EXPERIMENTAL AND NUMERICAL STUDIES OF SOLVENT NON-EQUILIBRIUM DISSOLUTION AND EXSOLUTION BEHAVIOR IN A HEAVY OIL SYSTEM

A Thesis
Submitted to the Faculty of Graduate Studies and Research
In Partial Fulfillment of the Requirements
For the Degree of

Doctor of Philosophy
in
Petroleum Systems Engineering
University of Regina

by
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Regina, Saskatchewan
July, 2020

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FACULTY OF GRADUATE STUDIES AND RESEARCH

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ABSTRACT

One of the most important mechanisms of foamy oil is the solvents’ non-equilibrium dissolution and exsolution behavior. Therefore, the real-time capturing of these dynamic properties is crucial in analyzing how foamy oil evolves under non-equilibrium state. In this research, various of solvent dissolution and exsolution tests were conducted in real-time visualization systems for direct quantifications of foamy oil behavior. Test conditions include visualization in both bulk phase and porous media. For bulk phase, visualization tests were realized in a high-pressure Hele-Shaw-like visual cell, and for porous media, a high-pressure etched glass micromodel was used. Tested solvent-heavy oil systems include CO₂-heavy oil and CO₂-C₃H₈-heavy-oil system. For the purpose of formulating an equilibrium PVT properties package to compare with non-equilibrium state, two-phase flash and live oil liquid-phase properties were measured by differential liberation tests. CO₂ dissolution and exsolution behavior have been tested in the visual cell. Pressure decay curves and oil swelling factor curves were achieved prior to numerically determine CO₂ intra-phase diffusion coefficient in oil phase. After diffusion stage, pressure depletion tests were conducted. It was found that foamy oil stability increased with higher initial GOR, higher pressure depletion rate, higher pressure drawdown level and longer solvent-heavy oil contact time from foamy oil volumetric curves. Constant Composition Expansion (CCE) tests with different pressure depletion rates have been conducted for CO₂-C₃H₈-heavy oil system in a closed system in the visual cell. Physical parameters such as phase volume ratio, solvent exsolution sequence and deviated vapor-liquid-equilibrium (VLE) K value, etc., have been achieved experimentally to show the solvent non-equilibrium exsolution behavior. Single bubble exsolution and dissolution behavior tests have generated a bubble-
mass-with-pressure/time relationship and have successfully guided the simulation study. Solvent diffusion and post-diffusion depletion tests conducted in micromodel have shown that the residual oil distribution and gravity would affect solvent solubility. Two types of static CCE tests as well as foamy oil continuous convective flowing (CCF) tests have been conducted to investigate foamy oil stability under static and convective conditions, and the vapor phase volume ratio indicated a higher foamy oil stability under convective conditions. Solvent flooding and post-flooding depletion tests have been carried out to study how efficient a cyclic solvent injection process could boost up the recovery factor. The qualitative phenomenon such as solvent viscous fingering was directly visualized.

Numerical simulations have been conducted to quantify and validate the experiments. CO₂ diffusion coefficients in oil phase and its kinetic exsolution rates were determined by history matching pressure decay curves and transient foamy oil volume curves. Identical foamy oil stability was found both experimentally and numerically. Dynamic adjustment of VLE K value and kinetic reaction model were applied to simulate CO₂-C₃H₈ mixture solvent exsolution behavior in the visual cell. Non-equilibrium K values were achieved. Experimental single bubble exsolution behavior was incorporated into simulation and achieved successful history matching. SCCE and CCF tests were simulated by kinetic reactions and it was found that the optimized reaction frequency factors indicated a higher foamy oil stability under convective conditions. Pressure decay tests in micromodel system have been simulated, and the solvent effective diffusion coefficient in porous media have been achieved as well as the solvent non-equilibrium dissolution kinetic reaction frequency factors, which was in accordance with the dissolution rate of the single bubble tests.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and utmost respect to my supervisor: Dr. Farshid Torabi, for his guidance, encouragement, suggestions and all kinds of support throughout my Ph.D. journey. I have greatly benefited from him in every aspect from scientific knowledge, creativity, experience to being a virtuous person, a humorous guy and a well-rounded human being. I felt greatly privileged to be under his supervision during these years of my study. Also, I am sincerely thankful for my co-supervisor, Dr. Fanhua (Bill) Zeng, for granting me the precious opportunity towards the gate of Ph.D. degree at the University of Regina, as well as for all the enlightening research discussions.

I am grateful for Dr. David Sinton to be my external examiner who is a renowned expert in terms of microfluidics and energy study and his precious advices and suggestions on my thesis. I am also grateful to Dr. Nader Mobed, Dr. Pairoon Tontiwachwuthikul, Dr. Na Jia for being my internal committee members and their educative and constructive suggestions on my research and thesis.

I would like to acknowledge the financial support from the Faculty of Graduate Studies and Research (FGSR) at the University of Regina (Graduate Research Fellowship), MITACS Canada, and Petroleum Technology and Research Centre (PTRC).

I am grateful to all my research group members for their help and support. I am thankful to all my other PTRC friends for research discussion. I am thankful to my oly-/powerlifting partners for their spot and encouragement to make me become strong and robust. I am thankful to all my soccer and basketball teammates for all the wonderful and fierce games and competitions.
DEDICATION

To my beloved Father and Mother, Zhen Wang and Ping Li, for their love and sacrifice without asking for any return.

To my beloved Aunt, Liping Wang, for her parent-like caring for my well-being.

To my beloved Girlfriend and Future Wife, Huiwen Xiao, for the mutual support and accompany in both of our arduous Ph.D. journey.

To my dearest Grandma Changru Gao, to all my beloved Uncles (Guocheng Qi, Kangfu Wu, Xiangyang He) and Aunts (Yun Li, Tong Li, Jing Li), to all my beloved Brothers and Sisters (Chuxin Qi, Yuedong Wu, Xingyu He), for their continuous support to build this strong family tree and giving me strength.

Also,

This thesis was written during the most severe outbreak of the Novel Coronavirus in China where tens of thousands of people are currently affected and accepting treatment:

To all the bravest Doctors, Nurses and relevant medical personnel in China, who have fought, are fighting and will fight against the virus, for their courage to confront what us normal people are afraid to confront, for their sacrifice and professional ethics to persist on their duty without flinch where death is a just step ahead, for their professional skills that bring back many lives. Without you, our lives will be at stake.

To all the international assistance from various countries that help China get through this toughest time of human history for their contribution.
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NOMENCLATURE

Notations

F \quad \text{free energy of a thermodynamic system, } ML^2 T^{-2}
N \quad \text{molar mass of a substance, } N
\mu_v \quad \text{chemical potential of vapor phase, } ML^2 T^{-2} N^{-1}
P_v \quad \text{pressure of vapor phase, } ML^{-1} T^{-2}
V \quad \text{volume, } L; \text{ vapor phase fraction}
\mu_L \quad \text{chemical potential of liquid phase, } ML^2 T^{-2} N^{-1}
P_L \quad \text{pressure of liquid phase, } ML^{-1} T^{-2}
A \quad \text{surface area of a spherical bubble, } L^2
\gamma \quad \text{thickness of bubble-mixture interface, } L
R \quad \text{spherical bubble diameter, } L
\sigma \quad \text{interfacial tension, } MT^{-2}
K_s \quad \text{Henry’s law solubility constant, } ML^2 T^{-2} N^{-1}
W \quad \text{crevice width of a nucleation site}
\text{R}_{\text{effective}} \quad \text{effective radius of a capillary coil viscometer, } cm
\mu_{\text{live oil}} \quad \text{live oil viscosity, } cP
\Delta P \quad \text{pressure differential between the two ends of a capillary coil viscometer}
q \quad \text{live oil viscosity measurement flow rate, } cm^3/min
L \quad \text{length of the capillary coil viscometer, } cm; \text{ liquid phase fraction}
P_1, P_2, P_3 \quad \text{pressure quantity of CCE test schematic, } kPa
V_1, V_2, V_3, V_4 \quad \text{volume quantity of CCE test schematic, } cm
Z \quad \text{real gas compressibility factor}
R \quad \text{universal gas constant, } 82.057 \text{ cm}^3 \text{atm} K^{-1} \text{mol}^{-1}
n \quad \text{molar mass of a substance, } mol
T \quad \text{temperature, } ^\circ K/^\circ C
PV \quad \text{pore volume, cm}^3
V%  volume fraction
MW  molecular weight, g/mol
ρ   density of a substance, g/cm³
SF  swelling factor, cm³/cm³
dP/dt pressure depletion rate, -kPa/min
y   component molar fraction in the vapor phase in flash calculation
x   component molar fraction in the liquid phase in flash calculation
rrf exsolution rate, 1/min
P_{prevailing} prevailing pressure in the system, kPa
P_{end} pressure at the end of the tests, kPa
P_r ratio of P_{prevailing} to P_{end}
P_{rrf} prevailing pressure in single bubble dissolution test
H   enthalpy
U   internal energy
S   entropy
A   Helmholtz free energy
Δg_{mix} dimensionless Gibbs free energy, departure function of an equation-of-state calculation
f_i  fugacity of a substance
z_i  total compositional feed of a substance i in a mixture system
f_i^V fugacity of substance i in vapor phase
f_i^L fugacity of substance i in liquid phase
Z_{V/L} root of compressibility factor in an equation-of-state calculation for vapor/liquid
λ   rate coefficient in exponential decay, 1/min
D   dispersion/diffusion coefficient, m²/s; cm²/min
\vec{u} velocity vector, LT⁻¹
R_{source/sink} source/sink term in a governing equation
\( \chi \)  
 molar fraction of a substance in liquid phase

\( y \)  
 molar fraction of a substance in vapor phase

\( \varphi \)  
 porosity

\( t \)  
 time, T

\( v \)  
 velocity, LT\(^{-1}\)

\( g, D \)  
 gravitational acceleration and potential from a datum

\( \text{CO}_2_\text{L} \)  
 \( \text{CO}_2 \) in dissolution state

\( \text{C}_3\text{H}_8_\text{L} \)  
 propane in dissolution state

\( \text{SGCO}_2 \)  
 solution gas \( \text{CO}_2 \)

\( \text{SGC}_3 \)  
 solution gas propane

\( \text{BBCO}_2 \)  
 dispersed \( \text{CO}_2 \) bubble

\( \text{BBC}_3 \)  
 dispersed propane bubble

\( \text{FGCO}_2 \)  
 free gas \( \text{CO}_2 \)

\( \text{FGC}_3 \)  
 free gas propane

\( Obj_V \)  
 objective function of foamy oil volume

\( \rightarrow \)  
 one-way reaction direction

\( \Leftrightarrow \)  
 two-way reaction direction

\( Obj_{V\text{gtotal}} \)  
 objective function of total vapor phase volume in the SCCE tests

**Subscripts and Superscripts**

\( i \)  
 denotation of a system, or a substance

\( V \)  
 vapor phase

\( L \)  
 liquid phase

\( T_1 \)  
 homogeneous nucleation

\( T_2 \)  
 heterogeneous nucleation

\( T_3 \)  
 heterogeneous nucleation of a bubble smaller-than-critical radius

\( T_4 \)  
 heterogeneous nucleation of a bubble larger-than-critical radius

\( M \)  
 mixture

XXII
I interface
MG mixture-bubble surface
initial initial state in the schematic of a CCE test
exsolution the exsolution gas in the schematic of a CCE test
atm atmospheric condition
CO₂ carbon dioxide
C₃H₈ propane
live oil live oil
dead oil dead oil
single gas solvent component if presented as a single substance in the system
ini initial state
decay pressure decay data points
BB_in vapor phase inside the micromodel
micromodel glass micromodel
PV pore volume, cm³
BB_image vapor phase fraction in the image domain after image processing
BB_out vapor phase outside the micromodel and in the collecting cylinder
liquid liquid phase
final final state
CO₂_dissolved CO₂ dissolution in the oil phase
mixture solvent-saturated live oil
res fg free gas under reservoir condition
res dg dispersed gas under reservoir condition
gas mixture solvent mixture of CO₂ and C₃H₈
initial_gas initial state of gas molar mass
initial_oil initial state of oil molar mass
vapor reservoir volume vapor phase volume under reservoir condition
dissolved_gas dissolution gas component
exsolved_gas  exsolution gas component
ig          ideal gas
equilibrium equilibrium state
non-equilibrium non-equilibrium state
CO₂_k       CO₂ dispersion/diffusion coefficient on k direction
abs         absolute
grid        a numerical grid in the numerical simulation
exp         experimental
num         numerical
t₀           last time step
t₁           current time step

Abbreviations
DNS          direct numerical simulation
CFD          computational fluid dynamics
SCCE         static constant composition expansion
CCF          continuously convective flowing
RRF(s)       kinetic reaction rate frequency factor(s)
RRF_1        RRF for solution CO₂ → bubbly CO₂
RRF_2        RRF for bubbly CO₂ → free gas CO₂
SG           solution gas
BB           bubble gas
VLK          vapor-liquid-equilibrium

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CHAPTER 1 INTRODUCTION

1.1 Research Background and Motivation

In the recent decades, heavy oil has been gradually showing the prominence to be one of the most important energy consumption resources as for its vast number of reserves discovered around the globe. Heavy oil accounts for 6 to 9 trillion barrels globally, which stands more than two-third of the world’s oil resources. Amongst, a vast number of the global heavy oil (about $350 \times 10^9 \text{ m}^3$ of crude heavy oil) exist in Alberta and Saskatchewan, Canada (S. Xu 2007). This shows the significance of effectively developing innovative techniques for heavy oil reserves in Canada for both environmental and economic benefits.

Heavy oil reserves can be developed by many different EOR techniques. Thermal methods such Steam Assisted Gravity Drainage (SAGD), Cyclic Steam Stimulation (CSS), Steam Flooding, etc. have been extensively used to utilize heat conduction as an effective means to reduce heavy oil viscosity so as to enhance the mobility. Solvent-based methods such as Vapor Extraction (VAPEX), solvent flooding, Cyclic Solvent Injection (CSI), etc. have also been extensively applied to utilize mass transfer mechanism to reduce heavy oil viscosity and enhance the mobility. Water-based injection methods are also very popular means to develop heavy oil fields, such as water flooding, chemical flooding (alkaline, surfactant, polymer), hot water flooding, low salinity water flooding, foam flooding, microbial, microemulsion etc.

For many of the western Canada heavy oil reserves, the pay zones are usually found to be thin, shallow and less consolidated. Therefore, under such circumstances, although thermal methods are the accounted for as the most effective heavy oil mobility enhancer,
thermal methods are usually not practical and economical due to the heat loss through the over- and under-burden of the reservoirs. Hence, other heavy oil development methods such as solvent-based injection processes come to handy.

In solvent-based injection techniques, solvent will usually be injected close to its dew point (under reservoir pressure and temperature) in order to maintain gaseous state to create further expansion into the deeper zones of the reservoirs, better pressure maintenance and larger contact interfacial area with the oil phase. By mass transfer, solvent will be dispersed in the reservoir and enhance the heavy oil in-situ quality. The gas-oil thermodynamic interaction thus comes into play. Heavy oil and bitumen usually have a viscosity ranging from 100 cp to 100,000 cp or even higher under various reservoir conditions. Under this high viscosity, the typical characteristics of conventional solution gas drive, which are defined as rapid reservoir pressure depletion rate, very short time endurance from zero initial gas exsolution to a high production GOR, fast declination of oil production rate and acceleration of continuous gas production rate, low recovery factors etc. are not matching with the abnormal performance of heavy oil reservoirs under foamy oil solution gas drive during primary production and follow-up solvent injection processes, namely, higher oil production rates with a lower/delayed production GOR. Unlike conventional solution gas drive in light oil reserves, the solution gas bubbles in heavy oil tend to be trapped longer and form foamy oil due to high viscosity, instead of forming a free continuous gas phase throughout pore space easily. The trapping of these solution gas bubbles in the oil phase will help remain the pressure of the reservoir to create a longer period of pressure differential between the reservoir and the production well, so that it leads to longer drive force endurance for the foamy oil production. This hysteresis of reservoir pressure decline
rate and bubble trapping could be attributed to the non-equilibrium solvent exsolution behavior of the solvent-heavy oil systems. In addition, unlike solvent-light oil systems in which the diffusion/dispersion coefficients (can be at miscible condition) are usually very high even in porous media due to the high mobility/low viscosity of the oil phase, the dissolution of solvent into heavy oil systems will go through a much longer time, and such solvent non-equilibrium dissolution behavior should also be understood in order to plan the best injection schemes to enhance the in-situ solvent mass transfer rate.

Meanwhile, with the increasing availability of CO₂ source and growing concern on reducing green house gas impact on the environment, CO₂ has been proved to be a very profound and efficient agent/solvent to be taken advantage of to recover heavy oil reserves as well as to be injected underground for storage in Canada. Incorporating with hydrocarbon gas during solvent injection, CO₂ could be a very promising solvent injection performance enhancer. Therefore, it is of great importance to study the solvent dissolution and exsolution behavior of CO₂-hydrocarbon solvent-heavy oil systems to test the feasibility of the injection schemes before any field-scale pilot tests. Due to a large number of operational parameters (such as solvent type, injection pressure, injection temperature, injection flow rate, solvent stream concentration, other additives etc.) and their mutual effects, it is significant to quickly and accurately screen out the optimum parameters in the laboratory study so as to generate a large base data set for solvent-heavy oil systems and provide it for field-scale pilot tests at the minimum time-cost. In the recent decades, the application of a nano-to-micro-to-milli-meter-scale experimental methodology for a rapid and accurate measurement of various research targets has been proposed. The idea of microfluidics, as a very important research tool in chemistry, biochemistry, biology,
thermo-physics, chemical engineering etc., has been recently extended to study heavy oil systems. Taking the advantage of the dimension and cost-reduction of such small-scale system, a large, time-efficient experimental data base for heavy oil reservoir development is highly feasible. Therefore, in this research, visualization techniques enlightened by the concept of microfluidics have been developed and proven its feasibility in terms of studying the non-equilibrium phase behavior of solvent-heavy oil systems. Also, for a microfluidics system, it could be easily coupled with other direct measurement methods such as Gas Chromatography (GC), Fourier-Transformed-Infrared-Spectroscopy (FTIR), UV/VIS spectrometer, mass spectrometer etc., to determine multiple types of fluid properties. Given the above condition, it is reliable to extensively implement microfluidics technique for heavy oil research.

1.2 Research Objectives

This research aims to deliver a profound understanding of the solvent non-equilibrium dissolution and exsolution behavior in heavy oil systems. In a solvent-based injection process, most typically, a procedure of solvent injection→soaking→pressure depletion would be implemented. In these procedures, solvent dissolution mainly happens in the first two stage where solvent is injected and soaked. Solvent exsolution mainly happens in the third stage where pressure depletion is to be applied to the reservoir, and how to take advantage of the foamy oil existence can better help improve the in-situ fluid compressibility and enhance the recovery factor. Hence, to understand solvent non-equilibrium solvent dissolution and exsolution can help better design each solvent injection stage.
The newly developed differential liberation tests for live oil properties measurement is aimed to provide a quick and accurate method to acquire basic equilibrium thermodynamic dataset, if a Pressure-Volume-Temperature cell is not available. CO₂ dissolution and exsolution tests helps to better understand how to properly choose the CO₂ injection parameters and production operational schemes for injection and production stage, respectively. CO₂-C₃H₈-heavy live oil system CCE pressure depletion tests were aimed to provide an accurate and novel experimental methodology for characterizing solvent non-equilibrium exsolution behavior. The parameters that indicate the existence of non-equilibrium were shown such as the total vapor/liquid phase volume ratio in the system etc., and these parameters can serve as appropriate technical guidelines for any CCE tests which are attempted to study non-equilibrium. Also, through such experimental methodology, by easily figuring out the beginning and the end of the non-equilibrium time frame, the well-bottom hole operational parameters can be better controlled to avoid the formation of continuous gas phase so as to maintain the foamy oil state in the reservoir. Single bubble dissolution and exsolution tests were aimed for characterizing bubble-scale behavior so as to compare with macro-scale for finding the bridge of upscaling bubble behaviors to Darcy-scale flow. Multiple types of tests were conducted in porous media system to investigate the non-equilibrium behavior. Diffusion tests and post-diffusion pressure depletion tests in closed-system micromodel with different orientation angles were aimed to show the effect of gravity on residual oil distribution and subsequent solvent solubility change. This can help better facilitate the variation of effective dispersion/diffusion coefficients under gravitational effect. Also, the effect of different pressure depletion rate applied in the post-diffusion exsolution tests can be directly
visualized to see the oil distribution in the reservoir to better guide the residual oil remobilization. SCCE tests and CCF tests were aimed to compare foamy oil stability under static condition and dynamic convection. This facilitates the understanding the in-situ fluid flow velocity and deviation from equilibrium saturation pressure could affect the foamy oil state. Solvent flooding and post-flooding pressure depletion tests were aimed to understand solvent channeling during the injection period and how it affected the subsequent soaking and pressure depletion periods. This type of test mimics the true operating condition of cyclic solvent injection. Non-equilibrium VLE K value section 6.2.1 was aimed to analyze how the adjustment from the equilibrium K value to the non-equilibrium K value can significantly help simulate the delayed/deviated solvent exsolution behavior. In a reservoir simulator, the molar fraction of each component as well as each phase in a numerical grid is normally controlled by equilibrium K value. Hence, under such equilibrium flash calculation, the molar fraction of each component and phase in a grid will reach equilibrium instantly. By applying a shifted K value, the delayed exsolution of solvent can be simulated. But this is limited to the case of continuous pressure depletion as discussed in section 6.2.3.1. CO₂ dissolution and exsolution numerical simulations were aimed to provide a methodology of simulating a pressure decay diffusion process in Darcy-scale simulator as well as using kinetic reactions to represent dynamic phase change as suggested in section 6.2.3.1. In traditional diffusion process simulation, the solution of a diffusion-convection governing equation set with different boundary conditions is purely dependent on the Fick 2nd law, which can result in a significantly limited ability to simulate a field-scale solvent soaking process with continuous pressure decay till equilibrium solubility is reached. Hence, how to effectively
and efficiently simulate diffusion process with the consideration of multiple physics in a Darcy-scale reservoir simulator is a crucial matter. At the same time, for a larger-field scale simulation, Direct Numerical Simulation (DNS) such as using full CFD equation set is not practical due to capability of the computers and complex algorithms, hence, in our field, simplifying complex physics into Darcy-scale simulator for field-scale numerical characterization is of crucial significance. Section 6.2.2 addresses such questions by conducting a history matching of pressure decay curves and oil swelling factor in a Darcy-scale simulator. Meanwhile, the dynamic phase change processes of solution gas $\rightarrow$ dispersed gas $\rightarrow$ free gas was also fulfilled to history match the foamy oil volume curves against time, providing a methodology to both experimentally and numerically examine various operational schemes’ effect on foamy oil stability. The simulation of SCCE and CCF tests were aimed to validate the experimental study and numerically represent the foamy oil stability in porous media condition. Last but not least, solvent diffusion tests in micromodel were simulated. The effective dispersion/diffusion coefficient and kinetic rate of solvent condensation onto oil-gas contact interface were aimed to be achieved to represent solvent dissolution in an effective porous media. Again, this simulation was also aimed to provide a methodology to simplify the complex phase change process of solvent dissolution “free gas $\rightarrow$ dispersed gas $\rightarrow$ solution gas” into flexible and convenient source/sink terms in Darcy-scale reservoir simulator. This methodology was validated by comparing to single bubble dissolution tests, and the physical trend of bubble-scale dissolution was found to be in the same physical trend of macro-scale dissolution tests. This indicates that the bubble-scale dissolution mechanism can be directly upscaled to represent gas phase dissolution in a Darcy-scale, just by
applying different rate coefficients to represent different dissolution rates found in different mediums.

### 1.3 Research Methodology

Experimentally, visualization techniques were mainly applied. The visualization technique was enlightened by the microfluidics research in the recent decades. The experimental setup overcomes the visualization shortcomings of traditional apparatuses such as a hardly-visual cylindrical PVT cell, or non-visual transfer cylinders. For an easier mass conservation calculation, a relatively larger-scale visualization system was developed based on the idea of microfluidics. The main visualization mediums are the utilization of a Hele-Shaw-like bulk phase high-pressure visual cell as well as etched glass micromodel with uniformly distributed porous media grains inside. The main purpose is to study solvent non-equilibrium dissolution and exsolution behavior both in bulk phase and porous media. For solvent dissolution tests, diffusion tests were conducted under both bulk phase and porous media. Pressure decay method was mainly utilized to capture the solvent solubility because a closed system allows for a more convenient material balance calculation. For solvent non-equilibrium exsolution tests, similarly, both bulk phase visual cell and glass micromodel engraved with porous media were tested. Constant Composition Expansion (CCE) tests with different operational schemes (pressure depletion rate, multiple initial pressure and temperature, etc.) were conducted in a closed system for a convenient material balance calculation. Solvent non-equilibrium exsolution behavior under continuous convection were conducted in an open system in glass micromodel, and the main focus was on the solvent exsolution behavior inside the porous media. Numerous
images would be captured during the experimentation for the quantification of the physical phenomenon.

Numerically, CMG CMOST optimization module and a MATLAB-controlled reservoir simulator were mainly used. In CMG CMOST module, relevant non-equilibrium parameters could be self-defined through the java script formula programming so as to utilize any pre-specified mathematical expressions. CMG reservoir simulator is not an entirely black box commercial software. In the MATLAB-controlled reservoir simulator, CMG STARS was connected to the application programming interface by MATLAB commands and was intelligently controlled by MATLAB programs to conduct a self-defined segmental numerical simulation and optimization based upon time step as well as material balance error. The history matching would be optimized in each pre-specified time step by extracting the simulation results and adjusting the parameters in the simulation run file according to any self-defined mathematical expressions and programming, such adding correlations between simulation results and adjustable parameters, adding any other physical terms, adding any numerical calculation based upon the simulation results in the previous time step etc. In this way, the reservoir simulator would no longer be inflexible compared to the usage of CMOST. Various types of optimization techniques can be added into the simulator, such as Nelder-Mead, ENKF, Genetic Algorithm (GA), Simulated Annealing etc. for the history matching process. In this MATLAB-controlled optimization module, Nelder-Mead method was used to determine solely the kinetic reaction rate frequency factors for SCCE and CCF tests, non-linear least squares method was used to determine CO\textsubscript{2} diffusion coefficients and kinetic reaction rate frequency factor, and GA as well Simulated Annealing methods were used.
to determine solvent effective diffusion coefficients and kinetic reaction rate frequency factor in solvent diffusion tests in glass micromodel porous media.

1.4 Thesis Outline

In Chapter 1, research background and motivation were discussed to show the importance of efficiently developing heavy oil reserves in Canada. In Chapter 2, literature review on non-equilibrium phase behavior studies of solvent-heavy oil systems have been conducted. These includes bubble-scale non-equilibrium behavior, experimental and numerical studies on solvent non-equilibrium dissolution and exsolution behavior. In bubble-scale non-equilibrium behavior, bubble nucleation types, growth patterns and other related mechanisms were included. For experimental studies, solvent diffusion tests, bulk phase PVT phase behavior, porous media PVT phase behavior, sandpack/core solvent-based processes, direct measurement of compositions and microfluidics technologies have been thoroughly investigated. For numerical studies, diffusion coefficient determination, reservoir simulation on foamy oil behavior, etc., have been investigated so as to fill the knowledge gap. In Chapter 3, experimental materials, setup, and procedures were demonstrated. Both bulk phase visual cell and glass micromodel system were implemented to study solvent non-equilibrium dissolution and exsolution behaviors. Various types of tests were introduced, aiming for the purpose of achieving the relevant parameters to describe the dynamics behind foamy oil phenomenon. In Chapter 4, solvent non-equilibrium dissolution and exsolution behavior have been studied in the bulk phase. Live oil differential liberation tests for CO₂-heavy oil and CO₂-C₃H₈-heavy oil system have been conducted. Equilibrium phase behavior of these solvent-heavy oil systems were obtained. CO₂ dissolution and exsolution behavior tests have been conducted by pressure
decay method and pressure depletion, respectively. Foamy oil generation and stability has been compared under different operational schemes. Live oil CCE pressure depletion tests were conducted using bulk visual cell to study the non-equilibrium exsolution behavior CO₂-C₃H₈-heavy oil. Different parameters describing the non-equilibrium phenomenon of the solvent-heavy oil system have been extracted including non-equilibrium K value, deviated liquid/vapor phase volume fraction, etc. Single bubble exsolution behavior has been, and the obtained mathematical relationship was incorporated into numerical simulation for validation. Similarly, single bubble dissolution behavior was studied by using two types of common bubble shapes and the obtained mathematical relationship against pressure and time were also incorporated into numerical simulation for validation.

In Chapter 5, experimental tests of solvent non-equilibrium dissolution and exsolution behavior in porous media were conducted in glass micromodel. These tests included solvent diffusion and post-diffusion pressure depletion tests, static Constant Composition Expansion (SCCE) tests, foamy oil continuously convective flowing (CCF) tests, solvent flooding and post-flooding pressure depletion tests (1 cycle only). Solvent diffusion and post-diffusion pressure depletion tests were aimed to investigate how residual oil distribution affected the subsequent solvent solubility in solvent injection stage. SCCE tests and CCF tests were aimed to study foamy oil stability under both static and dynamic conditions. Solvent flooding and post-solvent flooding pressure depletion tests were aimed to study how solvent channelling occurred in the porous media during injection stage, and how well the sweep efficiency would be at the stoppage of injection, since the solvent distribution after solvent injection would greatly affect the contact area with the oil and its solubility. In Chapter 6, numerical study has been conducted to validate the experimental
data. History matching tests were conducted by a newly developed MATLAB-controlled CMG STARS reservoir simulator with real-time optimization. The concept of introducing a non-equilibrium VLE K value to describe the deviation from equilibrium phase behavior was proposed, and bulk phase CCE tests were simulated by applying non-equilibrium K value. CO₂-in-oil diffusion coefficients under quasi-equilibrium condition were determined as well as CO₂ kinetic reaction rate frequency factors (RRFs) were determined to describe the dynamics of foamy oil volume expansion and decay. The achieved RRFs were in accordance with the experimental study, and it was both experimentally and numerically found that foamy oil stability increased with higher initial GOR, higher pressure depletion rate, higher pressure drawdown level, and longer solvent-heavy oil contact time. Bulk phase CCE tests of CO₂-C₃H₈-heavy oil system have been validated by two methodologies: non-equilibrium K value adjustment and kinetic reaction modeling. Both methodologies have successfully history matched the solvent non-equilibrium exsolution behavior. Foamy oil static Constant Composition Expansion (SCCE) tests and continuously convective flowing (CCF) tests were history matched by both non-gassy liquid and gassy-liquid setup in the numerical simulation. Kinetic reaction rate frequency factors describing foamy oil stability and solvent exsolution under both static and convective condition were achieved. Pressure decay curves of solvent diffusion tests conducted in glass micromodel were also history matched under quasi-equilibrium condition and non-equilibrium condition by adjusting the effective dispersion/diffusion coefficient of solvent in porous media and kinetic reaction rate frequency factors, respectively. The optimized solvent dissolution parameters were found to be in accordance with Taylor bubble dissolution behavior.
CHAPTER 2 LITERATURE REVIEW

In this chapter, past research work on foamy oil phenomena in the recent decades were discussed. The significance is to conclude the previous methodologies and find an innovative way to characterize the foamy oil flow.

2.1 Bubble-Scale Non-Equilibrium Exsolation Mechanisms

Unlike conventional light oil, for whose phase thermodynamic equilibrium can be easily reached or in other word, broken up, by changing the intensive parameters such as pressure and temperature of the system, heavy oil is indicating a different trend. For a gas-light oil system, excessive gas phase will exsolve out from the live oil mixture easily when the system pressure is depleted under saturation pressure. However, in a gas-heavy oil system, thermodynamic phase equilibrium is often difficult to reach within a short period of time due to the high viscosity of the liquid phase and the subsequent energy dissipation. Therefore, with the deviation from phase equilibrium, dissolved gas will not escape as freely as in a light oil system. Non-equilibrium phase behavior is therefore induced by this deviation from thermodynamic equilibrium.

The most important feature of a solvent injection in a heavy oil system is the existence of foamy oil flow due to the above-mentioned deviation from thermodynamic phase equilibrium. Gas bubble nucleation, bubble growth and coalescence, bubble break-up and formulating free gas are the most important dynamic properties of foamy oil. Thus, a better understanding of these dynamic properties is of crucial significance in monitoring how foamy oil evolves in order to guide and perfect the design of a solvent injection scheme.
In general, bubble dynamics include bubble nucleation, bubble growth, coalescence and break up. These processes indicate and determine how non-equilibrium affects the pore-scale mechanism of solvent injection process, and thus, by grasping the dynamics, it will be beneficial to take advantage of these features to enhance solvent injection performance.

2.1.1 Bubble Nucleation

Bubble nucleation is the first step for gas bubble to emerge in a system. And it is crucial for later stage bubble growth and formation of free gas phase.

Four main mechanisms are listed below based upon the experimental observations for gas exsolution and bubble nucleation in supersaturated systems: homogeneous nucleation, heterogeneous nucleation, nucleation based upon pre-existing gas cavities that have a radius smaller than the thermodynamic critical gas bubble radius to overcome the barrier energy, and nucleation based upon pre-existing gas cavities whose initial radius are larger than critical radius and has no nucleation energy barrier.

\textit{Homogeneous Nucleation}

The nucleation process is a process overcoming the energy barrier to generate new interface in an equilibrium system under a bulk phase with no physical media. Instead of going into molecular dynamics, a macro/bulk continuum theory based upon free energy minimization was deduced a century ago by Gibbs, and hence the famous Gibbs energy. Based upon bulk thermodynamics, the system Helmholtz free energy of a system containing volume V and N molecules of vapor at a chemical potential and pressure is (Obeidat 2003):

\[ F_i = N\mu_V - P_V V \] (2.1)
So, in order to form a droplet of $n$ molecules, and differentiate the chemical potential and pressure to an infinite small value, it is:

$$F_f = (N - \mu)\mu_V + n\mu_L - (V - V_L)P_V - V_L P_L + A\gamma$$ \hspace{1cm} (2.2)

Therefore, the difference between the initial state and the final state of the system yields:

$$\Delta F = F_f - F_i = n(\mu_L - \mu_V) - (P_L - P_V)V_L + A\gamma$$ \hspace{1cm} (2.3)

When the chemical potential between phases are the same, there exists a critical radius yielding the maximum free energy difference at a positive value:

$$\Delta F^{\text{max}} = -(P_L - P_V)\frac{4\pi}{3}R^3 + 4\pi R^2 \gamma$$ \hspace{1cm} (2.4)

Finally, the equation could be deduced as the following form for the classical homogeneous nucleation theory (Vachaparambil and Einarsrud 2018):

$$\Delta F^*_{T_1} = \frac{16\pi \gamma^3 (F^0_{I0} - F^0_{M})^3}{3(F^0_G - F^0_M)^2}$$ \hspace{1cm} (2.5)

This finally correspond analogously to the classical homogeneous nucleation theory (Obeidat 2003):

$$\Delta F^*_{T_1} = \frac{16\pi \sigma_{MG}^3}{3\Delta G^2_V}$$ \hspace{1cm} (2.6)

The critical radius could be yielded when the following condition is satisfied:

$$\frac{d\Delta F^*_{T_1}}{dR} = 0$$ \hspace{1cm} (2.7)

Then

$$R_c = -\frac{2\gamma(F^0_{I0} - F^0_{M})}{F^0_G - F^0_M}$$ \hspace{1cm} (2.8)

Which is analogous to classical nucleation theory:
\[ R_c = \frac{2\sigma_{MG}}{\Delta G_V} \]  
(2.9)

Where,

\[ \sigma_{MG} = \gamma(F_I^0 - F_M^0) \]

\[ \Delta G_V = -(F_G^0 - F_M^0) \]  
(2.10)

Therefore, the critical radius has to be reached in order to overcome the energy barrier for the gas bubble to form growable nucleus, and then the process becomes spontaneous. The following figure shows the relationship between system free energy and the critical radius under the balance of surface energy and volume energy:
Figure 2.1 System free energy formation vs. the bubble radius (Obeidat 2003)

Figure 2.2 Homogeneous bubble nucleation (Vachaparambil and Einarsrud 2018)
**Heterogeneous Nucleation**

In heterogeneous nucleation process, the supersaturated liquid mixture is in contact with a surface, and the following schematic Figure 2.3 shows the procedure of heterogeneous nucleation:

In this system, the excessive free energy that needs to be surpassed to form a new interface is written as the following:

\[
\Delta F^*_{T2} = \pi (-\cos^3 \theta + 3 \cos \theta + 2) \sigma_{MG} R^2 + \frac{R^3}{3} (F_G^0 - F_M^0)
\]  
(2.11)

From the equation, it is indicated that with pre-existing cavities/surface which allows a media for the phase change, the energy barrier is will be lower than homogeneous nucleation.

This finally corresponds analogously to the classical homogeneous nucleation energy equation:

\[
\Delta F^*_{T2} = \frac{4 \pi \sigma_{MG}^3}{3 \Delta \sigma_0} (-\cos^3 \theta + 3 \cos \theta + 2)
\]  
(2.12)

The energy barrier ratio between heterogeneous and homogeneous nucleation is therefore:

\[
\frac{\Delta F^*_{T2}}{\Delta F^*_{T1}} = \frac{-\cos^3 \theta + 3 \cos \theta + 2}{4}
\]  
(2.13)
Figure 2.3 Heterogenous bubble nucleation (Vachaprambil and Einarsrud 2018)

Figure 2.4 Ratio of heterogeneous nucleation to homogenous nucleation (Vachaprambil and Einarsrud 2018)
The figure 2.4 shows the energy barrier difference between homogeneous and heterogeneous nucleation:

Therefore, from the figure we can see, from contact angle at zero to completely non-wetting, the heterogeneous nucleation energy barrier is always equal or smaller than the homogeneous nucleation energy barrier.

The energy barrier is different from the other bubble nucleation theory which is only dependent on local variables (X. Li and Yortsos 1995):

\[
K_s C - P_L \geq \frac{\sigma}{W}
\]  
(2.14)

Where \(K_s\) is solubility constant, \(C\) is the local concentration of the solute in the solution mixture, \(P_L\) is the local liquid phase pressure, and \(W\) is the crevice width where the bubble grows. The above equation is analogous to heterogeneous nucleation, considering local properties, which will be discussed later in the pore-network modelling of gas exsolution processes under pressure depletion.

**Nucleation Based on Pre-existing Gas Cavities with Radius Smaller than Critical Radius**

The following figure 2.5 shows a nucleation process where there exists a gas cavity with a radius smaller than critical radius:

The energy barrier form is therefore:

\[
\Delta F^*_{T,3} = \pi(-cos^3 \theta + 3cos \theta + 2)(\frac{4\pi \sigma_{MG}^3}{3(F_G^0 - F_M^0)^2}) - \sigma_{MG}R_1^2 - \frac{(F_G^0 - F_M^0)}{3}R_1^3
\]  
(2.15)
Figure 2.5 Nucleation based upon pre-existing gas cavities smaller than critical radius (Vachaparambil and Einarsrud 2018)

Figure 2.6 Nucleation based upon pre-existing gas cavities larger than critical radius (Vachaparambil and Einarsrud 2018)
Nucleation Based upon Pre-existing Gas Cavities with a Radius Larger than Critical Radius

The figure 2.6 shows the process of a nucleation process where pre-existing gas cavities is having a radius larger than critical radius:

When the pre-existing gas bubble radius has surpassed the critical value, the energy barrier could be calculated using eq to substitute any \( R_1 \geq R_c \), and the result is zero. This means that in the 4\(^{th}\) type of nucleation, there is no need to form a critical nucleus. The pre-existing bubble mainly grows due to mass transfer under this case, and relevant study on diffusion driven nucleation in cavities was conducted before (Groß et al. 2018; Groß and Pelz 2017).

Bubble Nucleation Processes: Instantaneous Nucleation (IN) and Progressive Nucleation (PN)

In bubble nucleation theory, the sequence of the bubble nucleation has also been extensively studied: instantaneous nucleation and progressive nucleation. The former indicates that all the bubble nucleus are all formed at once when the phase equilibrium is deviated and then the bubbles grow on the nucleus (Firoozabadi 1996; Kashchiev and Firoozabadi 1993; X. Li and Yortsos 1995). For progressive nucleation, new bubble nucleus are continuous forming according to the extent of deviation from phase equilibrium, and bubbles grow continuously on these progressively occurring nucleus. Many studies have been conducted on characterizing the above two nucleation sequences (Arora and Kovscek 2003a; Bora 1998; Bora, Maini, and Chakma 2000; Geilikman, Dusseault, and Dullien 1995; X. Li and Yortsos 1991; Rupam, Amit, and Maini 2003;
Some argued that PN model did not verify what the experimentation showed according to the mathematical model deduced for the experimentation. Some argued that the bubble nucleation could not be treated as simply instantaneous due to the nature of the porous media where the pressure needs time to expand and affect the phase equilibrium at each point in the reservoir. And this assumption fits the equation where local variables such as nucleation site characteristics, local concentration gradient etc. are essential for bubble nucleation. (Sheng 1997) concluded that instantaneous nucleation was a part of the progressive nucleation when the condition of a sudden high pressure differential and one-time pressure drop is applied to the system.

In the work of (Arora and Kovscek 2003a), they claimed that their experimental results showed the feasibility of both IN and PN model. The bubble nucleation sequence has yet to be finally determined even till now due to the limitation of experimental apparatus, which can not fulfill the ability to visualize many very small micro-scale at the same time to determine the nucleation processes. Therefore, assumptions have to be made in many of the numerical model that covers the usage of both IN and PN processes.

### 2.1.2 Bubble Growth, Coalescence and Breakup

After a bubble or several bubbles nucleate at specific sites according to the upper mentioned bubble nucleation types, these bubbles will grow at a specific rate which is related to many physical parameters such as mass and heat transfer (in the case nucleation boiling), or by momentum transfer yielding compression or expansion due to change in force balance across the gas-liquid interface due to its compressible flow nature.

In total, bubble growth will be dominated by the following influential factors: mass transfer, heat transfer, and momentum transfer.
Mass transfer occurs by different mechanisms, such as compositional changes on the component-interface due to condensation and evaporation, also mass diffusion and dispersion will affect the mass transfer. Heat transfer mainly occurs through supplying heat/energy to the substance to break the phase equilibrium and yielding a phase change at the component interface. Momentum transfer is mainly dominated by the hydrodynamic forces of the system. In bulk phase, liquid inertia will play a very important role while in porous media, local pressure gradient, capillary pressure and viscous force plays an important role of controlling the bubble growth.

Gas bubble growth in bulk phase and porous media have been studied by many scholars before. In bulk phase, back to very early times, Gillmore (1952) has studied the growth and collapse of a spherical bubble in viscous compressible liquid. Scriven (1959) has derived the equation set for mathematically describing single gas bubble growth. The equation set includes continuity, momentum, energy flow, and mass flow. However, the equation set was rather a theory than a solvable equation set, and thus, many of the later studies have made simplifications and proper assumptions on the Scriven theory and developed many gas bubble growth theoretical models.

Szekely et al. (1971) proposed a mathematical model to describe the growth of a stationary spherical gas bubble in a supersaturated liquid due to solute diffusion. The effect of surface tension, viscosity and liquid inertia were investigated by coupling together into a continuity and motion equation and by formulating dimensionless parameters. Motion equation and solute diffusion equation were coupled together through two boundary conditions. The physical view was that the bubble expansion was caused by pressure difference inside and on the bubble surface. The pressure within the gas bubble was related
to the pressure on the bubble-liquid surface by considering the surface tension and viscous force, which was governed by the rate of mass transfer into the bubble. Experiments were designed and conducted to observe a bubble growth using a probe to act as a nucleation site. The experiment was well matched by the numerical analysis, for systems at low pressure where the liquid inertia was the main factor affecting the bubble growth. The concentration profile of the gas-liquid surface was expressed by the equilibrium law of mass transfer, say, Raoult’s law or Henry’s law.

On the basis of the previous work, Szekely and Fang (1973) proposed a modified model to re-consider the concentration profile by applying surface kinetics theory to represent a more realistic physical phenomenon, instead of using the equilibrium law between the surface of two components. Again, the effect of liquid inertia, viscous forces and surface tensions were investigated on the bubble growth, and surface kinetics was added as a new physics to describe bubble growth under non-equilibrium situations. The only focus of Szekely and Martins (1971) and Szekely and Fang (1972) was on the growth of a single spherical bubble, which posed many limitations on practical use. For instance, a single bubble in a diluted solution was not enough to explain multiple bubble nucleation, growth, and other dynamics when deviating from equilibrium.

Later on, many studies has been conducted on the growth of gas bubble in bulk viscous Newtonian fluid (Arefmanesh, Advani, and Michaelides 1992; Cable and Frade 1987; Gor and Kuchma 2009; Gor, Kuchma, and Kuni 2011; Jones, Evans, and Galvin 1999; Lillico et al. 2001; Rosner and Epstein 1972).

Gor et al.(2011) investigated gas bubble growth dynamics in a supersaturated solution by Henry’s and Sievert’s solubility law. Diffusion contributed to the bubble growth in their
modeling. Also, the Laplace pressure was studied on the bubble growth. The difference between Henry’s law and Sievert’s law in terms of the chemical equilibrium caused different growth dynamics for the investigated bubble. Based upon the assumption of steady state mass diffusion, for the case of homogeneous nucleation, bubble dynamics governing equations were solved analytically for both solubility laws. Three characteristic stages of bubble growth for both solubility laws were defined, namely, bubble radius growth with an increasing rate, growth rate decreasing, gradually comparable in-bubble Laplace pressure with external liquid pressure as growth rate decreasing, respectively. A case of nucleation of water vapor bubbles in magmatic melts. And for Sievert’s law, an analytical treatment of the bubble dissolution in a pure solvent was achieved.

The above-mentioned studies focused on the characterization of gas bubble growth in liquid phase by considering gas concentration, diffusion coefficient, temperature, pressure etc. These models included the simplified interface motion, mass transfer between multicomponent system in two-phase fluid, but the complexity of the models limit their usage to a very narrow area. Therefore, in order to simplify the model assumptions, Jones et al. (1999) described the relationship between bubble growing radius and time to be a power function. Meanwhile, Sheng (1997) concluded in a numerical model by simple assumption that the evolved gas bubble mole number to be the same growth pattern as gas bubble radius versus time (Jones, Evans, and Galvin 1999), then instead of characterizing bubble-scale, volumetric scale of foamy oil could be describe through a power function of time to consider non-equilibrium effect in heavy oil system.

In porous media, gas bubble growth has also been studied extensively. The main influential factor on bubble growth in porous media were mainly concluded to be pore structure and
geometry. This could be shown in the equation where porous media local parameters affect the gas exsolution in porous media.

Wong et al. (1999) has indicated three major mechanism of how a gas bubble grows in supersaturated fluid: the diffusion of the gas molecules from the ambient live oil which increases the mass of the gas bubble, the expansion under pressure depletion due to the compressibility of gas phase, and also the coalescence of multiple bubbles.

