Experimental Study of Heavy Oil Recovery Mechanisms during Cyclic Solvent Injection Processes (Master's thesis, Schulich School of Engineering).
- Robinson, D. B., & Peng, D. Y. (1978). The characterization of the heptanes and heavier fractions for the GPA Peng-Robinson programs. Gas processors association.
- Shen, C. (2015, June). A practical approach for the modeling of foamy oil drive process. In SPE Canada Heavy Oil Technical Conference. OnePetro.
- Sheng, J. J., Maini, B. B., Hayes, R. E., & Tortike, W. S. (1997). Experimental study of foamy oil stability. *Journal of Canadian Petroleum Technology*, 36(04).
- Sheng, J. J., Maini, B. B., Hayes, R. E., & Tortike, W. S. (1999). A non-equilibrium model to calculate foamy oil properties. *Journal of Canadian Petroleum Technology*, 38(04).

- Shi, Y., Li, X., & Yang, D. (2016). Nonequilibrium Phase Behavior of Alkane Solvent (s)-CO₂-Heavy Oil Systems Under Reservoir Conditions. *Industrial & Engineering Chemistry Research*, 55(10), 2860-2871.
- Tharanivasan, A. K., Yang, C., & Gu, Y. (2006). Measurements of molecular diffusion coefficients of carbon dioxide, methane, and propane in heavy oil under reservoir conditions. *Energy & fuels*, 20(6), 2509-2517.
- Uddin, M. (2005, November). Numerical studies of gas exsolution in a live heavy oil reservoir. In *SPE International Thermal Operations and Heavy Oil Symposium*. OnePetro.
- Wang, D. (2019). Experimental and Numerical Studies of Foamy Oil Displacement Mechanisms in Heavy Oil Reservoirs (Master's thesis, Schulich School of Engineering).
- Wang, H. (2020). Experimental and Numerical Studies of Solvent Non-Equilibrium Dissolution and Exsolution Behavior in a Heavy Oil System (Doctoral dissertation, The University of Regina (Canada)).
- Wang, H., Torabi, F., Zeng, F., & Xiao, H. (2020). Experimental and numerical study of non-equilibrium dissolution and exsolution behavior of CO₂ in a heavy oil system utilizing Hele-Shaw-like visual cell. *Fuel*, 270, 117501.

- Yang, C., & Gu, Y. (2005). New experimental method for measuring gas diffusivity in heavy oil by the dynamic pendant drop volume analysis (DPDVA). *Industrial & engineering chemistry research*, 44(12), 4474-4483.
- Zheng, S., & Yang, D. (2017). Determination of Individual Diffusion Coefficients of C₃H₈/n-C₄H₁₀/CO₂/Heavy-Oil Systems at High Pressures and Elevated Temperatures by Dynamic Volume Analysis. *SPE Journal*, 22(03), 799-816.
- Zhou, X., Jiang, Q., Yuan, Q., Zhang, L., Feng, J., Chu, B., ... & Zhu, G. (2020). Determining CO₂ diffusion coefficient in heavy oil in bulk phase and in porous media using experimental and mathematical modeling methods. *Fuel*, 263, 116205.
- Zhou, X., Zeng, F., Zhang, L., Jiang, Q., Yuan, Q., Wang, J., ... & Huang, X. (2020). Experimental and mathematical modeling studies on foamy oil stability using a heavy oil–CO₂ system under reservoir conditions. *Fuel*, 264, 116771.