Bora et al. (1998; Bora, Chakma, and Maini 2003; Bora, Maini, and Chakma 2000) claimed that the bubble coalescence is a three-step process. Firstly, bubbles gather together due to bulk convection during pressure depletion, then secondly, when the bubbles colloid together, the liquid film of the two bubbles starts to drain and form a liquid film thickness. When this thickness has reached a certain critical value, the two bubbles would merge. And when the pressure depletion is high, the high velocity of flow would not allow two bubbles to get in contact sufficiently long time, and thus, bubble stability will be higher and kept dispersed.

2.2 Experimental Studies on Solvent Non-Equilibrium Dissolution and Exsolution Behavior

In this chapter, experimental studies, typically for solvent-heavy oil system, on solvent solubility and foamy oil non-equilibrium phase behavior will be reviewed. These studies, from different perspectives, investigate the non-equilibrium phase behavior related to foamy oil regime.

2.2.1 Solvent Diffusion Test
In general, there are direct methods and indirect methods to determine the concentration of solutes in a solution and the diffusion coefficients.

For direct methods, it usually includes gas chromatography which detects the compositional fraction in a mixture. The effective molecular diffusion coefficients of nitrogen in a sandpack model was measured by Cruz et al. (2007). They have implemented gas chromatography to directly examine the solvent mass fraction in the sampled oil phase. And thus, diffusion coefficients were found by matching the concentration profile with a mathematical model. By using gas chromatography, it is quite expensive and time-consuming, and the measured points were not smooth enough.

Magnetic Resonance Imaging (MRI) is another way to directly measure diffusion coefficients. By MRI, the concentration gradients in a test chamber could be plotted out. Diffusion coefficients in heavy oil recovery methods such as VAPEX, has been studied by Jon et al (2007).

Imaging methods were also implemented by a methodology named dynamic pendant drop shape analysis (DPDSA). Yang and Gu (2007; 2005; 2006a; 2006b) have conducted numerous tests for dynamically measuring the diffusion coefficients between solvent and heavy oil. By measuring the drop shape, that is, the dynamic varying volume of the oil drop, solvent diffusion coefficients were determined by applying finite element method to solve for the convection-diffusion equation and Laplace equation of capillarity. The pendent oil drop volume was dynamically fitted with the numerical results.

Diffusion coefficients have also been determined by methods utilizing CT scanning (Araujo et al. 2013; Song, Kantzas, and Bryan 2010a, 2010b; L. Y. Tang et al. 2013; Song, Kantzas, and Bryan 2010a, 2010b; L. Y. Tang et al.)
and NMR (Nuclear Magnetic Resonance) as a means of direct measurement (Fayazi, Kryuchkov, and Kantzas 2017, 2019). For instance, Wen et al. (2005; 2010) applied NMR technique to determine diffusion coefficients between solvent and bitumen. Usually, a density profile of the sampled oil phase can be detected, and diffusion coefficients were able to be found by history matching the concentration profile of solvent phase in the oil phase with mathematical modeling. Although CT scanning technology is very convenient and straightforward methodology of measuring fluid density profile, the cost of the experimentation is usually high and materials are specifically required, and also the resolution of CT scanning varies. With a very similar manner, NMR method was applied to measure the diffusion coefficients in a VAPEX process in a saturated sandpack. The proton density of the oil and gas samples in the test chamber can be detected as diffusion processes continue which alters the mobility of solvent and oil molecules. However, NMR technology is not able to generate a spatial and temporal data to generate a concentration profile in the test fluid. Thus, Magnetic Resonance Imaging (MRI) is usually employed for an accurate measurement of spatial concentration characteristics.

For indirect methods, pressure decay method has been the most common methodology to determine diffusion coefficients between phases. Riazi (1996) for the first time introduced a novel method to determine diffusion coefficients by using a pressure drop profile against elapsing time. The pressure decay profile was matched by applying a semi-analytical solution to the 1D diffusion equation from Fick’s second law without convection. The most important feature of this method for a single solvent was there was no need to measure the compositional change, and mass transfer was assumed to occur only from gas phase to oil phase. Zhang et al. (2000) had utilized pressure decay method to measure the
diffusivity of CO₂ and CH₄ into heavy oil samples. While in their measurement, even it was conducted in the PVT cell, they did not consider the swelling effect of oil after diffusion. Upreti and Mehrota (2000) measured CO₂ diffusion coefficient into bitumen samples at multiple pressure up to 4MPa and temperature from 25 to 90°C. In the diffusion process, the diffusion coefficient was assumed to be independent of pressure. In the whole pressure decay range, the diffusion coefficient was dependent upon the concentration gradient. In addition, in their findings, they claimed that diffusion coefficient would increase with incrementing temperature, which was contrary to a common understanding that under a higher temperature, the viscosity of the heavy oil phase would drop, which might lead to a lower diffusivity of solvent into the oil phase. Tharanivasan et al. (2006) applied pressure decay method on characterizing the diffusion coefficients of 3 different types of solvent, methane, propane, and carbon dioxide into heavy oil. Analytical solution was applied to match the pressure decay profile with 3 types of different gas-oil interface boundary condition, equilibrium, quasi-equilibrium, and non-equilibrium interphase penetration. Studies conducted by Li et al. (2015), Zheng et al. (2016), and Shi et al. (2017) have conducted diffusion coefficient measurement by pressure decay method in PVT cell under multiple reservoir pressure and temperature conditions. They have combined equation of state in terms of determining the dynamic swelling factor during diffusion processes, as well as the concentration profile variation along the diffusion path.

Traditional PVT cells have been used for measuring bulk phase diffusion pressure and swelling factor evolution against time (H. Li 2013; H. Li and Yang 2015; Shi 2017; Zheng and Yang 2016). In solvent solubility measurement tests, solvent would be injected to get in contact with the oil phase in a confined space. Two types of injection schemes have
been widely used. The first is by connecting the gas-oil co-existing system to a constant pressure source for solvent supply. In this way, a high-accuracy and high-pressure digital mass flow meter has to be used to accurately capture the solvent flow rate to quantify the solubility. In another way, a high-pressure syringe pump such as ISCO® pump, Cetoni® pump etc. can be directly connected to the system after filling up with a fixed amount of gaseous solvent inside the pump transfer cylinder. Then, by setting a constant-pressure mode, the solvent solubility into oil phase can be quantified through the recording the volume variation of the pump transfer cylinder body. This as well requires a high-accuracy pump volume recording unless the oil sample in the test is large enough. The second is by injecting solvent to a confined space already saturated with a fixed amount of heavy oil at an initial pressure, and subsequently sealing the system to conserve mass. Hence, a closed thermodynamic system would be formed and mass transfer happens under a concentration gradient between the gas cap and the oil phase. Then according to the real gas law and the pressure decay in the system, one is able to quantify the solubility of the solvent into the oil. However, no matter under which above schemes, the time cost and material sample size for measurement in some of the bulk phase apparatuses are usually higher, and usually a set of test in a traditional 3D cylindrical PVT cell can take up to 10+ days to reach equilibrium even at high injection pressure at 4.48MPa(Kavousi et al. 2014; Kavousi, Torabi, and Chan 2013). For a diffusion test with visualization in a small volume scale, if a constant pressure is applied, then the measurement of the gas flux to compensate for the gaseous solvent mass loss in the gas cap due to interphase mass transfer under molecular diffusion should be very accurate. Therefore, in order to reduce the time cost of the test as well as conserve the mass, a microfluidics-inspired methodology of utilizing a Hele-Shaw-
like cell to conduct diffusion tests was established. Pressure decay instead of constant pressure was applied to measure the diffusivity of CO$_2$ into heavy oil in a very small and confined space, where gas chamber pressure can be rapidly measured and recorded for numerical simulation. Due to the volume size of Hele-Shaw-like cell, the time cost to reach equilibrium diffusion ending pressure is way shorter than using a 3D cylindrical cell. With high clarity of visualization, the swelling factor can also be measured as part of the history matching data set for determining the diffusion coefficient.

2.2.2 Solvent Exsolution Behavior in Bulk Phase

In this subchapter, studies from the past decades on foamy oil PVT phase behavior in bulk phase will be discussed. Prior to a porous media test, a bulk phase test could help generate an overall understanding of the PVT phase behavior of a certain measured system.

Supersaturation is an important phenomenon in foamy oil existence. The pressure difference between bubble point and actual system pressure was defined as the supersaturation degree of the system. Kamath and Boyer (1995) had concluded that live oil undergoing pressure depletion that was deviated from the bubble point pressure would induce a supersaturation, and once, a certain supersaturation was reached, the gas bubbles would begin to evolve. Sheng (1997) conducted multiple tests on foamy oil stability under bulk phase PVT cell. These tests included foamy oil pressure depletion under different scenarios. Different pressure depletion rates, initial oil column height, initial GOR, dead oil viscosity, asphaltene content etc. have been considered in the experimental studies. Albartamni (2000) has conducted a series of CCE tests on CO$_2$-heavy oil system in visual PVT cell with mainly two pressure depletion rate, 41 and 800kPa/day. Also, bulk phase viscosity was measured for foamy oil undergoing the above-mentioned pressure depletion.
rate. Three types of viscometers were used: Cambridge viscometer, Capillary viscometer, and Haake viscometer. The three viscometer showed different foamy oil viscosity measurement value. Specially, Haake viscometer results were not reliable because of the free gas phase within the testing chamber. Cambridge viscometer showed results that high pressure depletion rate induced lower foamy oil viscosity. Bennion et al. (2003) conducted non-equilibrium phase behavior tests on methane-heavy oil system under different pressure depletion rates. Oil formation volume factor, solution gas oil ratio, density and viscosity of the live oil system have been measured. It was concluded that pressure depletion rate has a very important effect on the bubble formation and growth, as well as live oil phase density. Goodarzi et al. (Goodarzi et al. 2007) have utilized CT scan and NMR techniques to measure live oil and foamy oil properties in a PVT cell. The essential parameters measured were oil density, oil and gas formation volume factor, solution gas GOR, and oil viscosity as a function of pressure. Both equilibrium and non-equilibrium conditions were applied to the PVT cell by using different pressure decline rates. Alshmakhy (2012) studied foamy oil viscosity under various conditions. Shear/flow rate exerted on the foamy oil, gas volume fraction dispersed in oil, type of viscometer etc. were experimentally evaluated. Cambridge viscometer, capillary viscometer, and slimtube packed with sand were used. It was found that the type of viscometer has showed significant effect on the final measurement. The capillary viscometer has showed different behavior than the rest of the three. He concluded that the apparent viscosity of the foamy oil was shear rate dependent. Zhou et al. (2017) studied three types of pressure decline method on a methane-heavy live oil system. Constant pressure depletion rate, constant volume withdrawl and step-by-step pressure depletion have been tested on the system. For
the former two methods, foamy oil relative volume changes over time were very similar. The concentration of solution gas presented a strong exponential relationship with time. And the rate of solution gas becoming dispersed gas increased as the pressure depletion rate increased. For the free gas phase, the mole number showed proportionality to square of time variable. The pseudo bubble point claimed in the research decreased with the increasing pressure depletion rate. Sun et al. (2017) conducted study on equilibrium and non-equilibrium PVT behavior of foam oil using experiments and PVT correlations. They concluded that foamy oil exhibits stable GOR, high FVF, low density and viscosity. Certain correlations for equilibrium PVT and non-equilibrium PVT phase behavior of foamy oil have been developed to better represent their characteristics. For tests utilizing pressure-volume responses in non-visual bulk phase transfer cylinders (Luo et al. 2018), the real-time vapor/liquid phase ratio and detailed foamy oil bubble form cannot be visualized, and the description of bubble-scale dynamics will be limited. Bryan et al. (Bryan et al. 2018) utilized low field NMR to test the non-equilibrium solvent release behavior of methane-propane/ and methane-CO₂/heavy oil systems. They proposed that a well-calibrated NMR can help measure the viscosity of the liquid phase when dissolution gas liberates from the solution. The impact of live oil viscosity on the rate of solvent release has been studied. Sun et al. (2019) has designed a high pressure high temperature PVT cell to testify a comprehensive experimental study of gas-oil interfacial properties to understand how to generate foamy oil. A new setup was applied to measure the gas-oil interfacial single film stability under reservoir conditions. And the product was collected and used for direct compositional test by NMR and FTIR to understand foamy oil generation in terms of chemical characterization. Zhou et al. (Zhou, Zeng, et al. 2020) have
conducted pressure depletion tests to study foamy oil stability using CO₂-heavy oil system in PVT cell. All the above-mentioned usage of 3D cylindrical PVT cell was bothered by a lower level of visualization for solvent exsolution, due to the heavy oil coating on the inner walls of the test chamber.

2.2.3 Solvent Exsolution Behavior in Porous Media

Tremblay et al. (Tremblay, Sedgwick, and Vu 1999) have conducted CT imaging of wormhole growth under solution-gas drive. They visualized the formation and growth of wormhole system in which oil flowed through a horizontal sandpack and out of a production port. The pressure gradient causing the wormhole to grow and expand was due to the liberation and expansion of the solution gas methane in the live oil. They found that wormhole grew to a certain size and stopped growing due to the lack of pressure gradient to mobilize the sand. But they concluded that in the field whose oil production rate was much higher than laboratory tests, wormholes can form easily in uncemented regions. Sahni et al. (Sahni et al. 2004) have studied heavy-oil solution gas drive experiments through CT scanning technique. The in-situ phase saturations along the sandpack model was quantified. Gas phase exsolution below true bubble point was investigated with dimensionless scaling as well as mechanistic modeling. Critical gas saturation was found and both the behavior before and after such critical gas saturation was studied. Phase mobilities were obtained. They concluded that the non-equilibrium effect mostly depended on viscosity and depletion rate. Critical gas saturation was correlated and they indicated that the dispersed gas flow might happen close to near wellbore region of near wormhole region under field-pressure gradients and flow rates. Tang et al. (G.-Q. Tang et al. 2006) tested heavy oil solution gas drive in both consolidated sandpack with confining pressure
applied as well as unconsolidated sandpack without the confining effect. They applied CT scan to investigate the saturation profile inside porous media. They showed that overburden pressure can support the pore-pressure and partially reduce the pressure depletion rate inside the sandpack, and hence resulted in different features of bubble behavior. Also, critical gas saturation was higher and the oil-gas relative permeability was greater in consolidated sandpack. Direct imaging methods will certainly provide an accurate measurement of the fluid distribution inside a confined space up to a very high resolution. However, due to the high-cost nature, strict model materials (usually aluminum core holders) and dimensional requirement, sophisticated operating procedures etc. of radioactive methods such as CT scan, it is often not practical and economical to conduct every single test in this type of equipment. Often, a dynamic scanning, such as synchrotron CT scan, of fluid flow behavior in a sandpack model would be very demanding but at much higher cost compared with a static CT scan, and thus, most of the CT scan results are intermittent. Also, the choice of the resolution of the CT scan might vary the operational cost of the experiment. As an example, a pixel of the scanned image might contain pore space, residual oil, and solvent gas, and if higher resolution has to be achieved to distinguish all phases, it increases the operational time and cost.

Xu (2007) has conducted a series of live oil depletion tests in sandpack model to examine the basic mechanisms on dispersed gas bubble formation and testify the nucleation theory based upon the experimental results. Totally 14 sets of live oil depletion tests were conducted using different pressure depletion rate and pressure depletion schemes, such as continuous pressure depletion rate and step pressure decline. He concluded that the concept of explosive nucleation might not be correct. The bubble size was maintained by
an equilibrium rate between the process of bubble break-up and coalescence. And the critical gas saturation where gas started to flow out of the sandpack increased with the increasing pressure depletion rate. Abusahmin (2010) has studied multiple parameters that affect foamy oil performance in a production test, including GOR, saturation pressure, and the type of oil used in the study. Primary pressure depletion tests were conducted in 2-meter long sandpack to mimic in-situ condition. Each foamy oil system was fully investigated in terms of GOR, oil compressibility, live oil viscosity, surface tension and foam stability. Zhou et al. (2016) has studied the foamy oil flow in heavy oil-solvent systems by pressure depletion in a sandpack. Three types solvent were studied, including methane, propane and methane-propane mixture. Multiple parameters have been analyzed, such as cumulative oil, cumulative gas, production GOR, pressure gradient along the sandpack etc. The optimum pressure depletion rate to induce more foamy oil flow for a 1m long sandpack has been figured out. This could be a reference to the pilot test on which pressure control schemes to be chosen to last foam oil flow longer. Other studies also utilized sandpack model and coreflooding systems to perform pressure depletion tests to examine the effect of the foamy oil existence and various of solvent types on the production performance under various pressure operational schemes(Bashir Suleman Abusahmin, Karri, and Maini 2017; B. Busahmin and Maini 2019; S. Li, Li, and Wang 2015).

2.2.4 Microfluidics System Studies

In order to minimize time cost of multi-phase equilibrating time and achieve higher observation resolution with less manual- and expenditure-cost, microfluidics system has been utilized recently for multiple kinds of phase behavior tests.
Bora (1998) and Bora et al. (Bora, Chakma, and Maini 2003) conducted a series of flow visualization studies within an etched glass micromodel of homogeneous and heterogeneous pore network. Pore scale phenomenon during pressure depletion was observed directly. The bubble nucleation of the system followed a progressive nucleation process and it was a very random event occurring mainly on the pore walls. However, the contribution of nucleation of the gas bubbles in the porous media seemed to have very little effect on determining the distribution of gas-oil dispersion. He concluded that the pressure decline rate was the most important parameter that affected the foamy oil phase behavior in the pore scale experiments. The pressure depletion rate determined the spanning pattern of gas-oil dispersion along the pores. Compressibility of the produced fluid, asphaltene contents and viscosity effects on the foamy oil phase behavior in micromodel were also analysed by Bora (1998) and Bora et al. (2003). Bora et al. (2003) also developed and modified the mathematical expressions for the nucleation rate of foamy oil gas bubbles for various oil systems. Maini (1999) conducted two series of micromodel experiments to visualize the gas bubble formation and flow in the porous media. He examined the effects of depletion rates as well and the asphaltene effect on the bubble dynamics, and eventually reached very similar conclusion as Bora (1998). Turta et al. (2002) used micromodel to determine the extent of supersaturation needed for bubble nucleation and the distribution of the nucleation sites. The study showed that gas did not necessarily start to nucleate in the part of lower pressure in the micromodel.

Lago et al. (2002) conducted a series of pressure depletion tests in micromodel and image processing was applied to analyse the three steps of gas behavior in the heavy oil flow. Gas bubbles nucleated in heavy oil had a smaller size compared to that of light oil. During
depressurization process, the nucleated bubbles grow to a critical size. Then, the already nucleated gas bubbles started to flow and migrate to “seek” for other bubbles and coalesce, while the new bubbles kept nucleating under continuous pressure drawdown before the pressure drawdown stopped. When the pressure drawdown stopped at a certain pressure, the nucleation of new gas bubbles stopped while the flow of the bubbles continued. In the research, the figure of gas saturation against gas bubble diameter during the 0.115 kPa/s depressurization was plotted by image processing to show the evolution of bubble size.

Shahabi-Nejad et al. (2005) performed a series of experiments to study the effect of pressure depletion rate, micromodel grain saturation history and water existence on the gas bubble nucleation processes, gas phase transition and fluid flow movements. They found out that it was of great significance to establish the correct initial conditions prior to conducting any physical experiments, because the grain saturation history and sequence would greatly affect the nucleation process of the gas bubbles. Oil-wet, water-wet, and mixed-wet conditions were applied to investigate the bubble nucleation, bubble growth, critical gas saturation etc. It was concluded that under no pre-existing gas bubbles system, it was hard to promote a significant foamy oil behavior even at high pressure depletion rate two orders of magnitude than the field rate. In light oil system, gas/oil interface snap-off happened at the pore throat due to capillary force, but in heavy oil tests in this research, such snap-off did not happen due to the high dead oil viscosity and very low GORs. This might contribute to a different gas relative permeability in an up-scale study. When the pre-existing gas bubbles was already present in the micromodel, foamy oil behavior occurred. And many small bubbles were trapped and flowing with the oil phase.
Li et al. (2012) conducted microscopic visualization experiments on heavy oil from Orinoco belt. Effects of pressure depletion rate and temperature on foamy oil microflow characteristics were investigated. There were bubble divisions, merging, deformation during transportation in the porous media. Gas bubbles had a higher stability under a higher pressure depletion rate. The temperature exerted some effect on the bubble nucleation pressure. Lower bubble nucleation pressure would appear under a higher temperature field. Also, higher temperature would increase the gas bubble velocity mainly due to the oil viscosity reduction. However, a much too high temperature would decrease the oil viscosity to a larger extent and lead to much higher gas bubble mobility and thus, reducing the recovery factor.

Bjorndalen et al. (2012) investigated solvent exsolution behavior from gas-heavy oil mixture during pressure depletion tests. Several types of solvent and solvent mixture, namely CO$_2$, C$_1$, C$_3$ and CO$_2$-C$_3$ mixture, were tested in an etched glass micromodel. Under the same operating scheme, CO$_2$-based tests produced the most nucleation sites than all the other solvent types. This provided the insight about using what type of solvent to generate the highest bubble nucleation number density.

Liu et al. (2013) proposed that the stability of foamy oil was the dominant factor affecting the life of foamy oil. They conducted visualized experiment under higher temperature high pressure to quantify the main factors affecting the stability of the foamy oil. These factors included temperature, solution GOR, pressure decline rate and the pore sizes. It was indicated that 70 °C was a critical temperature beyond which foamy oil would become very unstable. It was worth mentioning that foamy oil stability would be higher if the pore sizes approached closer to the real reservoir condition.
Li et al. (2015; Lu et al. 2015) conducted experimental study on the performance of foamy oil under different initial solution GORs in micromodel systems. It was showed that the differences between equilibrium bubble point and pseudo bubble point decreased as the initial solution GOR decreased. There should exist a low limit for the triggering of foamy oil phenomenon. For practical purposes, when the reservoir solution GOR became lower than the critical low limit of foamy oil triggering point, the solution gas separated from the produced oil could be re-injected into the reservoir to increase the foaminess of the heavy oil, so as to extend the foamy oil production time.

Xu et al. (Y. Xu et al. 2017) have physically simulated the full-pressure-temperature phase envelope with 1000 microfluidics chambers. In their tests, a hydrocarbon mixture of 80% propane and 20% methane was contained in the microfluidics system for the full PVT phase envelope measurement. They have successfully reproduced the phase envelope of the hydrocarbon mixture. However, such hydrocarbon mixture is in gaseous form under ambient condition, and therefore, the microfluidics control of such fluid is relatively easier than handling two-phase system with one phase being liquid state under ambient condition, let alone solvent-heavy oil mixture. Later, some literatures have applied bitumen sample into the microfluidics system for solvent solubility tests. Both gaseous solvent and liquid solvent have been tested, including CO₂-bitumen diffusivity test (Fadaei, Scarff, and Sinton 2011), propane-bitumen diffusivity test (Talebi et al. 2017), toluene-bitumen diffusivity test (Fadaei, Shaw, and Sinton 2013) etc. The above studies mainly targeted a quiescent condition so that the effect of flow resistance to the bitumen sample imposed by the geometry can be neglected, and only static molecular diffusivity can be measured.
Equilibrium phase behavior tests of gas and black oil have been tested before in microfluidics chips (Fisher et al. 2013; Sharbatian et al. 2018). Fisher et al. (Fisher et al. 2013) have conducted equilibrium black oil GOR measurement in a microfluidics chip. Their goal was to determine the gas-oil two-phase equilibrium state so as to achieve equation-of-state parameters. Therefore, light crude oil samples with °API gravity ranging from 37.2~63.8 have been used to form live oil and conduct pressure depletion tests. The phase behavior of such gas-black oil system under pressure depletion was almost instantaneously equilibrated thermodynamically. Sharbatian et al. (Sharbatian et al. 2018) have conducted CO$_2$-light oil phase behavior tests in microfluidics system, including the measurement of solubility, diffusivity, extraction pressure and swelling factor turning point, miscibility and wettability contact angle etc.

Molla and Mostowfi (Molla and Mostowfi 2017) have conducted equilibrium PVT measurement for saturation pressure and phase-volume ratio in small-scale microfluidics chip. Long serpentine channel was engraved on the chip for measurement with very small amount of volume at 5µL. Compared with the previous study conducted by Mostowfi et al. (Mostowfi, Molla, and Tabeling 2012), the microfluidics system in this study was changed to a closed system by using two sample bottles to contain and maintain the fluid and the system pressure. During the tests, the GOR measurement was conducted by optical method due to large difference in refractive index between opaque black oil phase and vapor phase. The vapor phase volume fraction inside the serpentine channel was measured through image processing and this value was used as the equilibrium phase-ratio of the overall system. The vapor phase volume fraction was then compared and validated with the tests conducted under the same pressure and temperature condition in traditional PVT
cell. In this series of study, due to the high API gravity and very low water-like viscosity of the oil phase, the liberation of solution gas out of the oil phase was at ease. Therefore, equilibrium state under pressure depletion was almost instantaneously reached. However, in heavy oil study, the high viscosity will hinder the exsolution of the vapor phase, and therefore, forming foamy phenomenon. Within such small micro serpentine channel (narrow capillary at 50×50µm), the injection of heavy oil into such dimension will be risky because of the high frictional resistance to the viscous flow by the 2D channel, as well as the potential of channel plugging by asphaltene precipitation. In addition, for such a long capillary at 80mm, according to Poiseuille’s law, the heavy oil pressure differential between the two capillary ends can be significantly larger than when the channel was saturated with light oil. Hence, the whole channel might not be at a uniform pressure, and when conducting phase behavior analysis, the system pressure should be uniform everywhere in order to eliminate the effect of pressure gradient disturbance on the phase-ratio measurement. In addition, other many high-clarity visualization and microfluidics-based methodologies have been widely used to characterize the solvent-heavy oil mutual interactions for a higher time-efficiency and lower material cost(Bao et al. 2017; Bashir Busahmin et al. 2017; Fadaei, Scarff, and Sinton 2011; Fadaei, Shaw, and Sinton 2013; Sell et al. 2013; Sharbatian et al. 2018; Talebi et al. 2017; Y. Xu et al. 2017). Although the usage of microfluidics overcome most of the difficulties of the non-visual or hardly-visual tests, the numerical modeling of such small pore-scale might have to resort to either Direct Numerical Simulation (DNS) simulations such as Computation Fluid Dynamics (CFD) simulations, or pore network simulations, which is fundamentally different from a Darcy-scale reservoir simulator, and the upscaling of such pore-scale mechanisms requires a
decent amount of research. Hence, a proper scale of experimentation device that can both be simulated by Darcy-scale simulator as well as possessing the advantages of microfluidics devices were experimentally established in this thesis.

2.3 Numerical Studies on Solvent Non-Equilibrium Dissolution and Exsolution Behavior

2.3.1 Diffusion Coefficient Determination

Yang (2005, 2006a, 2006b) has conducted diffusion coefficient calculation by utilizing a finite element method based upon the experimental study of dynamic pendant drop volume analysis (DPDVA). The volume of the dynamic pendant oil drop was calculated based upon the solvent concentration distribution inside the oil drop. In the calculation, the weak form of the dimensionless Fick’s second law was derived and diffusion coefficient was solved for by matching the volume change of the pendant drop. Tharanivasan (2006) has conducted diffusion coefficient calculation by a non-intrusive pressure decay method to determine the diffusion coefficient of a methane, propane, and carbon dioxide-heavy oil system under reservoir pressure and temperature conditions. Fick’s second law with 3 types of boundary conditions were applied in the study. The boundary conditions include equilibrium condition, quasi-equilibrium condition and non-equilibrium condition (flux). The pressure was the main target to be matched. Without considering the swelling factor, the mathematical model has proven the feasibility to match the pressure decay curve and result in a suitable diffusion coefficient. Zhou et al. (Zhou et al. 2020) have conducted diffusion tests in a CO₂-heavy oil system both under bulk phase and porous media.
Pressure decay curves of both conditions were history matched by analytical solution of 1D diffusion equation based upon Fick’s 2nd law.

However, purely by using diffusion-convection equation to solve larger lab-/field-scale problem is not practical as Multiphysics will be difficult to consider and boundary conditions cannot be as simple, uniform and regular shaped. Hence, to validate Darcy-scale simulator in terms of diffusion process simulation is significant for improving reservoir simulation, especially when any kind of solvent dissolution is to be simulated. Numerically, for the diffusion tests, inspired by dynamic wormhole modeling in a Darcy-scale simulator (Istchenko and Gates 2014), instead of using diffusion-advection partial differential equation (PDE) set with specified boundary conditions (3 types of boundary conditions: equilibrium, quasi-equilibrium, non-equilibrium) like most of the diffusion coefficient numerical determination (H. Li 2013; H. Li and Yang 2015; Shi, Zheng, and Yang 2017; Zheng and Yang 2016), a MATLAB-controlled reservoir simulator was applied to dynamically alter the value of the diffusion coefficient in the simulator at different stage of time to simulate Darcy-scale pressure decay behavior under molecular diffusion.

2.3.2 Foamy Oil Numerical Simulation

In the reservoir simulator study on foamy oil characterization, CMG was the mainly analysis subject as the kinetic model built in the simulator could simulate the foamy oil with utmost flexibility than other simulation techniques for Darcy-scale flow.

Coombe and Maini (Sheng 1997) has proposed a non-equilibrium reaction model to define chemical-like transformation to simulate the deviation from equilibrium status. They
assumed that the gas dissolved in the oil would firstly become micro bubble that has gas-like density, and then they would transform into free gas. Sheng (1997) has developed a dynamic model on simulating foamy oil phenomenon. In his model, three different methods were developed to simulate the process of bubble nucleation, bubble growth and bubble disengagement. All the bubble nucleation pattern was assumed to be instantaneous nucleation. Power law model of bubble growth were described for the first two models, and exponential law was considered for the third model. In the first model, the bubble growth history was stored. And second and third did not consider bubble growth history for the sake of being implemented into a simulator. It utilized a local equilibrium to consider time effect. Model 3 with exponential bubble growth and decay was the least sensitive to time step size than power law function in model 2. Reactions were incorporated into governing equations as a source term by adding intermediate component. Bulk phase foamy oil expansion tests were well matched by the model as well as the sandpack depletion tests. This newly developed model was a renovation in foamy oil simulation which later was incorporated into CMG STARS Process Wizard module considering pseudo chemical reaction with tunable reaction frequency factors and reaction orders. This way enables the dynamic foamy oil properties change during the pressure depletion processes.

Luigi et al. (1998) studied the sensitivity of the activation energy and the frequency factor of the foamy oil pseudo chemical reaction in CMG STARS® foamy oil module. The range of the upper two parameters was determined, which defined the non-equilibrium of the oil-gas dispersion system. The adjustment of the parameters matched the foamy oil behavior for well SDZ-182 in Orinoco belt in Venezuela. During the simulation, the
modification of the activation energy values and frequency factors of the first reaction (nucleation) had much less sensitivity to the final results than that of the second reaction (dispersed gas to free gas), because the time for the first reaction was much too slower than the second one. The first reaction mainly depended on the pressure decline rate and the gas-into-oil diffusion, and the second reaction was greatly affected by the temperature except for pressure decline rate, especially under vapor injection which would cause bubble instability, and thus, leading to a faster reaction rate.

Lillico et al. (2001) developed a numerical model to describe the gas bubble nucleation kinetics in a live heavy oil. In the model, colloidal and interfacial sciences were incorporated to study the nucleation and initial coalescence of gas bubbles. Volume expansion laboratory measurements were conducted, and the pressure deficit drove the bubble formation. Homogeneous nucleation was supported by the model that the scale of critical bubble radius (from 0.03 to over 3 μm) was at a much smaller scale than the pore size. There was no bubble break up processes in the model but only the coalescence. The bubble number density was estimated by matching the experimental data, and the number density reached quite of a maximum value of 1.6×10^{13} bubbles per ml during the initialization of the nucleation when supersaturation was high. The amount of the energy forming the new interface of the multiple bubbles was also calculated.

Arora and Kovscek (2003b) developed a mechanistic population balance model to describe the process of bubble nucleation and growth in both light and heavy oil. The bubble nucleation theories were tested, namely, instantaneous and progressive nucleation (IN and PN). The IN model showed good match to pressure data both for light and heavy oil, with the total number density of nucleated bubbles per volume of rock as an adjustable
parameter. The bubble number density increased when the oil withdrawal rate increased and when the surface tension decreased. All the bubble nucleated at the equilibrium bubble point pressure, and no supersaturation threshold was required for the onset of the bubble nucleation. The PN model had superior performance to IN model except that it needed more computational cost and the pre-defined porous media cavity size. The population balance model was analogous to the mass balance equations, so they proposed that this model could be incorporated into the already existing reservoir simulators.

Bayon et al. (2002) has conducted a series of pressure depletion tests under reservoir conditions on a 2-meter long sandpack model. The targeted subjects for history matching were recorded including oil and gas production, in-situ gas saturation profiles, critical gas saturations etc. Two main modelling techniques were applied. The first one was black oil model by IMEX, and the second one was chemical-like simulator. Two dynamic processes were set, namely, the solution gas transformation to dispersed gas, and the transformation from dispersed gas to free gas. An interpolation set of relative permeability curve was used to interpolate the relative permeability of the gas phase between dispersed gas and free gas. Also, kinetic reaction frequency factors were set for each test. The newly developed methodology has generated a set of tuning parameters that were not relying on the pressure depletion rate. Compared with the black oil model where the relative permeability is the main adjustable parameter, the chemical-like simulator added more tunable parameters in the simulation including a comprehensive set of reaction frequency factor and reaction order as well as the relative permeability curves.

Bayon et al. (2002) compared two models in simulating a long 2-meter sandpack pressure depletion tests. One method partitioned the solvent phase into 3 components, solution gas,
dispersed gas and free gas. And the other method partitioned the solvent phase into 4 components, in which two types of dispersed gas were considered, mobile and immobile dispersed gas phase. Since the components were different, therefore, in the two models, the relative permeability models were different from each other.

Chen and Maini (2005) conducted a series of numerical simulations of foamy oil depletion tests using CMG IMEX and CMG STARS foamy oil module (mainly in CMG STARS). The sensitive parameters affecting the simulation most were identified as: oil viscosity, frequency factors k1 and k2, Krocw, Krgcl, Sgcr, Sorg, Pnorm and Snorm. Cumulative gas was very sensitive to the frequency factors with a positive proportional relation. Oil relative permeability at connate water saturation Krocw had a positive proportional relation with cumulative oil and gas production. The critical gas saturation Sgc increased cumulative gas production significantly when Sgc decreased. The range of picking Pnorm and Snorm would greatly affect the performance of history matching. The results showed that foamy oil modules in CMG STARS could match the production data quite well for the macroscopic sandpack primary depletion tests, and up-scaling of the simulation for megascopic reservoir scale should be further developed. The following figure shows the adjustable parameters for the simulation.

By using CMG STARS foamy oil module, Uddin (2005) performed numerical simulation to study gas exsolution in heavy live oil reservoir. Eight sets of constant withdrawal rate tests and four sets of pressure depletion tests were history matched. A five-component kinetic model was utilized, including water, oil and the component from the TEF model. The bubble nucleation was symbolized by dissolved gas to dispersed gas, and the bubble growth by dispersed gas to free gas. For sufficiently low rate tests, the numerical
simulation showed no significant changes in tuning the model parameters, such as frequency factors, reaction energies etc. The successfully matched oil and gas production data of pressure depletion tests indicated the ability of the model to simulate field scale production. Uddin (2011) also used similar kinetic equations and chemical-like simulator module to numerically simulate the gas evolution and transport behaviors in natural gas-hydrate reservoirs. Uddin (2012) and Shen (Shen 2015) again developed a mechanistic foamy oil chemical-like reaction model to quantify the gas exsolution and transport in CMG STARS foamy oil module. The study included two parts: the first part was to develop a kinetic model with five components and four reactions to simulate foamy oil flow in live oil reservoir; part two was to develop a set of analytical function to quantify gas bubbles partition and gas oil relative permeability as a function of capillary number in reservoir condition. Based on the two purposes, gas exsolution behavior associating with capillary number was studied by history matching the withdrawal tests. An analysis of micro model tests to define capillary number effect on the gas bubble partition was carried out. Lastly, radial drainage pressure depletion tests were history matched to develop a set of relative permeability (also depending on the capillary number of the grid block) for field scale modeling.

Ivory et al. (2010) numerically investigated cyclic solvent injection process by using CMG STARS foamy oil module to represent the physical behavior of the experimental results. Cyclic solvent injection as a follow-up technique after primary depletion has been proved to be effectively in thin and shallower heavy oil reservoirs. The CSI process involves great amount of foamy oil generation, and therefore, the understanding of the transient phase behavior of foamy oil flow before and after bulk vapor injection could help better
understand the CSI process, such as solvent-oil distribution after bulk vapor injection, solvent diffusion during soaking period, solvent-oil distribution during production, etc. In their numerical modeling, non-equilibrium rate equations were formulated by chemical-like simulator. The deviation and delay time for solvent to reach equilibrium concentration either by dissolving or ex-solving into and out of the oil phase under the current pressure and temperature, were modeled by the foamy oil module in CMG STARS. Besides the kinetic frequency factors, the reduced gas-phase permeability due to foamy oil mechanism was also included. It was found that a significant oil swelling occurred during solvent injection period which would reduce solvent injectivity and the penetration of solvent into deeper oil. Under a fixed pressure injection scheme, the quantity of injected gas was found to be sensitive to the solvent solubility in oil (as the C$_3$H$_8$ and CO$_2$ solubility simulation profile during injection, soaking and production), kinetic dissolution rate frequency factor, K values, gas-phase diffusion coefficients, molar densities in the oil phase, gas relative permeability and capillary pressure. The final oil production was highly sensitive to the efficiency of gas dissolution into the oil during solvent injection and the rate of gas exsolution during depressurization.

Abusahmin (2010) concluded that in his simulation based upon CMG STARS, foamy oil simulation parameters tuned in one specific test in the same rock-fluid system could not provide good matching results to other experiments at different pressure depletion rates. So these parameters have to be tuned for specific pressure depletion rates each time running the simulation.

The post-CHOPS simulation included two major parts mainly, the geo-mechanical sand production and the foamy oil non-equilibrium phase behavior. Simulations were performed for different kinds of techniques of cyclic solvent injection, such as mixture solvent injection, pressure maintenance for longer foamy oil endurance, cyclic solvent injection pilot tests etc. And the contribution of foamy oil non-equilibrium kinetics defined by the foamy oil module gave reasonable prediction and matching of the in-situ oil and gas production data, showing the importance of considering the foamy oil pseudo chemical reaction mechanism in the study of solvent injection. This could help define the gas components in the reservoir and their individual contribution. Similarly, Shen (2015) also applied pseudo chemical reaction mechanism to simulate and history match the foamy oil flow occurred in pressure depletion and constant volume withdrawal tests. And some analytical solutions of bubble nucleation, growth and coalescence were given in the appendix for future reference.

Most recently, Oskouei et al. (2017) developed a kinetic model for non-equilibrium dissolved gas ex-solution from static heavy oil. The model considered both equilibrium and non-equilibrium processes of bubble exsolution behavior. Three steps of foamy oil formation and decay were developed as bubble nucleation, bubble growth and formation and bubble coalescence and decay. Reaction orders and reaction frequency factors were determined by history matching both the conventional and non-conventional PVT tests of the Driza heavy oil.

Lu et al.(X. Lu et al. 2019, 2020) have conducted numerical simulation study on the foamy oil behavior in heavy oil/methane and heavy oil/propane system. The focus was to history match the production data. Hence, the order of magnitude of the kinetic reaction rates were
very high since the live oil inside the sandpack model was directly produced into atmospheric pressure, and surface flash took place. This requires to tune the reaction rate frequency factors to very high values so as to history match the production GOR under surface flash.

Zhou et al. (Zhou et al. 2020) have conducted foamy oil stability analysis by both experimental and mathematical modeling. The targeted system was a CO₂-heavy oil system under reservoir conditions. By dividing foamy oil volume expansion into two processes: expansion and decay, they proposed a dynamic reaction rate model to describe foamy oil stability in bulk phase. Gas phase reaction rate k1 and k2 were employed to describe the two processes respectively. Both parameters were found to be in the order of magnitude at $10^{-3}$ min⁻¹, as the pressure depletion rate was small and the experimental study was conducted in a bulk cylindrical chamber, in which the volume expansion of the oil phase was not too significant.
CHAPTER 3 EXPERIMENTAL MATERIALS, SETUP AND PROCEDURES

In this chapter, the experimental materials, setup and procedures for the characterization of the non-equilibrium phase behavior of solvent-heavy oil systems will be presented.

3.1 Experimental Materials

3.1.1 Heavy Oil Sample

In this study, a heavy bitumen sample from Plover Lake, Saskatchewan, of western Canada at original viscosity of 132,000cP was chosen for the experimental tests. For a visualization system, due to the very confined geometry of the system, a fluid sample with much too large viscosity will bring forth hassle due to the possibility of micromodel fracking under large flow resistance to the viscous flow. If a very viscous fluid sample has to be used, it is highly suggested that the micromodel system should be heated up to reduce the flow resistance. Hence, in this study, in order to test the feasibility of the micromodel system in terms of non-equilibrium phase behavior characterization, the heavy oil sample was modified manually to reach a lower viscosity range for the research purpose. Kerosene was added to heavy oil sample at a specific volume ratio, and subsequently, the mixture was stirred for up to 24 hours in a sealed environment (preventing the vaporization of kerosene) to become uniform and the diluted heavy oil was continuously tested by Brooksfield viscometer until desired viscosity (1500cP @ 20°C in this study) was reached. Then, heavy oil was sent for a compositional analysis, up to C60+ by the simulated distillation method. The table 3.1 below shows the heavy oil compositional analysis results:
Table 3.1 Heavy Oil Compositional Analysis

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>mol%</th>
<th>Carbon Number</th>
<th>mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.00</td>
<td>C31</td>
<td>0.994</td>
</tr>
<tr>
<td>C2</td>
<td>0.00</td>
<td>C32</td>
<td>0.967</td>
</tr>
<tr>
<td>C3</td>
<td>0.00</td>
<td>C33</td>
<td>0.907</td>
</tr>
<tr>
<td>C4</td>
<td>0.00</td>
<td>C34</td>
<td>0.865</td>
</tr>
<tr>
<td>C5</td>
<td>0.00</td>
<td>C35</td>
<td>0.835</td>
</tr>
<tr>
<td>C6</td>
<td>0.00</td>
<td>C36</td>
<td>0.760</td>
</tr>
<tr>
<td>C7</td>
<td>0.00</td>
<td>C37</td>
<td>0.684</td>
</tr>
<tr>
<td>C8</td>
<td>0.00</td>
<td>C38</td>
<td>0.666</td>
</tr>
<tr>
<td>C9</td>
<td>8.566</td>
<td>C39</td>
<td>0.670</td>
</tr>
<tr>
<td>C10</td>
<td>11.209</td>
<td>C40</td>
<td>0.618</td>
</tr>
<tr>
<td>C11</td>
<td>8.863</td>
<td>C41</td>
<td>0.570</td>
</tr>
<tr>
<td>C12</td>
<td>2.726</td>
<td>C42</td>
<td>0.553</td>
</tr>
<tr>
<td>C13</td>
<td>2.150</td>
<td>C43</td>
<td>0.540</td>
</tr>
<tr>
<td>C14</td>
<td>2.429</td>
<td>C44</td>
<td>0.541</td>
</tr>
<tr>
<td>C15</td>
<td>2.446</td>
<td>C45</td>
<td>0.544</td>
</tr>
<tr>
<td>C16</td>
<td>2.537</td>
<td>C46</td>
<td>0.522</td>
</tr>
<tr>
<td>C17</td>
<td>2.467</td>
<td>C47</td>
<td>0.525</td>
</tr>
<tr>
<td>C18</td>
<td>2.399</td>
<td>C48</td>
<td>0.494</td>
</tr>
<tr>
<td>C19</td>
<td>2.374</td>
<td>C49</td>
<td>0.458</td>
</tr>
<tr>
<td>C20</td>
<td>2.209</td>
<td>C50</td>
<td>0.449</td>
</tr>
<tr>
<td>C21</td>
<td>2.065</td>
<td>C51</td>
<td>0.419</td>
</tr>
<tr>
<td>C22</td>
<td>1.879</td>
<td>C52</td>
<td>0.368</td>
</tr>
<tr>
<td>C23</td>
<td>1.699</td>
<td>C53</td>
<td>0.324</td>
</tr>
<tr>
<td>C24</td>
<td>1.552</td>
<td>C54</td>
<td>0.345</td>
</tr>
<tr>
<td>C25</td>
<td>1.428</td>
<td>C55</td>
<td>0.362</td>
</tr>
<tr>
<td>C26</td>
<td>1.378</td>
<td>C56</td>
<td>0.326</td>
</tr>
<tr>
<td>C27</td>
<td>1.291</td>
<td>C57</td>
<td>0.298</td>
</tr>
<tr>
<td>C28</td>
<td>1.248</td>
<td>C58</td>
<td>0.274</td>
</tr>
<tr>
<td>C29</td>
<td>1.184</td>
<td>C59</td>
<td>0.260</td>
</tr>
<tr>
<td>C30</td>
<td>1.090</td>
<td>C60+</td>
<td>18.596</td>
</tr>
</tbody>
</table>

MW: 374 g/mol  Density: 0.97302 g/cm³  μ:1500 cP@20°C
From the above compositional analysis, it is indicated that the addition of kerosene reduced the viscosity of the heavy oil sample to a large fold from 132,000cP down to 1500cP, and the percentage of the lighter components from C₈ to C₁₆ up to C₃₀ is much larger than the original bitumen sample at 132,000cP. Also, the addition of kerosene into the heavy oil would greatly reduce the heavy oil density, which can be substituted by toluene in the future study if density property of the oil sample is aimed to be kept constant. A higher content of light hydrocarbon components in the heavy oil sample will impose an effect on the dissolution/solubility behavior of the solvent. The density of the original bitumen dropped from 0.999 g/cm³ to 0.97302 g/cm³ under ambient condition.

3.1.2 Gaseous Solvent, Pressure Control and Pumping System

Pure CO₂ solvent at 99.99% purity level and a mixture solvent sample of Carbon dioxide (CO₂ 85% mole fraction) + Propane (C₃H₈ 15% mole fraction) (supplied by Praxair Canada) at a purity of 99.99% was mainly used as the solvent type to conduct all the tests. And prior to each test, nitrogen gas at a purity of 99.97% was used for leakage test. For the back pressure regulator at the physical model outlet and ISCO pump, de-ionized water was utilized to act as a pressure transfer medium in transfer cylinder.

3.2 Experimental Setup

The experimental setup is mainly composed of three categories: live oil recombination and differential liberation test unit, physical model unit (including bulk phase visual cell and micromodel systems) and data acquisition unit. Detailed explanations are elaborated in the following paragraphs.

3.2.1 Live oil Recombination and Differential Liberation Test Unit
Live oil recombination is the most important preliminary procedure before all the tests. In order to conduct all the non-equilibrium phase behavior tests, equilibrium properties of the solvent-heavy live oil systems have to be known beforehand for the comparison of the deviation from equilibrium state. Therefore, live oil recombination and differential liberation test unit was designed to fulfill the purpose. With the help of live oil properties analysis, we can obtain a series of meaningful data for understanding solvent injection processes, including phase mole/volume fraction under equilibrium, oil phase swelling factor, solvent solubility and composition, GOR, in-situ density, in-situ viscosity, etc. The device for recombining live oil is composed of solvent gas cylinder, gas pressure regulator, digital pressure gauge, injection tubing and valves, two stainless-steel high-pressure transfer cylinders, two high pressure 500mL ISCO pumps.

By linking the two stainless steel cylinders together, a path for gas-oil system to travel back and forth in the two cylinders is created, hence creating a mixing effect. The figure 3.1 below shows the apparatus for recombining solvent-heavy live oil systems.
Figure 3.1 Live oil recombination unit
Live oil differential liberation test unit was designed to fulfill the purpose of measuring various live oil properties under different pressure. The design shown in figure 3.2 is complicated due to the fact that pressure maintenance of live oil system is extremely important, and if the pressure is not controlled accurately, the properties test will not be accurate enough to represent live oil properties. And therefore, the valves and their position setting are of crucial significance in designing the differential liberation unit for two-phase flash equilibrium tests.

In the live oil differential liberation unit, several stainless-steel transfer cylinders were used to transfer fluid for different purposes. In addition, the live oil differential liberation unit is composed of a capillary coil viscometer, an Anton Parr® densitometer, Swagelok® high-pressure miniature (40mL) live oil sampler, several back-pressure regulators, digital mass flow meter, an advanced infrared gas composition analyzer, ISCO pumps, etc. Each of the items in the differential liberation units contribute to the measurement of the equilibrium properties of solvent-heavy live oil systems.
Figure 3.2 Live oil differential liberation unit
3.2.2 High-Pressure Bulk Phase Visual Cell

As illustrated above, physical model contains multiple units for corresponding functions. For the highly visual Hele-Shaw cell, it is mainly serving as the observation window of the whole experimental process. The size of the Hele-Shaw cell goes by length×width×depth as 30.5cm×5cm×0.02cm. The aperture size of the visual cell can be adjusted by inserting metal shim stocks or gaskets of different thickness, from 100µm to 600µm. The designed pressure of the Hele-Shaw cell is at 10MPa. Stainless steel plates serve as confining pressure. Due to the very thin nature of the Hele-Shaw cell aperture, the physical phenomena could be easily observed by putting a LED light at the back of the model and a high-speed camera or a microscope at the front. Highly accurate digital pressure gauge at an error of ±0.5kPa was utilized to capture pressure change during each individual test. Both reservoir-conditioned flash and surface-conditioned flash apparatus was installed prior to and after the BPR exit of the system, respectively. A back-pressure regulator was set at the outlet of the model to serve as a pressure barrier. At the downstream of the model outlet BPR, a digital gas mass flow meter was set to capture the flow rate of the produced gas under atmospheric pressure. In order to verify the captured data of the digital gas mass flow meter (DFM), a DBR stainless steel cylinder was installed at the downstream of the DFM to store the produced gas, preventing produced gas from leaking out. Therefore, a closed system was formed. The DBR transfer cylinder was controlled by maintaining a fixed pressure at atmospheric pressure using ISCO pump, therefore, when gas was flushed into the transfer cylinder, the floating piston would retreat to receive the produced gas to maintain the prespecified pressure.
Figure 3.3 Original bulk phase visual cell setup (simplified version in figure 3.8 (d))
### 3.2.3 High-Pressure/Temperature Micromodel System

In this research, a micromodel apparatus was utilized to fulfill the purpose of solvent-heavy live oil non-equilibrium measurement under the presence of porous media. A uniform porous media pattern on glass micromodel was designed by AutoCAD, and transferred into LaserCAD to be processed by Boss Laser® engraving machine. The designed pressure upper limit for the glass micromodel was 4MPa. With a micromodel high-pressure/temperature holder in the research group, the upper limit of the operating pressure can rank up to 40MPa and temperature at above 100°C. For the non-equilibrium tests conducted in glass micromodel including static Constant Composition Expansion CCE (SCCE) tests, foamy oil continuously convective flowing (CCF) tests, solvent diffusion and pressure depletion tests, solvent flooding and post-flooding pressure depletion tests, the operating pressure was all controlled under 1.5MPa and under ambient temperature (20°C), and thus, no micromodel high-pressure/temperature holder was needed.
Figure 3.4 Micromodel system setup (a) solvent dissolution and exsolution test (b) static Constant Composition Expansion (SCCE) test (c) continuously convective flowing (CCF) test (d) solvent flooding and post-flooding pressure depletion tests
3.2.4 Data Acquisition System

A LED light source was positioned at the back of the visual cell and microfluidics system for the facilitation of the image capturing. A digital scale (±0.005g accuracy, max weight 650g) was used to measure weight of the surface-flashed oil phase weight and live oil collecting sampler to determine oil density. Digital pressure gauge was linked to computer and record the pressure reading. Digital mass flow meter (AALBORG®) was connected to capture gas flow volumetric readings. A high-speed and high-resolution automatic camera was utilized to capture the real-time images of the system. Different resolution could be chosen for the image quality. Image processing will utilize the captured pictures and quantify the experimental data. An advanced infrared gas compositional analyzer, as an alternative to gas chromatography, was positioned at the outlet of both the live oil unit and the visualization cell to capture the dynamic solvent compositional change at solvent exsolution from live oil phase during pressure depletion stage. Teledyne® ISCO pumps in the experimental system were linked to computer via RS232-USB port and LABVIEW user interface, and therefore, the pump information shown on the pump controller could be recorded down and form CSV excel file to instantaneously obtain pump data. Heise® digital pressure transducers were utilized to record the pressure of the system at any time with the HyperTerminal® interface.
Figure 3.5 LabView user interface and pump data real-time acquisition interface
3.3 Experimental Procedures

In this section, detailed experimental procedures on measuring solvent-heavy oil non-equilibrium phase behavior will be illustrated. The procedures include live oil differential liberation tests, bulk phase visual cell tests, and micromodel tests. Especially, for microfluidics-based study, it is extremely crucial to maintain a smooth and meticulous control on the system in order not to break up the delicate glass parts.

3.3.1 Live Oil Differential Liberation Tests

Prior to any tests, solvent-heavy live oil was recombined in the live oil recombination unit for the preparation of equilibrium properties tests. Subsequently, live oil would be undergoing two procedures for the equilibrium properties measurement: 1, two-phase flash under reservoir condition; 2, live oil liquid-phase flash under surface condition. The two-phase flash under reservoir condition is aimed to provide the equilibrium phase mole and volume ratio in a solvent-heavy live oil system under certain pressure and temperature in a closed system. The live oil liquid-phase flash under surface condition to achieve the oil phase properties, such as solvent solubility, GOR, viscosity, density etc.

3.3.1.1 Live Oil Vapor-Liquid-Two-Phase Flash Tests under Reservoir Condition

Prior to any tests, CO$_2$-C$_3$H$_8$-heavy live oil was prepared by mixing the dead oil and gaseous solvent at an initial mole fraction of oil-to-solvent 45.879:54.121 at P=4000kPa in transfer cylinders with the aid of the ISCO pump. The pressure was set and oil and gas were pushed back and forth within the transfer cylinders to create a mixing effect. The gas solubility was considered reaching equilibrium state at a final stable pressure variation within 10kPa after a day. Then, live oil vapor-liquid two-phase flash tests was conducted
to achieve equilibrium phase mole/volume ratio prior under reservoir condition. The
detailed procedures of live oil differential liberation tests are listed as the following for
clarity:

(1) Live oil sample was recombined in live oil mixing unit by injection of CO$_2$-C$_3$H$_8$
mixture and dead oil sample at a mole fraction of 45.88:54.12 at $P_{inj}=4000$ kPa based
upon the dead oil volume injected in the transfer cylinder; Then by pushing the gas-oil
mixture back and forth inside the live oil mixing unit, live oil was recombined to
dissolve all the free gas phase into the oil phase;

(2) The freshly prepared live oil was stored in one of the transfer cylinders, named C1,
and transported into the other transfer cylinder, named C2, for 60~80 mL (in order to
prepare enough live oil volume for density measurement in Swagelok® miniature
sampling cylinder) to be used as the live oil two-phase flash experimentation; such
volume should not be too large so as to make sure all the exsolution gas volume can
be contained in C2, and thus, requiring less transfer cylinder to process the two-phase
flash;

(3) By controlling the ISCO pump 2 linked to C2, the pressure of the live oil single
phase system in the C2 was reduced to the targeted pressure, for instance, 3500 kPa,
and thus, since the pressure in C2 was reduced, and therefore the volume of C2 will be
expanded. Due to the viscous effect, the gas exsolution might not reach equilibrium
easily under static condition. Therefore, in order to fully expelled the trapped gas in
the live oil phase after volume expansion and pressure reduction of C2, by using An
extra cylinder, C4, the gas-foamy oil contained in C2, was pushed back and forth
between C2 and C4 at the targeted pressure as the same procedure in step 1; after at
least 20 strokes, the fluid was transferred back to C2 and let rest at fixed pressure for a day with pressure being monitored to vary less than ±5kPa;

(4) After step 3, the fluid system in C2 is now assumed to be in equilibrium; then starting to push the fluid in C2 towards the C3 as the receiving cylinder under targeted pressure; between C2 and C3, there is a very small sandpacked column installed, and this sandpacked column is to detect whether liquid phase has started be pushed through it. In the process of pushing fluid from C2 towards C3, the pressure is kept being monitored and if the pressure suddenly increases at a rapid rate, it is assumed that the liquid starts to invade into the sandpacked column. Then the shut down the pump and turn off the valve linking the outlet of the sandpacked column. Record pump 2 and pump 3 volume for liquid and vapor phase volume, respectively for two-phase flash phase mole/volume fraction calculation; then push the vapor phase in C3 through the back-pressure regulator towards the digital gas flow meter and gas compositional analyzer for solvent composition analysis.

(5) Shut down the valve from C2 towards C3, and pressurize the system from C2 towards the BPR by nitrogen. Then start to push the fluid in C2 towards the capillary coil viscometer and density measurement chamber to measure live oil phase viscosity and density; then under surface flash, the live oil will be separated into two-phase fluid, the oil phase is collected in the flask sealed by rubber plug for oil mass calculation, and gas phase is flashed through the outlet of the rubber plug into the digital mass flow meter to detect the solution gas GOR/solubility and solvent compositional change.

(6) Step 1~4 is repeated for the characterization of two-phase flash in order to achieve the vapor-liquid phase mole/volume ratio, vapor phase solvent composition ratio at
certain pressure and temperature, and step 5 is repeated for the characterization of liquid phase solution GOR, solution gas composition analysis, live oil viscosity, live oil density etc. Since live oil is always depleted from initial pressure at 4000kPa, and therefore, the mass balance can be conveniently calculated based upon the initial mole ratio between solvent and heavy oil. The detailed procedure is discussed in the section 3.3.1.2 in the following paragraphs.

**3.3.1.2 Live Oil Liquid-Phase Surface-Condition Flash Tests**

After conducting the two-phase flash properties tests following step 1 to 4 in section 3.3.1.1, basic properties of the liquid phase in the CO2-C3H8-heavy live oil system was then measured by surface-condition flash following the step 5. These properties include oil phase swelling factor, solvent solubility and dissolved composition, GOR, in-situ density and in-situ viscosity. The methodology of obtaining each property is shown as:

- **Oil swelling factor:**
  
  By pumping a certain volume $V_{pump}$ using the ISCO pump, the live oil was driven out of the live oil cylinder towards the surface-condition flash unit. Then after the live oil flowed out of the BPR into the collecting flask, the amount of mass of the collected oil was recorded. The collected oil was left in the flask for sufficiently long time, and the dissolved gas would flash out eventually under surface condition. By weighting method, the volume of the de-gassed dead oil could be calculated based upon the known dead oil density and the collected weight of the dead oil, hence $V_{deadoil}$. Then swelling factor $SF$ was calculated as the ratio of $V_{pump}: V_{deadoil}$.

- **Solution GOR:**
By applying the same technique, the live oil sample was collected in the oil/gas flash separator. A digital mass flow meter and gas bubbler apparatus were both used to measure the flashed gas volume at atmospheric pressure, $V_{\text{gas}}$. The ratio of $V_{\text{gas}}:V_{\text{dead oil}}$ is the gas-oil-ratio of live oil sample at different saturation pressure.

- **Solvent solubility and exsolution composition:**
  
  By acquiring the GOR, one can translate the value into a mole fraction of solvent in solvent-heavy oil mixture at different saturation pressure, and hence the solvent solubility in both $\text{wt}\%$ or $\text{mol}\%$ could be achieved. And by letting the flashed gas flow through the infrared gas compositional analyzer, the molar fraction of each solvent component in the mixture solvent could be detected, and once the reading became stable after a period of time, one can take an average of the reading as the solvent exsolution composition at the prevailing pressure. And the following figure 3.6 shows the CO$_2$ reading of the exsolution mixture solvent during live oil properties test at one saturation pressure.

- **In-situ density:**
  
  A live oil sampler of fixed value (40mL cylindrical sampler from Swagelok®) was parallelly connected to the live oil properties test apparatus. Live oil was passed through the sampler, and then the sampler was detached from the apparatus and weighed. The live oil weight was achieved by calculating the difference between the filled sampler and empty sampler, and thus by knowing the volume of the sampler, the density of the live oil could be calculated by universal law: \( \text{mass} = \text{density} \times \text{volume} \). The second measurement technique was utilizing a parallelly connected Anton Parr® densitometer to measure the density, however, due to a strict requirement of the
sampling technique inside the densitometer chamber, the reading of the densitometer sometimes could not stabilize, and any small pressure fluctuation caused by the transfer of live oil phase would greatly elongate the time to reach a stabilized reading. Hence, sampling and weighing method by universal physics law mass=density×volume is a more direct and accurate method to measure density in this study.

- **In-situ viscosity:**

A capillary coil viscometer was applied to measure live oil viscosity at different pressures. The Poiseuille’s Law served as the theoretical basis as the following equation:

\[
\mu_{live\ oil} = \frac{\pi (r_{effective})^4 \Delta P}{8 q L}
\]  

(3.1)

Where, \(r_{effective}\) is the cross-sectional radius of the capillary coil tubing, \(\Delta P\) is the pressure differential between the inlet and the outlet of the capillary coil tubing, \(q\) is the set pumping volume flow rate of the ISCO pump, and \(L\) is the length of the total capillary coil tubing. A flow rate of 0.25 cm³/min was applied to test the live oil viscosity.
Figure 3.6: An example schematic of continuous solvent compositional measurement.
3.3.2 Non-Equilibrium Tests in Bulk Phase Visual Cell

In this series of tests, non-equilibrium phase behavior of solvent-heavy live oil systems was measured in the bulk phase visual cell. Solvent dissolution/diffusion tests on CO₂-heavy oil system was conducted by the traditional pressure decay method. Different pressure decay curves were obtained under various operating pressure. The pressure decay curves would also serve as the history matching objectives to achieve the diffusion coefficient of CO₂ in heavy oil phase in the numerical simulation studies in Chapter 6. For solvent exsolution/pressure depletion tests, both CO₂- and CO₂-C₃H₈-heavy live oil systems were tested. The only difference was that, for CO₂-heavy oil system, the pressure depletion was conducted right after the end of the diffusion processes, while for mixture solvent, the pressure depletion was begun with fully saturated live oil phase.

3.3.2.1 Solvent Dissolution/Diffusion Tests

For solvent dissolution/diffusion tests, the applied methodology was pressure decay method (Riazi 1996). Traditionally, pressure decay tests were conducted in a PVT cell or a non-visual transfer cylinder. The shortcomings are either time-consuming (requiring a long time before the whole system reaches equilibrium state due to requiring a much larger fluid volume and diffusion penetration depth) or non-visual (no observations can be done to visually determine the swelling factor, hence often yielding a relatively larger solvent solubility due to the ignorance of the swelling factor). Therefore, A novel PVT phase behavior methodology utilizing high-pressure Hele-Shaw-like visual cell has been developed to conduct study on solvent dissolution and exsolution behavior of a CO₂-heavy live oil system. The experimental setup overcomes the visualibility shortcomings of traditional apparatus. The dynamic oil-gas interface can be accurately captured due to the
thin nature of the Hele-Shaw cell. Dead oil diffusion tests were conducted by pressure
decay method in the visual cell. Several different initial gas injection pressures were tested.
Firstly, the dead oil was injected from the bottom of the Hele-Shaw-like model. Secondly,
the BPR pressure was set to a pressure higher than the estimated initial CO\textsubscript{2} injection
pressure. Then the valves at the bottom of the Hele-Shaw-like cell were shut, and carbon
dioxide was injected from the top of the model after vacuuming the system up to -90kPag
for more than 10 minutes. After CO\textsubscript{2} injection, the system was closed by shutting the
valves off to create a closed system. Last, the LED light was positioned behind the Hele-
Shaw-like cell, and the high-speed automatic camera was used to capture images at a
specific time interval during the pressure decay period. After the pressure in the Hele-
Shaw-like model reached a flat trend, and was not fluctuating for at least one day, the
pressure decay test will be ended. Dynamic pressure and oil phase volume during the test
would then be achieved by digital pressure gauge and processed image, respectively. The
pressure and oil phase volume data would be used to calculate the CO\textsubscript{2} solubility as well
as CO\textsubscript{2}-in-oil diffusion coefficients by reservoir simulation in Chapter 6 as the history
matching objective data.

The schematics of a pressure decay test for solvent solubility and solvent-in-oil diffusion
coefficient determination is shown in the following figure:
Figure 3.7 Solvent dissolution/diffusion tests were mainly conducted on CO$_2$-heavy oil system (Etminan 2012)
As can be seen from figure 3.7, gas pressure in the vapor phase of the closed system will decline as the molecular diffusion happens. With a high pressure of gas injection, the concentration of CO$_2$ solvent in the gas phase is higher than that of the oil phase. Under such concentration difference, a Brownian movement of solvent molecules will occur and in macro point of view, diffusion. As time goes by, with more and more gas molecules diffuse into the oil phase, the concentration in the gas phase will be lower, and the diffusion process will be slower. That is why in pressure decay curves, the pressure drops at a very sharp rate at the beginning of the test and then gradually flattens out.

3.3.2.2 Solvent Exsolution/Pressure Depletion Tests

Pressure depletion tests were conducted in the bulk visual cell to test the non-equilibrium solvent exsolution behavior of a solvent-heavy oil system. The formation of foamy oil and the detailed gas bubble behavior under different pressure depletion schemes were tested by visualization and subsequently quantified by image processing. Solvent exsolution behavior of mixture solvent was captured instantaneously by gas compositional analyzer. During pressure depletion, the BPR was regulated by the ISCO pump and the DBR cylinder at the downstream of the BPR was set to atmospheric pressure on the pump controller. In other words, when the BPR pressure was depleted down to a certain value, dissolved solvent would form exsolution and expand through the BPR. When the live oil mixture expanded out of the visual cell, the high-pressure liquid trap would help to separate the gas-oil mixture and let out the gas through the BPR and eventually into the gas analyzer and the DBR transfer cylinder. Since the ISCO pump was directly linked to the displacing fluid end of the DBR cylinder, and the ISCO pump was set at atmospheric pressure, and thus, when the gas exsolution “touched” the piston of the transfer cylinder,
the pressure would be propagated along the pump fluid containing chamber, and the ISCO pump would maintain the pressure accordingly by withdrawing the volume of the displacing fluid inside the DBR transfer cylinder. Hence, the volume data shown on the ISCO pump controller would be the indicator of how much gas was received from the live oil system in order to determine the overall mass balance and other properties of the system such as total vapor/liquid volume/mole fraction of the system. The understanding of these parameters helps to characterize the non-equilibrium of the solvent-heavy oil system.

(1) CO₂-Heavy Oil System

For CO₂-heavy oil system, the solvent exsolution, or rather, pressure depletion tests were conducted right after each set of diffusion tests. When the pressure decay curve became less fluctuated and flattened out, the diffusion process was considered to be ceased. Then, by controlling the back-pressure regulator, the system pressure was adjusted by letting excessive gas phase out of the BPR to fulfill the purpose of pressure depletion. With such pressure drawdown from the equilibrium pressure at the end of the pressure decay tests, the dissolved CO₂ component in the oil phase would be unstable due to thermodynamically deviation from saturation pressure, and tent to form exsolution. Then, by capturing images and conducting image processing, the volumetric behavior of foamy oil phase can be quantified. The experimental data would then be used to serve as the history matching objective data in numerical simulation in Chapter 6 to describe the dynamic exsolution behavior of solvent out of the oil phase. During the tests, the immediate pressure depletion refers to -300kPa/min for a rapid drop.

(2) CO₂-C₃H₈-Heavy Live Oil System
Unlike the above-mentioned CO₂-heavy oil system, in this series of tests, the oil sample that was used to conduct pressure depletion tests were a directly pre-recombined live oil sample as shown in section 3.3.1. With a certain mole fraction of mixture solvent CO₂-C₃H₈ to dead oil, live oil was recombined for direct pressure depletion tests. Also, all the tests were conducted in a closed system. As shown in figure 3.8 (a) and (b), the initial fill-up percentage of the live oil in the visual cell was divided into fully-filled and half-filled. For a fully-saturated visual cell test, the visual cell was 100% saturated with live oil and there was not a free gas cap, while for a half-saturated cell, the fill-up percentage was around 44%, and there was a high-pressure free gas cap in the system. The live oil used in all the tests were under over-saturated condition, which meant that under the initial pressure of the test, the mixture solvent was at its maximum solubility, and the free gas cap would not dissolve into the live oil phase to alter its composition. Since the infrared gas compositional analyzer was mainly operated under atmospheric pressure, and therefore, as shown in figure 3.8(d), a BPR and a high-pressure liquid trap made by Swagelok ¼” stainless tubing was used for conducting a reservoir-condition flash, and the exsolution gas could be discharged out of the BPR and received into the transfer cylinder set at atmospheric pressure by ISCO pump after flowing through the gas analyzer. Under such circumstance, the oil phase was always under reservoir condition. For quantifying the non-equilibrium liquid/vapor phase mole/volume ratio, it is essential to have the assumption that the oil phase volume change was negligible compared to gas phase volume after solvent exsolution. By reading the volume of the received gas volume on the pump controller, one can easily figure out the total vapor phase volume that was exsolved out of the live oil phase.
Per figure 3.8 (d), the detailed experimental procedures of CCE tests in the bulk phase visual cell are as the following:

**Fully-saturated cell tests (live oil saturated at 100% of visual cell volume):**

1. To ensure a single phase state of live oil, prior to any live oil saturation in the visual cell, live oil was transferred back and forth between DBR transfer cylinder 1 (denoted as C1) and DBR transfer cylinder 2 (denoted as C2) to make sure a uniform dissolution of gas in the oil phase was reached.

2. The bulk phase visual cell was connected into the system. By opening valve 1 and closing valve 2, the live oil from C1, was transferred into the visual cell.

3. By closing valve 5, and opening valve 6, the live oil can be received back into C2. C2 was set at saturation pressure of the live oil at constant mode by ISCO pump to receive the live oil.

4. After several PVs of live oil was transferred from C1 to C2, the valve 1 and valve 6 were closed. By opening valve 2, live oil received in C2 was transferred back into C1 till the volume reading on C2 became zero, indicating the C2’s floating piston had reached the end and no more vacant volume was existed in C2.

5. By switching the 3-way valve towards the exhaust, the C2 pressure was released to atmospheric pressure. This is because the gas compositional analyzer works only under atmospheric pressure.
6. Valves 1, 2, 5 and 6 were all closed. By opening up valve 3 and 4, high-pressure gas (in this case, CO₂) was injected into the stainless-steel liquid trap to pressurize the system to the live oil saturation pressure.

7. By closing valve 3 and opening valve 5, the pressure of the live oil in the visual cell was maintained by the very small amount of high-pressure CO₂ in the liquid trap as well as the very short tubing before BPR. The BPR was maintained at live oil saturation pressure at all time to make sure the over-saturated state of the live oil.

8. By controlling the BPR pressure at different pressure operational schemes, the live oil in the visual cell was de-pressurized, and expelled out of the visual cell towards the liquid trap so that the oil stayed under reservoir condition, while the exsolution gas flowed out of the BPR, flowed through the gas compositional analyzer and finally collected in the C2 where the pressure was set under Constant Pressure mode by ISCO pump at atmospheric pressure.

9. The volume of the flashed gas phase was recorded by the ISCO pump controller and the data was simultaneously transferred through RS-232-USB cord to laptop LabView interface at pre-specified time step and data frequency.

**Partially-saturated cell tests (including half sample at 44% of visual cell volume, and small sample at 16% of visual cell volume):**

1. To ensure a single phase state of live oil, prior to any live oil saturation in the visual cell, live oil was transferred back and forth between DBR transfer cylinder 1 (denoted as C1) and DBR transfer cylinder 2 (denoted as C2) to make sure a uniform dissolution of gas in the oil phase was reached.
2. Liquid trap was removed from the experimental setup. Valves 1, 2 and 6 were closed, valves 3, 4 and 5 were opened. CO₂ high-pressure gas stream was injected into the bulk phase visual cell at live oil saturation pressure. This aims to pressurized the visual cell prior to oil saturation.

3. When the pressure in the visual cell was stabilized at the live oil saturation pressure, valve 3 was closed.

4. By opening up valve 1, 4 and 5, live oil from C1 was connected and pressurized by the CO₂ gas cap in the visual cell. The BPR was maintained at live oil saturation pressure at all time.

5. Live oil in C1 was injected into the visual cell till a certain volume was reached to partially saturated the visual cell.

6. The injection was stopped and valve 1 was closed. By controlling the BPR pressure at different pressure operational schemes, both the pre-existing gas cap and the live oil phase inside the visual cell was de-pressurized, so the live oil phase was undergoing two-phase flash under reservoir condition inside the visual cell and was not flowing out of the visual cell. Meanwhile, the pre-existing gas cap and the exsolution gas out of the live oil phase flowed towards the BPR, flowed through the gas compositional analyzer and finally collected in the C2 where the pressure was set under Constant Pressure mode by ISCO pump at atmospheric pressure.

7. The volume of the flashed gas phase was recorded by the ISCO pump controller and the data was simultaneously transferred through RS-232-USB cord to laptop LabView interface at pre-specified time step and data frequency.
Figure 3.8 Schematics of mixture solvent exsolution behavior tests under different fill-up percentage of the visual cell: (a) fully-saturated visual cell (b) half-saturated visual cell (c) schematic of CCE MBE calculation (d) simplified bulk phase visual cell setup
As shown in figure 3.8 (c), the solvent mass in such a closed system can be quantified. For system 1 and 2, if \( P_1 V_1 / Z_1 = P_2 (V_1 + V_2) / Z_2 \), it indicates that there is no excessive gas exsolved from the live oil to change the molar mass of the gas phase. Noted that the volume of the flashed gas out of the liquid trap and towards the atmospheric pressure should be firstly converted back into the prevailing reservoir condition according to the real-gas law where \( V_2 \) is the targeted parameter:

\[
\frac{P_{atm} V_{atm}}{Z_{atm}} = \frac{P_2 V_2}{Z_2}
\]

For system 1 and 3, when the pressure was reduced to \( P_2 \), if \( P_1 V_1 / Z_1 \neq P_2 (V_1 + V_3) / Z_2 \), it indicates that there is excessive gas exsolved from the live oil and has already escaped to the gas phase, like the red dots in figure 3.8 (c) system 3. For instance, if the initial gas cap is \( \text{CO}_2 \), and the dissolution gas in the live oil include \( \text{CO}_2 \) and \( \text{C}_3\text{H}_8 \), then in order to calculate the excessive gas molar mass, we have the following relationship:

\[
\Delta V_{BB} + V_4 + V_{3\text{res}} = \frac{Z_2 (n_{\text{CO}_2}^{\text{initial}} + n_{\text{CO}_2}^{\text{exsolved}} + n_{\text{C}_3\text{H}_8}^{\text{exsolved}})RT}{P_2}
\]

Here \( V_{3\text{res}} \) is converted into reservoir condition from the flashed gas volume collected in the DBR transfer cylinder \( V_{3\text{atm}} \), \( Z \) is a function of the molar ratio of \( (n_{\text{CO}_2}^{\text{initial}} + n_{\text{CO}_2}^{\text{exsolved}}) \): \( n_{\text{C}_3\text{H}_8}^{\text{exsolved}} \). \( n_{\text{CO}_2}^{\text{initial}} \) is the \( \text{CO}_2 \) gas cap molar mass at the beginning of the test. Then by compositional analysis of the molar fraction of \( \text{CO}_2 \) to \( \text{C}_3\text{H}_8 \), the \( Z \) factor can be calculated, and hence the total molar mass of the gas phase. By knowing the \( n_{\text{total}}^{\text{exsolved}} = n_{\text{CO}_2}^{\text{initial}} + n_{\text{CO}_2}^{\text{exsolved}} + n_{\text{C}_3\text{H}_8}^{\text{exsolved}} \), the individual molar mass of \( \text{CO}_2 \) and \( \text{C}_3\text{H}_8 \) can be calculated by the known molar fraction. And according to real-gas law,
\[ V_{\text{single gas}}^{\text{CO}_2} = \frac{Z_{\text{CO}_2}(n_{\text{total}}^{\text{vapor}} - n_{\text{initial}}^{\text{vapor}})RT}{p_{\text{atm}}}, V_{\text{single gas}}^{\text{C}_3\text{H}_8} = \frac{Z_{\text{C}_3\text{H}_8}(n_{\text{total}}^{\text{vapor}})RT}{p_{\text{atm}}} \] (3.4)

\[ V_{\%}^{\text{vapor}} = \frac{\Delta V_{BB} + V_4 + V_{3}^{res}}{V_{\text{visual cell}} + V_{\text{cylinder}}^{res}} \] (3.5)

Hence, if each solvent component exsolution is presented as single gas in the system (also without gas cap), the volume of the individual component under atmospheric pressure can be calculated with the above equation set. This was used in the section 4.2.2 and the numerical simulation section 6.2.3. By the above-proposed methodology, the gas cap can be regarded as the piston inside a cylindrical PVT cell but in gaseous phase. In order to prevent further dissolution of gas cap into liquid phase, the tested live oil must be under supersaturated state under test pressure if there is any gas cap existed in the system so as to prevent more dissolution.

### 3.3.2.3 Single Bubble Exsolution and Dissolution Behavior Tests

Single bubble nucleation and growth behavior was investigated by manually creating a crevice on the edge of the shim stock. By meticulously cutting 2 pieces of shim stock and insert into the visual cell to clamp and form a gap of width at 850µm with a depth of 200µm, a crevice was sitting on the edge of the shim stock by manual cutting tool. Then live oil was saturated into the visual cell for pressure depletion tests. In this series of tests, the aim was to figure out the exsolution behavior of single bubbles reacting to pressure depletion rate, and extract the relationship of bubble growth volume against prevailing pressure and the corresponding time. In order to see if such bubble-scale bubble volume growth rate against prevailing pressure can be up-scaled and represent the macro-scale bubble exsolution behavior in porous media, the experimental relationship was
incorporated into the numerical simulation to verify if successful history matching of experimental data can be achieved. The experimental data was illustrated in Chapter 4 section 4.2.3. Numerical simulation based upon the relationship was elaborated in Chapter 6.

Single bubble dissolution behavior was investigated in the visual cell to see the bubble dissolution rate against prevailing pressure and time. After single bubble exsolution tests shown in figure 3.9 (b) (red arro:0.85mm), there were both gas and liquid phase randomly distributed in the visual cell. To ensure that the oil phase was out of solvent saturation, the system was rested under atmospheric pressure for at least two days to liberate all the dissolution gas. And then, by positioning the visual cell perpendicular to the ground, the system was re-pressurized by ISCO pump shown in figure 3.9 (a). The reason why to position the model perpendicular to the ground was that, by doing so, the excessive gas bubbles would be “crushed” by the newly injected high-pressure gas stream, and due to the wall effect, some of the bubble at the bottom of the observation gap would flow up along the shim stock edge, and some other smaller bubbles might be trapped in the oil phase. Therefore, instead of paying attention to all the bubbles in the system, we mainly focused on a single bubble as shown in figure 3.9 (c). After the re-pressurization of the solvent back into the narrow Hele-Shaw gap and randomly picking up one of the bubbles, the system was sealed by shutting off the ISCO pump that was re-pressurized to the live oil saturation pressure, and pressure decay was allowed to happen in the narrow gap. Since the system was then static without bulk motion, molecular diffusion would take place and gas bubble started to dissolve back into the oil phase slowly. By subsequently by continuously capturing the dissolution of the chosen single bubble, the bubble volume and
mass against pressure and time could be investigated. Based upon the initial volume and pressure, bubble mass can be calculated according to the real gas law: \( PV=ZnRT \), and hence, at the end of the pressure decay period, the final volume can be quantified through image processing and the final mass of the bubble can then be calculated. Another type of single bubble dissolution test was conducted by injection of a fixed amount of solvent and dead oil column into the narrow observation gap as shown in figure 3.9 (d). Procedures are detailly listed as the following. The visual cell was vacuumed and saturated from one end with a certain amount of dead oil. Then solvent was injected from the other end. Subsequently, another oil column was injected at the same side where the solvent was injected to form a “sandwich” on the vapor phase. The valve on the first side was shut down to create a closed system, while the other end which was connected to the dead oil injection transfer cylinder was gradually injected to the system. In addition, on the side of the visual cell, there are several ports that can be connected with tubing. With one of the ports being open, the excessive gas column can be expelled to control the amount of the initial gas column. Then the gas column was pressurized to an initial high pressure by adjusting the dead oil injection side with ISCO pump controller. The valve for dead oil injection side was later turned off to seal down the system. Pressure decay method was then used to characterize the mass transfer rate from vapor phase into liquid phase. With an extracted relationship between bubble dissolution rate against prevailing pressure and time, such relationship could also be incorporated into reservoir simulation to characterize the solvent dissolution processes in Chapter 6. Figure 3.9 briefly shows the time-elapse volume variation of a single gas bubble under these two types of tests. In section 4.2.4, single bubble dissolution behavior will be analyzed in details.
Figure 3.9 Single bubble dissolution processes under (a) solvent re-pressurization into post-pressure depletion gas-oil system and the isolation of a single bubble; (b) (red arrow: 0.85mm) and (c): bubbles and single bubble in the gap (d) controlled injection of a fixed amount of solvent column (red arrow: 0.85mm)
3.3.3 Non-Equilibrium Tests in Porous Media: Micromodel System

In this section, the experimental procedures of non-equilibrium phase behavior tests conducted in porous media: micromodel system will be illustrated. The following table and figure show the dimension details of glass micromodel used in this study:

Table 3.2 Glass Micromodel Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length, cm</td>
<td>12.3</td>
</tr>
<tr>
<td>Width, cm</td>
<td>3.8</td>
</tr>
<tr>
<td>Depth, cm</td>
<td>0.0123</td>
</tr>
<tr>
<td>Porosity, %</td>
<td>56</td>
</tr>
<tr>
<td>Pore Volume, cm(^3)</td>
<td>0.3219</td>
</tr>
<tr>
<td>Absolute Permeability to Water, Darcy</td>
<td>18</td>
</tr>
</tbody>
</table>

Figure 3.10 Glass Micromodel
3.3.3.1 Solvent Mixture Dissolution and Exsolution Tests

High-pressure glass micromodel was utilized to conduct the solvent dissolution and exsolution tests on dead oil system. Unlike section 3.3.3.1, there was not displacement process in the tests, which means there is no port for production of oil phase, and the whole system was static. At first, the micromodel was partially saturated with a small and fixed amount of heavy oil volume from one side of the model. Then, after the oil saturation, the valve of the dead oil injection side was turned off to seal down the system where oil phase cannot escape. Then, as shown in figure 3.11(b), the bright space where the red/white arrows are indicates the porous space where solvent was saturated at a pre-specified pressure. The arrow direction shows the solvent injection and diffusion direction like in figure 3.4(a) or 3.11(a) red: diffusion and green: exsolution. When the system pressure reached the pre-specified pressure, the solvent injection was shut down, and pressure decay was allowed to investigate diffusion processes in porous media like figure 3.11(a) red arrow. After the pressure decay curve reached equilibrium or near-equilibrium value, the gas cap was let out into the ISCO pump cylinder to expand the system volume, and thus, reducing the system pressure at a specific rate. A CSI cycle was then completed in such a micromodel system without oil production. Then a new cycle began by compressing the solvent contained in the ISCO pump cylinder back to the micromodel at the same injection pressure. Pressure decay curve was recorded for each set of test to see how solvent spatial distribution affected the curve, and how different pressure depletion rate altered the solvent spatial distribution in the micromodel after each cycle of pressure depletion. Both horizontal and vertical positioning of the micromodel was conducted to see the effect of gravity drainage on solvent dissolution and exsolution.
Figure 3.11 Solvent dissolution and exsolution processes in a micromodel (a) apparatus (b):(left-pointed arrow: dissolution; right-pointed arrow: exsolution)
3.3.3.2 Static Constant Composition Expansion (SCCE) Tests

Static Constant Composition Expansion (SCCE) tests were mainly conducted to mimic the CCE test in traditional PVT cell. Unlike PVT cell, there is no floating piston inside the micromodel and therefore, the volume expansion and compression were mainly controlled by directly connecting the micromodel outlet to an ISCO pump. The rod-driven piston inside the ISCO pump pressure chamber was treated the same as the floating piston inside a tradition PVT cell. Although control on micromodel is not as convenient as manipulating a PVT cell in terms of volume calculation, but due to the 2D nature of the micromodel, the fluid interface can be easily captured and quantified by image processing. In SCCE tests, live oil was used in the system to directly investigate the effect of pressure depletion on the non-equilibrium phase behavior of the solvent-heavy live oil system. SCCE tests have been conducted under multiple step-wise pressure depletion, aiming to compare with the foamy oil continuously convective flowing (CCF) tests under the same operating pressure.

The experimental schematics can be seen from figure 3.4 (b) and figure 3.12. The glass micromodel was linked in the closed loop of ISCO pump set in which live oil was stored inside. Then, live oil was discharged into the system to first expel the air out of the micromodel, and then by switching the 3-way valve, the live oil was re-pushed back in the closed loop. When around 2~3 PV of live oil was flooded through the micromodel, the pre-existing air was all displaced out of the all the tubing and single-phase live oil was continuously observed in the micromodel, the injection direction of live oil was switched back by 3-way valve into the closed loop. During the live oil saturation process, one of the ISCO pump cylinders in the closed loop was displaced to a zero volume. Eventually, a closed system was formed as shown in figure 3.4(b) and figure 3.12. Noticeably, for
microfluidics devices, the tricky part is the existence of the dead volume of the system, and hence, aiming to reduce the dead volume, HIP® tubing at 0.006” I.D. was used to form the connection tubing listed as the red lines in figure 3.4 (b), and the valves used in the study were ultra-low flow metering valves from Fitok® company that fits the connection of 1/16” tubing. In order to reduce the pressure differential caused by the small diameter tubing during the experimental processes, Poiseuille’s law was applied to calculate the anticipated pressure drop at various injection rate of heavy oil at various of viscosity values. Then, after such calculation, the tubing length was controlled at no more than 1.5cm and 3.0cm in straight and curved link respectively for tubing parts where 1/16” tubing was used (1/16” female nut plus ferrule size at 0.7cm long), and during the injection of heavy oil, the tubing link which was used as the path to pass through liquid into the micromodel was slightly wrapped and heated by heating tape to further reduce the heavy oil viscosity when they flow in the tubing. By measuring the dead volume of the closed system using ultra-low volume gas syringe, including low-flow metering valves, connections and tubing, it was measured to be around 0.025cm³, which is about 7.8% of the high-pressure glass micromodel pore volume at 0.3174cm³. In the experimental recording, the maximum decimal places of the ISCO pump available in the laboratory which is recordable is at 0.01mL (Teledyne ISCO “current” version D-series pump controller), therefore, with very small saturated live oil sample volume, the variation of the pump recording was very small as well and some of the volume expansion was not recorded due to the minimum value that can be read. The main parameter in these series of tests is the vapor phase volume fraction in the glass micromodel under pressure depletion. Since the actual solvent compositional change inside the visual glass micromodel cannot be measured, the phase
volume fraction of a closed system under unstable two-phase condition (according to Tangent Plane Distance analysis) will serve as the most direct and convenient parameter to be acquired to indicate the non-equilibrium phenomenon in the closed system as in our studies. The vapor phase volume fraction is a direct indicator because the difference between non-equilibrium and equilibrium vapor volume fraction in the porous media can clearly show how the non-equilibrium and unstable foamy oil phase evolves throughout the whole pressure depletion process. In a closed system built by connecting a micromodel and pump cylinder which collects the flashed gas phase out of the expelled oil from the micromodel, the assumption is that the oil phase that is driven out of the micromodel into the pump cylinder maintains its volume unchanged due to the negligible swelling/shrinkage factor. Then by recording the ISCO pump controller data, the withdrawn volume of total gas-oil mixture in the pump cylinder can be known. The vapor phase volume can be calculated by subtracting the pump volume data by the known produced/expelled oil volume. Hence, the volume of the flashed gas phase can be achieved to calculate the overall system vapor volume fraction and its deviation towards the equilibrium value. The following equations show how to achieve the vapor phase volume fraction of the overall system by acquiring the vapor volume fraction in the micromodel:

\[
V_{BB, in} = P V_{\text{micromodel}} \times \phi_{PV} \times V\%_{BB, image} \tag{3.6}
\]

\[
V_{BB, out} = V_{ISCO \text{ Pump}} - P V_{micromodel} \times \phi_{PV} \times V\%_{BB, in} \tag{3.7}
\]

\[
V_{vapor, total} = V_{BB, in} + V_{BB, out} \tag{3.8}
\]

\[
V\%_{vapor, total \_system} = \frac{V_{vapor, total}}{V_{liquid} + V_{vapor, total}} \tag{3.9}
\]
Where,

\( V_{\%BB_{image}} \): vapor phase volume fraction in micromodel

\( PV_{micromodel} \): micromodel pore volume

\( \phi_{PV} \): micromodel porosity

\( V_{BB_{in}} \): vapor phase volume in micromodel

\( V_{ISCO_{pump}} \): pump collected fluid volume

\( V_{BB_{out}} \): vapor phase volume collected in pump transfer cylinder

\( V_{vapor_{total}} \): total vapor phase volume in the closed system

\( V_{liquid} \): liquid phase volume

\( V_{\%vapor_{total\_system}} \): total vapor phase volume fraction in the closed system
Figure 3.12 Schematics of SCCE tests in micromodel
3.3.3.3 Foamy Oil Continuously Convective Flowing (CCF) Tests

In the CCF tests, instead of a closed system, the micromodel was in an open system. The inlet flow rate was controlled by ISCO pump and the outlet was controlled by BPR to allow fluid to flow out of the micromodel. This is because if we used the same HIP® small diameter tubing, a continuous injection of foamy oil under two-phase dispersed flow might build up a large pressure inside the micromodel, and hence the risk of micromodel fracking would be high. Therefore, unlike SCCE tests where dead volume of the system needed to be minimized and the total volume of the system is an important experimental parameter, CCF tests most focused on the effect of continuous flow on the variation of vapor phase volume ratio through the micromodel using Eulerian view. Thus, in order to achieve uniform Darcy-velocity and reduce the pressure build-up caused by tubing geometry in the micromodel, a relatively larger diameter tubing of 0.07” I.D. was used at the model outlet. The foamy oil was induced by creating a pressure differential between the inlet and the outlet of the micromodel. The inlet pressure of the live oil was controlled by a BPR which maintained the saturation pressure to prevent bulk gas from forming exsolution before entering the micromodel. Then by adjusting the BPR and setting up the outlet pressure, a pressure differential between saturation pressure and prevailing pressure can be created. Under such pressure deviation from equilibrium saturation pressure, the live oil injected was immediately put under unstable thermodynamic state (saturation-pressure deviation) and hence, according to the value of the pressure differential, the solution gas formed to different extents. In order to achieve a uniformly distributed displacement velocity of foamy oil in the micromodel, the foamy oil was pre-flushed through the micromodel at the set flow rate and outlet pressure at least 1.5~2 pore volume and more
pore volume at higher pressure differential and flow velocity. The vapor phase volume fraction was observed to be varying less than ±10% and the measurement began. If the variation of vapor phase volume fraction was higher than 10%, it means that the flow velocity cannot overcome the exsolution tendency caused by pure pressure differential, and the foamy oil flow injection rate would be adjusted at a step of 0.002mL/min on ISCO pump controller until the variation fell below ±10%. Hence, by recording the whole process and quantify the vapor phase volume fraction in the micromodel, the effect of continuously convective condition on the foamy oil stability can be examined. This test mimics the true condition of foamy oil flowing in a small section of the reservoir under certain flow rate and deviation from equilibrium saturation pressure.
Figure 3.13 Schematics of CCF tests in micromodel
3.3.3.4 Solvent Mixture Flooding and Post-Flooding Pressure Depletion Tests

Before soaking and pressure depletion stages of a CSI process, solvent injection is the first step to transfer energy into the reservoir by continuously injection of solvent at a specific rate. Solvent distribution in the reservoir after injection into the reservoir has a very significant effect on the following soaking and pressure depletion stages. For example, solvent gravity override might result in a less efficient solvent-oil contact area, and more oil would be expelled to the bottom of the reservoir that would naturally hinder its mobility due to density difference. Solvent viscous fingering is also another “headache” for solvent injection, in which solvent channeling will be highly possible that also reduces the contact between solvent and heavy oil phase. Once if the advantageous path for gaseous solvent is formed in the reservoir, it is highly possible that the recovery factor is going to be lowered, and the injected solvent will be wasted into some theft zone.

Hence, in order to physically observe the CSI processes, solvent flooding and post-flooding pressure depletion tests were conducted in micromodel system by using mixture solvent of 85 mol% CO₂ and 15 mol% C₃H₈. The oil sample used in the study was dead oil, aiming to see how solvent channeling would happen under a large viscosity ratio (0.0148cp:1500cp @ 20°C) in the solvent injection period.

In figure 3.14, a glimpse of solvent channeling was observed and this figure generally shows how the CSI process was conducted in the micromodel. Unlike sandpacked models, glass micromodel is more fragile, and non-meticulous control of injection might result in fracking of the glass. In the micromodel, in order to investigate the viscous fingering phenomenon, it is essential to have an open system in the micromodel to allow for the displacement of oil by gas, and therefore, two-well pattern was used. As can be seen figure
3.14, the red arrow indicates the direction for solvent injection into dead heavy oil phase where viscous fingering happened. After the breakthrough of gas, both the injection and production end of the micromodel were shut to allow for soaking period. During soaking period, solvent dissolved into heavy oil phase mainly by molecular diffusion. Pressure decay method was used to indicate the efficiency of gas mass transfer. After soaking period, as indicated by the green arrow, the production port was still set at the same side of flooding tests, and pressure depletion was applied to the production end by controlling the BPR pressure at different rates.

Totally 7 sets of solvent injection-soaking-production tests were conducted in the micromodel system which would be illustrated in detail in Chapter 5.
Figure 3.14 Solvent flooding and post-flooding CSI processes in micromodel system
3.3.4 Image Processing and Experimental Data Quantification

High resolution pictures were taken by Dinoeye® high-speed and resolution automatic camera. All the pictures captured were analyzed by ImagePro Plus 6.0 and an automated image processing code in MATLAB. Quantification of the visualized dynamic solvent-heavy oil system behavior in various tests was realized.

(1) Image processing of solvent dissolution and exsolution behavior in bulk phase visual cell

The advantage of utilizing a bulk phase visual cell compared with traditional PVT cell can be seen from figure 3.15. On the left-hand side, traditional PVT cell was utilized to conduct solvent-heavy oil phase behavior study. The black arrow indicates the floating piston of the cylindrical PVT cell, which separates the displacing fluid from the test fluid. The red and green arrow indicate the vapor phase and the liquid phase, respectively. It can be seen that during pressure depletion, the actual observable part that distinguishes between vapor and liquid is the interface of the green and red arrow. While for the part covered by green arrow, only a bulk and dark liquid phase can be observed. This is due to the 3D nature of the cylindrical PVT cell. For an equilibrium state characterization where the magnetic stirrer at the bottom of the cell agitates, a relatively clearer gas-oil interface can be seen. But for non-stirring case where non-equilibrium behavior is to be induced, a heavy oil coating on the glass tube wall will impose difficulty determining the exact fluid interface. For the bulk phase visual cell developed in this study, like (b) in figure 3.14, the 2D nature of the visual cell clearly shows the evolution of the fluid interface. The floating piston of the tradition PVT cell was replaced by utilizing a DBR transfer cylinder or directly using
ISCO pump fluid collecting chamber, and in order to reduce dead volume of the system at the greatest extent, as-short-as-possible tubing connections were used and fluid collecting transfer cylinder was directly connected to the outlet of the visual cell with zero initial volume. In such a setup, the DBR transfer cylinder or ISCO pump can be regarded as the floating piston in the traditional PVT cell. Volume expansion/compression of the system can be realized by controlling the transfer cylinder/ISCO pump. While the only difference between a traditional PVT cell and the bulk phase visual cell is that, for a traditional PVT cell, since the floating piston is directly positioned in the system and therefore, an initially single-phase live oil can be restored back to single-phase again even after pressure depletion by continuously pressurizing the floating piston and running the magnetic stirrer. While, for the bulk visual cell, it will be difficult to fully restore the system back to single-phase after pressure depletion on the live oil, this is simply because the piston in the DBR transfer cylinder or ISCO pump cannot reach into the narrow gap and there is no stirrer to efficiently agitate the system. Hence, for the bulk phase visual cell, in order to do every another test, live oil sample has to be re-discharged into the visual cell for at least 3~5 PV every time a new test is aimed to be conducted. Due to the very small volume that is needed in the visual cell, the experimental efficiency is still high.
Figure 3.15 Comparison between traditional PVT cell and bulk phase visual cell on the observation of gas-oil interface
Bulk phase characterization of non-equilibrium phase behavior includes solvent dissolution and exsolution behavior. For solvent dissolution, diffusion tests by pressure decay method was the main methodology. By taking pictures during the whole diffusion test at a certain time interval, the dynamic swelling behavior of the heavy oil under solvent dissolution was captured and analyzed by processing the pictures. The figure below shows the idea of how to yield the swelling factor through image analysis. From figure 3.16, the initial height of the gas-oil interface was known at the intersection of the two red arrows in the picture of the left-hand side, and thus, the initial dead oil volume and the gas cap volume can be calculated. At the end of the pressure decay test, the swelled gas-oil interface was indicated as the intersection of the two green arrows on the right-hand side, and the final solvent-saturated oil volume and the gas cap volume can be calculated. Based upon the volume and the recorded system pressure, the dissolved gas mole can be calculated and thus the solubility of CO₂ at each equilibrium pressure.
Figure 3.16 Image processing of live oil phase swelling phenomenon during pressure decay tests
Bulk phase characterization of foamy oil also includes pressure depletion tests. Unlike diffusion tests where solvent dissolution is the main mechanism, solvent exsolution under the interruption of stable state is the main mechanism in pressure depletion tests. Therefore, inevitably, a much “messier” gas-oil interface will be observed during solvent exsolution. In a traditional PVT cell, such “messy” gas-oil interface is almost non-visualizable due to the 3D nature, and it will be difficult to determine the appropriate boundary between foamy oil phase and gas phase during pressure depletion. This dynamic gas-oil interface, however, can be efficiently captured by our bulk phase visual cell as shown in figure 3.16.

From the figure 3.17 (a), it is seen that the foamy oil region is Area 2 on the left, and the free gas chamber region is the Area 1. The picture was taken during the generation and expansion of the foamy oil phase. On the right-hand side, the processed image shows that the Area 2’ is the area of the pseudo foamy oil phase, and its volume variation against time could be taken as the foamy oil endurance, or stability. And hence, the half life of the foamy oil mixture could be quantified.

The figure 3.17 (b) shows the whole process of how foamy oil was generated and stabilized over time. The red line indicates the initial height of the live oil interface, from which, the initial volume could be determined. Then by certain pressure depletion rate, the dissolved gas in the live oil mixture started to form exsolution. The foamy oil was generated and went through the processes: expansion $\rightarrow$ peaking $\rightarrow$ decay. The foamy oil phase volume is recorded as per discussed for figure 3.17 (a). Hence, the whole volume variation processes of foamy oil phase can be quantified.
Figure 3.17 Foamy oil phase volume quantification (a) foamy oil phase region (b) foamy oil volume variation at time-elapse order
Figure 3.18 shows the image processing procedures for bulk phase foamy oil bubbles. The live oil was saturated into the visual cell at an initial pressure. Then by pressure depletion, a certain area of the visual cell was magnified and the gas bubbles were captured. By image processing, various parameters of the bubbles could be determined. Figure 3.18 lower figure shows the example of calculating the histogram of bubble number density versus bubble mean diameter against time. It can be seen that, the greater number of smaller bubbles there were, the higher peak the histogram was towards to the origin side of the X axis. Then as time elapsed, smaller bubbles tended to coalesce together and form thicker/larger bubble, which is called Ostwald Ripening, and the histogram slowly shifted towards more right-hand side on the X axis, indicating larger bubbles were gradually taking places in the observed area. When the bubbles were finally thickened and coalesced as continuous gas cluster, continuous gas phase was formed and the peak of the histogram dropped and flattened eventually.
Figure 3.18 Schematics of dynamic histogram of the evolution of gas bubble number density versus mean bubble diameter
(2) Image processing of solvent dissolution and exsolution behavior in porous media micromodel system

In porous media, the image processing technique could be a bit “trickier”, as the porous grain might have very similar color as the gas bubbles because of the transparency through light. One may encounter a situation that during screening the color scale for the bubbles, the grains might be included as well. There are roughly two ways to address this issue. The first one is the screen out the brighter region of the image and toggle off the objects that belong to the solid phase in the porous media. The second one is the find out the color histogram after eroding the boundary regions of the picture such as the perimeter of the grains and bubbles. Then by giving a certain limitation in object counting, such as choosing roundness of the objects, or giving an appropriate limit for light density etc., one may be able to screen out the targeted objects in the picture. For the first method, if the counting area is not too big, which contains less amount of grains, it is feasible and more accurate. With the aid of watershed splitting, smaller objects could be easily defined its statistical properties in the image. And for the second method, the counting area could be bigger with more grains in it, so the time for screening the grains from the bubbles will be shorter for each image to be processed. But the accuracy will be slightly lower than the first method. In our case, the first method could be used to count the bubbles and the overall vapor phase volume fraction in the pictures.

The following figures show how to extract the vapor phase from the picture and conducting the statistical analysis:
Figure 3.19 Extraction of vapor phase from porous media (red arrow: 1mm)
Figure 3.20 Procedures of vapor phase extraction from image by screening RGB segmentation and toggling objects off in an example domain of 1cm by 0.75cm
CHAPTER 4 EXPERIMENTAL STUDY OF SOLVENT NON-EQUILIBRIUM DISSOLUTION AND EXSOLUTION BEHAVIOR IN A HEAVY OIL SYSTEM UNDER BULK PHASE

4.1 Live Oil Differential Liberation Tests

Prior to any non-equilibrium tests, equilibrium live oil properties were measured through live oil differential liberation tests according to the steps shown in section 3.3.1. Main parameters such as solvent solubility, equilibrium solvent-heavy oil mixture mole fraction, total vapor-liquid volume/mole fraction, individual solvent mole fraction in vapor phase and liquid phase, live oil swelling factor, live oil density, live oil viscosity etc. were meticulously measured. Then based upon the equilibrium properties, an equilibrium PVT properties package was formulated to compare with the non-equilibrium data.

4.1.1 CO₂-Heavy Oil System

The following tables show the live oil properties of the CO₂-heavy oil system. These properties would be used later as the data input into CMG WINPROP for the purpose of generating a live oil mixture package into CMG STARS for history matching conducted in reservoir simulation in Chapter 6. Unlike mixture solvent, the measurement of total vapor-liquid phase volume/mole fraction as well as the solvent individual composition in vapor and liquid phase was unnecessary. For single solvent component mixture, the main properties were achieved for the liquid phase as below:
Table 4.1 CO₂ solvent solubility in heavy oil

<table>
<thead>
<tr>
<th>Saturation pressure, kPa</th>
<th>Oil mole fraction, %</th>
<th>Solvent mole fraction, %</th>
<th>Solvent weight fraction, %</th>
<th>Solvent solubility, g solvent/100g oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>3894.2</td>
<td>51.55</td>
<td>48.45</td>
<td>9.96</td>
<td>11.05</td>
</tr>
<tr>
<td>3383.7</td>
<td>55.56</td>
<td>44.44</td>
<td>8.60</td>
<td>9.41</td>
</tr>
<tr>
<td>2879.3</td>
<td>63.72</td>
<td>36.28</td>
<td>6.28</td>
<td>6.69</td>
</tr>
<tr>
<td>2263.7</td>
<td>70.48</td>
<td>29.52</td>
<td>4.69</td>
<td>4.93</td>
</tr>
<tr>
<td>1798.8</td>
<td>73.13</td>
<td>26.87</td>
<td>4.14</td>
<td>4.32</td>
</tr>
<tr>
<td>1268.4</td>
<td>81.85</td>
<td>18.15</td>
<td>2.54</td>
<td>2.61</td>
</tr>
</tbody>
</table>

Table 4.2 CO₂-heavy live oil properties

<table>
<thead>
<tr>
<th>Saturation pressure, kPa</th>
<th>Swelling factor</th>
<th>Live oil density, g/cm³</th>
<th>Live oil viscosity, cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>3894.2</td>
<td>1.132</td>
<td>0.94005</td>
<td>288.4474</td>
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<tr>
<td>3383.7</td>
<td>1.136</td>
<td>0.93720</td>
<td>401.1869</td>
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<tr>
<td>2879.3</td>
<td>1.101</td>
<td>0.94337</td>
<td>498.514</td>
</tr>
<tr>
<td>2263.7</td>
<td>1.074</td>
<td>0.95042</td>
<td>654.4738</td>
</tr>
<tr>
<td>1798.8</td>
<td>1.063</td>
<td>0.95537</td>
<td>964.2422</td>
</tr>
<tr>
<td>1268.4</td>
<td>1.039</td>
<td>0.96138</td>
<td>1378.373</td>
</tr>
</tbody>
</table>
Figure 4.1 CO₂ solubility and CO₂ mole fraction in live oil
Figure 4.2 CO₂-heavy live oil density and viscosity
It can be seen from figure 4.2 live oil density, that around 3900kPa, the density of the live oil was heavier even though more CO₂ was dissolved into it. This might be due to the fact that, when the live oil was prepared, an excessive CO₂ gas cap was injected together with the heavy oil phase into the live oil recombination unit. When the gas-oil system was fully rocked after many back-and-forth stroke, excessive CO₂ gas cap extracted the light components in the heavy oil phase at high pressure as the heavy oil was heavily blended with kerosene. Therefore, the density of the live oil at higher pressure increased instead. However, in all of our experiments, in order to reduce the effect of CO₂ extraction of the light components from the heavy oil phase, lower pressure (<3320kPa) of CO₂ injection was conducted in the experimental study.

### 4.1.2 CO₂-C₃H₈-Heavy Oil System

The following tables show the live oil properties of the CO₂-C₃H₈-heavy oil system. These properties would also be used later as the data input into CMG WINPROP for the purpose of generating a live oil mixture package into CMG STARS for history matching conducted in reservoir simulation in Chapter 6. For a mixture solvent, the measurement of total vapor-liquid phase volume/mole fraction as well as the solvent individual composition in vapor and liquid phase in two-phase flash was necessary to accurate describe the thermodynamic behavior. Therefore, both two-phase flash and liquid phase properties were conducted for this live oil system.
Table 4.3 Mixture solvent solubility in liquid phase

<table>
<thead>
<tr>
<th>Saturation Pressure, kPa</th>
<th>Oil Mole Fraction, %</th>
<th>Solvent Mole Fraction, %</th>
<th>Solvent Weight Fraction, %</th>
<th>Solvent Solubility, g solvent/100g oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>3919.3</td>
<td>45.878</td>
<td>54.121</td>
<td>14.360</td>
<td>16.768</td>
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<td>3349.6</td>
<td>49.001</td>
<td>50.999</td>
<td>12.887</td>
<td>14.794</td>
</tr>
<tr>
<td>2809.1</td>
<td>54.263</td>
<td>45.737</td>
<td>10.699</td>
<td>11.981</td>
</tr>
<tr>
<td>2254.3</td>
<td>58.858</td>
<td>41.142</td>
<td>9.038</td>
<td>9.936</td>
</tr>
<tr>
<td>1692.1</td>
<td>63.132</td>
<td>36.868</td>
<td>7.665</td>
<td>8.301</td>
</tr>
<tr>
<td>1160.7</td>
<td>74.915</td>
<td>25.084</td>
<td>4.543</td>
<td>4.759</td>
</tr>
<tr>
<td>707.2</td>
<td>82.611</td>
<td>17.388</td>
<td>2.905</td>
<td>2.992</td>
</tr>
</tbody>
</table>

Table 4.4 Live oil two-phase flash compositional analysis (part 1)

<table>
<thead>
<tr>
<th>Saturation Pressure, kPa</th>
<th>Oil Mole Fraction in Live Oil Mixture, %</th>
<th>Solvent Mole Fraction in Live Oil Mixture, %</th>
<th>CO₂ Mole Fraction in Solution Gas, %</th>
<th>C₃H₈ Mole Fraction in Solution Gas, %</th>
<th>CO₂ Mole Fraction in Exsolution gas, %</th>
<th>C₃H₈ Mole Fraction in Exsolution gas, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3919.3</td>
<td>45.878</td>
<td>54.121</td>
<td>46.003</td>
<td>8.119</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3349.6</td>
<td>49.001</td>
<td>50.999</td>
<td>42.328</td>
<td>8.672</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2809.1</td>
<td>54.263</td>
<td>45.737</td>
<td>36.815</td>
<td>8.921</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2254.3</td>
<td>58.858</td>
<td>41.142</td>
<td>32.731</td>
<td>8.410</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1692.1</td>
<td>63.132</td>
<td>36.868</td>
<td>29.146</td>
<td>7.721</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1160.7</td>
<td>74.915</td>
<td>25.084</td>
<td>16.249</td>
<td>8.835</td>
<td></td>
<td></td>
</tr>
<tr>
<td>707.2</td>
<td>82.611</td>
<td>17.388</td>
<td>9.940</td>
<td>7.447</td>
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<td></td>
</tr>
</tbody>
</table>

Table 4.5 Live oil two-phase flash compositional analysis (part 2)

<table>
<thead>
<tr>
<th>Saturation Pressure, kPa</th>
<th>Liquid phase mole fraction, %</th>
<th>Vapor phase mole fraction, %</th>
<th>CO₂ Mole Fraction in Solution Gas, %</th>
<th>C₃H₈ Mole Fraction in Solution Gas, %</th>
<th>CO₂ Mole Fraction in Exsolution gas, %</th>
<th>C₃H₈ Mole Fraction in Exsolution gas, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3919.3</td>
<td>100</td>
<td>0</td>
<td>85.002</td>
<td>14.998</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>3349.6</td>
<td>93.628</td>
<td>6.371</td>
<td>82.998</td>
<td>17.002</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2809.1</td>
<td>84.549</td>
<td>15.451</td>
<td>80.494</td>
<td>19.506</td>
<td>96.277</td>
<td>3.723</td>
</tr>
<tr>
<td>2254.3</td>
<td>77.948</td>
<td>22.052</td>
<td>79.558</td>
<td>20.442</td>
<td>92.914</td>
<td>7.086</td>
</tr>
<tr>
<td>1692.1</td>
<td>72.671</td>
<td>27.328</td>
<td>79.056</td>
<td>20.944</td>
<td>90.827</td>
<td>9.173</td>
</tr>
<tr>
<td>1160.7</td>
<td>61.241</td>
<td>38.759</td>
<td>64.778</td>
<td>35.222</td>
<td>93.014</td>
<td>6.985</td>
</tr>
<tr>
<td>707.2</td>
<td>55.535</td>
<td>44.464</td>
<td>57.168</td>
<td>42.832</td>
<td>91.044</td>
<td>8.955</td>
</tr>
</tbody>
</table>

123
Table 4.6 Live oil liquid phase properties (part 3)

<table>
<thead>
<tr>
<th>Saturation Pressure, kPa</th>
<th>Swelling factor</th>
<th>Live Oil Density, g/cm³</th>
<th>Live Oil Viscosity, cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>3919.3</td>
<td>1.271</td>
<td>0.89802</td>
<td>182.859</td>
</tr>
<tr>
<td>3349.6</td>
<td>1.237</td>
<td>0.90563</td>
<td>229.858</td>
</tr>
<tr>
<td>2809.1</td>
<td>1.194</td>
<td>0.91561</td>
<td>258.578</td>
</tr>
<tr>
<td>2254.3</td>
<td>1.159</td>
<td>0.92172</td>
<td>318.190</td>
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<tr>
<td>1692.1</td>
<td>1.129</td>
<td>0.93232</td>
<td>512.491</td>
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<tr>
<td>1160.7</td>
<td>1.079</td>
<td>0.94349</td>
<td>587.4696</td>
</tr>
<tr>
<td>707.2</td>
<td>1.047</td>
<td>0.95579</td>
<td>1336.75</td>
</tr>
</tbody>
</table>
Figure 4.3 Solvent solubility and mole fraction in live oil for CO$_2$-C$_3$H$_8$-heavy live oil system
Figure 4.4 Phase mole fraction in two-phase flash and live oil density for CO$_2$-$C_3$H$_8$-heavy live oil system
Figure 4.5 Live oil viscosity for CO$_2$-C$_3$H$_8$-heavy live oil system
Figure 4.3~4.5 shows the results of CO$_2$-C$_3$H$_8$-heavy live oil system differential liberation tests. The equilibrium PVT phase behavior results of CO$_2$ solvent alone and CO$_2$-C$_3$H$_8$ mixture solvent coexisting with heavy oil will be used as the objective history matching data and formulation of a PVT package in CMG WINPROP module in Chapter 6 to conduct reservoir simulation.

### 4.2 Solvent Dissolution and Exsolution Tests on Solvent-Heavy Oil Systems

#### 4.2.1 CO$_2$-Heavy Oil System

##### 4.2.1.1 CO$_2$ Dissolution Behavior Tests

Based upon the mass balance in a closed system, the following equation can be used to calculate the mass of CO$_2$ transferred into heavy oil after the diffusion process:

$$n_{CO_2 \_ dissolved} = \frac{P_{\text{ini}}V_{\text{ini}}}{Z_{\text{ini}RT}} - \frac{P_{\text{final}}V_{\text{final}}}{Z_{\text{final}RT}}$$  \hspace{1cm} (4.1)

Where, $n_{CO_2 \_ dissolved}$ is the final mole of CO$_2$ dissolved in the heavy oil, $P$, $V$, $Z$, $R$ and $T$ are pressure, volume, real gas deviation factor, universal gas constant, and temperature of the system. The caption $\text{ini}$ and $\text{final}$ indicate the initial and final state of the system.

Then assuming when the chamber pressure reached equilibrium state without obvious pressure variation in the system, the following equation can be used to calculate the effective density of the CO$_2$-dissolved heavy oil density assuming molecular weight of the mixture follows a linear superposition:
\[ MW_{\text{mixture}} = \sum_{i}^{n} MW_i \times n_{\%_i} \]  

(4.2)

Where, \( i \) is the individual component, \( n \) is the total number of components, \( MW_i \) is the molecular weight of the component \( i \), and \( n_{\%_i} \) is the mole fraction of component \( i \) in the mixture. In our case, the above equation can be expressed as:

\[ MW_{\text{live oil}}(P, T) = MW_{\text{CO}_2} n_{\%_\text{CO}_2} + MW_{\text{dead oil}} n_{\%_\text{dead oil}} \]  

(4.3)

\[ \rho_{\text{live oil}} = \frac{n_{\text{mixture}} MW_{\text{live oil}}}{V_{\text{live oil}}} \]  

(4.4)

Where,

\[ n_{\text{mixture}} = n_{\text{CO}_2, \text{dissolved}} + n_{\text{dead oil}} \]  

(4.5)

And,

\[ SF_{\text{live oil}} = \frac{V_{\text{live oil}}}{V_{\text{dead oil}}} \]  

(4.6)

Where, \( n_{\text{CO}_2, \text{dissolved}} \) and \( n_{\text{dead oil}} \) is the number of moles of \( \text{CO}_2 \) diffused into the heavy oil and initial saturated dead oil; \( SF_{\text{live oil}} \) is the swelling factor/formation volume factor of dead oil saturated with solvent; \( V_{\text{live oil}} \) is the recorded live oil volume during the diffusion process; \( V_{\text{dead oil}} \) is the initially saturated volume of dead oil in the test chamber.

The above equation sets are under the assumption that when the system pressure reached equilibrium, the concentration field of \( \text{CO}_2 \) inside the live oil was uniformly distributed, and hence, the calculated density of the live oil from the high-pressure visual cell tests can represent a uniform live oil mixture.

The gas cap was injected into the system at an initial pressure. And the system was closed while the gas cap pressure dropped. After certain period of time, the gas cap pressure will reach a steady state, meaning very small fluctuations (±3kPa to be the pressure transducer
accuracy) will occur. At this stage, we can assume that the system had arrived equilibrium state, that is, full solubility of CO\(_2\) at a certain final pressure.

According to image analysis, the initial and final volume of the oil and gas phase can be determined, and from recorded pressure data, initial and final pressure of the gas cap can be determined. Real gas Z factor at different pressure was achieved from CMG WINPROP. The universal gas constant R, and temperature were all assumed as fixed constants. The dissolved CO\(_2\) number of moles can be calculated from the above determined parameters.

The following table summarizes the CO\(_2\) solubility/diffusion test results:

**Table 4.7 Summary of CO\(_2\) diffusion tests**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>(P_{\text{initial}}), kPa</th>
<th>(P_{\text{final}}), kPa</th>
<th>Contact Time, min</th>
<th>(\text{CO}_2) mol%</th>
<th>(\text{CO}_2) wt%</th>
<th>(\frac{g}{100\ \text{g}})</th>
<th>Saturation GOR, (\text{cm}^3/\text{cm}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(equilibrium)</td>
<td>1555</td>
<td>1266</td>
<td>4980</td>
<td>18.24</td>
<td>2.57</td>
<td>2.65</td>
<td>13.98</td>
</tr>
<tr>
<td>2(equilibrium)</td>
<td>2231</td>
<td>1800</td>
<td>4000</td>
<td>26.88</td>
<td>4.17</td>
<td>4.36</td>
<td>22.93</td>
</tr>
<tr>
<td>3(equilibrium)</td>
<td>2623</td>
<td>2158</td>
<td>3000</td>
<td>29.57</td>
<td>4.74</td>
<td>4.98</td>
<td>26.31</td>
</tr>
<tr>
<td>4(equilibrium)</td>
<td>3320</td>
<td>2755</td>
<td>906</td>
<td>36.29</td>
<td>6.33</td>
<td>6.75</td>
<td>35.70</td>
</tr>
<tr>
<td>5(transient)</td>
<td>2623</td>
<td>2530</td>
<td>120</td>
<td>7.96</td>
<td>1.01</td>
<td>1.02</td>
<td>/</td>
</tr>
<tr>
<td>6(transient)</td>
<td>2623</td>
<td>2385</td>
<td>540</td>
<td>17.96</td>
<td>2.53</td>
<td>2.60</td>
<td>/</td>
</tr>
<tr>
<td>7(transient)</td>
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<td>3.89</td>
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<tr>
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<td>2160</td>
<td>28.02</td>
<td>4.41</td>
<td>4.62</td>
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</tbody>
</table>
From the above table 4.7 we can see, test 1 to 4 were conducted under equilibrium state, indicating that the solvent CO₂ has sufficiently long time to contact with dead heavy oil, in order to reach the equilibrium state of thermodynamic condition. Test 5 to 8 were conducted at a fixed initial pressure, but different solvent-heavy oil contact time, hence different final pressure. This indicated that the oil and the solvent CO₂ were not contacted sufficiently well, and transient solubility of these tests was calculated.

The following figures show the results of CO₂ diffusion tests in the newly bulk phase visual cell under ambient temperature (20°C). These experimental results will be incorporated into the developed MATLAB-controlled reservoir simulator in Chapter 6 as the history matching objectives, including pressure decay curves and dynamic swelling factor curves.
(a) $P_{ini}=1555\text{kPa}$

(b) $P_{ini}=2231\text{kPa}$
Figure 4.6 Diffusion pressure decay and swelling factor curves for different injection pressure in (a)~(d)

(c) $P_{ini}=2623\text{kPa}$

(d) $P_{ini}=3320\text{kPa}$
Table 4.8 Swelling factor and density data of diffusion tests

<table>
<thead>
<tr>
<th>Diffusion process equilibrium pressure, kPa</th>
<th>Live oil density measurement</th>
<th>Swelling factor, cm³/cm³</th>
<th>Density measured from visual cell tests, g/cm³</th>
<th>Density measured from live oil tests, g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1266</td>
<td>1268.4</td>
<td>1.039</td>
<td>0.9612</td>
<td>0.9613</td>
</tr>
<tr>
<td>1800</td>
<td>1798.8</td>
<td>1.063</td>
<td>0.9552</td>
<td>0.9554</td>
</tr>
<tr>
<td>2158</td>
<td>2200.7</td>
<td>1.074</td>
<td>0.9510</td>
<td>0.9504</td>
</tr>
<tr>
<td>2755</td>
<td>2879.3</td>
<td>1.100</td>
<td>0.9443</td>
<td>0.9434</td>
</tr>
</tbody>
</table>

Table 4.8 shows the measured swelling factor of live oil at different equilibrium pressure of diffusion tests as well as the density calculated from mass balance and observed volume expansion of heavy oil under CO₂ dissolution. It can be seen that the two density values are quite close to each other, proving the feasibility of such methodology in terms of characterizing the dynamic solubility of solvent into heavy oil.

In the next section, the experimental results pressure depletion under various pressure operational schemes will be analyzed to investigate how these parameters affect the foamy oil generation and stability during time elapse. The solvent exsolution behavior can then be numerically simulated according to these foamy oil volumetric variation curves.

4.2.1.2 CO₂ Exsolution Behavior Tests

In this section, the experimental results of pressure depletion tests will be illustrated to show the foamy oil generation and stability under various of pressure operational schemes. The foamy oil volumetric variation curves will be also used as the history matching subject in the subsequent sections of numerical simulation of solvent exsolution process.
**Effect of initial GOR**

In this section, the effect of initial GOR on foamy oil volumetric variation curve is shown in the following figure 4.7.

As it is indicated in the figure 4.7, higher initial GOR will have a larger area of foamy oil expansion and decay. This is very straightforward to understand, as higher content of gas dissolution will provide higher amount of gas to form exsolution and hence, increasing the foamy oil stability. Therefore, a higher solvent injection is preferred under formation fracking limit to achieve a higher dissolution in order to release more elastic energy to expel oil out of the reservoir in depletion stage of a solvent injection process.

**Effect of pressure depletion rate**

The effect of pressure depletion rate on foamy oil generation and stability are plotted in the following figures 4.8. From figure 4.8, it is indicated that an immediate depletion to atmospheric pressure will induce a high expansion of foamy oil volume at a relatively earlier time, but the enduring time is relatively shorter than a high continuous pressure depletion rate, -90kPa/min in this series of tests. Comparing two different pressure depletion rates, at -90kPa/min and -50kPa/min, it can be seen that higher pressure depletion rates was able to induce larger foamy oil volume expansion. At a lower pressure depletion rate, the whole system tent to equilibrium exsolution, due to a lower rate of thermodynamic condition shifting from equilibrium to non-equilibrium.
Figure 4.7 Effect of initial GOR on foamy oil volumetric behavior

Figure 4.8 Effect of pressure depletion rate on foamy oil volumetric behavior
Effect of pressure drawdown level

From figure 4.9, pressure drawdown level also have significant effect on the foamy oil volumetric behavior. When the system was depleted to a higher prevailing pressure 500kPa in this case, more gas was still dissolved in the heavy oil that could not escape, and the viscosity of the live oil remained lower with still a certain amount of gas dissolved. At a lower prevailing pressure 1atm in this case, most of the gas formed exsolation and contributed to the volume expansion of foamy oil. Also, since the gas were mostly exsolved, the remaining heavy oil in the system would tend to have a higher viscosity that helped to trap the gas bubbles and limit their mobility. Therefore, when the pressure was depleted to a higher prevailing pressure, the foamy oil stability area was less than the case of low prevailing pressure.

Effect of solvent-heavy oil contact time

From figure 4.10, it is clearly indicated that a shorter solvent-heavy oil contact time will result in lower solvent solubility, and the concentration of solvent will highly probably to be distributed at the regions close to the gas-oil interface. Therefore, when the pressure was depleted, the dissolved gas had an “easy” way out of the heavy oil, and escaped very quickly. However, when solvent contacts heavy oil for a longer period of time, the diffusion penetration in the heavy oil phase will be deeper, as well as a higher number of mass can be transferred. Thus, it is reasonable that a longer solvent-heavy oil contact time will result in a higher foamy oil expansion and stability area as shown in figure.
Figure 4.9 Effect of pressure drawdown level on foamy oil volumetric behavior

Figure 4.10 Effect of contact time on foamy oil volumetric behavior
4.2.2 CO$_2$-C$_3$H$_8$-Heavy Oil System

In this section, the experimental study of CCE pressure depletion tests on CO$_2$-C$_3$H$_8$-heavy oil system have been conducted to study the non-equilibrium phase behavior. Unlike CO$_2$-heavy oil test where dead oil was mainly used, the series of CO$_2$-C$_3$H$_8$-heavy oil system was mainly using live oil instead of dead oil, and the solvent exsolution behavior was mainly studied. The detailed experimental tests are listed in the following table:
Table 4.9 CO$_2$-C$_3$H$_8$-heavy oil system CCE pressure depletion tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Saturation Pressure, kPa</th>
<th>Pressure Depletion Scheme</th>
<th>Initial Live Oil Volume Occupancy in the Visual Cell, %</th>
<th>Initial Fluid Types in Visual Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1200</td>
<td>$\frac{dP}{dt} = -20$ kPa/min</td>
<td>44</td>
<td>Live oil + gas cap</td>
</tr>
<tr>
<td>2</td>
<td>1200</td>
<td>$\frac{dP}{dt} = -50$ kPa/min</td>
<td>44</td>
<td>Live oil + gas cap</td>
</tr>
<tr>
<td>3</td>
<td>1200</td>
<td>$\frac{dP}{dt} = -100$ kPa/min</td>
<td>44</td>
<td>Live oil + gas cap</td>
</tr>
<tr>
<td>4</td>
<td>1200</td>
<td>$\frac{dP}{dt} = -300$ kPa/min</td>
<td>44</td>
<td>Live oil + gas cap</td>
</tr>
<tr>
<td>5</td>
<td>1200</td>
<td>$\frac{dP}{dt} = -20$ kPa/min</td>
<td>100</td>
<td>Live oil</td>
</tr>
<tr>
<td>6</td>
<td>1200</td>
<td>$\frac{dP}{dt} = -300$ kPa/min</td>
<td>100</td>
<td>Live oil</td>
</tr>
<tr>
<td>7</td>
<td>1200</td>
<td>$\frac{dP}{dt} = -300$ kPa/min</td>
<td>16</td>
<td>Live oil + gas cap</td>
</tr>
<tr>
<td>8</td>
<td>1200</td>
<td>$\frac{dP}{dt} = -300$ kPa/min</td>
<td>16</td>
<td>Live oil + gas cap + 10,000 ppm Sodium Dodecyl Sulfate (SDS) solution</td>
</tr>
</tbody>
</table>
From the table 4.9, we can see a total of 8 tests were conducted in the visual cell. Test no.1 to 4 were conducted under the same initial live oil volume occupancy, but with different pressure depletion rates. Test no.5 and 6 were conducted with full initial live oil occupancy in the visual cell, while with 2 different pressure depletion rates. These two tests were aimed to test the solvent exsolution sequence during pressure depletion. Without the gas cap, it is more direct to test out the solvent compositional change in live oil when being depleted out of the visual cell. Test no.7 was conducted with a smaller initial live oil volume occupancy to compare with test no.4 in terms of the effect of the live oil initial drainage height. For test no.8, a 10,000 ppm SDS surfactant solution was initially injected into the bulk phase, and subsequently the live oil was saturated into the visual cell. This was aimed to compare the foamy oil stability under the existence of a surfactant to test no.7 which had no surfactant. The effect of pressure depletion scheme on live oil bulk volume dynamics were analyzed. During pressure depletion, the exsolution gas phase which was highly visual in the bulk chamber has two parts: the free gas phase and the dispersed phase, $V_{res\ fg}$ and $V_{res\ dg}$, and the composition mole fraction, pressure, temperature etc. are assumed to the same, the following schematics show the assumption of the PVT phase behavior analysis:

In figure 3.16 (a), the **Area 2’** represents the foamy oil phase, and the **Area 1’** represents the gas phase. The gas phase is forming exsolution from the supersaturated oil phase during pressure depletion. Therefore, the assumption for the PVT phase behavior is that the dispersed gas phase in **Area 2’** part share the same physical properties with the free gas phase in **Area 1’** during pressure depletion tests.
Also, the oil-phase shrinkage effect under gas dissolution was not considered from the image processing. Despite the chamber thickness is only 200 microns, heavy oil phase was still able to form a bit of coating on the observation window, and it is fairly difficult to accurate calculated the actual oil phase coverage during a dynamic process where oil phase expanded very rapidly. Therefore, the oil phase volume is assumed to be non-varying and its volume is considered to be equal to initial live oil phase volume. According to this assumption of oil phase volume, then the dispersed gas volume is taken to be the difference between the foamy oil phase volume subtracted by initial live oil phase volume.

4.2.2.1 Dynamic Foamy Oil Phase Volume

Test no.1 to 4 were all conducted under the same initial live oil height/volume, which occupied 44% of the bulk chamber. The difference between the tests are the pressure depletion rate, which is -20kPa/min, -50kPa/min, -100kPa/min, -300kPa/min, respectively. The aim is to examine how pressure depletion rate affects the foamy oil non-equilibrium phase behavior.

The first analysis is to show the difference between foamy oil dynamic relative volume as indicated in Area2’ in figure 3.16,
Figure 4.11 Foamy oil relative volume vs. time (test no.1 to 4)
As it is indicated from the figure 4.11, pressure depletion rate at -300kPa/min induced the earliest volume expansion of the foamy oil phase. Then when the pressure was depleted to atmospheric pressure, the expansion of the foamy oil phase reached its maximum capability at a relative volume peak around 1.99 and maintained for a relatively long time. Within this period, the dissolution gas had exsolved out from the oil phase totally which was indicated by the free gas volume in figure. And the volume change at the late stage of the tests were mainly a natural convection flow of gas driven by gravity to exchange “place” with oil phase. For the case of -100kPa/min, it is indicated that the foamy oil started to expand at around 12min where the initial cell pressure was declined to atmospheric pressure. As time went by, the relative volume of the foamy oil phase expanded to around 2.1 at its peak value, then started to fall down gradually at a slightly larger negative slope than the case of -300kPa/min. The decline trend of -100kPa/min case shows a more gradual trend than in the case of -300kPa/min. The foamy oil height lasted longer and the relative volume was higher than in the case of -300kPa/min. For test no.3 where -50kPa/min was applied, the trend was very similar to the case of -100kPa/min, except for the initial stage where the foamy oil phase volume expansion rate against time is higher, and at later stage, it seemed that relative volume of foamy oil phase was a bit higher. For test no.1, which has the lowest pressure depletion rate, the initial stage of the foamy oil phase expansion was very similar to the case of -50kPa/min and -100kPa/min. But in the middle of foamy oil expansion process, the exsolved gas partially escaped and form free gas at the interface of the free gas cap and bulk oil, hence, some fluctuations occurred during oil phase expansion. The foamy oil expanded to its peak at around 2.2 of relative volume, which was the highest among all the tests. At the mid and late stage of the oil phase, the
experimentation was stopped, but the trend in the blue curve in figure 4.11 shows that a depletion rate of -20kPa/min will be extrapolated to yield higher foamy oil relative volume.

For test no.5 and 6, since these two tests were conducted with the visual cell saturated with 100% of live oil, and hence, the foamy oil phase as an integrity of dispersed gas phase and supersaturated oil phase did not exist, and they were not accounted for in the analysis of foamy oil phase relative volume.
Figure 4.12 Foamy oil relative volume vs. time (test no. 4 and 7)
For test no.4 and 7, the aim is to determine how the initial live oil column height affects the foamy oil phase volumetric behavior. As it is indicated in figure 4.12, when the initial live oil column height was lower, that is, with a smaller amount of live oil sample in the visual cell, the foamy oil phase tended to have a higher expansion maximum peak. The highest relative volume of test no.7 reached around 3.4, and the expansion started about 10mins later than the case of initially half saturated in the cell. This might be due to oil phase reaction to pressure propagation in the porous media-analogous cell. When the initial live oil sample was small (test no.7 was around 3 folds smaller than test no.4), the free gas cap reacted slower to the pressure depletion controlled by the back-pressure regulator and the CCE test gas collecting transfer cylinder. In terms of overall foamy oil stability, both tests had a very similar region of foamy oil stability, lasting around 80 minutes long.
Figure 4.13 Foamy oil relative volume vs. time (test no.7 and 8)
Figure 4.13 shows the foamy oil phase volumetric stability between test no.7 and no.8, where the difference is whether there was aqueous phase presented. In test no.8, a 1 wt% of SDS solution mixed with deionized water was injected into the visual cell prior to saturating live oil. The reason is to see how an aqueous phase, especially for a surfactant solution, affects the foamy oil phase volumetric stability during pressure depletion. The initial live oil saturation volume was the same for both tests. From the figure, it is indicated that the early stage of foamy oil phase expansion presented similar trend, and the expansion rate against time (the slope) was very alike for both tests. This meant that the surfactant solution in the system did not influence the foamy oil phase expansion in the early stage. This was mainly due to the fact that the surfactant solution was positioned above the live oil mixture prior to pressure depletion, and the convection of oil phase was not strong enough yet to penetrate surfactant solution and let the surfactant solute act on the dispersed gas bubbles in the foamy oil phase. But in the later stage after around 30 mins, the foamy oil phase volume began to decrease for the case without surfactant, while the foamy oil phase with surfactant solution kept stable for a very long time and decreased very slowly. The phenomenon was mainly due to the fact that the surfactant was blended into the oil phase while expansion, and the surfactant helped to keep the foamy oil endurance longer.

4.2.2.2 Total Vapor Phase Reservoir Volume

In this sub-chapter, the total vapor volume in the visual cell against time and pressure of the system will be analyzed, the brief schematics of the analysis is shown as figure 4.14:
Figure 4.14 Schematic of total vapor phase volume measurement in the closed system (a) fully-saturated (b) half-saturated
The white parts inside the closed system indicates that total vapor volume in the system. For the visual cell part, the white part was directly visualized and quantified by image processing, and for the white part in the cylinder which was non-visualizable, the total collected fluid volume (including both oil phase and gas phase) was recorded by ISCO pump controller. As can be seen from figure 3.8, since the oil was not produced out of the BPR, the oil in liquid trap underwent a reservoir-condition flash. As discussed previously, the volume shrinkage of oil phase under gas exsolution was not considered as the gas-oil interface was never static in the visual cell, and it would be difficult to trace how oil phase shrunk when solution gas exsolved as under pressure depletion, the evolution and motion of the gas-oil interface would be too rapid. In addition, in real physics, the formation volume factor of heavy oil with gas dissolution will not change much. The same assumption goes for foamy oil non-equilibrium phase behavior characterization in Chapter 5 where the fluid was in porous media. Because oil phase was the wetting phase in a gas-oil system, a film of oil phase would tend to form around the porous grains, which makes the tracing of the exact oil phase formation volume factor even harder. Therefore, knowing the total volume collected in the transfer cylinder, and by subtracting the volume of gas phase inside the visual cell, the total vapor volume in the system can be known.

Figure 4.15 Shows the total vapor volume behavior for test no.1 to 4. As can be seen from the graph, the required time for the solution gas to fully exsolve out of the live oil mixture was different for tests under different pressure depletion rates. The slope of total vapor volume against time increased with the incremented pressure depletion rate. For each set of the tests, the total vapor volume reached its maximum when the pressure inside the system was depleted to atmospheric pressure.
Figure 4.15 Total vapor reservoir volume in the closed system (test no.1 to 4)
Figure 4.16 Total vapor reservoir volume in the closed system fully saturated with live oil (test no. 5 and 6)
From figure 4.16, it shows that when the visual cell was fully saturated with live oil, the total vapor volume under certain pressure depletion rate was showing a similar trend to test no.1 and 4 where half the visual cell was saturated, except for the total amount of the gas volume, also indicated in figure. When the visual cell was fully saturated, it could be viewed as a “production” experiment of live oil under pressure depletion, and according to the assumption that the oil shrinkage effect is neglected, the oil volume that was “produced” out of the visual cell will be the subtraction between the initial live oil volume and final visible oil phase volume in the visual cell.

Figure 4.17 is plotted to show the total vapor reservoir volume behavior between tests of different saturation extent of live oil in the visual cell. Although the total amount of gas presented in the closed system was at different value according to the live oil saturation content inside the visual cell, the exsolution behavior was very similar for tests at high pressure depletion rate, -300kPa/min, in this research. And for low pressure depletion rate at -20kPa/min, the exsolution was delayed very little, 3 minutes from 45 to 48 in the time scale in figure 4.17, and overall the exsolution behavior seemed similar. Although the free gas exsolution behavior was similar, however, when the saturated live oil content was different in the visual cell, the non-equilibrium volumetric behavior was not all the same. This could be validated in the next section where liquid phase volume fraction of each test was plotted to compare with the equilibrium condition.
Figure 4.17 Total vapor reservoir volume vs. time (test no.1, 4, 5, 6)
4.2.2.3 Total Liquid Phase Volume Fraction Deviation from Equilibrium Condition

During a Constant Composition Test (CCE) for PVT phase behavior, a fluid system inside and outside the visual cell are viewed as a whole integrity. The total gas and liquid phase volume fraction under multiple pressure and temperature conditions are the most straightforward parameters to be observed in the test to examine the phase distribution of a fluid system. In this sub-chapter, the liquid phase volume fraction of the solvent-heavy live oil system undergoing pressure depletion was thoroughly studied for the 8 sets of tests conducted. The liquid phase volume fraction of the system was visualized and obtained from image processing. The deviation of the tests from equilibrium shown in each figure shows the non-equilibrium regime of the solvent-heavy live oil system. The equilibrium liquid phase volume fraction was calculated based upon Peng-Robinson equation-of-state after performing phase stability test according to the Tangent Plane Distance (TPD) rule. The given composition feed of the system was the mole fraction of the live oil used in the experimental study, and two-phase flash calculation was carried out if phase stability test indicated an unstable mixture and a two-phase condition would prevail.
Figure 4.18 Liquid phase volume fraction vs. pressure (test no.5, 6 and equilibrium condition, the horizontal red arrow showing the pressure range for non-equilibrium existence)
From figure 4.18, test no.5 and 6 were plotted against the equilibrium liquid phase volume fraction yielded from live oil differential liberation tests. The equilibrium liquid phase volume fraction was obtained at multiple pressure points in the experimental tests, and for the sake of forming a continuous line to clearly show the deviation from equilibrium condition, the pressure and solvent solubility mole fraction relationship was interpolated. Test no.5 and 6 were chosen because the ease of characterizing the oil phase volume during pressure depletion according to the assumption. From the figure, we can see that at the initial stage of pressure depletion, the liquid phase volume fraction had already deviated from equilibrium. A higher pressure depletion rate started to move “closer” to the equilibrium line earlier than a slower pressure depletion rate, however, when the pressure was continuously decreasing to the mid stage, a higher pressure depletion rate started to deviate more than the case of a lower pressure depletion rate. The red arrow on the graph shows the deviation of the prevailing liquid phase volume fraction from equilibrium liquid phase volume fraction. At the later stage of the tests, case of lower pressure depletion rate, the blue line in figure 4.18, started to merge with equilibrium line at around 250kPa, while the case of higher pressure depletion rate, the orange line in the figure, still deviated 2 times more than blue line. The figure clearly shows the non-equilibrium pressure region deviated from equilibrium condition. The non-equilibrium regime happening when and at what condition are clearly shown in the graph.
Figure 4.19 Liquid phase volume fraction vs. pressure (test no.1, 4 and equilibrium condition)
From figure 4.19, it is shown that for tests in which the visual cell was half saturated with live oil, the trend appeared to be different than tests in which the visual cell was fully saturated. For a pressure depletion rate at -300kPa/min, the liquid phase volume fraction was very close to the equilibrium condition. However, for a relatively lower pressure depletion rate at -20kPa/min, the deviation behavior from equilibrium was evident, and it showed a similar trend to test no.5 shown in figure 4.18. This clarifies that if non-equilibrium phase behavior is meant to be achieved, it is important to choose how much live oil sample to be saturated and what pressure depletion rate to be chosen prior to conducting the tests. With a free gas cap, the live oil phase would be in contact with a large interface adjacent to the free gas cap. In this case, dissolution in the live oil phase had a better “exit”, and hence, in a very confined and thin aperture space, high mass transfer exchange rate would advance the exsolution than the rate of exsolution inside of the live oil phase, causing the whole system to reach equilibrium much faster than in a fully saturated visual cell. On the contrary, a lower depletion rate would be helpful to reduce the mass transfer rate due to the excessive energy applied to the system was at lower rate, therefore, the tendency to reach equilibrium was mainly controlled by the highly viscous oil phase, and in this case, with a smaller saturated volume of live oil in the visual cell, a lower pressure depletion rate might as well generate very evident non-equilibrium liquid phase volume fraction behavior.
Figure 4.20 Liquid phase volume fraction vs. pressure (test no.1, 3, and 4)
From figure 4.20, we can see that with the same initial amount of live oil saturated in the visual cell, the non-equilibrium phenomenon was more evident with a lower pressure depletion rate at -20kPa/min. And as pressure depletion rate increased, the liquid phase volume fraction tended to move towards the equilibrium condition.

From figure 4.21, cases with the same pressure depletion rate -20kPa/min but with different visual cell live oil initial saturation volume were compared with its corresponding equilibrium condition. Evidently, non-equilibrium phenomenon was more obvious in a fully saturated visual cell than that of a half-saturated cell, as the deviation of liquid phase volume fraction was higher in a fully saturated case.

From figure 4.22, it shows that in a test with very small amount of live oil sample saturated in the visual cell, when compared to figure 4.18, there existed a certain degree of non-equilibrium phenomenon for a high pressure depletion rate at -300kPa/min. But still, the degree of deviation from equilibrium condition was still very small, and trend was more towards equilibrium.
Figure 4.21 Liquid phase volume fraction vs. pressure (test no.1, 5 and corresponding equilibrium condition)
Figure 4.22 Liquid phase volume fraction vs. pressure (test no.7 and equilibrium condition)


4.2.2.4 Solvent Exsolution Sequence

In this section, solvent exsolution sequence at the production well during pressure depletion process would be plotted. This solvent exsolution profile would be serving as the target parameter for CMG CMOST to history match the solvent exsolution rate of each solvent in the live oil system.

Totally 2 sets of the total tests which showed the most significant non-equilibrium phase behavior were plotted to show the solvent exsolution behavior. Since the majority of the dissolved gas in the live oil phase was CO$_2$, therefore, in each of the figure in figure 4.23, the total exsolution volume of CO$_2$ was always higher than C$_3$. For half-saturated visual cell under 20kPa/min depletion rate, the CO$_2$ content in the produced gas stream was high at the beginning. This was due to the fact that the free gas chamber saturated in the visual cell initially was CO$_2$. Then when the pressure was depleted to around 20mins after initial pressure, C$_3$ started to form exsolution out of the live oil, and hence, the detection of the fraction of C$_3$ started to rise at that moment. For depletion with -20kPa/min in a fully-saturated visual cell, both CO$_2$ and C$_3$ did not form exsolution until the pressure was depleted to around 650kPa to 590kPa. Then both solvents started to evolve out of the live oil. For CO$_2$, the pseudo-bubble point detected by the compositional analysis was a bit earlier than C$_3$, and exsolution rate was higher as well. It is shown that for the same pressure depletion rate at -20kPa/min, the exsolution timing for C$_3$ was quite close to each other for both half- and fully-saturated visual cell. These solvent compositional change at the production well and total cumulative gas volume would be the data input for history matching of individual solvent component non-equilibrium exsolution rate.
Figure 4.23 Solvent compositional change under exsolution (a) 20kPa/min half sample (b) 20kPa/min full sample
Figure 4.24 Total liquid volume fraction in the system
By the definition of vapor-liquid-equilibrium (VLE) K value, the experimental K value in such a closed system was calculated based upon the recorded total vapor reservoir volume in the previous section 4.2.2.2 *Total Liquid Phase Volume Fraction Deviation from Equilibrium Condition* and the composition of the free gas phase:

$$K = \frac{y_{gas \, mixture}}{x_{gas \, mixture}}$$ (4.7)

$$n_{total} = n_{initial \_gas} + n_{initial \_oil}$$ (4.8)

$$n_{exsolved \_gas} = \frac{PV_{vapor \, reservoir \, volume}}{Z_{gas \, mixture}RT}$$ (4.9)

$$x_{gas \, mixture} = \frac{n_{dissolved \_gas}}{n_{dissolved \_gas} + n_{initial \_oil}} = \frac{n_{initial \_gas} - n_{exsolved \_gas}}{n_{initial \_gas} - n_{exsolved \_gas} + n_{initial \_oil}}$$ (4.10)

In such a closed system, the total mole of solution gas and oil were known beforehand. By such, the total number of molar mass $n_{total}$ of the live oil can be calculated by the summation of $n_{initial \_gas}$ and $n_{initial \_oil}$. During pressure depletion, combining the volume of gas collected in the DBR transfer cylinder as well as the vapor phase volume inside the visual cell, the exsolution gas molar mass $n_{exsolved \_gas}$ can be calculated according to real gas law as shown in equation 4.9. Hence, the molar fraction of solvent in the form of dissolution can be calculated by equation 4.10, and subsequently the $K$ value by equation 4.7. The following figures 4.25 and 4.26 show the non-equilibrium molar mass of solution gas and $K$ value.
Figure 4.25 Total number of molar mass of gas-in-solution vs. equilibrium condition
Figure 4.26 K value w.r.t vapor phase vs. equilibrium condition
Figure 4.24 shows the total liquid volume fraction in the test chamber for tests with both half-saturated and fully-saturated visual cell. The total liquid volume fraction in the system indicates the deviation from equilibrium. This figure puts all the tests together to show the discrepancy of deviation from equilibrium under different pressure depletion rate. For half-saturated visual cell, the total liquid volume fraction was very close to equilibrium for high pressure depletion rates at -300kPa/min, -100kPa/min and -50kPa/min. Then for lower pressure depletion rate at -20kPa/min, the non-equilibrium phenomenon started to show, that is, the deviation from the equilibrium liquid volume fraction became obvious.

For tests where the visual cell was fully-saturated, as resembling to a fully-saturated reservoir production test, the non-equilibrium phenomena were even obvious. This might be due to the confining space that hindered the rapid exsolution of gas phase from the oil phase. Hence, a fracture-like geometry could yield results resembling to actual sandpack live oil pressure depletion tests. It is seen that, for a fully-saturated visual cell, the non-equilibrium region is larger for a higher pressure depletion rate at 300kPa/min, and for 20kPa/min, the volume fraction was firstly deviated from the equilibrium liquid volume fraction until reaching a certain pressure where the liquid volume fraction started to merge with each other and dissolution gas tend to exsolve in an equilibrium manner.

From figure 4.25, it is shown that the calculated mole number of the remaining dissolved gas in the oil phase during pressure depletion followed the same trend as figure 4.24. Very obvious deviation was observed for tests with fully-saturated visual cell at either high or low pressure depletion rate, as well as for tests with half-saturated visual cell under lower pressure depletion rate. The calculation of the liquid phase mole fraction was by the gas equation of state, \( PV=ZnRT \), where \( P \) and \( V \) were direct parameters obtained from image
processing and ISCO pump data acquired in LABVIEW user interface, and Z factor from compositional analysis of the production gas inside the DBR cylinder.

According to the mole number calculated from the experiments, the dynamic non-equilibrium K value under pressure depletion was obtained by using the definition of K value equation, \( \frac{y_i}{x_i} \). For tests with half-saturated visual cell, the deviation of K value from equilibrium was not obvious until a lower pressure depletion rate was applied. It is seen that in the right-hand side figure 4.26 in the middle row, the pseudo-bubble point started at around 570kPa where the dissolved gas started to form exsolution and got sensed by the ISCO pump system. For fully-saturated visual cell, a deviation of K value from equilibrium K value was also observed. It can be seen that the dissolved gas started to form exsolution at around 650kPa which can be regarded as the pseudo-bubble point pressure.

The above-mentioned information was very useful for a further simulation on non-equilibrium phase behavior in CMG STARS foamy oil module, to obtain the pseudo chemical reaction factors of the dissolved gas. The deviated K value data could be used as an important input into the simulator to consider for the pseudo bubble point, where gas started “reaction”. Also, the cumulative gas volume in the DBR cylinder controlled by ISCO pump would be serving as one of the production history data in CMG CMOST history matching.

**4.2.3 Single Bubble Exsolution**

This test was aimed to obtain the exsolution rate of a single bubble from the live oil mixture out of a nucleation site, and achieve a pressure-dependent exsolution rate that could be
used as an input into CMG STARS foamy oil module to conduct history matching of gas exsolution behavior.

The nucleation site was manually cut on a 200micron thick brass shim stock to limit the exsolution number of gas bubble to one bubble at a time. Although the actual number of the nuclei of gas bubble at the nucleation site was more than one due to its physical dimension, the nucleation site still served well to confine the gas bubble exsolution number to be only one bubble during pressure depletion. Since it was aimed for obtaining macro properties from a micro-scale and compare their similarity, visualizing only one bubble helped serve the purpose. Therefore, it is safe to say that the methodology of confining single bubble growth is highly feasible, and it could be used to quantify single bubble growth.
Figure 4.27 Bubble nucleation from nucleation site (red arrow indicating a gap length=0.85mm)
Figure 4.28 Tracked bubble volume evolution against time from nucleation site
Figure 4.27 and 4.28 shows the volume evolution of the single bubble. The actual bubble exsolution started at 496.6kPa after pressure was depleted from 1200kPa at a depleted rate of -20kPa/min. The time started to count when the first bubble appeared and grew. The pressure was continuously depleted until atmospheric pressure was reached. There were totally 5 bubbles appeared in the nucleation site along the whole pressure depletion processes, and the frequency was getting higher and higher as pressure was deviated more and more from pseudo bubble point. There were other bubbles formed in the system from other nucleation sites which was not accounted for. The only area accounted for as mentioned previously was one nucleation site with one bubble.

By obtaining the volume evolution of the single bubble, real gas equation of state was applied to the bubble to calculate for the molar mass change in the gas bubble. Three periods of bubble growth were extracted to regress the bubble exsolution rate against time and prevailing pressure, which can be seen from the following three figures:
Figure 4.29 Single bubble molar mass for three time-sequenced bubble under pressure depletion
The bubble exsolution rate was shown to be in an exponential relationship with time, by introducing a reduced pressure, \( P_r = \frac{P_{\text{prevailing}}}{P_{\text{end}}} \), the pressure-exsolution rate relationship could be generated in the following table:

**Table 4.10 Single bubble exsolution rate vs. \( P_r \)**

<table>
<thead>
<tr>
<th>Average pressure, kPa</th>
<th>( P_r ), kPa/kPa</th>
<th>Exsolution rate, 1/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>376.6 (0-12min)</td>
<td>3.722772</td>
<td>0.3141</td>
</tr>
<tr>
<td>156 (15.5-18.5min)</td>
<td>1.544554</td>
<td>0.8277</td>
</tr>
<tr>
<td>105 (19.3-21min)</td>
<td>1.039604</td>
<td>1.7789</td>
</tr>
</tbody>
</table>

The relationship between reduced pressure versus exsolution rate is in a power form. The coefficient 1.6948 in figure is the coefficient for these three exsolution rate based upon average pressure in the system.

For simplicity, the equation form was revised to:

\[
rrf = \frac{A}{P_r}
\]  

(4.11)

Followed by MATLAB regression tool box, the result was yielded as below in figure 4.30. The coefficient for reduced pressure versus exsolution rate was 1.646, and this parameter will be input as the initial guess in Chapter 6 for history matching formula input in CMG CMOST module.
Figure 4.30 Single bubble exsolution rate against time
### Results

**General model:**

\[ f(a) = \frac{A}{a} \]

**Coefficients (with 95\% confidence bounds):**

\[ A = 1.646 \ (0.793, 2.499) \]

**Goodness of fit:**

- \( SSE: 0.1113 \)
- \( R\text{-square}: 0.8993 \)
- \( \text{Adjusted R-square}: 0.8993 \)
- \( \text{RMSE}: 0.2359 \)

---

**Figure 4.31** MATLAB-regressed relationship between single bubble exsolution rate and time
4.2.4 Single Bubble Dissolution

In this section, a single bubble dissolution volume fraction against pressure decay was studied to generate a general expression for CMG CMOST formula section, in order to describe the vapor phase dissolution when injected into the reservoir. Since diffusion coefficient is a very sensitive numerical parameter to numerical settings such as grid size, numerical error, etc., therefore, it is important to develop a methodology that can describe vapor dissolution in oil, in which situation that, the gas chamber mass will be decreasing by condensation. This gas chamber mass condensation and dissolution into the heavy oil would reduce the gas chamber pressure and form the pressure decay as observed in regular diffusion coefficient measurement. However, in a numerical simulation, gridding would impose a strong effect on the selection of an “appropriate” diffusion coefficient. This is because in a reservoir simulation, the real-time oil-gas interface is not impossible to be captured due to the nature of the Darcy flow governing equation in a Finite Difference simulator. The saturation profile is the only parameter indicating how much each phase of fluid is distributed in a grid. Therefore, an intra-phase diffusion was used in such simulator rather than an inter-phase diffusion. Plus, with the local equilibrium flash calculation, the local grid containing multiple fluid phases will reach equilibrium immediately if non-equilibrium mass transfer mechanisms are not used. According to the above description, it is necessary to understand the dissolution phenomenon of solvent in contact with oil with another approach in reservoir simulation—pseudo-chemical kinetic reaction mechanism. This is similar to modeling foamy oil gas exsolution behavior, while in a reversed order.
Based upon such non-equilibrium mass transfer mechanism in reservoir-scale simulator, experimental study should also be developed accordingly to measure the parameters that could eventually be able to be fit into the numerical modeling and represent the dissolution mechanism in a “Darcy” way. In this section, a single bubble dissolution in a confined channel was analyzed. The bubble volume variation against pressure decay was analyzed through image processing.

Two types of bubble dissolution tests were conducted as per discussed in Chapter 3 section 3.3.2.2, which is again shown in figure 4.32. For figure 4.32(a), the traced bubble was a spherical bubble with large contact area with the surrounding oil phase, and for figure 4.32(b), the tracked bubble was a Taylor bubble, which was surrounded by a very thin liquid film with two sides forming a meniscus contacting the bulk oil phase. Figure 4.33 shows the pressure decay curve for these two types of bubble under the dissolution process.
Figure 4.32 Single bubble distribution in solvent reinjection in a closed system (a) spherical bubble (b) Taylor bubble
Figure 4.33 Pressure decay curve for single bubble dissolution process
Figure 4.34 Bubble volume change against time (a) spherical bubble (b) Taylor bubble
Table 4.11 Bubble dissolution rate at different time segments during pressure decay

<table>
<thead>
<tr>
<th>Time, min</th>
<th>Spherical bubble, l/min</th>
<th>Taylor bubble, l/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0~60mins</td>
<td>0.024</td>
<td>0.003</td>
</tr>
<tr>
<td>60~120mins</td>
<td>0.01</td>
<td>0.002</td>
</tr>
<tr>
<td>120~180mins</td>
<td>0.006</td>
<td>0.001</td>
</tr>
<tr>
<td>180~240mins</td>
<td>0.006</td>
<td>0.0009</td>
</tr>
<tr>
<td>240~300mins</td>
<td>0.006</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Figure 4.35 Bubble dissolution rate against time (a) spherical bubble (b) Taylor bubble
Figure 4.36 Bubble dissolution rate against prevailing pressure in the system (a) spherical bubble (b) Taylor bubble
It can be seen that from figure 4.34, that a spherical bubble has a higher overall dissolution rate than a Taylor bubble. This is mainly because for a spherical bubble, the interfacial area between the bubble and the surrounding oil phase was larger than that of a Taylor bubble. An exponential relationship was used in regression, as it fits the physics that the gas bubble volume shrinks at an initial volume, and eventually flattens under zero concentration gradient between the bubble and the surrounding oil. It can be seen that the overall trend of bubble volume against time is in a step-wise exponential relationship. The time segments were divided into 60mins per step, and the exponential relationship was found. Since this was an exsolution processes, the coefficient in the exponent is negative, indicating the process of initial gas bubble volume gradually getting smaller and smaller, and eventually, bubble volume stopped varying. Table 4.11 summarizes the bubble dissolution rate against time for plotting in figure 4.35. From figure 4.35, the bubble dissolution rate was plotted against time. This relationship was later verified in the history matching of micromodel diffusion tests in Chapter 6 by a dynamic optimization of a MATLAB-controlled reservoir simulator. Also, it can be seen that the bubble dissolution rate of a spherical bubble is higher than a Taylor bubble due to the difference in interfacial area with the surroundings.

For a history matching processes conducted directly by CMG CMOST optimization module, a dynamic adjustment of bubble dissolution rate along time elapsing was not possible as the simulation run has to be conducted from zero to end. In addition, the adjustment of reaction frequency factors in the original simulator itself only can be either a constant value indicated by “FREQFAC” or a pressure-dependent value “FREQFACP”. Therefore, in order to dig out a relationship that can be fitted into the CMOST formula
module where one can define their own equations for parameters to be used in the simulation run, the bubble dissolution rate against prevailing pressure in the system was plotted in figure 4.36 and the relationship can be described as:

\[ rrf = A \times \exp(B \times P_{rf}) \]  \hspace{1cm} (4.12)

where \( P_{rf} \) is the prevailing pressure of the system, \( A \) can be taken as the dissolution rate at the equilibrium pressure of a pressure decay test, which could be very close to zero value. By equation 4.12, a table of “FREQFACP” can be formed in the simulator and the relationship can be used in CMG CMOST formula module. Grasping the exponential behavior between bubble dissolution rate and prevailing pressure in the system, the history matching in CMG CMOST module is enlightened. The first step is to analyze the pressure decay curve, in-situ total vapor and liquid phase volume/mole fraction, and the corresponding equilibrium pressure of the regression relationship of the pressure decay curve. Then by roughly knowing the equilibrium pressure that the system might eventually reach, the \( P_{rf} \) lower limit could be set to this equilibrium pressure and the \( P_{rf} \) upper limit could be set to the injection pressure of the solvent at the beginning of the pressure decay. Then by formulating such a relationship in CMOST self-defined formula section, one is able to history match the pressure decay curve to indicate the rate of solvent dissolution. Multiple sets of exponential relationship under multiple pressure segments can be used if more accurate history matching results are to be achieved. The numerical simulation example of utilizing such relationship to history match the pressure decay curve was shown in Chapter 6.
CHAPTER 5 EXPERIMENTAL STUDY OF SOLVENT NON-EQUILIBRIUM DISSOLUTION AND EXSOLUTION BEHAVIOR IN A HEAVY OIL SYSTEM UNDER POROUS MEDIA:

MICROMODEL SYSTEM

In Chapter 5, experimental study of the non-equilibrium phase behavior of CO$_2$-C$_3$H$_8$-heavy live oil system was investigated by utilizing a micromodel system engraved with porous media. The tests include solvent diffusion and pressure depletion tests in micromodel mimicking CSI processes, static Constant Composition Expansion (SCCE) tests of live oil system in a micromodel, foamy oil continuously convective flowing (CCF) tests and solvent flooding and post-flooding soaking-pressure depletion tests.

5.1 Solvent Diffusion and Post-Diffusion Pressure Depletion Tests

In this subchapter, solvent diffusion tests were conducted in the micromodel under a partially-saturated condition to see the evolution of oil phase under solvent diffusion in the porous media as well as the follow-up post-diffusion pressure depletion tests to understand how the solvent diffusion affected the frontal advancement/distribution of the solvent-saturated oil phase when pressure is depleted. The tests were conducted in a closed system similar to a CCE test in PVT cell to make sure the composition of the system was always constant.

Micromodel system was positioned both horizontal and vertical to the ground, in order to understand how gravity would affect the gas-oil distribution after each CSI cycle. Firstly, the solvent stored in the ISCO pump cylinder under atmospheric pressure was compressed
into the free space in the micromodel to the desired injection pressure, and the injection was stopped. Then, the injected solvent was allowed to diffuse into heavy oil for a period of time. After the diffusion process, the micromodel was depleted by withdrawing the displacing fluid in the ISCO pump cylinder to expand the total volume of the closed system at certain pressure rate. The purpose of this series of tests was to examine how the gas-oil interface moved during the pressure depletion, and how it affected the solubility of solvent in a new cycle of solvent injection stage. The solvent solubility was quantified by image processing and pressure decay method and the “recovery factor” of cyclic solvent injection from the image processing bounding box was also quantified.

5.1.1 Horizontal Test

In this section, micromodel positioned horizontally to the ground has been used for solvent diffusion and pressure depletion tests. Pressure decay method was used to quantify the solubility of solvent in porous media.

5.1.1.1 Diffusion Tests

Table 5.1 Initial volume/mole feed composition for diffusion tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Initial dead oil volume fraction, %</th>
<th>Initial gas chamber volume fraction, %</th>
<th>Initial liquid phase mole fraction, %</th>
<th>Initial vapor phase mole fraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.418</td>
<td>94.582</td>
<td>24.42</td>
<td>75.58</td>
</tr>
<tr>
<td>2</td>
<td>25.35</td>
<td>74.65</td>
<td>24.89</td>
<td>75.11</td>
</tr>
<tr>
<td>3</td>
<td>24.89</td>
<td>75.11</td>
<td>24.88</td>
<td>75.12</td>
</tr>
<tr>
<td>4</td>
<td>24.82</td>
<td>75.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>24.82</td>
<td>75.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In total as summed up in Table 5.1, 5 sets of diffusion and pressure depletion tests were conducted. Since the oil phase swelling in the porous media is hard to be captured due to
the fact that the oil phase is the wetting phase in a gas-oil system and therefore, the grains in the micromodel would be covered by a thin film layer of oil phase. Also, after each round of pressure depletion, the light component would be extracted out the heavy oil phase, resulting in a colored porous media which formed the “third” phase in image processing. To sum up, due to the above-mentioned facts, the oil volume in the reservoir was considered constant and the value to be taken as the volume is the oil volume injected at the beginning of the test. Figure 5.1 shows the gas-oil interface distribution during the soaking period of cycle 1 to 5. On the figure, the red arrow indicates the initial state of pressure depletion process of Cycle N+1 (which is also the final state of diffusion process of cycle N). The gas-oil interface distribution was affected by the residual oil profile after each set of pressure depletion. The diffusion of solvent into heavy oil phase was affect by the distribution of the gas and oil in the porous media. The curves for a pressure decay test was plotted in the following up paragraphs. Solvent solubility in the system was sorted in the chart and plotted against time. As it is seen on figure 5.1, the gravity did not pose any effect on the distribution of the gas and oil saturation. The only driving force to advance the gas-oil interface towards the micromodel outlet was the pressure differential as well as the viscosity-reduction of the oil phase at the gas-oil contact. Since the condensation and diffusion of solvent mainly focused on the gas-oil contact, it can be seen that the frontal oil phase interface was advancing along pressure gradient direction, and it was “ripped” off the bulk oil phase due to solution of solvent that reduced the frontal viscosity. For the bulk oil phase in the deeper part of the micromodel, the solubility of solvent was lower than the frontal part, and therefore, that part of bulk oil phase tent to stay static without obvious movement.
Figure 5.1 Diffusion profile for each cycle (a) initial diffusion (b) post-cycle 1 diffusion (c) post-cycle 2 diffusion (d) post-cycle 3 diffusion (e) post-cycle 4 diffusion
Figure 5.2 Diffusion pressure decay curve versus time
Figure 5.3 Utilizing MATLAB Toolbox to match pressure decay data vs time
Table 5.2 Horizontal diffusion test results

<table>
<thead>
<tr>
<th>Test No</th>
<th>Initial pressure, kPa</th>
<th>Final pressure, kPa</th>
<th>Solvent mole fraction in live oil, %</th>
<th>EOS calculated equilibrium solvent mole fraction in live oil, %</th>
<th>Vapor phase mole fraction, %</th>
<th>EOS calculated equilibrium vapor phase mole fraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1057</td>
<td>977.6</td>
<td>21.51</td>
<td>25.16</td>
<td>69.10</td>
<td>67.61</td>
</tr>
<tr>
<td>2</td>
<td>1056</td>
<td>974.8</td>
<td>21.85</td>
<td>25.10</td>
<td>68.95</td>
<td>67.61</td>
</tr>
<tr>
<td>3</td>
<td>1056.9</td>
<td>980.5</td>
<td>20.75</td>
<td>25.21</td>
<td>68.52</td>
<td>67.05</td>
</tr>
<tr>
<td>4</td>
<td>1057.6</td>
<td>951.8</td>
<td>26.10</td>
<td>24.42</td>
<td>66.32</td>
<td>67.30</td>
</tr>
<tr>
<td>5</td>
<td>1055.8</td>
<td>978.3</td>
<td>21.45</td>
<td>25.17</td>
<td>67.93</td>
<td>67.19</td>
</tr>
</tbody>
</table>

Figure 5.2 and 5.3 show the pressure decay curves of each CSI cycle. Table 5.2 shows the results of the diffusion tests in the glass micromodel. The calculation was based upon the ignorance of the swelling factor of the dead oil phase during diffusion. The reason is that, in a porous media, the grains are typically oil-wet in a gas-oil system, and hence, as it can be observed in the figure that oil might form a very thin layer of oil film on the grain surface while expanding its volume, however, due to the capability of the camera, it was very difficult to accurately measure the volume of the oil phase which was covering on the grain surface. Therefore, under this circumstance, the swelling factor was ignored during calculation. The effect of ignoring the swelling factor will result in a higher estimation of the live oil density in the micromodel. Other than that, the solubility measurement was in a good trend. From figure 5.2, it is indicated that, for the initial diffusion process, since the contact area between solvent and heavy oil was small, therefore, the pressure decay was not as rapid as the other diffusion processes after pressure depletion. The pressure drop of the initial diffusion process was the lowest, indicating the solvent solubility was relatively lower. For post-cycle 1 diffusion, it can be seen that the pressure decay curve reached a globally minimum value, indicating the highest solvent solubility in the oil phase. This is
mainly due to the pressure depletion of the cycle 1. After pressure depletion, the heavy oil phase in the reservoir was “broken up” by gas exsolution and pressure gradient. And therefore, with more oil being dispersed outward from the image bounding box area mentioned in 5.1.1.2, larger interfacial area of bulk oil phase was exposed to the solvent chamber. Therefore, after the first cycle of depletion, the solvent solubility in the heavy oil was improved, and hence, a higher pressure drop from the initial injection pressure. Overall for the first post-pressure depletion diffusion processes, the solvent solubility was similar to each other. But for the post-cycle 3 diffusion, the pressure decay curve showed a higher pressure differential, indicating more solvent was dissolved. This can be seen from figure 5.1, that after pressure depletion of cycle 3, the oil phase was broken up and scattered out in the micromodel. This facilitated a larger contact area between solvent and oil. Then according to figure 5.1, the gas-oil profile for cycle 4 and 5 pressure depletion was almost the same, but the pressure decay had less pressure drop than post-cycle 3 diffusion. This might be due to the fact that after 4 cycles of pressure depletion, the light components in the heavy oil phase was extracted by solvent and evaporated out of the heavy oil phase under pressure depletion. The extracted light component can be seen clearly on the picture where the color is darker than gas while lighter than crude oil. The light component can be observed in the following figure 5.4 where the color was defined as red. However, the quantification of the amount of light component extraction would not be feasible. Hence, the light component extraction could only be observed qualitatively.
Figure 5.4 Distribution of the extracted volatile lighter component
5.1.1.2 Post-Diffusion Pressure Depletion Tests

In this section, the post-diffusion pressure depletion tests for each cycle has been shown to see how the gas-oil interface advanced during pressure depletion, and how this interface distribution affected the solvent diffusion.

Table 5.3 Residual oil saturation in bounding box

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Pressure depletion rate, kPa/min</th>
<th>Final residual oil saturation in bounding box, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>86.14</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>86.74</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>84.76</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>/</td>
</tr>
</tbody>
</table>
Figure 5.5 Bounding box for oil phase volume fraction image processing (red arrow indicates the direction of pressure depletion)
Figure 5.6 Image processing procedure for bounding box oil phase volume fraction
Figure 5.7 Oil phase volume fraction within image processing bounding box during each CSI cycle
Figure 5.5 and 5.6 show how to quantify the oil saturation in the bounding box set up for image processing. Figure 5.7 shows the oil phase saturation in the bounding box for each pressure depletion cycle. It can be seen that for the residual oil saturation in the bounding box, it did not follow the trend of decreasing monotonously. This shows that solvent exsolution might push some of the oil back into bounding box. The reason was that there was counter-current flow happened due to local pressure gradient and capillary force heterogeneity. In a drainage process, if the pressure of the two pores linked by one throat has a pressure differential that the pressure of the non-wetting phase in one pore is larger than the wetting phase in the other pore, then the non-wetting can push away the wetting-phase if the $dP$ is larger than the capillary resistance caused by the throat. But if the pressure differential is reversed, it is possible that the wetting-phase will push the non-wetting phase, which is also called imbibition. Under such complex pore network system, counter-current flow happens and resulted in such a saturation increase. Thus, under micro-scale, the pressure depletion would significantly change the gas-oil distribution. This counter-current phenomenon can be studied by utilizing full CFD or dynamic pore network modeling.

For the last cycle, instead of a closed system, the vapor phase in the micromodel was let out from the micromodel for a compositional analysis. The gas extraction from the micromodel was conducted by linking the micromodel to a BPR instead of a transfer cylinder. Then by controlling the BPR pressure at 900kPa (preventing gas from forming continuous exsolution from the oil phase), a portion of the gas was let out from the micromodel into the gas sensor to detect the composition of CO$_2$ and C$_3$. The following figure 5.8 shows the carbon dioxide composition in the bled-out gas stream.
Figure 5.8 CO₂ concentration in the extracted gas stream at P=900kPa for 3 minutes of continuous flow-through sampling
Table 5.4 Solvent composition in vapor and liquid phase at the end of diffusion tests for cycle 5

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$ mole fraction in live oil, %</th>
<th>C$_3$ mole fraction in live oil, %</th>
<th>Overall solvent mole fraction in live oil, %</th>
<th>CO$_2$ mole fraction in vapor phase, %</th>
<th>C$_3$ mole fraction in vapor phase, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle 5 pressure depletion (averaged value)</td>
<td>11.07</td>
<td>10.38</td>
<td>21.45</td>
<td>88.21</td>
<td>11.79</td>
</tr>
<tr>
<td>Equilibrium condition</td>
<td>13.01</td>
<td>12.16</td>
<td>25.17</td>
<td>89.02</td>
<td>10.98</td>
</tr>
</tbody>
</table>

From the above table 5.4, it is seen that the measured solvent compositions in the bled-out gas vapor phase was quite closed to the equilibrium condition, however, the overall solvent mole fraction in the live oil phase was lower than the equilibrium value. This might be due to the fact that, after 5 cycles of diffusion and pressure depletion, the light component in the heavy oil phase was extracted out to the gas-oil interface and even further from the gas-oil frontal interface. Therefore, in the calculation by equation-of-state, if without considering the compositional change of the oil phase, the calculation was always meant for the initial heavy oil phase which, in our case, contained lots of lighter component as indicated in GC analysis in Chapter 3. Thus, the equilibrium solubility would always be higher than actual condition with in-situ oil down-grading.

5.1.2 Vertical Test

In this section, solvent diffusion and pressure depletion tests were conducted with a micromodel being placed vertically to the ground. Therefore, the effect of gravity would
occur. The following tables shows the result of the pressure decay tests for solvent diffusion process in each cyclic solvent injection cycle.

5.1.2.1 Diffusion Tests

Table 5.5 Initial volume/mole feed composition for diffusion tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Initial dead oil volume fraction, %</th>
<th>Initial gas chamber volume fraction, %</th>
<th>Initial liquid phase mole fraction, %</th>
<th>Initial vapor phase mole fraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.418</td>
<td>94.582</td>
<td>24.86</td>
<td>75.14</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>24.96</td>
<td>75.04</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>24.78</td>
<td>75.22</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>24.20</td>
<td>75.80</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td>24.25</td>
<td>75.75</td>
</tr>
</tbody>
</table>

Table 5.6 Vertical diffusion test results

<table>
<thead>
<tr>
<th>Test No</th>
<th>Initial pressure, kPa</th>
<th>Final pressure, kPa</th>
<th>Solvent mole fraction in live oil, %</th>
<th>EOS calculated equilibrium solvent mole fraction in live oil, %</th>
<th>Vapor phase mole fraction, %</th>
<th>EOS calculate equilibrium vapor phase mole fraction, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1058</td>
<td>975.1</td>
<td>22.21</td>
<td>25.11</td>
<td>68.86</td>
<td>67.65</td>
</tr>
<tr>
<td>2</td>
<td>1056.7</td>
<td>961.1</td>
<td>24.56</td>
<td>24.84</td>
<td>67.86</td>
<td>67.76</td>
</tr>
<tr>
<td>3</td>
<td>1056.5</td>
<td>977.6</td>
<td>21.51</td>
<td>25.16</td>
<td>69.11</td>
<td>67.61</td>
</tr>
<tr>
<td>4</td>
<td>1059</td>
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<td>22.84</td>
<td>24.93</td>
<td>68.48</td>
<td>67.61</td>
</tr>
</tbody>
</table>
Figure 5.9 Diffusion pressure decay curves versus time
Figure 5.10 Diffusion profile for each cycle (a) initial diffusion (b) post-cycle 1 diffusion (c) post-cycle 2 diffusion
Figure 5.11 Diffusion profile for each cycle (d) post-cycle 3 diffusion (e) post-cycle 4 diffusion (f) post-cycle 5 diffusion (red dotted circle showing the oil downward drainage during diffusion by gravity)
Figure 5.9 to 5.11 show the pressure decay curves and solvent diffusion profile for all the diffusion tests in a vertically positioned micromodel. It can be seen that, for the initial diffusion process, the result was very similar to the test conducted in a horizontally positioned micromodel. This makes sense because the solvent was in contact with the original oil without any compositional change by light component extraction. For the post-cycle 1 diffusion, it can be seen that the overall pressure decay was higher than that of horizontal test. This can be proved by the distribution of the oil and gas after the first cycle of pressure depletion. It can be seen from figure 5.13 (b) left-hand side, that after the first cycle of pressure depletion, the gravity tended to pull the diluted oil at the gas-oil interface towards a lower position, and hence, with the aid of gravity, more of the deeper bulk oil phase in the upper part of the reservoir could be exposed for a solvent to increase its solubility.

After the 2\textsuperscript{nd} cycle of pressure depletion at a pressure depletion rate of 10kPa/min, the gas-oil distribution at the beginning of the diffusion process of cycle 3, was very similar to the gas-oil distribution of the pressure depletion from cycle 2 according to figure 5.13 (c). Hence, due to the extraction of light component from cycle 2 diffusion whose pressure decay was the highest, the cycle 3 diffusion did not dissolve as much of oil as cycle 2 diffusion. Also, a 10kPa/min pressure depletion rate was not able to effectively break up the oil phase into dispersed droplets, which also resulted in a decreased solubility of solvent.

Then after the diffusion process of cycle 3, the pressure depletion rate was raised up to 100kPa/min to examine the effect of gas-oil interface advancement under higher pressure depletion rate. It was found that, by utilizing a higher depletion rate, the gas-oil distribution
profile would be effectively broken up to smaller oil droplets in the porous media, which enhanced the ease of mass transfer. Therefore, in figure 5.11 (d), the post-cycle 3 diffusion has presented a higher solubility of solvent into heavy oil phase. In the next cycle, by using the same pressure depletion rate, lighter components were extracted more aggressively from the heavy oil phase, and hence, the solvent mass transfer was less efficient as indicated by the post-cycle 4 diffusion process in figure 5.9 and 5.11 (e). In order to see if further increasing the pressure depletion rate would cause higher solvent solubility in the next round of diffusion, 300kPa/min as pressure depletion rate was used. However, after 4 cycles of huff and puff, even though the 300kPa/min depletion rate had broken up more dispersed oil droplets in the porous media, the lighter component in the heavy oil had been extracted out of the oil phase to a great extent. Therefore, in the last 2 cycles of diffusion, the solvent solubility did not change drastically, which was reflected on figure 5.9.

5.1.2.2 Post-Diffusion Pressure Depletion Tests

Table 5.7 Residual oil saturation in bounding box for vertical tests

<table>
<thead>
<tr>
<th>Test no.</th>
<th>Pressure depletion rate, kPa/min</th>
<th>Initial residual oil saturation in bounding box, %</th>
<th>Final residual oil saturation in bounding box, %</th>
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</thead>
<tbody>
<tr>
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<td>3</td>
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</tr>
<tr>
<td>6</td>
<td>300</td>
<td>47.18</td>
<td>49.34</td>
</tr>
</tbody>
</table>
Figure 5.12 Residual oil saturation in bounding box for vertical tests (black: beginning; green: ending)
Figure 5.13 Gas-oil distribution after each cycle of pressure depletion (left: initial state; right: final state) (a) cycle 1 -10kPa/min (b) cycle 2 -10kPa/min (c) cycle 3 -100kPa/min
Figure 5.14 Gas-oil distribution after each cycle of pressure depletion (left: initial state; right: final state) (d) cycle 4 - 100kPa/min (e) cycle 5 - 300kPa/min
Table 5.7 sums up the residual oil saturation in the bounding box in image processing for vertical tests, and figure 5.12 shows the initial and final residual oil saturation in the bounding box against cycle number. Again, resembling to horizontal tests, the oil phase saturation in the bounding box was not always decreasing monotonously. Without gravity pull on the diluted gas-oil interface, the final state of cycle N pressure depletion stage should have the same residual oil saturation as the initial state of cycle N+1 diffusion stage. However, due to the existence of gravity acting on the diluted gas-oil interface, that part of the dilute interface tent to “slide” down and eventually out of the bounding box, allowing for more bulk oil phase to be exposed to the solvent chamber. This phenomenon can be clearly observed from figure 5.10 to 5.11. In addition, with a higher pressure depletion rate as indicated in figure 5.13 (c) and figure 5.14 (d) to (e), the oil phase can be recovered more from the bounding box and the rapid expansion of gas phase broke the oil into smaller droplets which enhanced the solvent solubility in the next round of CSI cycle.

5.2 Static Constant Composition Expansion (SCCE) Tests

In this subchapter, the characterization of non-equilibrium foamy oil phase behavior was conducted through CCE tests in micromodel system. In order to characterize the extent of non-equilibrium, the initial pressure of micromodel was depleted to a certain pressure at a certain pressure depletion rate. The exsolution gas was received by the pump transfer cylinder at the down stream of the system, and the volume expansion was indicated by the data achieved from the pump controller. Therefore, the system was kept as a closed system for constant composition.
5.2.1 SCCE Test Type 1

The first set of CCE pressure depletion test conducted in the micromodel was at a continuous pressure depletion rate at 20kPa/min and the whole system was eventually depleted to 500kPa. A continuous pressure depletion rate was applied to investigate the feasibility of utilizing micromodel system to conduct non-equilibrium phase behavior tests for a solvent-heavy oil two-phase system. In the attempted experiment of SCCE type 1, however, there was some excessive CO₂ gas in the system, therefore, the equilibrium vapor phase volume fraction was considered by calculating the given system in a pre-existing two-phase condition. Figure 5.15 shows the vapor phase volume fraction in the micromodel against prevailing pressure and time. By considering the pre-existing gas as the vapor phase and the live oil as the liquid phase, a two-phase flash calculation based upon the given vapor and liquid mole fraction for the equilibrium vapor volume fraction line was calculated to compare with the experimental vapor phase volume fraction inside the micromodel. It can be seen that under the confinement of the geometry and high viscosity of the oil phase, the liberation of gas phase tent to stay non-equilibrium. As pressure was further decreased, the vapor phase volume fraction gradually increased but still far from reaching equilibrium. The actual phase change processes of the live oil in the micromodel before and after reaching the final destined pressure at 500kPa was shown in figure 5.16 and figure 5.17 for direct visualization.
Figure 5.15 Vapor volume fraction (a) against prevailing pressure (b) against time.
Figure 5.16 Phase change processes of solvent-heavy oil system in micromodel under SCCE test type 1 (subplot 1~10 shows the time-elapsed order of solvent exsolution at a time segment of 5mins from 1400kPa~500kPa)
Figure 5.17 Phase change processes of solvent-heavy oil system in micromodel under SCCE test type 1 (subplot 1~10 shows the time-elapsed order of solvent exsolution after reaching 500kPa and maintained the pressure for another 10 minutes)
Figure 5.18 Magnified section for vapor phase volume fraction characterization
Figure 5.19 Vapor volume fraction of a zoomed-in portion of the micromodel geometry (1cm by 0.75cm)
Figure 5.20 Time-series of zoomed-in micromodel section for vapor volume fraction characterization (domain dimension: length=1cm, width=0.75cm)
The above figures 5.18 and 5.20 show the measurement of the vapor phase volume fraction in a 1cm by 0.75cm geometry area that is closed to the outlet of the micromodel where the pressure propagation is almost instantaneous with the connected ISCO pump cylinder. The magnified section in figure 5.18 is aimed to compare the vapor phase volume fraction between the whole micromodel scale and a very localized scale. It was assumed that a part of the micromodel near the outlet would have the fastest reaction to pressure depletion, and hence chosen as the observation area. From figure 5.18, it can be seen that the overall trend of vapor phase volume fraction evolution between the two measurements are similar to each other, while for the small observation section, there are more fluctuations. This is because the small section has both an “inlet” and an “outlet”, while the total micromodel was sealed down from one side, where there would not be any fluid supply into the system. Figure 5.20 shows the actual phase change process in the small section of the micromodel.
Figure 5.21 Overall system vapor volume fraction versus equilibrium condition
Figure 5.21 shows the vapor phase volume fraction in the total system including the micromodel and pump fluid collecting chamber. It can be seen that from figure 5.21 (a) that the live oil system was under non-equilibrium state during the whole pressure depletion processes even though a free gas phase pre-existed in the live oil system. Given enough time, the solution gas would eventually libertate completely from the oil phase. Figure 5.21 (b) shows the vapor phase volume fraction inside the micromodel as well as in the ISCO pump cylinder. It can be seen that there is a clearer difference between the gas exsolution behavior under a porous media and a bulk phase even though the system was a closed system and under reservoir condition. Worth noticing, due to the inability of “current” version ISCO pump controller in volume display accuracy under Constant Pressure Mode, the recorded volume of liberated gas collected in the pump chamber might possibly be smaller than the recorded value as the controller would round up the number to a minimum decimal place of 0.01cm$^3$ when any movement of the rod piston occurred. Hence, on figure 5.21 (b), on the left-hand side of the blue dotted line, when the pump was controlled for pressure depletion, the reading of the pump was maintained at 0.01cm$^3$. After 11 minutes, the pump controller started to read a gradual increase in the volume instead of maintaining a fixed number, indicating the volume sensor had enough accuracy to read the volume change of the rod piston when collecting the fluid out of the micromodel. Since it is impossible to create a polymerized liquid piston in the micromodel for a porous media, therefore, the non-equilibrium phase behavior that occurred inside the porous media is what should be paid attention to. Hence, in Chapter 6 when conducting reservoir simulation, two ways can be used to address the difference in gas exsolution behavior between micromodel and the ISCO pump cylinder. One is to use keyword “PTYPE” and
“PVTSET ##” in PVT Regions settings to define different PVT properties to multiple grid cell regions. The other is by dynamically changing the reference condition and surface flash K value to mimic the gas exsolution from the oil phase in a bulk phase region.

5.2.2 SCCE Test Type 2

In this section, the experimental results of SCCE tests will be elaborated to investigate the non-equilibrium of solvent-heavy live oil system under the presence of a porous media. The main parameter of non-equilibrium extent indication is the vapor volume fraction dynamic variation against time and pressure depletion. The vapor volume fraction was quantified through automatic image processing of a large photo set.

Figure 5.22 shows the whole process of SCCE tests at different pressure segment. The red triangular marker in the figure indicates the equilibrium vapor phase volume fraction at the prevailing pressure of the system, which is calculated by Peng-Robinson equation-of-state with the given initial conditions in the closed system (prevailing pressure and temperature, and initial solvent-heavy oil mole fraction of the saturated live oil system assuming the system was uniform). It is clearly shown that there is a gap between the equilibrium line and the non-equilibrium line. At first when the hydrostatic pressure of the system was instantaneously lowered to 1100kPa from saturation pressure, there were barely any gas bubbles formed in the micromodel even after 30 minutes of equilibrating time. This proved that the thermodynamic bubble point of the live oil was deviated from the true bubble point. Then, the system pressure was depleted instantaneously to 900kPa from 1100kPa, and after around 5 minutes, there was a sudden increase in the vapor phase volume fraction in the micromodel. This phenomenon indicated that the pseudo-bubble point pressure of the live oil system lied around 900kPa. Although vapor phase volume
fraction increased to a larger extent, it still did not reach equilibrium. This can be due to the suppression of porous media on the formation of large connected gas clusters. System pressure was then depleted to 700kPa, but the vapor phase volume fraction did not seem to rise up at a higher rate. When the pressure was further depleted to 500kPa, the vapor phase volume fraction again increased at a very high rate. This can be attributed to the compressibility of the vapor phase as well as the excessive deviation from live oil saturation pressure. When the pressure was further reduced to 300kPa, the incremental rate of vapor phase volume fraction against time was similar to 500kPa. Eventually, when the system was depleted to atmospheric pressure, it showed that the vapor phase volume fraction in the micromodel was still lower than equilibrium line by around 35%. However, according to figure 5.25, the live oil phase that was expelled out of the micromodel was approaching to equilibrium at 83.86% of vapor phase volume fraction. The reason might be highly possible due to the fact that the tubing link between the outlet of the micromodel and the receiving transfer cylinder was at a quite small diameter, and when the pressure was depleted far from the saturation pressure, the exsolution of solvent further increased the viscosity of the oil phase. With a very small diameter and a relatively higher oil phase viscosity, there might be a pressure build up before and after the tubing link. Because the effect of system dead volume had to be minimized to increase the accuracy of the measurement in micromodel, pressure transducer was not placed before the tubing link at the outlet, and the pressure recorded was the pressure after the link, that is, the pressure inside the receiving cylinder. Therefore, the expelled oil phase underwent surface flash, while the live oil phase inside the micromodel might undergo pressure build up that resulted in a lower vapor phase volume fraction. But above all, even when the system was
depleted to the atmospheric condition, non-equilibrium still existed in the whole system, indicating part of the solvent was still in dissolution form no matter inside the micromodel or in the receiving cylinder.
Figure 5.22 Vapor phase volume fraction in the micromodel during SCCE tests
Figure 5.23 Phase change processes of solvent-heavy oil system in micromodel under SCCE tests (subplot 1~7 shows the time-elapsed order of solvent exsolution)
Figure 5.24 SCCE tests pump collected fluid data
Figure 5.23 shows the actual phase change processes of solvent-heavy oil system in micromodel under SCCE tests. From subplot 1 to 7, the processes of phase change from single phase live oil to gas-oil two-phase flow are clearly visualized. At first, when the pressure was kept at 1100kPa in subplot 1, it can be seen that very limited exsolution of vapor phase was observed even though the pressure was kept constant under saturation pressure at 1200kPa, for almost 30 minutes. Then by further reducing the pressure to 900kPa, it can be seen that at subplot 2, for the initial 5 minutes, no obvious exsolution gas was observed. After around 5 to 6 minutes, the exsolution rate suddenly increased and the vapor phase volume fraction increased to a clearly observable level in subplot 3. By further reducing the pressure in the system to 700kPa, 500kPa, 300kPa, and finally 100kPa, the phase change processes in the micromodel became more and more evident from visualization as shown in subplot 4~7.

Figure 5.24 shows the pump data recorded during all the SCCE tests. The total system volume is by the addition of the micromodel pore volume and the pump collected volume due to the exsolution of solvent and free gas formation during pressure depletion. The vapor phase volume is calculated by assuming that the expelled oil out of the micromodel into the ISCO pump chamber remained the same volume (ignoring the volume shrinking effect of solvent exsolution on the oil phase), and then this value was subtracted directly by the total pump collected volume. It can be seen that under surface condition (100kPa, 20°C) in the last SCCE test point, the total pump collected value suddenly increased, which indicated that the exsolution rate of solvent increased drastically and according to figure 5.24, the tendency to reach back to equilibrium state was very strong.
Figure 5.25 Overall system vapor volume fraction versus equilibrium vapor volume fraction.
Figure 5.26 Reproducibility of the SCCE test in the micromodel
Figure 5.25 shows the overall system vapor volume fraction which is the sum of the reservoir-condition vapor volume in the micromodel and the vapor volume collected in the transfer cylinder as shown as the red and green frame in figure 3.12, respectively. Hence, under such comparison, it can be seen that the vapor volume fraction under non-equilibrium deviates from the equilibrium vapor volume fraction, indicating that the exsolution of the solvent out of the oil phase inside the porous media was suppressed and required enough time to reach re-equilibrium. Worth noticing, due to the inability of “current” version ISCO pump controller in volume display accuracy under Constant Pressure Mode, the recorded volume of liberated gas collected in the pump chamber might possibly be smaller than the recorded value as the controller would round up the number to a minimum decimal place of 0.01cm$^3$. Judging from the overall trend, it is safe to say that the liberated gas collected at the end of 1100kPa test pressure should be smaller than 0.01cm$^3$, which indicated a non-equilibrium vapor volume fraction smaller than 10% in figure 5.25. In the above figure 5.26 shows the reproducibility of the experimental results for the SCCE tests. The vapor phase volume fraction in the micromodel was compared against 5 repetitions. The pseudo-bubble point pressure of the live oil system of each reproducibility test was very close to each other. It can be seen that the overall reproducibility of the tests was good, although certain level of error existed. The reason for such variation up to at most 15% of differences is due to the size of the sample used in the experiments as well as the apparatus control accuracy. Microscopically, the distribution of the solvent inside the heavy oil phase above saturation pressure cannot be guaranteed to be perfectly uniform, and therefore, with smaller fluid size sample, it is highly possible that the saturated live oil sample in the micromodel will have slightly
different properties, and an extremely small scale might exaggerate such non-uniformity. The outlet tubing used in the SCCE tests might have imposed some effect inside the micromodel as smaller-diameter tubing could induce pressure build-up inside the micromodel. This can be seen by all the tests when the pressure was dropped from 900kPa to 700kPa. 700kPa was closed to the pseudo-bubble point measured in bulk phase visual cell, hence, when the pressure was dropped to 700kPa, sudden release of dissolution gas might build up the pressure inside the micromodel while it can be hard to flow out of the micromodel due to the Jamin effect of gas phase piling up at the tip of the tubing.

5.3 Foamy Oil Continuously Convective Flowing (CCF) Tests

In the CCF tests, the foamy oil was induced by creating a pressure differential between the live oil inlet and the model outlet as shown in figure 3.13. Again, the vapor volume fraction of the foamy oil against time and pressure depletion was quantified from image processing. CMG Results Graph Module was used to plot the series of large data set of vapor volume fraction against time for different flow rate and operation pressures as the CMG readable FHF file format. For each set of CCF tests, the experimentation time was set to be long enough to see the trend of the vapor volume fraction change for a micromodel-based methodology. Under such experimentation setting, the effect of in-situ Darcy velocity on vapor volume fraction can be more clearly investigated. In order to show the dynamic fluctuations of the observed vapor volume fraction of the foamy oil, the Y axis of all the CCF tests were all set to be 0.35 to yield a shorter Y axis distance so the fluctuations could be more easily observed. Figure 5.27 shows all the CCF test results under various operation pressure and injection velocity. It can be clearly seen that the vapor phase volume fraction under a continuously convective condition kept stable for a long period of testing time.
Figure 5.27 Vapor phase volume fraction of various CCF tests at different operating pressure and injection rate: (a) 1200~950kPa (b) 950~700kPa (c) 700kPa (d) 700~500kPa (e) 500~400kPa (f) 400~150kPa
Figure 5.28 Foamy oil vapor volume fraction in porous media for P=700kPa at (a) 0.001mL/min (b) 0.006mL/min
From figure 5.28, from the same outlet pressure at 700kPa in CCF test, it can be clearly seen that at first, the flow velocity of the foamy oil through the micromodel was set to be at 0.001mL/min while having a relatively large pressure differential of 500kPa from saturation pressure. After continuously observing the growing vapor volume fraction, it can be seen that at such velocity, the shear effect was not able to compete with the tendency to undergo phase change under thermodynamic deviation from equilibrium, and therefore the gas cluster sizes are relatively larger in a more consecutive form. Then in order to see how gas-oil mixture velocity can reduce the vapor volume fraction and maintain foamy oil stability, higher injection rate was adjusted to be 0.006mL/min from the inlet of the micromodel. As it is shown in the blue curve in the subplot (c) in figure 5.27, the rate of vapor volume fraction growth under thermodynamic deviation was surpassed by the effect of the higher velocity, and hence, the vapor volume fraction in the micromodel was observed to decrease overtime.

From subplot (d)–(f) in figure 5.27, it shows that even though the pressure differential between saturation pressure and operation pressure at the model outlet was getting higher, if the foamy oil flow velocity was set high enough from the inlet port of the micromodel, the vapor volume fraction would maintain relatively low throughout the flowing test time, which indicates that the higher flow velocity was able to overcome the effect of the gas exsolation tendency caused by thermodynamic deviation.
Figure 5.29 (a) Lateral comparison between different SCCE tests (b) bubble size shifting under flow condition (Fu, Cueto-Felgueroso, and Juanes 2016)
The comparison between all the CCF tests is plotted in figure 5.29 (a). The X axis was purposely plotted as the consecutively incremental time to laterally compare the trend of the vapor phase volume fraction in micromodel under different operation pressure and flow velocity schemes. Worth noticing, the true Darcy-velocity of the foamy oil phase in the micromodel was hard to be accurately determined. This is because even when the flow rate was set to a small value, the true velocity was still dominated by the applied pressure differential. Therefore, the actual Darcy velocity of the foamy oil was contributed together by pressure differential and the displacing rate at the inlet of the micromodel. For CCF tests, it can be seen that when the model pressure differential was set to 500kPa, if the flow velocity was not adjusted and maintained to be 0.001mL/min, the vapor phase volume ratio was in an uprising tendency. This means that the foamy oil was unstable under such flowing velocity, while by increasing the velocity from 0.001mL/min to 0.006mL/min, it can be seen that the vapor volume fraction started to fall down again and maintain stable until the pressure differential was further increased to 600kPa. Again, at outlet pressure around 450~400kPa, the vapor phase ratio in the micromodel was in an uprising trend. Therefore, in order to testify if flow velocity could affect the foamy oil stability, higher injection rate was adjusted to 0.01mL/min. It can be seen that the vapor phase volume ratio decreased again. Although high flow velocity was able to yield a higher foamy oil stability, the average vapor phase volume ratio under higher pressure differential from live oil saturation pressure (indicated by the black dotted line), was around 10% higher than the average vapor phase volume ratio under lower pressure differential (indicated by red dotted line). This indicates that under larger pressure differential from saturation pressure, the tendency for thermodynamic phase change was stronger. Figure 5.29 (b) shows a
numerical simulation result of continuous flow effect on the coarsening of bubbles in bubble-scale (Fu, Cueto-Felgueroso, and Juanes 2016). It is concluded that under continuous background flow for a non-equilibrium mixture, recurrent pinch off of small bubbles from large coalesced bubble patches would always occur. Under non-equilibrium state, newly formed bubbles at smaller sizes would be consumed into bulk liquid phase by Ostwald Ripening mechanism. If the rate of bubble shredding effect imposed by the shear effect is larger than the rate of diffusive mass flux from oil into larger bubbles, then excessive mass of dissolution gas concentration would be presented in the liquid phase, while larger bubbles are shredded into smaller bubbles that have a high possibility to be dissolved back to liquid phase again under Ostwald Ripening. Hence, if the rate of shearing can overcome or equate to the rate of exsolution under non-equilibrium, the vapor phase volume ratio would be decreasing or stabilized, respectively. Figure 5.30 shows the overall comparison between SCCE tests and CCF tests. The same color indicates the same operation condition for clearly comparison between SCCE and CCF test results. The SCCE test at system pressure of each pressure was plotted against the CCF tests at pressure close to the SCCE test pressure. It can be seen that for SCCE test, the vapor volume fraction was higher and less stable than all the CCF tests. This has shown the great effect of flowing velocity on the stability of foamy oil. For the SCCE test, the undergoing time for the test was shorter than CCF tests, while the tendency to reach equilibrium vapor volume fraction was stronger, which is indicated by the red dotted line on the figures. For the CCF tests, the vapor volume fraction maintained stable and lower under convective environment throughout a long period of time. The effect of flow velocity of the foamy oil mixture in the micromodel had greatly contributed to the foamy oil stability.
Figure 5.30 Overall comparison between SCCE tests and CCF tests
5.4 Solvent Flooding and Post-Flooding Pressure Depletion Tests

In this chapter, experimental study of solvent flooding and post-flooding cyclic solvent injection tests (just 1 cycle) were conducted to study the mechanism of solvent-heavy oil system under solvent injection processes. For all the tests, solvent flooding tests were conducted firstly due to the fact that in a micromodel which is fully saturated with dead heavy oil, there is no path at all for solvent to get into the main heavy oil-bearing area of the micromodel, and hence the subsequent solvent soaking and pressure depletion tests could not be effectively carried on. Totally, 7 sets of solvent flooding tests and 7 subsequent sets of solvent soaking and pressure depletion tests were conducted. The following table shows the detailed parameters of the conducted tests.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Solvent flooding stage</th>
<th>Solvent injection rate, cm³ res/min</th>
<th>Solvent flooding outlet pressure, kPa</th>
<th>Post-flooding soaking and pressure depletion state</th>
<th>Post-flooding solvent soaking time, min</th>
<th>Pressure depletion rate, kPa/min</th>
</tr>
</thead>
<tbody>
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<td>0.01</td>
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<td>290</td>
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<td>2</td>
<td>0.05</td>
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<tr>
<td>3</td>
<td>0.1</td>
<td>1000</td>
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<td>10</td>
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<tr>
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<tr>
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<td>1000</td>
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</tr>
</tbody>
</table>
Solvent flooding tests were conducted firstly in order to achieve two objectives. First, to understand how injection rate of solvent affects the performance of solvent flooding and subsequent viscous fingering that occurs when a less viscous fluid displaces a more viscous fluid. Then by directly observing the performance of the solvent flooding, it is evident to understand how gas contacts oil and its relationship to the well, as well as the efficacy between cyclic and continuous solvent injection. Also, in the future work, the upscaling and pore-network modelling of gas displacing oil could be conducted to generate the relative permeability to gas and oil under displacing mechanism. Second, for the experimental purpose sake, the prior solvent injection could create a path for solvent to get into the micromodel without creating a very high pressure differential between the two ends of the model when the tests conducted were not under the shield of the high pressure/high temperature micromodel holder.

5.4.1 Solvent Flooding

Recovery Factor
Figure 5.31 Solvent flooding recovery factor comparison between different solvent injection rate

Table 5.9 Solvent flooding result table

<table>
<thead>
<tr>
<th>No.</th>
<th>Solvent injection rate, cm$^3$$_{res}$/min</th>
<th>Recovery factor</th>
<th>Solvent breakthrough time, min</th>
<th>$Nca$, capillary number</th>
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<td>0.1273</td>
<td>33</td>
<td>1.55e-7</td>
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<tr>
<td>3</td>
<td>0.1</td>
<td>0.155</td>
<td>38</td>
<td>3.10e-7</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.119</td>
<td>29</td>
<td>1.55e-6</td>
</tr>
</tbody>
</table>
In figure 5.31, the recovery factor of the solvent flooding tests was plotted. It is seen that, at the highest solvent injection rate at 0.5cm$^3_{\text{res}}$/min, the breakthrough of the solvent was the earliest, and the recovery factor was the lowest. At a moderate solvent injection rate at 0.1cm$^3_{\text{res}}$/min, the recovery factor was raised and surpassed test no.4. But when the solvent injection rate was reduced to a lower value at 0.05cm$^3_{\text{res}}$/min, the recovery factor was lower and when the injection rate was further reduced to 0.01cm$^3_{\text{res}}$/min, the recovery factor raised up again. This abnormal behavior might be due to the fact of the non-uniform distribution of oil saturation in the micromodel prior to solvent flooding. For test no.1, 3, and 4, the trend is very obvious, that is, a lower solvent injection rate would yield a higher recovery factor and a later solvent breakthrough time.

Figure 5.32 shows the pressure differential during solvent flooding, and it is clearly that a higher solvent injection rate would yield a high pressure differential during flooding processes. And the turning point of the pressure drop curves show the breakthrough of the solvent to the production well.

**Repeatability of the Solvent Flooding Tests**

Four sets of solvent flooding under the same solvent injection rate were conducted to examine the repeatability of the solvent flooding under the same operation condition. The following figure shows the recovery factor of the four tests:
Figure 5.32 Pressure differential during solvent flooding
Figure 5.33 Repeatability of the solvent flooding test under same solvent injection rate
As it is indicated in the figure 5.33, the repeatability of the solvent flooding tests was decent, except for the one set. The breakthrough of the 0.1 cm$^3$/min 2nd set of flooding test was way earlier than the other three tests. From the figure 5.34 below, it is indicated that at the very first stage, injected gas travelled along the edge of the micromodel and flowed much faster towards the production well than the other tests where the gas chamber mainly focused on flowing in the middle section of the model. For the outlier, even though the gas break through very early, it still managed to flow toward the middle of the micromodel eventually and created obvious fingers and thus, yielding a very similar recovery factor.
Figure 5.34 Outlier test with the early breakthrough time (12mins)
Figure 5.35 (a) Viscous fingering during solvent flooding (at a time segment of 0, 10, 20, 30, BT) (b) repeatability of solvent flooding tests at Nca=3.10E-7, 0.1cm³/min)
Figure 5.35 Shows the viscous fingering phenomenon for different solvent injection rate with various capillary number $Nca$. As it is indicated in the picture, a lower solvent injection rate would form a relatively “thicker” finger as well as a delayed breakthrough during flooding process. It showed that the fingers tend to form in the upper part of the micromodel due to the local heterogeneity which created a flow-ease path. Once the solvent has break through and created a path for solvent to exist in the micromodel, the recovery factor no longer increased, and subsequent soaking and pressure depletion processes would be carried out to utilize the remaining solvent energy in the model to understand to what extent a following up cyclic solvent injection process could enhance the recovery factor.

The following table shows the final recovery factor of the solvent flooding tests, and the screening of the recovery factor will be useful for the comparison of post-solvent flooding cyclic solvent injection.

Table 5.10 Recovery factor of all the solvent flooding tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Solvent injection rate, cm$^3_{res}$/min</th>
<th>Recovery factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>0.155</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.127</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.156</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.119</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>0.156</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>0.155</td>
</tr>
<tr>
<td>7</td>
<td>0.1</td>
<td>0.152</td>
</tr>
</tbody>
</table>
5.4.2 Post-Flooding Soaking and Pressure Depletion Tests

In this subchapter, the experimental results of post-flooding cyclic solvent injection tests will be analyzed to understand the effectiveness of solvent soaking and pressure depletion on the performance of stimulate the oil recovery factor.

According to the table 5.11, the post-solvent flooding tests were arranged to be compared with each other shown in the following table:

Table 5.11 post-solvent flooding cyclic solvent injection comparison

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Soaking time, min</th>
<th>Pressure depletion rate, kPa/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, 4</td>
<td>√</td>
<td>×</td>
</tr>
<tr>
<td>1, 3</td>
<td>√</td>
<td>×</td>
</tr>
<tr>
<td>1, 5, 6, 7</td>
<td>×</td>
<td>√</td>
</tr>
</tbody>
</table>

Comparison between Test No.2 and 4

For test No.2 and 4, the comparison was based upon the soaking time effect on the final recovery factor under a fixed pressure depletion rate.
Figure 5.36 Recovery factor increment

Figure 5.37 Oil production rate under pressure depletion (test no.2 and 4)
Figure 5.36 shows the results of the effect of utilizing post-solvent flooding cyclic solvent injection to boost up the recovery factor of the reservoir. The experimental studies were conducted only using 1 cycle of solvent injection, soaking and production. As we can see from the figure 5.36, even under the same pressure depletion rate, the solvent soaking time has significant effect on increasing the recovery factor. This means the longer the solvent got in contact with oil, where in test no.4 for 1000 minutes of soaking time, the more solubility of the solvent could be achieved, and thus, the more upgrading of in-situ oil it would yield. In addition, the initial profile of gas-oil saturation after solvent-flooding would also affect the final recovery factor. Notably, there are some “ups and downs” in the recovery factor plot. This might be due to the accuracy of image processing as well as the flowing-back phenomenon of fluid from outlet into the main model under the capillary pressure in a very confined space, or it might be due to the fact that under pressure depletion, the heavy oil phase would be swelling and therefore, when the image processing was conducted, it accounted for the oil phase volume as the residual oil volume inside the reservoir, and hence, it might yield more oil in the model, and these bumps in the figure could be regarded as the expansion of oil phase during gas exsolution. The total trend is incrementing.
Figure 5.38 Soaking pressure drop during soaking period (test no.2 and 4)
Figure 5.38 shows the trend of pressure depletion during soaking period. It is clearly indicated that the pressure drop for a longer solvent soaking time would yield a higher pressure drop, and hence, a higher solubility of gas into heavy oil phase. Therefore, with more dissolved gas content, when under pressure depletion, the more gas could form exsolution and provide more expansion energy for the oil to be driven out of the micromodel.
Figure 5.39 Exsolution behavior of propane from the oil phase (test no.2 and 4)
Figure 5.40 Cyclic solvent injection production period profile of test no.2 and 4
The figure 5.39 shows the exsolution behavior of propane during pressure depletion for the two tests. It shows that propane tended to form exsolution out of the heavy oil phase earlier for the case in which the soaking time was longer at 1000 minutes. It might be due to the fact that a longer soaking time yielded a high solubility of solvent into the heavy oil, and under lower pressure, as indicated by the live oil tests, propane tended to dissolve more into oil phase than carbon dioxide.

Therefore, the oil closer to the production well would have more propane in solution, and the viscosity of the oil near the production well would be reduced to a greater level. When it was produced, propane content in the produced oil will be flashed out, and its content should be higher. When this portion of oil finished producing, the propane exsolution rate reduced and subsequently, more carbon dioxide started to flash out of the oil phase. For a relatively shorter time of soaking, the propane was dissolved into the heavy oil at a higher rate than carbon dioxide, but meanwhile not fully saturated into the solvent-contacted oil, and thus, more carbon dioxide left in the free gas phase. When the pressure was depleted, free gas phase tended to flow out first and subsequently the solvent-saturated oil. In figure 5.40 above, the upper part shows the gas-oil distribution of test no.2 and 4 at the point of turning, and the lower part shows the fluid profile of test no.4. The upper picture shows that the gas chamber was very close to the production well as well as the deeper part of the reservoir. Therefore, when the pressure was depleted, it is clear that the free gas would flow out firstly, and subsequently the live oil. The majority of the production gas was detected to be carbon dioxide in the free gas, indicating that a majority of propane was dissolved near the production well. For the lower part, more solvent-dissolved live oil was near the well, and therefore, when the pressure was depleted, the live oil would flow out
firstly, and subsequently the free gas phase. The live oil mixture produced at the first several minutes was saturated with more carbon dioxide than propane, as the production progressed, the deeper part of the live oil was produced and it was indicated to be saturated with more propane as propane detection started to rise.

Comparison between Test No.1 and 3
Figure 5.41 Recovery factor increment

Figure 5.42 Oil production rate
Figure 5.43 Soaking pressure drop during soaking period (test no.1 and 3)
Figure 5.44 Cyclic solvent injection production period profile of test no.1 and 3
Figure 5.45 Exsolution behavior of propane from the oil phase (test no. 1 and 3)
The figure 5.41 shows very similar trend to the comparison between test no.2 and 4. A longer soaking time yield a higher oil production eventually. The pressure drop of a longer soaking time of solvent with heavy oil yielded more solubility into heavy oil, and therefore, in the next figure 5.45, it showed a similar trend of propane exsolution behavior where in the upper part of the figure, the free gas chamber was closer and expanded to the well region, and therefore, free gas tend to produce in prior to oil, and the carbon dioxide content in the produced free gas was higher than propane which had dissolved into heavy oil in majority. And the lower part of the figure shows that at a longer soaking time and a relatively higher injection pressure, more solubility was achieved, and therefore, the live oil near the well tend to produce first and hence the propane detected during live oil production was way earlier than a shorter soaking time.

The continuous detection of propane content in the flowing gas stream might also be affected by its flow rate, humidity, temperature etc. And therefore, at a higher flow rate like the case in both of the upper part of figure 5.39 and figure 5.45, the detection of propane content might contain error due to higher gas flow rate, that is, in the blue label in figure, the detection of propane did not rise until around 45 mins passed. That is to say, the actual propane content might be higher than the shown number, but since the flow rate is getting faster and faster during pressure depletion (pressure=550kPa at 45mins) when the pseudo bubble point has been passed, the actual high flow rate might affect the reading. And hence, the actual propane might be higher or lower or fluctuate more than a straight line. That best way to validate the propane content during the mid section of pressure depletion is to collect the gas and run through a gas chromatography test to compare with the tunable infrared filter of the gas sensor system. The total trend shows correct exsolution
behavior, that is, the final ratio of C$_3$/($C_3$+CO$_2$) reached around 15%, which resembles to the original solvent mole fraction of injection, 85% CO$_2$+15% C$_3$.

*Comparison between Test No.1, 5, 6, and 7*

In this subchapter, the comparison between test no.1, 5, 6 and 7 will be discussed to analyze how the pressure depletion rate affects the final recovery factor and solvent exsolution behavior.
Figure 5.46 Comparison between tests of different pressure depletion rate (a) recovery factor (b) oil production rate
Figure 5.46 shows the recovery factor of tests with similar initial residual oil saturation but with different pressure depletion rate value. It is shown that all the tests followed a trend that, an intermediate pressure depletion rate at 20kPa/min showed the highest recovery factor boost than the other two tests at 5kPa/min, 10kPa/min, and 50kPa/min. The oil production rate follows the same trend as the cumulative recovery factor curve. After a high peak of oil production, at the earlier stage of the pressure depletion, the oil production rate greatly reduced and oil recovery dropped down significantly.
Figure 5.47 Pressure drop during soaking period of tests with different pressure depletion rate

Table 5.12 Pressure decay for tests with different pressure depletion rate

<table>
<thead>
<tr>
<th>Pressure depletion rate, kPa/min</th>
<th>Initial pressure, kPa</th>
<th>Total pressure drop from initial pressure, kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1054.5</td>
<td>135.8</td>
</tr>
<tr>
<td>10</td>
<td>1000</td>
<td>96.2</td>
</tr>
<tr>
<td>20</td>
<td>1021</td>
<td>124.1</td>
</tr>
<tr>
<td>50</td>
<td>1035</td>
<td>126.4</td>
</tr>
</tbody>
</table>
As it is indicated in the figure 5.47, due to the accuracy of the pressure gauge and pressure regulator, the initial pressure of the solvent injection deviated with each other to an average around 20kPa, so roughly it was assumed that the initial pressure was regarded the same for all the tests. It is seen from the figure that, even though the test no.1 has the highest pressure drop (highest solvent solubility), it was not necessarily yielding the highest recovery factor under a relatively low pressure depletion rate. For test no.4, even though the initial pressure and soaking pressure drop was the lowest among the actual data, it was not necessarily yielding the lowest recovery factor. As for test no.6, a higher pressure drop with a higher pressure depletion rate did not perform the best in terms of expelling the oil out. The optimal case in the upper tests were a pressure depletion rate of 20kPa/min.
Figure 5.48 Oil production process: scattered gas phase to connected gas cluster to free gas streaming
Figure 5.49 Free gas chamber in-situ growth: unfavoured mobility ratio
As is indicated in the above figure 5.48 inside the red dotted box, before the gas chamber break through to the production well, the performance of oil production was mainly focused on producing oil, and hence, a higher oil production rate was observed. However, when the gas chamber started to coalesce and grow towards the production under the pressure depletion, the unfavoured mobility ratio between oil and gas dominated the flow pattern, and the oil production rate greatly reduced with high gas production rate.

It is indicated in figure 5.49 that after gas has break through the production well, the gas chamber would mostly grow in-situ-ly, and expand to the production well in the main gas channel without efficiently “taking” oil out of the model, and hence, a great deal of heavy oil was left in the post-cyclic solvent injection well. It could be confirmedly induced that after the gas production rate, the gas chamber shape barely changed which indicated that only free gas expanded and flowed out of the model. Severe gas channeling formed at this moment.
Figure 5.50 Comparison of the final oil-gas distribution profile for tests with different pressure depletion rates
The above figure 5.50 shows the final oil-gas distribution profile in the micromodel. From up to down the picture indicates the recovery profile of 5kPa/min, 10kPa/min, 20kPa/min and 50kPa/min. The overall gas chamber profile resembles to each other as gas tend to channel through the favourable zone in the same model. It is indicated that at a relatively high rate, say 50kPa/min, of depletion, the gas phase was likely to channel faster under a greater pressure drop and high mobility. And at relatively lower pressure depletion rate, the gas mobility was reduced but the oil mobility was also reduced with less pressure drive. Hence in the above tests, test no.1 and 5 showed lower recovery factor than an optimal pressure depletion rate at 20kPa/min. However, it should not be the only criteria to judge if one pressure depletion rate is better than another because the distribution of gas chamber inside the model follows a random trend, that is to say, if the free gas chamber happens to be near the wellbore region, the likelihood of early gas channeling and breakthrough with very little oil production will be higher than where the gas chamber is way deeper inside the reservoir. Therefore, it is important to figure out if the injected solvent could be sent further into the reservoir to conserve the energy and allow a longer distance of expansion to generate greater oil-expelling effect.
Figure 5.51 Propane mole fraction in the produced gas stream under different pressure depletion rate
Figure 5.52 Gas-oil interface distribution effect on propane exsolution
The above figure 5.51 shows the propane exsolution behavior of tests with different pressure depletion rate. From the figure 5.52, it is indicated that at 5kPa/min, the gas chamber was very close to the production well, and under such low pressure depletion rate, the oil phase was slowly driven out of the well as well as the bulk gas phase, and therefore, with majority of the production fluid to be gas (high production GOR), the CO₂ content in the produced gas was high at the first stages. And as the dissolved propane started to form more exsolution, the propane detection started to rise. For the second row, the test with 10kPa/min, the case was similar to test with depletion rate at 5kPa/min. The majority of the gas production at the first stages were CO₂ due to the formation of high gas chamber content close to the production well. For the 3rd column, the pressure depletion rate was raised up to 20kPa/min, and it is observed that although the initial gas chamber content was high close to the production wellbore, the exsolution of propane was detected way earlier than the tests with low pressure depletion rate. For the 4th column in which the test was under the highest pressure depletion rate at 50kPa/min, the propane exsolution was the earliest. It is concluded that propane exsolution behavior is highly affected by the pressure depletion rate. Lower pressure depletion rate would yield a more delayed propane exsolution but not necessarily a higher recovery. Also, the rate of propane exsolution was similar for pressure depletion rate as indicated with the red dotted line in figure, the only differences observed in the tests were the time or rather, the pseudo-bubble point for propane to start forming exsolution.
CHAPTER 6 NUMERICAL STUDY OF SOLVENT NON-EQUILIBRIUM DISSOLUTION AND EXSOLUTION BEHAVIOR

6.1 Non-Equilibrium VLE K Value

In this section, the behavior of K value deviation from equilibrium state of the closed system CCE tests will be analyzed. The analysis is mainly focused on the two sets of the test, -20kPa/min in both fully-saturated cell and half-saturated cell in section 4.2.2. Since closed system was applied to each set of experiment, there was no mass exchange of the system, and thus, constant composition was achieved and the intensive parameters affecting the system thermodynamic is pressure $P$ and temperature $T$.

When performing a phase stability test with Tangent Plane Distance (TPD) method, Gibbs free energy minimization can be used to indicate the stability condition of the thermodynamic system of the given compositions. Peng-Robinson equation-of-state was mainly used in this study to calculate the phase stability and with the results from equilibrium state calculation, deviations from equilibrium state can be formulated either by changing the “flash” algorithm in a reservoir simulator, or by modifying the Gibbs free energy curves in a Phase Field modeling for phase change phenomenon. According to the departure function in terms of Gibbs free energy from Peng Robinson equation-of-state:

$$H = U + PV \rightarrow \frac{H - H_{ig}}{RT} = \frac{U - U_{ig}}{RT} + \frac{PV - RT}{RT} = \frac{U - U_{ig}}{RT} + Z - 1 \quad (6.1)$$

$$A = U - TS \rightarrow \frac{A - A_{ig}}{RT} = \frac{U - U_{ig}}{RT} - \frac{S - S_{ig}}{R} \quad (6.2)$$
\[
\Delta g_{\text{mix}} = \frac{G - G_{\text{ig}}}{RT} = \frac{H - H_{\text{ig}}}{RT} - \frac{S - S_{\text{ig}}}{R} = \ln \left( \frac{f}{P} \right) \tag{6.3}
\]

Where,

\[
\ln \left( \frac{f}{P} \right) = Z - 1 - \ln(Z - B) - \frac{A}{B\sqrt{8}}\ln \left( \frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B} \right) \tag{6.4}
\]

Where \( H \) is enthalpy, \( U \) is the internal energy, \( S \) is the entropy, \( G \) is the Gibbs free energy.

For a closed thermodynamic system with multiple components, the departure function of Gibbs free energy is expressed as:

\[
\Delta g_{\text{mix}} = \Delta \left[ \sum^n_i z_i \ln(f_i) - \ln(P) \right] \tag{6.5}
\]

Where \( z_i \) is the overall feed composition of the thermodynamic system. This equation is the most crucial part of a phase stability test.

And, take the fugacity of component \( i \) in gas phase for instance, the Peng-Robinson equation-of-state departure function for component \( i \) is expressed as (H. Li and Yang 2016; Zheng and Yang 2017):

\[
\ln \left( \frac{f_{iV}}{y_{iV}P} \right) = \left( \frac{b_i}{b} \right)_V (Z_V - 1) - \ln(Z_V - B_V) - \frac{A}{B\sqrt{8}} \left( \frac{2 \sum_{j}^{n} y_j a_{ij}}{a} - \frac{b_i}{b} \right) \ln \left( \frac{Z_V + (1+\sqrt{2})B}{Z_V + (1-\sqrt{2})B} \right) \tag{6.6}
\]

Where, \( Z_i \) is the total feed composition for each component of the thermodynamic system, and \( f_i \) is the fugacity of the component \( i \), for which the fugacity equality holds for an equilibrium state:

\[
f_{iV} = f_{iL} \tag{6.7}
\]

The phase stability test was carried out according to the Tangent Plane Distance (TPD) algorithm from (Nghiem and Li 1984), the first initial guess by assuming the system as a
single phase in most of the situation, had yielded a larger Gibbs free energy than the Gibbs free energy of a trial of a second phase in the system. The differences between the single-phase Gibbs free energy and the two-phase Gibbs free energy of the system is expressed as:

\[ \Delta g_{\text{mix}} = \left[ \Sigma^n_i z_i \ln(f_i) \right]_{\text{two-phase}} - \ln(P) - \left[ \Sigma^n_i z_i \ln(f_i) \right]_{\text{single-phase}} - \ln(P) = \left[ \Sigma^n_i z_i \ln(f_i) \right]_{\text{two-phase}} - \left[ \Sigma^n_i z_i \ln(f_i) \right]_{\text{single-phase}} \]  \hspace{1cm} (6.8)

From the above equation, if the value of \( \Delta g_{\text{mix}} \) is smaller than zero, it indicates that the system is unstable, and the mixture is in a tendency to form multiple phases, in this case, two phases. By this TPD calculation, if given a total feed of the compositions of the system, prevailing pressure and temperature, one can calculate the phase stability of the mixture.

And if the system was not stable after performing the TPD analysis, multiphase flash algorithm according to the following relationships were conducted:

\[
\ln(f_i^L) - \ln(f_i^V) = 0 \\
x_i L + y_i V - z_i = 0 \\
\sum_i^N x_i = 1 \\
\sum_i^N y_i = 1 \\
\sum_i^N z_i = 1 \\
L + V = 1
\]

\[
K_i^{\text{equilibrium}} = \frac{y_i}{x_i} \\
K_i^{\text{non-equilibrium}} = f(K_i^{\text{equilibrium}})
\]  \hspace{1cm} (6.9)
Where $f(K_i^{\text{equilibrium}})$ is a function indicating the deviation from equilibrium K value, and the function form can either be by pre-specifying prior to running the simulation or by regression after the all the segmental optimization under dynamic adjustment of relevant parameters.

Some of the previous literatures (Indrupskiy et al. 2017) show the deviated two-phase flash for a light hydrocarbon mixture system by adding a convergence standard due to the chemical potential difference to the equilibrium flash algorithm after performing the equilibrium TPD phase stability analysis:

$$\ln(f_i^L) - \ln(f_i^V) = \omega_{i \rightarrow V} \quad (6.10)$$

Where,

$$\omega_{i \rightarrow V}(t + \Delta t) = \frac{C(\mu_i^L - \mu_i^V)}{CR} = \ln f_i^L(\tilde{x}(t + \Delta t), p(t + \Delta t)) - \ln f_i^V(\tilde{y}(t + \Delta t), p(t + \Delta t))$$

$$= [\ln f_i^L(\tilde{x}(t), p(t + \Delta t)) - \ln f_i^V(\tilde{y}(t), p(t + \Delta t))] e^{-\lambda \Delta t} \quad (6.11)$$

Where, $\mu$ is the chemical potential of different phases, $C$ is a parameter of reservoir properties and dynamic flow parameters. Since the relaxation of the chemical potential difference towards current time step always requires to know the fugacity of the components from last time step, hence, the equation set 6.9 has to be incorporated into the continuity equation set. By directly implementing the above phase flash equation set without pre-specifying VLE K value table or K value coefficient formula before solving Darcy-flow equation set, the flash problem can add up another 2N+2 degrees of freedom (i.e. if N=2 with component a and b, then $y_a, x_a, y_b, x_b, L, V$) in the equation set added into
the governing equation sets for each component, hence, increasing the number of unknowns if Fully-Implicit method is applied to solve the non-linear equation set. In addition, the TPD phase stability analysis was conducted under an equilibrium assumption, which means, even though the phase flash calculation uses a deviated convergence standard for the equilibrium condition of the system, the TPD analysis itself might not yield a stable condition if non-equilibrium is incorporated.

Instead, the problem can be simplified by the calculation of equilibrium K value according to equation set 9 for each pressure and temperature of the grid at each time step, then a modification can be used to shift the equilibrium K value to a non-equilibrium value, and hence, without solving for additional flash problems in the given governing equation set and changing the convergence standard of equilibrium equation-of-state algorithm. This is resembling to equation set 6.11, but instead of conducting relaxation on fugacity and requiring the flash equations set to be added into the Darcy-flow equation, the relaxation is directly conducted on the already pre-specified VLE K value table or K value coefficient formula under given total compositional feed, pressure and temperature to reduce the degrees of freedom when solving flowing problems with phase change. In addition, this way of dealing with K value shift and modeling non-equilibrium phase behavior based upon separate mass balance equation for each component in each phase is more versatile as multi-component multi-phase flash Eos calculation may not all be well-developed like a simple gas-oil system. If the system contains multiple-components and multiple-phases, for instance, a system of mixture solvent containing CH₄, C₃H₈, CO₂, etc, heavy oil component including light and heavy pseudo-components, as well as aqueous phases such steam, water, or any other chemical solutions such polymer, surfactant, etc., then only
counting on Eos to calculate multi-component multi-phase flash is unreliable as the mutual thermodynamic behavior of such system is too complicated to be accurately described by prevailing Eos developed in recent decades. Hence, for such complex system, an interphase mass transfer source/sink term representing the non-equilibrium phase behavior between different phases will be more practical and suitable than a relatively simple system only containing hydrocarbon mixtures which can be already well-described by Eos flash algorithm. In our study, the system contains only two-phase flash for a typical solvent-heavy live oil system so the implementation of a deviated flash calculation based upon equilibrium condition is enough.

In an isothermal non-equilibrium process, usually 2 pressure operational conditions will occur. First, a continuous pressure depletion rate until some setpoint of pressure. Second, a sudden pressure drawdown to a certain pressure setpoint, and this setpoint can be higher or lower than the pseudo-bubble point pressure. Under these two pressure operational conditions, for solvent-heavy live oil system, the possibility of the occurrence of solvent non-equilibrium exsolution is very high due to the high viscosity of the oil. Then with such non-equilibrium, the index indicating the thermodynamic condition of the system will be deviated from equilibrium state.

The following figures 6.1, 6.2, and 6.3 show the 3 different scenarios of K value evolution under different pressure operational schemes:
Figure 6.1 Schematics of $K$ value deviation from equilibrium state under continuous pressure depletion at certain $dP/dt$

Figure 6.2 Schematics of $K$ value deviation from equilibrium state under a transient pressure drawdown to a certain fixed pressure level at $P > P_{\text{pseudo-bubble point}}$
Figure 6.3 Schematics of K value deviation from equilibrium state under a transient pressure drawdown to a certain fixed pressure level at $P<P_{\text{pseudo-bubble point}}$.
Figure 6.1 shows the K value deviation of a continuous pressure depletion. As pressure is reduced stepwise, the \( K_{\text{equilibrium}} \) will rise until the setpoint of the pressure drop. For \( K_{\text{non-equilibrium}} \), the K value will deviate from the equilibrium value as the pressure drops until finally the exsolution rate of the solvent once again equals to the exsolution rate of equilibrium state. The solvent will not form exsolution until pseudo-bubble point is reached.

Figure 6.2 shows the K value deviation from equilibrium state under a transient pressure drawdown to a certain fixed pressure level which is above the observed or pre-specified pseudo-bubble point pressure. It can be seen that the \( K_{\text{non-equilibrium}} \) is getting close to \( K_{\text{equilibrium}} \) at a very slow rate, which indicates that even though the system pressure is above pseudo-bubble point pressure, it is still lower than the true equilibrium thermodynamic bubble point pressure. Under such circumstances, the dissolved gas may still exsolve out of the oil phase, but at a very slow rate.

Figure 6.3 shows the K value deviation at a pressure drawdown to below the pseudo-bubble point pressure. Under such condition, the dissolved gas tends to form exsolution at a much higher rate than the system of pressure higher than pseudo-bubble point pressure. Hence, the \( K_{\text{non-equilibrium}} \) value will tend to get close to and merge with the \( K_{\text{equilibrium}} \) value at a certain pressure shown as the \( P_{\text{re-equilibrium}} \) in the figure.

### 6.2 Solvent Non-Equilibrium Dissolution and Exsolution Behavior

In this subchapter, reservoir simulation was applied on characterizing solvent-heavy oil non-equilibrium phase behavior through analyzing the above-mentioned experimental data.
With reservoir simulator, which characterizes fluid flow in Darcy-scale in porous media, therefore, it is reasonable to apply the technique on our tests which were conducted mainly in a confined space with/without porous media.

6.2.1 Equilibrium PVT Phase Behavior Modeling

In this section, equilibrium live oil properties obtained from live oil differential liberation tests were input into CMG WINPROP module for parameter regression. Both CO\(_2\)-heavy oil system and CO\(_2\)-C\(_3\)H\(_8\)-heavy oil system were history matched in the PVT simulator. Totally 13 sets of live oil properties were input for the history match. Saturation pressure calculation was applied on CO\(_2\)-heavy oil system as there was only a single solvent component involved. Two-phase flash calculation (phase mole/volume ratio, solvent mole fraction in each phase, etc.) was applied on CO\(_2\)-C\(_3\)H\(_8\)-heavy oil system as the individual solvent composition variation is vital to the live oil properties and later-on reservoir simulation. Important regressions of live oil physical properties are listed in figure 6.4~6.8 to show the regression results for both types of solvent-heavy live oil properties.


**CO$_2$-C$_3$H$_8$-Heavy Live Oil System**

![Graph](image)

Figure 6.4 WINPROP history matching of live oil properties (a) live oil density (b) live oil viscosity
Figure 6.5 WINPROP history matching of live oil properties (a) total liquid phase mole fraction (b) oil component mole fraction in live oil
Figure 6.6 WINPROP history matching of live oil properties (a) CO$_2$ mole fraction in live oil (b) CO$_2$ mole fraction in vapor phase
CO$_2$-Heavy Live Oil System

Figure 6.7 Live oil saturation pressure and density regression
Figure 6.8 Live oil viscosity regression
From figure 6.7, it can be seen that the live oil density was not properly matched at saturation pressure of 3895 kPa. This is highly possible due to CO₂ extraction of the light components in heavy oil phase. However, in the PVT regression, the heavy oil phase composition was always kept constant and no compositional change was applied. But since the operating pressure of CO₂-heavy oil system was lower than 3895 kPa, and therefore, the compositional change of heavy oil phase was ignored and only the PVT properties below 3895 kPa was used in all simulation study.

6.2.2 CO₂ Dissolution/Exsolution Behavior

6.2.2.1 Pressure Decay Diffusion Tests

In this section, the dynamic CO₂ dissolution and exsolution behaviors were studied through conducting mathematical modeling combining MATLAB and CMG STARS. The proposed MATLAB-controlled reservoir simulator was able to pause, optimize and then restart towards a new time destination setpoint at a certain pre-specified time step to dynamically history match the targeted parameters.

For live oil properties achieved in the solvent dissolution processes, equation-of-state simulation was to be utilized to conduct PVT parameters regression corresponding to the solubility and density achieved at the end of each equilibrium solubility test under different pressure conditions. For the solvent dissolution processes, pressure decay methodology was utilized in the experimental study, and hence in the numerical study, the experimental pressure decay curves were to be matched by dynamically adjusting the diffusion coefficient of solvent into heavy oil. For the solvent exsolution processes, the simulation will be initiated based upon the final condition of the dissolution processes. Then, the
experimental volumetric curve of the foamy oil phase was to be matched by dynamically adjusting the pseudo-chemical reaction frequency factors of the kinetics processes proposed below.

In the numerical simulation of pressure decay diffusion tests, the mass transfer was mainly dominated by molecular diffusion, and hence, the pressure-volume-temperature conditions within a closed thermodynamic system was mainly affected by the molecular diffusivity, $D$ (m$^2$/s), of CO$_2$ solvent into heavy oil. Naturally, the diffusion coefficient of CO$_2$ into heavy oil in certain direction became the main parameter to be adjusted to history match the experimental pressure decay curves and the swelling factor curves. Reservoir simulator CMG STARS has provided an excellent platform to carry out the numerical tests, however, in this simulator, the setting of the parameter, $D$, is not a dynamic volume which cannot be adjusted once the simulation run is on. Hence, in order to more accurately capture the diffusion coefficient variations during the pressure decay to better history match the experimental data, a self-developed simulator combining MATLAB and CMG STARS was established. Also, instead of using CMG CMOST module for parameter optimization, self-developed optimization module by MATLAB using non-linear least-squares method was applied to adjust the diffusion coefficients and history match the experimental data.

**Optimization Technique for MATLAB-controlled History Match with CMG STARS Simulator**

During each pre-specified time step, nonlinear least-squares method was applied to history match the experimental data. The flowchart underneath shows the procedures of MATLAB-controlled CMG simulation:
Figure 6.9 Flowchart of MATLAB-controlled CMG optimization simulator
The programming and optimization procedure of the non-linear least-squares method can be found elsewhere in the wikipedia site, which is not overly explained in the main paragraphs.

In the simulation of CO₂ dissolution processes, diffusion coefficient $D$ (cm²/min as in Lab Unit per used), was the main parameters to be adjusted to history match the experimental pressure decay curve. In a Darcy-scale simulator, since there is no convection in a static pressure decay test, therefore the parameter controlling the pressure drop of the closed system is mainly by mass transfer due to concentration between the two phases, in this case, by molecular diffusion under concentration gradient. According to figure, the gridding of the system is shown, and the numerical model takes the following assumptions:

(1) In the numerical grid where gas and oil get in contact with each other, CO₂ and heavy oil are in instant equilibrium condition, indicating the condensation of solvent on the gas-oil interface is immediate, and the molar fraction of CO₂ on the interface is an equilibrium value;

(2) CO₂ diffusion coefficient acts in a one-way direction towards the oleic phase, diffusion in the bulk gaseous phase is neglected;

(3) Intra-phase diffusion is considered, where grids with non-zero oil and gas saturation “form” a so-called interface, and the mole fraction of solvent in heavy oil in these grids are in equilibrium immediately according to the equation-of-state to form a concentration gradient towards other grids where the oil saturation is 100%, so that only molecular diffusivity is available.
Figure 6.10 Numerical simulation grid system of a diffusion process
In a Darcy-scale simulator, there is no concept as the multiphase flow interface, instead, saturation profile in each grid is considered than the actual interface. Instead of solving for a pure diffusion-advection equation set based upon Fick’s 2nd law:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D \nabla c) - \nabla \cdot (\vec{u} c) + R_{\text{source/sink}}$$  \hspace{1cm} (6.12)

where the velocity field $\vec{u}$ should be pre-defined or computed from mass and momentum conservation equation sets, and the solution of the equation requires a defined multiphase interface to set up the boundary conditions, and thus it is not convenient to be coupled into Darcy-scale simulator to consider for Multiphysics in the system.

Instead, multiple continuity equation sets derived from mass conservation law based upon Darcy’s law are solved. Therefore, inter-phase mass transfer will not be considered as a molecular diffusion process across the multiphase fluid interface, but rather, it can be considered as a source/sink term in each component’s governing equation to reduce the necessity of accurate “locating” the actual multiphase flow interface. The inter-phase mass transfer in a Darcy-scale simulator can be described by two different mechanisms: first, an equilibrium condition from applying various equation-of-state per referred to in each grid with the existence of multiphase fluid, and second, a kinetic pseudo-chemical reaction term describing real-time non-equilibrium mass transfer across different phases.

In this thesis, the first mechanism of inter-phase mass transfer was used to describe the inter-phase mass transfer between CO$_2$ and heavy oil in grids containing both fluids with certain saturation values. The governing equation of the diffusion process of CO$_2$ within the oil phase is as follows:
Grids containing both gaseous CO₂ and oleic heavy oil (equilibrium inter-phase mass transfer determined by equilibrium K value from EOS calculation):

\[ K_{SGCO_2}(P,T) = \frac{y_{CO_2}}{x_{CO_2}} \]  

(6.13)

CO₂ in solution gas in oil phase:

\[ \frac{\partial \phi_{oil} \rho_{oil} \cdot \chi_{molar}^{molar}}{\partial t} = -\nabla \cdot (\rho_{oil} \chi_{oil}^{molar} v_{oil}^{molar}) + Q_{source/sink} + \phi \rho_{oil} D_{oleic}^{oleic} \frac{\partial^2 \chi_{molar}^{molar}}{\partial x^2} \]  

(6.14)

Grids containing only gaseous CO₂ (grid pressure determined by real gas law PV=ZnRT):

CO₂ in free gas in gas phase:

\[ \frac{\partial \phi_{gas} \rho_{gas} \cdot \chi_{molar}^{molar}}{\partial t} = -\nabla \cdot (\rho_{gas} \chi_{gas}^{molar} v_{gas}^{molar}) + Q_{source/sink} \]  

(6.15)

Grids containing both oleic CO₂ and oleic heavy oil (intra-phase mass transfer under molecular diffusion with concentration gradient):

\[ \frac{\partial \phi_{oil} \rho_{oil} \cdot \chi_{molar}^{molar}}{\partial t} = -\nabla \cdot (\rho_{oil} \chi_{oil}^{molar} v_{oil}^{molar}) + Q_{source/sink} + \phi \rho_{oil} D_{oleic}^{oleic} \frac{\partial^2 \chi_{molar}^{molar}}{\partial x^2} \]  

(6.16)

In which, the kinetic/Darcy velocity terms of component \(i\) in the direction of \(j\) are expressed as:

\[ v_{i,j} = -\frac{K_{abs} \cdot K_{r ij}}{\mu} (\nabla_j P_{gra} - \rho g \nabla_j D) \]  

(6.17)

Where, \(K_{abs}\) is the absolute permeability of the Hele-Shaw-like visual cell according to Reiss’s aperture/fracture permeability law which enables the Darcy-law for numerical simulation of the fracture-resembling Hele-Shaw-like cell, \(K_{r ij}\) is the relative permeability of component \(i\) in direction \(j\), \(\mu\) is the viscosity of the phase where component \(i\) is in,
\( \nabla_j \rho g \text{grid} \) is the pressure gradient towards \( j \) direction at the local grid, \( \rho g \nabla_j D \) is the gravitation potential of the phase where \( i \) is in towards \( j \) direction and reference datum.

From the above equation sets, it is clearly indicated that under static condition, the Darcy velocity of all phases in the closed system will be very close to zero, meaning that the hydraulic diffusivity is far less prominent than molecular diffusivity (in which \( v_{oil} \) in the equation is close to zero due to a small pressure gradient under quiescent condition), and thus, the diffusion coefficient \( D_{CO_2,K}^{oleic} \) becomes the dominated parameter to determine real-time solution CO\(_2\) component concentration profile in the heavy oil phase. For grids with both CO\(_2\) and oil presence, equilibrium equation-of-state calculated was carried out and form a higher concentration region of CO\(_2\), and then under such concentration gradient,

\[
\frac{\partial \chi_{molar}^{CO_2}}{\partial \chi} = \frac{\chi_{molar}^{CO_2,i} - \chi_{molar}^{CO_2,j}}{\Delta \chi_{i,j}},
\]

the condensed CO\(_2\) started to diffuse towards regions with lower concentration. The targeted history matching data is shown in the following:

\[
Obj_P = \sqrt{\frac{1}{No_P} \sum_{i=1}^{No_P} \left( \frac{P_{exp,i} - P_{num,i}}{P_{exp,i}} \right)^2}
\]

\[
Obj_SF = \sqrt{\frac{1}{No_SF} \sum_{i=1}^{No_SF} \left( \frac{SF_{exp,i} - SF_{num,i}}{SF_{exp,i}} \right)^2}
\]

Where \( Obj_P \) and \( Obj_SF \) is the objective function for pressure decay curves and oil swelling factors, respectively. \( No_P \) and \( No_SF \) is the number of data points of the pressure decay curves and oil swelling factors, respectively. \( P \) and \( SF \) indicate pressure and swelling factor data point, respectively. The indices \( exp \) and \( num \) indicate experimental and numerical value, respectively.
Figure 6.11 History matching of pressure decay curve and oil swelling factor at $P_{ini}=1555\text{kPa}$
Figure 6.12 History matching of pressure decay curve and oil swelling factor at $P_{ini}=2231$ kPa
Figure 6.13 History matching of pressure decay curve and oil swelling factor at $P_{ini}=2623\text{kPa}$
Figure 6.14 History matching of pressure decay curve and oil swelling factor at $P_{ini}=3320$kPa
Table 6.1 Diffusion coefficients achieved from history matching

<table>
<thead>
<tr>
<th>Injection pressure, kPa</th>
<th>Live oil viscosity at 20°C, cP</th>
<th>Average diffusion coefficient, ×10^{-9} m²/s</th>
<th>Swelling factor from simulation, cm³/cm³</th>
<th>Swelling factor from experimentation, cm³/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1555</td>
<td>1378.37</td>
<td>6.198</td>
<td>1.039</td>
<td>1.039</td>
</tr>
<tr>
<td>2231</td>
<td>964.24</td>
<td>8.016</td>
<td>1.063</td>
<td>1.065</td>
</tr>
<tr>
<td>2623</td>
<td>654.47</td>
<td>9.464</td>
<td>1.074</td>
<td>1.075</td>
</tr>
<tr>
<td>3320</td>
<td>498.51</td>
<td>25.333</td>
<td>1.101</td>
<td>1.103</td>
</tr>
</tbody>
</table>

From the above pressure decay curve figures 6.11~6.14, it is indicated that the fluctuation in the pressure decay curves were mainly caused by the variation in the ambient pressure. For all the simulations, the optimization time step was set as the value of the total diffusion time divided by 10. Due the existence of such experimental pressure fluctuations in the system, the automatic adjustment of the diffusion coefficient by the optimization technique might also fluctuate according to the experimental data. Although the diffusion coefficients fluctuated in a certain range, we managed to average them to evaluate the effect of injection pressure on the diffusion coefficients. Their average value proved that a higher injection pressure resulted in higher diffusion coefficient. From table, it can be seen that the diffusion coefficient increased from 6.198×10^{-9} m²/s to 25.333×10^{-9} m²/s when the injection pressure increased from 1555kPa to 3320kPa. The order of magnitude of diffusion coefficients are mostly in the range of 10^{-9} m²/s, while the for the highest injection pressure, the diffusion coefficient increased to the range of 2.533×10^{-8} m²/s. This is mainly due to the fact which was illustrated in the experimental material section. The light component from C₈ to C₁₆+~C₃₀ is very high in our diluted bitumen sample with a viscosity of 1500cP, and hence, the magnitude of order of diffusion coefficient in our CO₂-
light heavy oil system was mainly between CO₂-light oil system (viscosity at 2.43cP) at a range of ×10⁻⁶ m²/s and CO₂-bitumen system (viscosity from 10000~30000cP+) at a range of 10⁻¹⁰ m²/s~10⁻⁹ m²/s.

<table>
<thead>
<tr>
<th>Studies</th>
<th>Solvent</th>
<th>Oil viscosity at temperature, cP@°C</th>
<th>Test pressure, kPa</th>
<th>Diffusion coefficient, ×10⁻⁹ m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>CO₂</td>
<td>1500cP at 21.0°C</td>
<td>1555~3320</td>
<td>6.198~25.333</td>
</tr>
<tr>
<td>Nguyen et al. (Nguyen and Farouq Ali 1998)</td>
<td>CO₂</td>
<td>1000 cP at 23.0°C</td>
<td>1000</td>
<td>6</td>
</tr>
<tr>
<td>Zhang et al. (Zhang, Hyndman, and Maini 2000)</td>
<td>CO₂</td>
<td>5000 cP at 21.0°C</td>
<td>2800~3500</td>
<td>4.8</td>
</tr>
<tr>
<td>Du et al. (Du, Ma, and Gu 2019)</td>
<td>CO₂</td>
<td>1.48cP at 56.0°C (light oil case for comparison)</td>
<td>4149.2~5200.2</td>
<td>2880~4970 (period I: main pressure decay period)</td>
</tr>
<tr>
<td>Rojas et al. (Rojas and Farouq Ali 1988)</td>
<td>CO₂</td>
<td>4681 at 23.0°C</td>
<td>5500</td>
<td>3.59</td>
</tr>
<tr>
<td>Unatrakarn et al. (Unatrakarn, Asghari, and Condor 2011)</td>
<td>CO₂</td>
<td>21285 at 30°C</td>
<td>2665.5</td>
<td>34~35.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8154 at 30°C</td>
<td>2415.3</td>
<td>58~68</td>
</tr>
</tbody>
</table>

Based upon the equilibrium live oil properties tests, the final swelling factor or the live oil molar volume calculated from equation-of-state under certain pressure and temperature was quite successfully matched by adjusting the diffusion coefficient. From figure 6.11, 6.12, 6.13 and 6.14, it is indicated that the rate of oil phase volume change was dependent on the diffusion coefficient. A higher diffusion coefficient will result in a steeper increase of the calculated molar volume of the solvent-saturated oil phase, which is reasonable.
because the higher the diffusion coefficient, the higher mass transfer rate of CO$_2$ into heavy oil phase, and hence, a more rapid volume increase will occur.

6.2.2.2 Pressure Depletion Tests

In this section, the solvent exsolution behavior will be analyzed by applying pseudo-chemical kinetic reactions to the numerical simulator as well as the optimization module by adjusting the reaction frequency factors of the various of CO$_2$ component in the simulator. Instead of using K value to directly conduct two-phase flash calculation, the exsolution of solvent to form vapor phase was all represented by various non-equilibrium interphase mass transfer terms incorporated in the continuity equation of each component.

Model Description:

In the numerical modeling for pressure depletion tests, 4 components were defined to simulate the process of CO$_2$ exsolution behavior:

(1) dead heavy oil;

(2) SGCO$_2$: CO$_2$ in solution gas state, which is treated in oil phase as reference phase;

(3) BBCO$_2$: CO$_2$ in bubble form, which is dispersed in the oil phase and treated as oil phase with gas-like density according to the non-ideal gas law: $PV=ZnRT$;

(4) FGCO$_2$: CO$_2$ in free gas form, which is treated in gaseous phase as reference phase, obeying the non-ideal gas law: $PV=ZnRT$;

To describe CO$_2$ exsolution, a 2-step 1st-order pseudo-chemical reaction model was established and incorporated into the mass conservation equation sets of each individual component to describe the inter-phase non-equilibrium mass transfer:
Pseudo-chemical reaction 1:

\[ SGCO_2 \rightarrow BBCO_2 \]

Pseudo-chemical reaction 2:

\[ BBCO_2 \rightarrow FGCO_2 \]

By assuming the molecular weight of all the components to be constant during the simulation process, the kinetic form of pseudo-chemical reactions in the molar quantity, that is, the molar volumetric reaction rate in a grid for component \( i \) in phase \( j \) is formulated as the following:

\[ SGCO_2 \rightarrow BBCO_2 \]

\[ \frac{\partial m_{molar}^{SGCO_2}}{\partial t} = RRF_{SGCO_2 \rightarrow BBCO_2} \left[ \left( \frac{1}{\text{min}} \right)^1 \times \left( \frac{\text{mole}}{\text{cm}^3} \right)^{1-m} \right] \times \exp \left( -\frac{E_{ACT}}{RT} \right) \times \left( \phi_{oil} \chi_{SGCO_2}^m \rho_{oil}^{molar} \right)^m \left[ \left( \frac{\text{mole}}{\text{cm}^3} \right)^m \right] \] (6.20)

\[ BBCO_2 \rightarrow FGCO_2 \]

\[ \frac{\partial m_{molar}^{BBCO_2}}{\partial t} = RRF_{BBCO_2 \rightarrow FGCO_2} \left[ \left( \frac{1}{\text{min}} \right)^1 \times \left( \frac{\text{mole}}{\text{cm}^3} \right)^{1-m} \right] \times \exp \left( -\frac{E_{ACT}}{RT} \right) \times \left( \phi_{oil} \chi_{BBCO_2}^m \rho_{oil}^{molar} \right)^m \left[ \left( \frac{\text{mole}}{\text{cm}^3} \right)^m \right] \] (6.21)

Where, the unit of both \( RRF_{SGCO_2 \rightarrow BBCO_2} \) and \( RRF_{BBCO_2 \rightarrow FGCO_2} \) are dependent on the reaction order capital \( m \) of the pre-set pseudo-chemical reaction kinetics.

Therefore, by considering the following mass conservation equation sets for the 4 components:
**Oil Phase Components:**

Dead oil:

\[
\frac{\partial \phi_{oil} \rho_{oil} \chi_{dead \ oil}}{\partial t} = -\nabla \cdot (\rho_{oil} \nu_{oil} \chi_{dead \ oil}) + Q_{source/sink} \tag{6.22}
\]

SGCO\(_2\):

\[
\frac{\partial \phi_{oil} \rho_{oil} \chi_{SGCO_2}}{\partial t} = -\nabla \cdot (\rho_{oil} \nu_{oil} \chi_{SGCO_2}) + Q_{source/sink} - \frac{\partial m_{SGCO_2}}{\partial t} \tag{6.23}
\]

BBCO\(_2\):

\[
\frac{\partial \phi_{oil} \rho_{oil} \chi_{BBCO_2}}{\partial t} = -\nabla \cdot (\rho_{oil} \nu_{oil} \chi_{BBCO_2}) + Q_{source/sink} + \frac{\partial m_{SGCO_2}}{\partial t} - \frac{\partial m_{BBCO_2}}{\partial t} \tag{6.24}
\]

**Gas Phase Components:**

FGCO\(_2\):

\[
\frac{\partial \phi_{gas} \rho_{gas} \chi_{FGCO_2}}{\partial t} = -\nabla \cdot (\rho_{gas} \nu_{gas} \chi_{FGCO_2}) + Q_{source/sink} + \frac{\partial m_{BBCO_2}}{\partial t} \tag{6.25}
\]

The history matching objective function is shown as the following:

\[
Obj_{\_V} = \frac{1}{\sqrt{\sum_{i=1}^{N_{\_V}} (\frac{V_{\exp,i} - V_{\num,i}}{V_{\exp,i}})^2}} \tag{6.26}
\]

It is seen from the above equation, when the system was under pressure depletion, the term of molecular diffusion was not considered by setting the molecular diffusion coefficients to zero but instead, a non-equilibrium inter-phase mass transfer term was added into the governing equation as an extra source/sink term to describe the mass gain/loss of each
individual component. The parameters $R_{SGCO_2 \rightarrow BBCO_2}$ and $R_{BBCO_2 \rightarrow FGCO_2}$ were the two main factors determining the exsolution behavior of CO$_2$, and were used as the main adjustable parameters to history match the experimental volumetric curve of foamy oil expansion and shrinkage under pressure depletion.

In the equation sets, the term activation energy, $E_{ACT}$, was assumed to be zero for all the pseudo-chemical reactions. The energy threshold for such reaction to happen is the excess Gibbs free energy and deviation from equilibrium caused by pressure depletion. Therefore, although the activation energy was set to zero, the actual reactions happened by setting up a pseudo bubble point pressure, where above the pressure, no reactions will take place. For the 1$^{st}$ reaction where solution gas formed exsolution to become dispersed gas bubbles, the $R_{SGCO_2 \rightarrow BBCO_2}$ was optimized by MATLAB-controlled CMG simulation for the first stage where the foamy oil expansion was the main phenomenon. This was mainly attributed to the gas-like density setting for the oleic component BBCO$_2$. For the 2$^{nd}$ reaction rate, the reaction frequency factor $R_{BBCO_2 \rightarrow FGCO_2}$ was adjusted and optimized at a certain time step to history match the experimental data of the 2$^{nd}$ stage where foamy oil shrinkage or gas phase separation from oil phase was the main phenomenon, so as to extract the relationship between the dynamic exsolution rate and time.

(a) Exsolution processes under different initial GOR

The effect of initial GOR on the foamy oil volumetric behavior has been experimentally shown in the previous discussion, and in this section, the MATLAB-controlled CMG history-matched foamy oil volumetric change curve against time has been plotted and both of the two reaction frequency factors were extracted.
Figure 6.15 Foamy oil volumetric behavior history matching by MATLAB-controlled CMG STARS numerical simulation study (exsolution under different initial GOR: (a) 13.98cm$^3$/cm$^3$ (b) 22.93cm$^3$/cm$^3$ (c) 26.31cm$^3$/cm$^3$ (d) 35.70cm$^3$/cm$^3$ )
Figure 6.16 $RRF_{SGCO_2 \rightarrow BCO_2}$ factor for different initial GOR

The equation for the trend line is:

$$y = 0.0038e^{0.0664x}$$

with $R^2 = 0.8788$.
(1) GOR=13.98 cm³/cm³

(2) GOR=22.93 cm³/cm³

(3) GOR=26.31 cm³/cm³

(4) GOR=35.70 cm³/cm³

(a)
Figure 6.17 $RRF_{B_{CO_2}→F_{GCO_2}}$ factor against time for different initial GOR: (a) individual $RRF_{B_{CO_2}→F_{GCO_2}}$ against time (b) comparison between different cases

Table 6.2 Exponent of the transient $RRF_2$ for different initial GOR

<table>
<thead>
<tr>
<th>GOR, cm$^3$/cm$^3$</th>
<th>Exponent of RRFs, 1/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.98</td>
<td>0.1169</td>
</tr>
<tr>
<td>22.93</td>
<td>0.0366</td>
</tr>
<tr>
<td>26.31</td>
<td>0.0075</td>
</tr>
<tr>
<td>35.70</td>
<td>0.0090</td>
</tr>
</tbody>
</table>
Figure 6.15 shows the history matching results of foamy oil volumetric behavior under different initial saturated GOR value. The pre-specified time stepping was mainly divided into 2 parts: before apex time, and after apex time. In the simulation, the concept of apex time refers to the time point where the foamy oil volume expansion curve reaches the peak value. Before the apex time, the main parameters to be adjusted is the \( RRF_{SGCO_2 \rightarrowBBCO_2} \), which is the main factor determining the expansion of whole foamy oil phase as the BBCO\(_2\) component is assumed to be within oil phase but with a gas-like density according to real gas law \( PV = ZnRT \). At the same time, the \( RRF_{BBCO_2 \rightarrowFGCO_2} \) was also adjusted at the same time with a less weight than the \( RRF_{SGCO_2 \rightarrow BBCO_2} \). During the simulation before apex time, the 2 pseudo-chemical reaction frequency factors were achieved to history match the first phase of foamy oil volumetric curve: the expansion stage. When the system reached apex time, the simulation time stepping was evenly divided by the remaining time length of the foamy oil decay processes. By assuming the \( RRF_{SGCO_2 \rightarrow BBCO_2} \) as a constant, the foamy oil volume decay was history matched by mainly adjusting the \( RRF_{BBCO_2 \rightarrow FGCO_2} \) as this reaction frequency factor indicates the non-equilibrium mass transfer of bubbly CO\(_2\) transforming into free gas CO\(_2\) which will escape from the oil phase, resulting in a volume decay of the foamy oil phase. Same as the diffusion coefficient history matching mentioned above, the fluctuation of foamy oil volume during decay stage will affect the optimization of the \( RRF_{BBCO_2 \rightarrow FGCO_2} \) as well to be fluctuating in a certain range. But the overall trend is quite clear as shown in the figure 6.17 (a). it is indicated that the decay coefficients mainly formed an exponential distribution against time, and they vary according to different initial GOR values. For lower initial GOR, the decay coefficient \( RRF_{BBCO_2 \rightarrow FGCO_2} \) is higher than the case of higher initial GOR. This is reasonable because
lower initial GOR resulted in a lower amount of gas saturated in the heavy oil, and hence, compared to heavy oil with higher solvent saturation, the rate of solvent exsolution with low GOR under the same pressure condition will be higher, and there was less amount of “back-up storage” solvent to be exsolved. The rate of decay coefficient should be lower to maintain a more stable foamy oil phase, which is indicated in figure 6.17 (b). Therefore, the foamy oil stability of different initial GOR was numerically proved that higher level of solvent saturation will yield a more stable foamy oil during pressure depletion. Table 6.2 shows that a higher initial GOR resulted in a lower exponent, hence, better foamy stability.

(b) Exsolution processes under different pressure depletion rate

In this section, the effect of different pressure depletion rate on CO₂ exsolution behavior was analyzed. The foamy oil stability was different under immediate pressure drawdown and continuous pressure drawdown at a constant rate.
Figure 6.18 Foamy oil volumetric behavior history matching by MATLAB-controlled CMG STARS (exsolution under different pressure depletion rate (a) transient depletion to 1atm (b) -90kPa/min (c) -50kPa/min)
Figure 6.19 $RRF_{SGCO_2 \rightarrow BCO_2}$ factor for different pressure depletion rate

\[ y = 0.0188e^{0.0016x} \]

$R^2 = 0.994$
(1) -90kPa/min

(2) -50kPa/min
Figure 6.20 $RRF_{BB\text{CO}_2\rightarrow FG\text{CO}_2}$ factor against time for different pressure depletion rates: (a) individual $RRF_{BB\text{CO}_2\rightarrow FG\text{CO}_2}$ against time (b) comparison between different cases

Table 6.3 Exponent of the transient RRF_2 for different pressure depletion rates

<table>
<thead>
<tr>
<th>Pressure depletion rate, kPa/min</th>
<th>Exponent of RRFs, 1/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>0.0335</td>
</tr>
<tr>
<td>-90</td>
<td>0.0039</td>
</tr>
<tr>
<td>-300</td>
<td>0.0075</td>
</tr>
</tbody>
</table>
From the figure 6.18, the history matching was satisfactory with some fluctuations for continuous pressure drawdown cases as in figure 6.18 (b) and (c). This can be due to the fact that, when the system was undergoing a continuous pressure drawdown, the pressure was depleted linearly at a constant rate. Therefore, not like immediate drawdown to atmospheric pressure, dispersed gas bubble volume was also significantly affected by the prevailing pressure in the system. When the pressure was depleted to a certain level, the dissolved gas started to form exsolution, and this exsolution had a tendency to form free gas clusters and escape out of the oil phase to decay the whole oil phase volume. So at this time step, if the bubble decay rate was higher than the bubble exsolution rate, the whole foamy oil volume would tend to decay. However, as the pressure depletion went on, other small bubbles which were not able to form free gas clusters at the last time step, might react to the pressure depletion at this time step and expand according to real gas law, and therefore, if the hydraulic-induced bubble volume expansion rate was higher than the bubble decay rate at this time step, the foamy oil volume would, to a great extent of possibility, rise up again, and hence, forming such “ripples” in the numerical simulation curves. From figure 6.19, if a constant $R_{SGCO_2\rightarrow BBCO_2}$ was assumed, it can be seen that a higher pressure depletion rate yielded a higher $R_{SGCO_2\rightarrow BBCO_2}$ factor. From figure 6.20 (b), it can be seen that the $R_{BBCO_2\rightarrow FGCO_2}$ factor was quite close for immediate pressure depletion to 1atm and -90kPa/min. But from figure 4.8, it can be seen that the case of -90kPa/min depletion rate had resulted in the highest foamy oil stability, and this can be attributed to the above-mentioned hydraulic-induced foamy oil volume expansion. Under a continuous pressure depletion rate, the effect of hydraulic-induced bubble expansion was more prominent, as dispersed bubbles could have more time to expand than a sudden drop.
to atmospheric pressure. Table 6.3 shows that the exponent of RRFs for higher pressure depletioin rate is lower, hence, better foamy oil stability.

(c) *Exsolution processes under different pressure drawdown level*

In this section, history matching of exsolution behavior was conducted for experimetal tests under different pressure drawdown level. The following figures show the result of such pressure operational schemes:
Figure 6.21 Foamy oil volumetric behavior history matching by MATLAB-controlled CMG STARS (exsolution under different pressure drawdown level: (a) transient depletion to 1atm (b) transient depletion to 250kPa (c) transient depletion to 500kPa)
Figure 6.22 $R_{RF_{SGCO_2 \rightarrow BCO_2}}$ factor for different pressure drawdown level

$y = 0.0319e^{-0.003x}$

$R^2 = 0.7796$
(1) immediate pressure drawdown to 500kPa

\[ y = 0.1081e^{0.0196x} \]

\[ R^2 = 0.8339 \]

(2) immediate pressure drawdown to 250kPa

(a)
Figure 6.23 $RRF_{BBCO_2 \rightarrow FGCO_2}$ factor against time for different pressure drawdown level: (a) individual $RRF_{BBCO_2 \rightarrow FGCO_2}$ against time (b) comparison between different cases

Table 6.4 Exponent of the transient $RRF_{2}$ for different pressure drawdown levels

<table>
<thead>
<tr>
<th>Pressure drawdown level, kPaa</th>
<th>Exponent of RRFs, 1/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.0196</td>
</tr>
<tr>
<td>250</td>
<td>0.0034</td>
</tr>
<tr>
<td>100</td>
<td>0.0075</td>
</tr>
</tbody>
</table>

331
From figure 6.21, it can be seen that the MATLAB-controlled CMG optimization simulator history matched the foamy oil volumetric curves with different pressure drawdown level. From such simulations, the $RRF_{SGCO_2\rightarrow BBCO_2}$ for different pressure drawdown level was yielded. It can be seen from figure 6.22 that when the system pressure was drawdowned to a higher value, the $RRF_{SGCO_2\rightarrow BBCO_2}$ presented a lower value. This is because even though the system pressure had been lowered to a pressure lower than its thermodynamic bubble point, but there was still a decent amount of dissolution CO$_2$ in the heavy oil phase that could not escaped. But for higher pressure drawdown level, the whole system was depleted to a lower level where the dissolution of CO$_2$ was minimum at its thermodynamic equilibrium state, and therefore, more BBCO$_2$ exsolution formed, resulting in a higher $RRF_{SGCO_2\rightarrow BBCO_2}$ factor. From figure 6.23, it can be observed that the fluctuation of tests of higher pressure drawdown level was higher, and does not strictly follow an exponential trend as case (1) in figure 6.23 (a). Overall, it can be seen that from figure 6.23 (b), higher pressure drawdown level resulted in a higher foamy oil volume expansion and endurance, but the “relative stability” of the foamy oil phase can be higher in a higher pressure drawdown level as the decay coefficient $RRF_{BBCO_2\rightarrow FGCO_2}$ is showing lower value for immediate depletion to 500kPa and 250kPa than that of a immediate depletion to 1atm. Table 6.4 shows higher pressure drawdown level yielded a lower exponent for better foamy oil stability.

**(d) Exsolution processes under different CO$_2$-heavy oil contact time**

In this section, the effect of the different CO$_2$-heavy oil contact time after CO$_2$ injection on solvent exsolution process and foamy oil stability was history matched with the experimental foamy oil volumetric variational curve.
Figure 6.24 Foamy oil volumetric behavior history matching by MATLAB-controlled CMG STARS (exsolution under different solvent-heavy oil contact time: (a) 120mins (b) 540mins (c) 1020mins (d) 2160mins
Figure 6.25 $RRF_{SGCO_2 \rightarrow BCO_2}$ factor for different solvent-heavy oil contact time
(1) 120mins

\[
y = 0.4422e^{0.099x}
\]

\[R^2 = 0.8768\]

(2) 540mins

\[
y = 0.2333e^{0.0736x}
\]

\[R^2 = 0.7274\]

(3) 1020mins

\[
y = 0.3405e^{0.0205x}
\]

\[R^2 = 0.9488\]

(4) 2160mins

\[
y = 0.486e^{0.0113x}
\]

\[R^2 = 0.8224\]
Figure 6.26 $RRF_{BBOCO_2 \rightarrow FGCO_2}$ factor against time for different solvent-heavy oil contact time cases: (a) individual $RRF_{BBOCO_2 \rightarrow FGCO_2}$ against time (b) comparison between different cases

Table 6.5 Exponent of the transient RRF_2 for different solvent-heavy oil contact time

<table>
<thead>
<tr>
<th>Solvent-heavy oil contact time, min</th>
<th>Exponent of RRFs, 1/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>0.1000</td>
</tr>
<tr>
<td>540</td>
<td>0.0736</td>
</tr>
<tr>
<td>1020</td>
<td>0.0205</td>
</tr>
<tr>
<td>2160</td>
<td>0.0112</td>
</tr>
</tbody>
</table>
Figure 6.24 shows the history matching of the foamy oil volumetric curves under different solvent-heavy oil contact time, and the results are satisfactory. There are some “rippling” in the figure 6.22, which can be explained as the dynamic balancing of the two reaction frequency factors, and repetitive restart of the numerical model by dividing into multiple time steps and conducting history matching in each individual period. From figure 6.25, it is indicated that the $R_{SGCO_2 \rightarrow BCO_2}$ is not in a monotone increasing or decreasing value. This is understandable as when the solvent-heavy oil contact time was not long enough, the concentration of the CO$_2$ diffusion into the heavy oil phase was to be “shallower”, and hence, most of the CO$_2$ dissolution was close to the solvent-oil interface. When the system pressure was depleted by expanding the volume of the excessive gas cap, the CO$_2$ dissolution had a shorter distance to escape from the oil phase, and therefore, CO$_2$ reacted more rapidly to the pressure depletion, and the $R_{SGCO_2 \rightarrow BCO_2}$ factor was relatively higher. Then when the solvent-heavy oil contact time was longer, the diffusion depth was relatively deeper, and thus, the reaction of the CO$_2$ dissolution towards pressure depletion was slower than a shallower diffusion. Hence, a lower $R_{SGCO_2 \rightarrow BCO_2}$ factor was presented in the system with relatively longer solvent-heavy oil contact time. However, as the contact time approached equilibrium state, the diffusion of CO$_2$ into heavy oil phase was very close to equilibrium state, that is, the CO$_2$ concentration field was much more uniformly distributed in the oil phase and meanwhile, the concentration was higher than the tests of shorter contact time. Thus, when the pressure was depleted transiently to atmospheric pressure, the $R_{SGCO_2 \rightarrow BCO_2}$ factor again approached almost the same value of figure 6.16 with initial GOR x axis value as 26cm$^3$/cm$^3$. From figure 6.26 (a), it is clearly indicated that the $R_{BBO_2 \rightarrow FGCO_2}$ presents an exponential trend against time, which
means the decay rate of foamy oil volume increased exponentially with time increment. From figure 6.26 (b), it can be seen that the foamy oil stability was higher when the solvent-heavy oil contact time was longer, equivalent to the pressure depletion cases where higher initial GOR yielded a better foamy oil stability. Table 6.5 shows that the exponent for the tests with different solvent-heavy oil contact time, and it is found that a longer solvent-contact time would result in a lower exponent, indicating a better foamy oil stability. To sum up, Chapter 4.1.1, 4.1.2, 4.2.1, and 6.2.2 have been published in Elsevier Journal "FUEL" and can be found in the database by searching the title “Experimental and numerical study of non-equilibrium dissolution and exsolution behavior of CO₂ in a heavy oil system utilizing Hele-Shaw-like visual cell”. The paper concludes both the experimental and numerical studies of CO₂ dissolution and exsolution in heavy oil.

6.2.3 Pressure Depletion Tests in Bulk Phase Visual Cell

In this section, the non-equilibrium solvent exsolution behavior of the pressure depletion tests conducted in the bulk phase visual cell would be numerically simulated to investigate the non-equilibrium phase change in CO₂-C₃H₈-heavy live oil system. Totally, 2 different ways of describing the non-equilibrium exsolution behavior will be illustrated: first, the dynamic tuning of VLE K value for a direct two-phase flash; second, kinetic reactions representing the non-equilibrium interphase mass transfer between multiple components.

6.2.3.1 Dynamic Adjustment of K Value

Based upon the K value expression in Chapter 4.2.2, the experimental K value under non-equilibrium condition was yielded as the following figures 6.27 and figure 6.28 for fully-saturated cell and half-saturated cell, respectively.
Figure 6.27 Non-equilibrium K value from experimental study for gas component as one mixture (-20kPa/min fully-saturated cell test)

Figure 6.28 Non-equilibrium K value from experimental study for gas component as one mixture (-20kPa/min half-saturated cell test)
In figure 6.27 and 6.28, the equilibrium K value was calculated through equilibrium Eos calculation and plotted to compare against the experimental value. In both figures, the orange arrow shows the stable and unchanged period of K value, indicating that the exsolution of the dissolved gas was not initiated. When the pressure was further declined to a lower value below the pseudo-bubble point pressure, the system entered a solvent rapid exsolution period which is indicated by the blue arrow. In this period, the experimental non-equilibrium K value started to rise up and “chase” against the equilibrium value until at certain pressure, that the non-equilibrium and equilibrium K value curve merge with each other, that is, the period indicated by the red arrow. Then the overall system became equilibrium again.
Figure 6.29 Solvent composition change under pressure depletion (-20kPa/min fully-saturated cell test)

Figure 6.30 Solvent composition change under pressure depletion (-20kPa/min half-saturated cell test)
The figure 6.29 shows the solvent composition change under pressure depletion for the -20kPa/min fully-saturated cell test. It can be seen from the figure that the red dotted line is the line indicating the onset of the gas exsolution, and above 600kPa, no gas was detected as there was no gas exsolution above the pseudo-bubble point pressure at 600kPa. But for the purpose of a figure indicating the pressure range for the whole depletion process, the CO₂ mole fraction was assigned to 100% in the region where no gas exsolution was formed. Below 600kPa, where the red arrow points to the left region of the figure, the gas exsolution started to form out of the gas phase, and the solvent exsolution compositional change was therefore detected. When the system pressure was declined to atmospheric pressure, the detected solvent composition in the vapor phase was very close to the mole fraction of individual solvent at saturation pressure, indicating most of the dissolved gas had escaped from the oil phase. In figure 6.30, the visual cell was half-saturated with oil and high-pressure CO₂ gas cap as the initial condition. Under this condition, the free gas chamber at the first place was detected as CO₂ mole fraction as 100%. Then as the system pressure was declined, the free gas chamber maintained its CO₂ fraction as 100% due to the delayed exsolution of solvent. It is seen that even though the pressure was declined, the C₃H₈ did not exsolve out of the oil phase until the system pressure was reached around 400kPa, and after such pressure, the propane started to form exsolution and the free gas chamber composition changed. Comparing figure 6.29 and figure 6.30, it is clearly indicated that the K value measured from the experimental study is fitting the trend of the figure. From 1000kPa to 600kPa, the measured K value stay almost the same, indicating no gas exsolution had formed during this period of pressure depletion. Then when the pressure was further draw down, the gas exsolution started to
form and the K value started to raise its value. If the gas component was treated to be one mixture without characterizing its individual compositional change, then the pseudo-bubble point of the solvent-heavy live oil mixture can be set at $P=600\text{kPa}$, which can be an input for Eos calculation for a deviated K value. Between, 600kPa and 300kPa, the K value was rising towards the equilibrium value at a higher rate than the rate of the equilibrium K value, that is, with a higher incremental rate, the non-equilibrium K value might catch up with the equilibrium K value and the whole system became equilibrium again when the pressure was further draw down from 300kPa to atmospheric pressure. The three periods of non-equilibrium-to-equilibrium evolution processes are indicated in figure with 3 different colored arrows, with orange representing before-pseudo-bubble point pressure period, blue representing non-equilibrium K value increment towards equilibrium curve, and red representing the resuming of the equilibrium state. In order to understand how individual solvent’s non-equilibrium behavior was, $\text{CO}_2$ and $\text{C}_3\text{H}_8$ were separately treated as two components in the Eos calculation and numerical simulation to achieve their individual exsolution behavior. With the aid of MATLAB, the CMG simulator was applied to study the solvent exsolution behavior. The target objectives in our case are total vapor phase standard-condition volume, total $\text{CO}_2$ vapor phase standard-condition volume, and total $\text{C}_3\text{H}_8$ vapor phase standard-condition volume. By adjusting the K value table dynamically for each component, as long as the total vapor phase volume for each component can be history matched, the total vapor phase volume would be matched as well. Two methodologies of altering the K value during the simulation can be realized. First one is by giving a pre-specified relationship of non-equilibrium K value against system pressure, and directly formulating a K value table for the simulator to run without
periodically restarting the simulator. Second one is by extracting the grid pressure of the simulator at a pre-specified time step, that is for -20kPa/min as an example, the K value was altered every time step according to the pressure drop, the simulator was repetitively restarted and controlled by MATLAB after optimizing the K value table for each component after each certain time and pressure step. The simulated cases in our study here are the two most representative cases in which non-equilibrium prevailed: -20kPa/min fully-saturated cell test and -20kPa/min half-saturated cell test. Figure 6.31 and 6.32 show the history matching result for the total vapor volume change in the system. Figure 6.31 shows the total vapor volume of solvent exsolution under equilibrium K value, and it can be seen that there is a clear gap between both solvent components in the graph between the FHF file (experimental history data) and the IRF file (simulation results). Then by utilizing MATLAB-controlled CMG simulation, the total vapor volume in the closed system was matched by dynamically adjusting the K value table with an alternative pausing and restarting the simulator. It can be seen from figure 6.32 that the non-equilibrium solvent exsolution behavior was well matched with the experimental data by non-equilibrium K value shifted from equilibrium state calculated by equation-of-state. Since K value of single solvent component would not affect the exsolution behavior of any other solvent components, hence, by assuming single component existence in the exsolution gas collected in the pump transfer cylinder, the volume of single solvent component can be calculated using partial pressure. By knowing the total molar mass as well as the molar fraction of each component of exsolution gas under atmospheric pressure, individual component volume can be calculated as in figure 6.31, 6.32, 6.37 and 6.38.
Figure 6.31 Solvent exsolution volumetric behavior under equilibrium K value from live oil differential liberation tests (-20kPa/min fully-saturated cell test)

Figure 6.32 History matching of solvent exsolution volumetric behavior by applying non-equilibrium K value (-20kPa/min fully-saturated cell test)
Figure 6.33 Comparison of CO\textsubscript{2} mole fraction in free gas phase (-20kPa/min fully-saturated cell test)

Figure 6.34 Comparison of C\textsubscript{3}H\textsubscript{8} mole fraction in free gas phase (-20kPa/min fully-saturated cell test)
From figure 6.33 and 6.34, the comparison between equilibrium and non-equilibrium free gas chamber composition was shown for CO$_2$ and C$_3$H$_8$, respectively. The red dotted line indicates the time and pressure where the free gas phase started to form in the system, and the actual comparison is after this free gas phase initiating point at around 600kPa. It can be seen that the non-equilibrium composition of both solvent is “chasing” the equilibrium composition at a steeper rate, and at around 300kPa, the two curves merge together, indicating the equilibrium state is again reached in the closed system. Also, from figure 6.33, it is indicated that CO$_2$ exsolution rate was higher than that of C$_3$H$_8$ because CO$_2$ mole fraction free gas was always higher until around 350kPa where both of the solvent components reached equilibrium. Although CO$_2$ exsolved faster than C$_3$H$_8$, both of the solvent components were still under non-equilibrium as indicated by figure 6.31. What needs to be considered for the indication of non-equilibrium in this series of tests is the deviation of the actual amount of mass between experimental data and the equilibrium condition. As long as the mass of the solvent components were lower than the equilibrium state at any prevailing reservoir condition, regardless of the exsolution sequences, the system would be under non-equilibrium state.
Figure 6.35 CO₂ K value by non-equilibrium shifting from equilibrium state (-20kPa/min fully-saturated cell test)

Figure 6.36 C₃H₈ K value by non-equilibrium shifting from equilibrium state (-20kPa/min fully-saturated cell test)
Figure 6.37 Solvent exsolution volumetric behavior under equilibrium K value from live oil differential liberation tests (-20kPa/min half-saturated cell test)

Figure 6.38 History matching of solvent exsolution volumetric behavior by applying non-equilibrium K value (-20kPa/min half-saturated cell test)
Figure 6.35 and 6.36 show the comparison between equilibrium and non-equilibrium K value of both solvent compositions. It shows that for both solvent components, there is a period where the K value stays the same as the initial saturation pressure. When the pressure was declined to certain pressure, both the solvent components’ non-equilibrium K value started to rise up, indicating the free gas phase formation in the closed system. After the history matching, the non-equilibrium both CO$_2$ and C$_3$H$_8$ K value is in a power relation with the prevailing pressure in the system. Also, it can be seen that the C$_3$H$_8$ reached equilibrium exsolution rate at around 300kPa faster than CO$_2$ at around 200kPa.

Figure 6.37 and 6.38 show the history matching results for the half-saturated cell test. It can be seen in figure 40, the red star indicates the onset of gas exsolution from the oil phase after comparing the CO$_2$ volume with the real gas law $V=ZnRT/P$. Before the red star, the total vapor volume expansion was due to the existence of the initial CO$_2$ gas cap in the system. After the red star, the dissolved gas started to form. The exsolution of C$_3$H$_8$ appears to be later than the exsolution of CO$_2$. By adjusting the non-equilibrium K value, the total vapor volume was matched with the experimental data. Figure 6.39 and 6.40 show the difference of free gas composition under equilibrium and non-equilibrium state. In both figures, the gap between equilibrium and non-equilibrium is existing until the system pressure was gradually declined to a lower pressure at around 320kPa. From figure 6.41 and 6.42, non-equilibrium K value for CO$_2$ and C$_3$H$_8$ in a half-saturated cell test were plotted. The overall trend of K value shifting from equilibrium state is similar to the trend of a fully-saturated cell test. For C$_3$H$_8$, the non-equilibrium K value achieved from applying dynamic history matching seem to be a bit higher than equilibrium K value below the pressure of 400kPa.
Figure 6.39 Comparison of CO$_2$ mole fraction in free gas phase (-20kPa/min half-saturated cell test)

Figure 6.40 Comparison C$_3$H$_8$ mole fraction in free gas phase (-20kPa/min half-saturated cell test)
Figure 6.41 CO$_2$ K value by non-equilibrium shifting from equilibrium state (-20kPa/min half-saturated cell test)

Figure 6.42 C$_3$H$_8$ K value by non-equilibrium shifting from equilibrium state (-20kPa/min half-saturated cell test)
In a reservoir simulator, the molar fraction of each component as well as each phase in a numerical grid is normally controlled by equilibrium K value. Hence, under such equilibrium flash calculation, the molar fraction of each component and phase in a grid will reach equilibrium instantly. By applying a shifted K value, the delayed exsolution of solvent can be simulated in a continuous pressure depletion operational scheme. However, if in a pressure operational scheme where a transient pressure drawdown level was applied and then the pressure was fixed, similar to the figure 6.2 and 6.3, then a non-equilibrium K value might fail to simulate the solvent exsolution behavior. This is because that the adjustment of K value in the reservoir simulator is only relevant to the prevailing pressure and temperature value in a grid but not with time. Therefore, when a certain pressure drawdown level was applied, and the system pressure was then fixed, then the K value can only denote the fixed pressure. But solvent exsolution might not react to a sudden pressure drop immediately. Certain period of time might be needed for the solvent to exsolve. Under such circumstance, the closed system would have a volume expansion to keep to pressure constant as solvent tended to exsolve, and if non-equilibrium K value was applied, it can only represent the one value under that fixed pressure, and one value cannot efficiently simulate the continuous exsolution that expanded the system volume. Solution to this can be in two ways: first, a non-equilibrium K value can be adjusted as a function of time at a fixed pressure and temperature; second, kinetic reactions can be added to continuity equations as source/sink terms to indicate the non-equilibrium interphase mass transfer among different components, so as to represent the phase change process in a Darcy-scale reservoir simulator.
To sum up, Chapter 4.1.2, 4.2.2, 6.1 and 6.2.3.1 have been published in Elsevier Journal “FUEL” and can be found in the database by searching the title “A novel visualization approach for foamy oil non-equilibrium phase behavior study of solvent/live heavy oil systems”. The paper concludes both the experimental and numerical studies of CO₂-C₃H₈ solvent mixture exsolution behavior and how to properly define the concept of non-equilibrium as well as quantify the extent of non-equilibrium by using reservoir numerical simulation.

6.2.3.2 Kinetic Reactions of Solvent Exsolution

In this section, solvent exsolution behavior for bulk phase visual cell -20kPa/min fully-saturated cell and half-saturated tests were history matched by utilizing kinetic reactions in CMG setup to describe the dynamic and non-equilibrium interphase mass transfer processes of different components. The mathematical relationship applied for the pressure-exsolution rate relation was obtained from Chapter 4.2.3. Implementing such a relationship in CMOST formula section, one is able to generate a list of parameters to be substituted into the DAT file of CMG to recurrently update the parameter in the simulation. The history matching of 4 main parameters obtained in the CCE pressure depletion test: total liquid volume fraction, cumulative gas volume collected by the DBR transfer cylinder, and the cumulative individual component gas volume detected by the compositional analyzer, which was CO₂ and C₃H₈ in this case.
Figure 6.43 Simulation model buildup
In CMG STARS module, totally 7 components (no aqueous phase existed) were defined in the simulation. And totally 4 1st order kinetic reactions were defined for the solvent exsolution behavior simulation during the bulk phase visual cell CCE pressure depletion tests:

**1st reaction in oil phase: dissolved gas → dispersed gas bubbles:**

\[ CO_2_{L} \rightarrow BBCO_2 \]

\[ C_3H_8_{L} \rightarrow BBC_3 \]

**2nd reaction from oil phase to gas phase: dispersed gas bubbles → free gas clusters**

\[ BBCO_2 \rightarrow FGCO_2 \]

\[ BBC_3 \rightarrow FGC_3 \]

For the above each reaction, chemical reaction order was defined to be 1, and the stoichiometry for both reactant and product was set to 1, indicating the reaction product is solely for each reactant. The chemical reaction activation energy was set to 0 in our case, as it is a reaction induced by supersaturation in the liquid solution under pressure drop. Strictly speaking, the activation energy should be defined as the excess energy induced by the pressure depletion of the system. But in this case, the activation energy was set to 0 and the starting pressure for each reaction was set to a pressure lower than the saturation pressure as the pseudo bubble point pressure to compensate for the zero activation energy, which means that only when the system pressure reaches the pre-set pseudo bubble point pressure, the solvent would enter a spinodal decomposition region and exsolve out of the mixture. Before that, there is no reaction would be activated.
In the above reactions, the 1st reaction assumes that the dispersed gas bubbles are all in the oil phase, and the total liquid properties were affected by the gassy-liquid of BBCO₂ and BBC₃ component, as these two components were set to have a density resembling to gas phase. The 2nd reaction assumes that the exsolved gas bubbles would grow and coalescence together to form continuous gas phase, so the reaction would be a source term for the gas phase and a sink term for the oil phase by considering the physical meaning using continuity equations. The non-equilibrium K value table for CO₂ and C₃H₈ component was set according to the K value calculated in chapter 4.2.2 to consider for the delayed exsolution under non-equilibrium.

In this simulation, the targeted parameters were aimed for the non-equilibrium phase behavior using the source/sink kinetic terms rather than the flowing mechanism of foamy oil in the reservoir, and therefore, the relative permeability curve adjustment parameters in the CMOST module was not considered and set to a fracture-like curve set. The whole geometry was built as the same geometry as the visual cell and the permeability was estimated by the fracture/aperture permeability equation. The porosity was set to 0.99 and permeability was 1800 Darcy to mimic a confined Hele-Shaw space.

The history matching results of utilizing CMG CMOST self-defined formula module to simulate the non-equilibrium solvent exsolution behavior are listed in the following figures:
-20kPa/min half-saturated cell test:

Figure 6.44 (a) History matching of the gas reservoir volume inside the visual cell (red dotted line indicating the equilibrium liquid volume fraction under the same composition, pressure and temperature) (b) History matching of the cumulative STD gas collected in transfer cylinder from the bulk visual cell
Figure 6.45 (a) History matching of the cumulative STD CO$_2$ production from the visual cell (b) History matching of the cumulative STD C$_3$H$_8$ production from the visual cell
-20kPa/min fully-saturated cell test:

Figure 6.46 (a) History matching of the gas reservoir volume inside the visual cell (red dotted line indicating the equilibrium liquid volume fraction under the same composition, pressure and temperature) (b) History matching of the cumulative STD gas collected in transfer cylinder from the bulk visual cell
Figure 6.47 (a) History matching of the cumulative STD CO$_2$ production from the visual cell (b) History matching of the cumulative STD C$_3$H$_8$ production from the visual cell
Figure 6.48 Optimized kinetic reaction rate frequency factors value for -20kPa/min fully-saturated cell test (test no.1 in section 4.2.2)
It is noted that in figure 6.48, the A2 and A4 reaction frequency factor exponent indicated the exsolution processes of CO2 from dissolved state to gas phase and C3H8 from dissolved state to gas phase, respectively. In the chapter 4.2.3, the regressed single bubble exsolution rate exponent in the pressure-exsolution rate relationship was 1.646 considering the solvent mixture as one component. It is seen from the 1st row in figure 6.48 where the global error is the least, that A2 is 1.625 and A4 is 1.25. Since the majority of the exsolution gas was CO2 whose initial compositional fraction was high in the live oil, therefore, the exsolution behavior was more or less dominated by CO2, and the exsolution rate A2 for CO2 at 1.625 was very close to experimentally measured value at 1.646. The average of A2 and A4 is 1.43, and the order of magnitude was close to 1.646 as well. It is safe to say they are in the same range, which could be a very representative value for the exsolution rate exponent. From other A2 and A4 columns in figure 6.48, the average value of the two parameters are close to 1.646.

6.2.4 SCCE and CCF Tests

In order to investigate the non-equilibrium phase behavior of heavy oil in microfluidics system, it is essential to have a relatively larger pore space in the micromodel so as to minimize the effect of fractional resistance to the heavy oil flow caused by the narrow geometry of the model. By doing this, pressure propagation and distribution in the micromodel will be instantaneous and a uniform pressure-temperature-volume condition can be well controlled. Also, a real porous media pattern (whether homogeneous or heterogeneous) is preferred for the characterization of static and dynamic foamy oil non-equilibrium phase behavior. In the previous studies of foamy oil numerical simulation (Y. Bayon et al. 2002; Y. M. Bayon, Cordelier, and Nectoux 2002; Chang and Ivory 2013,
foamy oil phenomenon was mostly modeled to history match the production system data of the coreflooding/sandpack systems, and parameters selected for history matching usually contain multiple static model variables such as application of different relative permeability curve calculation laws and different relative permeability curve endpoints. Such adjustment is aimed to better tune the fluid flow behavior of the gas-foamy oil two-phase flow inside the porous media to match the production data, while the actual non-equilibrium phase behavior that affects the multi-phase distribution in the porous media was not independently considered. Although there are some studies that have numerically characterized foamy oil non-equilibrium exsolution behavior in bulk phase (Oskouei, Zadeh, and Gates 2017; Sheng 1997; Zhou et al. 2017), the experimental apparatus in such studies were mostly traditional PVT cell with relatively lower visualization level than microfluidics system, hence, resulting in a rather difficult reading of true gas-oil interface. Therefore, in this study, a high-pressure porous micromodel was designed and applied to the study of foamy oil generation and stability under pressure depletion with two tests. Static Constant Composition Expansion (SCCE) tests mostly focused on the static foamy oil non-equilibrium phase behavior, and Continuous Convective Flowing (CCF) tests was mainly aimed to study foamy oil stability under various dynamic conditions. With porosity and permeability measurement of the micromodel, the creeping-flow condition of reservoir fluid through such a micromodel of engraved porous media can be well represented by Darcy flow behavior, and therefore a MATLAB-controlled reservoir simulator was developed to conduct numerical simulation. By eliminating the fluid flow behavior effect
on the history matching of the non-equilibrium foamy oil phase behavior, the simulation study did not aim to adjust a large number of parameters related to relative permeability curve, and solely focuses on the adjustment of kinetic reaction frequency factors. An optimization module was incorporated into the numerical simulation for history matching by real-time tuning of kinetic reaction frequency factors which represent the rate of non-equilibrium interphase mass transfer of different components.

6.2.4.1 Model Setup for an Effective Porous Media

In this section, a combination of MATLAB and CMG reservoir simulator technique was applied to study the non-equilibrium phase behavior of solvent-heavy live oil system. The reservoir model was built based upon the porosity and permeability measurement of the high-pressure glass micromodel. The simulator assumes various of pseudo-chemical kinetic reactions to describe interphase mass transfer of different components so as to represent the non-equilibrium phenomenon in the experimentation. The following figure shows the schematics of the numerical model built for simulating solvent non-equilibrium dissolution/exsolution behavior in porous media:

In figure 6.49, the red part is where the micromodel was represented by the concept of “effective porous media”. The micromodel was assumed to be homogeneous in permeability and porosity according to the measurement by passing water through and recording the pressure differential between the two model ends. The green part is where the “piston area” of the closed system is positioned, and the fluid contained in the green part is water, which was set to have no thermodynamic interaction with gas and oil phase while only controlling the system pressure in the simulation by the producer at the end. When SCCE tests were simulated, no injection rate was set at the injector but opposite for
the CCF tests. In this numerical simulation, the goal is not to find how the adjustment of relative permeability curve effect on the non-equilibrium phase behavior of solvent-heavy live oil system undergoing pressure depletion, but rather the effect of the phase change kinetics represented by various of source/sink terms on each component in each phase. Therefore, the relative permeability curve was set to be fracture-like permeability where the flow ability of gas, oil and water phase through the porous media were very high, hence, the pressure propagation along the whole numerical grid was almost instantaneous, eliminating the relative permeability effect on the local grid pressure build-up and fluid flowing behavior.
Figure 6.49 Numerical grid systems (a) a closed micromodel-based PVT cell system for SCCE tests (b) an open system micromodel for CCF tests
Therefore, under such setup, the whole numerical grid system was large enough to form a closed system by preventing gas and oil phase from being produced out of the producer while being able to travel and expand freely through the grids and towards the producer under very small pressure resistance, and thus, a micromodel-based PVT cell was numerically established. The one good thing about conducting phase behavior tests in a 2D micromodel is that according to the physical permeability, porosity and creeping-flow condition (very low Reynolds number flow), the micromodel can be efficiently represented by a Darcy-scale simulator, while a traditional PVT cell with a much-too-large hollow space will tend to have unphysically large permeability value if Darcy-scale simulation is to be applied. Then the simulation has either to be turned to full CFD calculation or using pure Fick’s 2nd law where in both the situation, the actual interface of gas and oil has to be captured accurately for an efficient numerical simulation, and multiple physics will be challenging to be incorporated. In addition, for full CFD equation sets, given finite computer ability, it will severely limit the size of the numerical porous media model where a large number of solid boundaries are present, and complex fluid-solid interactions should be considered.

In the simulation, the foamy oil was assumed to be in 2 different forms: first, two-phase system without gassy-liquid setup, and second, pseudo single phase foamy oil with gassy-liquid setup. For two-phase system without gassy-liquid setup, the foamy oil system was considered to be in two-phase condition, free gas phase and oil phase, and within the oil phase, dispersed/bubbly component did not contribute the change of volume in the oil phase. Bubbly-dispersed gas phase only acted as the medium for solution gas in oil phase to be transferred into free gas phase. The process where solution gas being transferred to
dispersed gas only indicates the deviation from thermodynamic equilibrium. While in the
gassy-liquid setup, both the free gas and dispersed gas were considered to be existed in the
form dispersed/bubbly gas in the oil phase. Therefore, the volume variation of the
dispersed component directly affects the overall volume of the oil phase. Such a volume
variation contributed by the dispersed component can represent the vapor volume fraction
change in the experimentation.

(a) Non-Gassy-Liquid Setup:

In the numerical simulations, totally 7 components were incorporated into the simulator:

*Oil phase components:*

(1) Dead oil: a de-gassed state heavy oil sample

(2) SGCO2: CO\(_2\) component in dissolution state in the oil phase

(3) SGC3: C\(_3\)H\(_8\) component in dissolution state in the oil phase

(4) BBCO2: CO\(_2\) component in bubbly form which is dispersed in the oil phase

(5) BBC3: C\(_3\)H\(_8\) component in bubbly form and also dispersed in the oil phase

*Gas phase components:*

(6) FGCO2: CO\(_2\) component in free gas state

(7) FGC3: C\(_3\)H\(_8\) component in free gas state

In a Darcy-scale simulator, the structure of the actual pores and throats is usually ignored,
and the porous media is represented by an effective media with certain parameters such as
porosity, permeability etc. to indicate its ability to pass through fluids. Therefore, rather
than solving a complex set of CFD compressible equation sets which describe the gas-oil two-phase interaction between solid boundaries, the Darcy-scale simulator can simplify the problem and upscale to a larger oil-field scale for a more practical computational time cost. In Darcy-scale simulator, non-equilibrium interphase mass transfer can be applied to the continuity equation sets as source/sink terms, which can be a function of multiple parameters such as phase velocity, porous media permeability, pressure gradient, etc. Hence, such source/sink terms can be accounted for describing the non-equilibrium phase change in a numerical grid as the following:

(1) \( \text{SGCO}_2 \Leftrightarrow \text{BBCO}_2 \) (thermodynamically non-equilibrium dissolution/exsolution)

\( \text{CO}_2 \) in dissolution state becomes dispersed/bubbly state, which is trapped in the oil phase;

(2) \( \text{SGC}_3 \Leftrightarrow \text{BBC}_3 \) (thermodynamically non-equilibrium dissolution/exsolution)

\( \text{C}_3\text{H}_8 \) in dissolution state becomes dispersed/bubbly state, which is trapped in the oil phase;

(3) \( \text{BBCO}_2 \Leftrightarrow \text{FGCO}_2 \) (bubble coalescence/break-up)

Bubbly \( \text{CO}_2 \) coalesces and becomes free gas;

(4) \( \text{BBC}_3 \Leftrightarrow \text{FGC}_3 \) (bubble coalescence/break-up)

Bubbly \( \text{C}_3\text{H}_8 \) coalesces and becomes free gas;

For the pseudo-chemical kinetic reactions, the interphase mass transfer can be expressed as the source/sink term of each component in each corresponding phase:

\( \text{SGCO}_2 \Leftrightarrow \text{BBCO}_2 \):
\[
\frac{\partial m_{\text{SGCO}_2 \rightleftharpoons \text{BBCO}_2}}{\partial t} = RRF_{\text{SGCO}_2 \rightleftharpoons \text{BBCO}_2} \left[ \left( \frac{1}{\text{min}} \right) \left( \frac{\text{mole}}{\text{cm}^3} \right)^{1-m} \right] \cdot \exp \left( -\frac{E_{\text{ACT}}}{RT} \right) \cdot \left( \phi_{\text{oil}} \chi_{\text{SGCO}_2 \rightleftharpoons \text{BBCO}_2} \rho_{\text{oil}} \right)^m \left[ \frac{\text{mole}}{\text{cm}^3} \right]^m
\]  
(6.27)

\[
\frac{\partial m_{\text{BBCO}_2 \rightleftharpoons \text{FGCO}_2}}{\partial t} = RRF_{\text{BBCO}_2 \rightleftharpoons \text{FGCO}_2} \left[ \left( \frac{1}{\text{min}} \right) \left( \frac{\text{mole}}{\text{cm}^3} \right)^{1-m} \right] \cdot \exp \left( -\frac{E_{\text{ACT}}}{RT} \right) \cdot \left( \phi_{\text{oil}} \chi_{\text{BBCO}_2 \rightleftharpoons \text{FGCO}_2} \rho_{\text{oil}} \right)^m \left[ \frac{\text{mole}}{\text{cm}^3} \right]^m
\]  
(6.28)

\[
\frac{\partial m_{\text{SGC}_3 \rightleftharpoons \text{BBC}_3}}{\partial t} = RRF_{\text{SGC}_3 \rightleftharpoons \text{BBC}_3} \left[ \left( \frac{1}{\text{min}} \right) \left( \frac{\text{mole}}{\text{cm}^3} \right)^{1-m} \right] \cdot \exp \left( -\frac{E_{\text{ACT}}}{RT} \right) \cdot \left( \phi_{\text{oil}} \chi_{\text{SGC}_3 \rightleftharpoons \text{BBC}_3} \rho_{\text{oil}} \right)^m \left[ \frac{\text{mole}}{\text{cm}^3} \right]^m
\]  
(6.29)

\[
\frac{\partial m_{\text{BBC}_3 \rightleftharpoons \text{FGC}_3}}{\partial t} = RRF_{\text{BBC}_3 \rightleftharpoons \text{FGC}_3} \left[ \left( \frac{1}{\text{min}} \right) \left( \frac{\text{mole}}{\text{cm}^3} \right)^{1-m} \right] \cdot \exp \left( -\frac{E_{\text{ACT}}}{RT} \right) \cdot \left( \phi_{\text{oil}} \chi_{\text{BBC}_3 \rightleftharpoons \text{FGC}_3} \rho_{\text{oil}} \right)^m \left[ \frac{\text{mole}}{\text{cm}^3} \right]^m
\]  
(6.30)

<table>
<thead>
<tr>
<th>RRF Sign</th>
<th>SGi ⇐ BBi</th>
<th>BBi ⇐ FGi</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>Solution Gas → Dispersed Gas</td>
<td>Dispersed Gas → Free Gas</td>
</tr>
<tr>
<td>-</td>
<td>Dispersed Gas → Solution Gas</td>
<td>Free Gas → Dispersed Gas</td>
</tr>
</tbody>
</table>
In the above numerical study, the vapor volume fraction is mainly attributed to the gas phase whose stability will be affected by the in-situ Darcy velocity at each time step. As the gas phase velocity changes, the free gas CO$_2$ or C$_3$H$_8$ component will react accordingly, and undergoes corresponding kinetic reactions to decrease its content and transfer into oil phase, hence, the vapor volume fraction keeps fluctuating around a relatively stable value.

In the overall pressure depletion phase, the interphase non-equilibrium mass transfer of multiple components was under a dynamic condition. According to the optimized parameters of the kinetic reaction frequency factors, it shows that the above-mentioned reactions were not just under single direction. In the history matching, in order to show more clearly of direction of the interphase mass transfer of different components, both positive and negative values of kinetic reaction frequency factors occurred, and this has indicated the direction of the kinetic reaction was not always single. According to the experimental data, the simulator and the optimization module would make judgement to adjust the sign of the source/sink term in the continuity equation to indicate dynamic dissolution/exsolution.

For instance, in the BBCO$_2$ ⇌ FGCO$_2$ kinetics, if the $RRF_{BSCO_{2}\rightarrow FGCO_{2}}$ sign was yielded a positive value, it indicates that the reaction was going forward (exsolution BBCO$_2$ → FGCO$_2$), in this case, the CO$_2$ component in dispersed form in oil phase underwent phase change and became free gas CO$_2$ component in gas phase, and if the $RRF_{BSCO_{2}\rightarrow FGCO_{2}}$ term was yielded a negative value after the optimization module was done for the iteration in this time step, it indicates the kinetic reaction was going backward (dissolution) where CO$_2$ component in free gas phase underwent phase change and became dispersed CO$_2$ component in oil phase, and thus, the simulator would re-adjust the input file of the CMG.
automatically to indicate a new reaction direction from \( \text{BBCO}_2 \rightarrow \text{FGCO}_2 \) to \( \text{FGCO}_2 \rightarrow \text{BBCO}_2 \). Therefore, with the above specified kinetics, the dynamic dissolution/exsolution behavior of solvent components can be simulated by the MATLAB-controlled reservoir simulator. But for the clarity of reaction direction, positive (+) values in the RRF plots indicates the forward reaction while the negative (-) indicates the backward.

Table 6.7 Reaction patterns indicated by kinetic reaction frequency factors

<table>
<thead>
<tr>
<th>Sign of RRF</th>
<th>( \text{SG}_i \rightleftharpoons \text{BB}_i (+) )</th>
<th>( \text{SG}_i \rightleftharpoons \text{BB}_i (-) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{BB}_i \rightleftharpoons \text{FG}_i (+) )</td>
<td>Pure exsolution processes;</td>
<td>Competition of phase-change direction of ( \text{BB}_i ) component (either towards ( \text{SG}_i ) or ( \text{FG}_i ));</td>
</tr>
<tr>
<td>( \text{BB}_i \rightleftharpoons \text{FG}_i (-) )</td>
<td>Equilibrium-deviation-driven kinetics for solution gas ( \rightarrow ) dispersed gas processes; Free gas phase might undergo phase change back into dispersed state under multiple effects such as flowing velocity, porous media parameters, etc.</td>
<td>Pure dissolution processes;</td>
</tr>
</tbody>
</table>

From the above table, it indicates the 4 different possible combinations of kinetic reaction frequency factors. If, take \( \text{CO}_2 \) for example, for both the \( \text{RRF}_{\text{SGCO}_2 \rightleftharpoons \text{BBCO}_2} \) and \( \text{RRF}_{\text{BBCO}_2 \rightleftharpoons \text{FGCO}_2} \) to be positive (+) value, it means that the whole process is single-directional as a pure exsolution process. If both the factors are negative (-) value, it indicates a pure dissolution process of the free gas component. If \( \text{RRF}_{\text{SGCO}_2 \rightleftharpoons \text{BBCO}_2} \) is negative (-) while \( \text{RRF}_{\text{BBCO}_2 \rightleftharpoons \text{FGCO}_2} \) is positive (+), it indicates that the dispersed component \( \text{BB}_i \) will undergo phase change in both directions, and the vapor volume fraction will be affected by the inequality of the kinetic RRFs, that is to say, if the absolute...
value of $\text{RRF}_{\text{SGCO}_2 \equiv \text{BBCO}_2}$ is higher than that of $\text{RRF}_{\text{BBCO}_2 \equiv \text{FGCO}_2}$, then the free gas component incremental rate will be lower than the incremental rate of solution gas, and hence, the vapor volume fraction of the solvent-heavy live oil system will be decreased, and vice versa. In addition, under the assumption of the non-gassy-liquid properties, the dispersed gas in the oil phase will not share the same properties as the gas in the free gas phase, and therefore, in order to history match the free gas chamber volume fraction in the micromodel, the main mechanism behind is the process where the dispersed/bubbly gas in oil phase transforms into free gas phase. Last, if $\text{RRF}_{\text{SGCO}_2 \equiv \text{BBCO}_2}$ is positive (+) and $\text{RRF}_{\text{BBCO}_2 \equiv \text{FGCO}_2}$ is negative (-), it indicates that the system is under thermodynamic non-equilibrium, and the solution gas will have a tendency to form exsolution, while the already formed free gas phase is unstable, and may be affected by various of influential factors such flowing velocity, and other porous media-related parameters (porosity, permeability, local heterogeneity, reservoir pore-throat distribution, configuration and sizes, etc.). Then, overall vapor volume fraction may reduce, while the bubbly component will increase, in turn, the reservoir block pressure may bounce up as the compressibility of the oil phase is now high, and the bubbly gas is tightly trapped by heavy oil which cannot easily escape.

By incorporating the non-equilibrium interphase mass transfer source/sink terms, the governing equation sets for each component in each phase, hence, become as the following:

**Oil phase components mass balance equations:**

\[
\frac{\partial \phi_{\text{oil}}}{\partial t} \rho_{\text{oil}} \frac{m_{\text{molar}}}{\chi_{\text{dead oil}}} = -\nabla \cdot \left( \rho_{\text{oil}} m_{\text{molar}} \nu_{\text{oil}} \chi_{\text{dead oil}} \right) + Q_{\text{well,source/sink}} \quad (6.31)
\]

\[
\frac{\partial \phi_{\text{oil}}}{\partial t} \rho_{\text{oil}} \frac{m_{\text{molar}}}{\chi_{\text{SGCO}_2}} = -\nabla \cdot \left( \rho_{\text{oil}} m_{\text{molar}} \nu_{\text{oil}} \chi_{\text{SGCO}_2} \right) + Q_{\text{well,source/sink}} - \frac{\partial m_{\text{SGCO}_2 \equiv \text{BBCO}_2}}{\partial t} \quad (6.32)
\]
\[
\frac{\partial S_{oil} \rho_{oil} \chi_{SGC_3}^{\text{molar}}}{\partial t} = -\nabla \cdot \left( \rho_{oil} v_{oil} \chi_{SGC_3}^{\text{molar}} \right) + Q_{\text{well source/sink}} - \frac{\partial m_{SGC_3}^{\text{molar}}}{\partial t} \quad (6.33)
\]

\[
\frac{\partial S_{oil} \rho_{oil} \chi_{BBCO_2}^{\text{molar}}}{\partial t} = -\nabla \cdot \left( \rho_{oil} v_{oil} \chi_{BBCO_2}^{\text{molar}} \right) + Q_{\text{well source/sink}} + \frac{\partial m_{BBCO_2}^{\text{molar}} \equiv FGCO_2}{\partial t} - \frac{\partial m_{BBCO_2}^{\text{molar}} \equiv FGCO_2}{\partial t} \quad (6.34)
\]

\[
\frac{\partial S_{oil} \rho_{oil} \chi_{BBC_3}^{\text{molar}}}{\partial t} = -\nabla \cdot \left( \rho_{oil} v_{oil} \chi_{BBC_3}^{\text{molar}} \right) + Q_{\text{well source/sink}} + \frac{\partial m_{BBC_3}^{\text{molar}} \equiv FGCO_2}{\partial t} \quad (6.35)
\]

**Gas phase components mass balance equations:**

\[
\frac{\partial S_{gas} \rho_{gas} \chi_{FGCO_2}^{\text{molar}}}{\partial t} = -\nabla \cdot \left( \rho_{gas} v_{gas} \chi_{FGCO_2}^{\text{molar}} \right) + Q_{\text{well source/sink}} + \frac{\partial m_{FGCO_2}^{\text{molar}} \equiv FGCO_2}{\partial t} \quad (6.36)
\]

\[
\frac{\partial S_{gas} \rho_{gas} \chi_{FGC_3}^{\text{molar}}}{\partial t} = -\nabla \cdot \left( \rho_{gas} v_{gas} \chi_{FGC_3}^{\text{molar}} \right) + Q_{\text{well source/sink}} + \frac{\partial m_{FGC_3}^{\text{molar}} \equiv FGCO_2}{\partial t} \quad (6.37)
\]

**(b) Gassy-Liquid Setup:**

For our experimental study, since visualization gives a direct gas saturation in the closed system for all the SCCE and CCF tests, therefore, a pseudo single-phase method can be applied to study foamy oil in an integrity-manner. By considering foamy oil being composed of the following components:

**Oil phase components:**

(1) Dead oil;

(2) Solution gas (CO\textsubscript{2}-C\textsubscript{3}H\textsubscript{8} mixture);
(3) Dispersed gas (CO$_2$-C$_3$H$_8$ mixture), and behaving like free gas phase according to the real gas law, \( PV = ZnRT \)

In the above components, every component is considered to be in the oil phase. The whole numerical reservoir was filled with “bouncy” foamy oil pseudo single phase mimicking two-phase fluid in a closed system. Then, the overall vapor volume fraction in the confined system can be expressed as the variation of the dispersed gas volume in the oil phase according to the real gas law. With such a methodology, a single pseudo-chemical reaction is enough to represent the non-equilibrium volume change of the foamy oil phase. The reaction source/sink terms and the total governing equations for such a single-phase system simulation is:

**Oil phase components:**

\( SG_{gas\_mixture} \rightleftharpoons BB_{gas\_mixture} \): positive (+) reaction direction here is \( SG \rightarrow BB \) and vice versa

\[
\frac{\partial m_{SG=B_B}^{\text{molar}}}{\partial t} = RRF_{SG=B_B} \left[ \left( \frac{1}{\text{min}} \right)^1 \times \left( \frac{\text{mole}}{\text{cm}^3} \right)^{1-m} \right] \times \exp \left( - \frac{E_{\text{ACT}}}{RT} \right) \times \left( \phi_{\text{oil}} x_{SG=B_B} \rho_{\text{oil}} \right)^m \left[ \left( \frac{\text{mole}}{\text{cm}^3} \right)^m \right]
\]

(6.38)

And the governing equations for each component in oil phase can be derived as the following:

**Oil phase components mass balance equations:**

\[
\frac{\partial \phi_{\text{oil}} x_{SG}^{\text{molar}}}{\partial t} = -\nabla \cdot \left( \rho_{\text{oil}} x_{\text{dead oil}}^{\text{molar}} \right) + Q_{\text{well source/sink}}
\]

(6.39)

\[
\frac{\partial \phi_{\text{oil}} x_{SG}^{\text{molar}}}{\partial t} = -\nabla \cdot \left( \rho_{\text{oil}} x_{SG}^{\text{molar}} \right) + Q_{\text{well source/sink}} - \frac{\partial m_{SG=B_B}^{\text{molar}}}{\partial t}
\]

(6.40)
\[ \frac{\partial \phi_{oil} \rho_{oil} \chi_{BB}^{molar}}{\partial t} = -\nabla \cdot (\rho_{oil} v_{oil} \chi_{BB}^{molar}) + Q_{well\_source/sink} + \frac{\partial m_{SU=BB}^{molar}}{\partial t} \] (6.41)

In the numerical modeling with the consideration of gassy-liquid, under the assumption of the gassy-liquid properties, the dispersed gas in the oil phase will share the same properties as the gas in the free gas phase, and therefore, in order to history match the free gas chamber volume fraction in the micromodel, the main mechanism is to adjust the transformation between the bubbly phase and solution phase of solvent. Worth mentioning, the setup of the gassy-liquid properties for the simulation will better preserve the mass balance \((10^{-4} \sim 10^{-3})\) of the computation as it can vary the system pressure by its compressibility. Therefore, in the simulation process by single phase setup, the average pressure in the system was quite affected by the compressibility of the oil phase due to the bubbly component, and there was prominent pressure fluctuation phenomenon in the simulation results.

The equation below shows the calculation of the vapor volume fraction based upon the single-phase assumption of foamy oil, and hence, incorporated as the history matching objectives in the simulation as the following:

\[ n_{oil} = P_{micromodel} \cdot \rho_{oil}^{molar} \] (6.42)

\[ n_{BB} = \rho_{oil}^{molar} \cdot P_{micromodel} \cdot n_{\%BB} \] (6.43)

\[ V_{BB} = \frac{Zn_{BBRT}}{p} \] (6.44)

\[ V_{\%BB} = \frac{v_{BB}}{P_{micromodel}} \] (6.45)
From the above equation sets, it is indicated that the vapor volume fraction in the closed system was represented by the gas-like properties of the dispersed component in the oil phase. By obtaining the properties of the targeted numerical grid at each pre-specified time-step, the experimental vapor volume fraction of the micromodel can be history matched.

**6.2.4.2 History Matching and Optimization**

In the numerical study, the main purpose is to show the difference of solvent-heavy live oil non-equilibrium phase behavior between static and convective tests. In a static test, the effect of the in-situ Darcy-velocity was set to be irrelevant to the pseudo-chemical kinetic reaction frequency factors, while in a convective test, the interphase mass transfer between different components in different phases was related to the velocity of the phase, and hence, the adjustment of the coefficients indicating flow velocity effect was crucial to yield a decent history match. In the following figure 6.50, a schematic of vapor volume fraction history matching is shown to indicate how to segmentally adjust parameters and match the experimental data. The red lines are the trial and error and once the convergence standard was met, the optimization would enter a newer specified time step for the next optimization sequence. In the history matching process, due to the high adjustability of the simulator, a near-perfect and faster history matching results can be generated as long as the time step was step sufficiently small, but in order to maintain the integrity and commonality of the simulation, time step dt was usually chosen between 1~10 minutes instead of going towards an order of magnitude at $10^{-2}$~$10^{-1}$ min scale.

In addition, since the detailed composition of the solvent which was visualized in the micromodel was un-detectable by any means, therefore, instead of using individual solvent
component properties, the numerical model was further refined by conducting component-lumping of CO$\text{2}$ and C$_3$H$_8$ together to form a single component gas phase in CMG WINPROP. In addition, the other only achievable parameter in the experimentation is the system pressure recorded at the receiving transfer cylinder. Therefore, the history matching processes, these above-mentioned two experimental parameters were the main objectives to be simulated and matched for both SCCE and CCF tests. In SCCE tests, since the tests were conducted in a closed system, and therefore, one more parameter that is the fluid volume collected in the transfer cylinder by system volume expansion can be another constraint and objective to make the history matching of SCCE accurate.

Unlike CMOST whose optimization procedure is carried out throughout the whole preset simulation time, and thus, sometimes it can be hard to capture the exact behavior of the small fluctuations observed in the experimental study. While, in a time-step-wise-controlled simulator, the total time of the simulation can be broken up into very small fragments in order to capture the small fluctuations in the adjustment of the RRFs. Figure 6.50(a) shows the detailed procedures of the MATLAB-controlled reservoir simulator on history matching the solvent exsolution behavior and foamy oil stability in the effective porous media.
Start

Create input file, initiate the simulator and run for a specific initial time step

Run for the pre-specified Δt with initial guess of RRFs

Export and extract simulation results into MATLAB and compare with the trend of the experimental data to decide the kinetic reaction directions

Adjust the values of RRFs to testify the kinetic reaction (solvent phase change) directions

Simulation trend = experimentation trend

Y

Stop

Y

N

N

t_i > t_{total}

Write new reservoir properties and generate new executive simulator file for the next time step at \( i = i + 1 \)

Extract the optimized RRFs

Apply optimization module (i.e. Genetic Algorithm, Nelder-Mead, Simulated Annealing etc.) to history match experimental vapor phase volume fraction and system average pressure

(a)
Figure 6.50 History matching (a) algorithm and example of CCF tests at 700kPa 0.001mL/min (b) non-gassy-liquid setup (c) gassy-liquid setup

Figure 6.51 Simultaneous history matching of the 3 parameters in 700kPa SCCE tests (from left to right: system pressure, vapor phase volume fraction in the micromodel, total vapor phase volume collected in the micromodel and ISCO pump chamber)
In figure 6.50(b) and (c), an example of how the dynamic history matching of experimental vapor volume fraction and pressure under both non-gassy-liquid and gassy-liquid setup as well as the history matching objectives in figure 6.51 were shown. The system average pressure was also incorporated as a constraint of the history matching in order that the system pressure would not fluctuate too much just for the purpose of perfectly matching the vapor volume fraction. Two series of experimental data were used as the subjects to be matched, and in the optimization module, the weight of both candidates was set to be the same, and hence, the root-mean-squared relative error objective function is a combination of the two objective functions shown in the following equation:

**SCCE Tests Targeted History Matching Parameters:**

\[
Obj_{V\%} = \frac{1}{No_{V\%}} \sum_{i=1}^{No_{V\%}} \left( \frac{V\%_{exp,i} - V\%_{num,i}}{V\%_{exp,i}} \right)^2
\]

\[
Obj_{P} = \frac{1}{No_{P}} \sum_{i=1}^{No_{P}} \left( \frac{P_{exp,i} - P_{num,i}}{P_{exp,i}} \right)^2
\]

\[
Obj_{V_{total}} = \frac{1}{No_{V_{total}}} \sum_{i=1}^{No_{V_{total}}} \left( \frac{V_{total_{exp,i}} - V_{total_{num,i}}}{V_{total_{exp,i}}} \right)^2
\]

\[
Obj_{total} = w1 \times Obj_{V\%} + w2 \times Obj_{P} + w3 \times Obj_{V_{total}} \quad (6.46)
\]

Where, \( w1, w2 \) and \( w3 \) are the weights for the sub-objective functions in the total objective function. The total vapor phase volume was automatically plotted as linear relationship in MATLAB data set for the purpose of optimization. Because the actual experimental data was only collected at the beginning and the ending of the pressure depletion phase, and thus, all the data point between the first and the last point was set to null while the last data point was set to be a optimization constraint during the optimization processes, and the
parameter \(Obj_{Vgtotal}\) was only judged once at the end of the history matching processes. If the final history matching result was deviated from the last point of total gas volume in the system, the whole optimization procedure would be re-run until the last point the total gas volume in the system was matched.

**CCF Tests Targeted History Matching Parameters:**

\[
Obj_{V\%} = \sqrt{\frac{1}{N_0 \cdot V\% \sum_{i=1}^{N_0 \cdot V\%} (\frac{V\%_{exp,i} - V\%_{num,i}}{V\%_{exp,i}})^2}
\]

\[
Obj_{P} = \sqrt{\frac{1}{N_0 \cdot P \sum_{i=1}^{N_0 \cdot P} (\frac{P_{exp,i} - P_{num,i}}{P_{exp,i}})^2}
\]

\[Obj_{total} = w1 \cdot Obj_{V\%} + w2 \cdot Obj_{P} \quad (6.47)\]

The objective function was minimized by optimization in order to find out the kinetic frequency factors indicating the dynamic foamy oil behavior. The weights \(w1\) and \(w2\) were can be adjusted during the simulation. Since the pressure is sitting at a relatively larger order of magnitude \((10^2 \sim 10^3 \text{ kPa})\) than the vapor volume fraction \((10^{-1})\), therefore, the weight of pressure objective function sometimes should be adjusted with a relatively higher value in order to match up the pressure as well, and this can be manually/automatically handled by MATLAB to control the weight of objective functions during the history matching.

**(a) SCCE Tests (Non-Gassy Liquid Setup)**

In this section, history matching of SCCE tests under non-gassy liquid setup was conducted. The following figure shows the history matching results for each segment of the SCCE tests:
Figure 6.52 Dynamic history matching of vapor volume fraction in SCCE tests (Sub-figures (a) to (e): 1100kPa, 900kPa, 700kPa, 500kPa, 300kPa, 100kPa)
Figure 6.53 Comparison between equilibrium and non-equilibrium vapor phase volume fraction in micromodel for SCCE tests
Figure 6.52 shows the history matching of the vapor phase volume fraction in micromodel as well as the total vapor phase volume in the system. It can be seen that the overall history matching results was reliable for each pressure depletion stage of SCCE tests. Figure 6.53 shows the history matched vapor phase volume fraction in micromodel in total and compares the equilibrium condition and the non-equilibrium condition.

Figure 6.54 shows the simulation result for the total vapor phase volume in the closed system. It can be seen that the simulation results are very close to the experimental data, indicated by the red line and the black triangles. Meanwhile, the equilibrium vapor phase volume with the given feed of global composition of the live oil is also plotted to show the difference with the non-equilibrium vapor phase volume. It can be seen that the overall system was deviated from equilibrium and long-enough time might be needed for the system to reach equilibrium state, where the oil phase would be completely de-gassed.
Figure 6.54 Comparison between equilibrium and non-equilibrium vapor phase volume in the whole system
Figure 6.55 (a) RRF1 and RRF2 of SCCE tests (b) RRF2 of SCCE tests at each pressure depletion stage
Figure 6.55 shows both kinetic reaction frequency factors achieved from the history matching processes. It can be seen that under a fixed pressure, the kinetic reaction frequency factors still fluctuate, and a single value cannot satisfactorily history match the vapor volume fraction increment. In original CMG reservoir simulator setup, the kinetic reaction frequency factors can be adjusted in several different means by being constant, dependent on pressure, permeability, phase velocity etc. Fixed value indicated by the keyword “FREQFAC” can be replaced by “FREQFACP” to render the dependency of RRF on prevailing pressure. Under the setup by keyword “FREQFACP”, the kinetic reaction frequency factor will only have one value under each pressure but not varying with time. In figure 6.55 (b), however, the history matching shows that even under a fixed pressure, the kinetic reaction frequency factors might be a transient value. Since most of the previous literatures on foamy oil phenomenon study were conducted under a continuous pressure depletion at a certain rate against time, therefore, the keyword “FREQFACP” can be properly used under such condition as the prevailing system pressure did not maintain a constant value. While in order to investigate if a constant value of RRF can properly represent the non-equilibrium gas exsolution processes under a fixed pressure differential from saturation pressure, numerical tests have been conducted, and it was found that a single RRF was not able to accurately history match the experimental data. This is because at the setpoint where the system pressure was suddenly dropped to a certain value instead of a constant $dP/dt$, and therefore, with the innate settings of CMG, one fixed pressure corresponds to one fixed RRF, and no transient value/relationship with time can be input. In figure 6.55 (b), by dynamic tuning of the kinetic reaction frequency factors, it can be seen that RRF varied under a fixed prevailing pressure. In the beginning
of each pressure depletion stage, the RRF2 was observed to be higher. This is because the pressure was instantaneously dropped down, and during such drastic drop down, the local non-equilibrium circumstance was created rapidly, the tendency for gas to ex-solve was strong. Before pseudo-bubble point at around 900kPa, the system almost had no tendency to form exsolution gas, and therefore, the blue curve was at a low and steady value. While when the pressure was dropped down to 900kPa, the pseudo-bubble point pressure, in a very short period of time, dissolution gas started to form exsolution at a high rate, reacting to the disturbance to the thermodynamic equilibrium. Then, the rate for gas exsolution started to decay and finally became steady. Hence, as can be seen in figure 24, the green part indicating the exsolution behavior at 900kPa, the vapor phase increased a higher rate at first, and then gradually decay to a steady rate. But since the system was under non-equilibrium, given enough time if the pressure was fixed at 900kPa, vapor phase volume ratio would eventually reach equilibrium, and that is why the overall trend of the curve was upwards. The same phenomenon was also observed for the rest of the pressure depletion stage, where the RRF was high near the time nodes of the pressure depletion, and decayed to a relatively smaller value with variation, and then at the end of each pressure stage, the RRF started to rise up again, showing the tendency to reach equilibrium at the fixed prevailing pressure if given enough time.

(b) CCF Tests (Non-Gassy Liquid Setup):

In this section, the history matching of CCF tests under non-gassy-liquid setup has been studied.
Figure 6.56 Dynamic history matching of vapor volume fraction in CCF tests (Sub-figures (a) to (e): 900kPa at 0.001mL/min, 700kPa at 0.001mL/min, 700kPa at 0.006mL/min, 500kPa at 0.006mL/min, 300kPa at 0.01mL/min)
Figure 6.57 Dynamic history matching of system pressure in CCF tests (Sub-figures (a) to (e): 900kPa at 0.001mL/min, 700kPa at 0.001mL/min, 700kPa at 0.006mL/min, 500kPa at 0.006mL/min, 300kPa at 0.01mL/min)
Figure 6.56 shows the history matching of the CCF tests at the same operation pressure as the SCCE tests from 900kPa, 700kPa, 500kPa down to 300kPa. The history matching was satisfactory. It can be seen that under continuously convective condition, the vapor phase volume fraction in the micromodel was observed to be more stable than quiescent SCCE tests under the same operation pressure. Figure 6.57 shows the history matching of the system pressure under continuous flowing of foamy oil. It can be seen that the pressure history matching is not as “bouncy” as the real recorded pressure. This is due to the fact that under non-gassy-liquid setup, the dispersed gas component in the oil phase does not behave as the real gas which contributes to the variation of the foamy oil compressibility. Therefore, the simulated system pressure was not shown as a bouncy trend like the experimental recorded data. In the following section, a gassy-liquid setup will be illustrated and the history matching of system pressure was more accurate as the simulator considered the compressibility of foamy oil.
Figure 6.58 RRF values for (a)–(e): 900kPa at 0.001mL/min, 700kPa at 0.001mL/min, 700kPa at 0.006mL/min, 500kPa at 0.006mL/min, 300kPa at 0.01mL/min
Figure 6.59 Optimized kinetic reaction frequency factors of solvent mixture component by history matching of CCF tests

Figure 6.60 Lateral comparison of RRF2 between SCCE and CCF tests at 900kPa, 500kPa and 300kPa
Figure 6.58 shows the kinetic reaction frequency factors achieved from the dynamic history matching. From figure 6.58 (a), it can be seen that when the model outlet pressure was set to be 900kPa, the live oil was continuously injected into the system and form foamy oil under a pressure differential of 300kPa. Even though under a very low injection rate at 0.001mL/min, such 300kPa pressure differential would cause a velocity inside the micromodel. Based upon the experimental data in figure 6.56 (a), since the fluctuation of vapor phase volume fraction under 900kPa at 0.001mL/min was not large, therefore in the history matching simulation, with a flowing velocity created by both injection and pressure differential, the foamy oil kept flowing inside the model, and the free gas phase would be continuously carried away by the oil phase. Because the fluctuation in the experimental data was not large, and the kinetic reaction frequency factors achieved was also not fluctuating, indicating a good foamy oil stability. When the pressure was further reduced to 700kPa with a low injection velocity 0.001mL/min, it can be seen from figure 6.56 (b) that the vapor phase volume fraction increased, and the competition between injection rate or thermodynamic deviation from stable state (above live oil saturation pressure) on controlling the increment of vapor phase volume ratio can be shown according to the kinetic reaction frequency factors. From figure 6.58 (b), it can be seen that the achieved RRF1 was quite high in the simulation, while the RRF2 was lower. This is because under a higher velocity caused by the pressure differential at 500kPa from the saturation pressure, the foamy oil flow was faster in the micromodel. With a fracture-like permeability, the free gas phase inside the numerical grid would be “flushed” away faster. While under such high pressure differential from saturation pressure, deviation from thermodynamically stable state would render the system to enter into the spinodal region with a higher rate. In
order to satisfy the amount of phase change from dispersed component into free gas component, the solution component had to be transformed into the dispersed component at a high rate to supply the amount of the needed dispersed component. But since the experimental data from figure 6.56 (b) was still quite low compared to SCCE tests, the actual phase change from dispersed component into free gas component was slow, and hence, the history matching tuned the RRF2 to be small compared to RRF1. When injection rate of foamy oil was raised up to 6 times higher at 0.006mL/min, it can be seen from figure 6.58 (c) that initially RRF1 was high due to the above-mentioned same reason as in figure 6.58 (b), and later on RRF became low and stable. Since the velocity of displacement of foamy oil was high plus the pressure differential applied, the foamy oil would flow at higher velocity, and the velocity for gas phase would also be higher. From figure 6.56 (c), it can be seen that the experimental vapor phase volume ratio was low, and the RRF2 achieved from history matching was also low. Such low vapor phase volume ratio in the micromodel was contributed mainly by the application of higher flow velocity where the exsolution rate of gas out of the moving live oil phase was lower than the hydraulic effect where the exsolution gas was immediately carried away by the moving oil. Under this test, a higher flowing velocity of foamy oil can prevent the formation of large exsolution gas cluster. This can also be proved in the trend of the vapor phase volume ratio in figure 6.56 (c) as less and less fluctuation was observed.

However, in the experimental study, it was found that when a high velocity and pressure differential was applied to continuously supplied foamy oil phase, there was a phenomenon that when the foamy oil hit the solid boundaries in the micromodel, the nucleation sites on these boundaries contributed to a faster gas nucleation and bubble
formation. If the in-situ velocity was too high, the nucleation of gas bubbles had not enough time to form then the oil phase would be flushed away. If the velocity is too low resembling to a static volume expansion test, the stability of foamy oil would be relatively lower as the observed in the SCCE tests in this study, where the vapor phase volume ratio kept increasing against time to reach equilibrium. In our series of tests, the velocity applied to the foamy oil flow was well controlled to prevent forming a much too large pressure build-up in the micromodel. Thus, observing and comparing from figure 5.29, the velocity applied to the model did have significant effect on enhancing the foamy oil stability indicated by reducing the vapor phase volume fraction, but the applied velocity just partially overcome the effect of gas exsolution phenomenon due to the thermodynamic deviation from saturation pressure. Therefore, in the numerical simulation, in order to maintain the vapor volume ratio in the micromodel (to history match the experimental data), a higher RRF2 was achieved for CCF tests conducted at a higher velocity as shown in figure 6.59. This is because under a high permeability for both gas and liquid phase in the numerical setup, the flow ability for both fluid types through the porous media was at ease so that the gas phase would easily flow away from the grid to the next one, and the RRF2 had to be tuned to a higher value to keep up the formation of gas phase and balance out the effect of convection that carried the gas away. This explains why in figure 6.59, that the gray curve would suddenly go up and reach a higher value at 0.006mL/min than when foamy oil injection rate was at 0.001mL/min. Higher velocity tent to push both gas and liquid out of the grid, while in order to maintain and history match the experimental data, a higher RRF2 value was automatically adjusted. This also indicates that even though the injection velocity was raised up several times, the gas exsolution induced by
pressure/thermodynamic deviation from live oil saturation pressure still kept forming and meanwhile reducing a certain extent by around 10% due to the fluid flow. The same analysis goes to the behavior when the model outlet pressure was adjusted to 500kPa at 0.006mL/min and 300kPa at 0.01mL/min, explaining why the RRF2 was higher when the pressure differential and injection velocity was higher. Assuming in a Eulerian grid point of view, considering two extreme cases, first, if the velocity is too high, then the hydraulic diffusivity of the gas and oil phase will be very high, and no matter how deviated from the saturation pressure, the rate of gas exsolution due to thermodynamic deviation from saturation pressure will never be higher than the rate that the bulk oil phase carries away the exsolution gas bubbles formed in that grid. Then, the gas saturation in that Eulerian grid will be low even down to zero by strong convection. Second, if the velocity is zero which is under a static condition, the gas exsolution will be solely due to the thermodynamic deviation from saturation pressure, and no convection is presented. Then the gas saturation in the Eulerian grid will keep increasing until the exhaustion of the available solution gas. In our CCF experiments, only limited ratios between foamy oil injection rate and supersaturation pressure can be tested (scenarios between the two above-mentioned extreme cases), and to avoid infinite pressure build-up in the micromodel, high injection velocity was ignored. In figure 6.60, it can be seen that both the RRFs for 900kPa SCCE and 500kPa SCCE tests were higher than CCF tests at the same pressure. This has indicated that the effect of hydraulic diffusivity rate was larger than the effect of non-equilibrium exsolution, and hence, by continuous convection, the exsolution rate reduced. However, when it came to 300kPa, it was highly possible that in SCCE tests, the outlet tubing diameter was too small for newly exsolved gas to escape and pressure might have
built up in the micromodel, resulting in a relatively small increment in vapor phase volume inside the micromodel. Therefore, the RRFs for SCCE at 300kPa was lower. In a CCF test, the outlet tubing has larger diameter that can prevent pressure build-up in the micromodel, and hence, hydraulic diffusivity can easily carry away the exsolved gas inside the micromodel at 300kPa, and the RRFs value was still low, but slightly higher than 500kPa as the deviation from saturation pressure increased by 200kPa.

(c) CCF Tests (Gassy-Liquid Setup):

In order to ignore the numerical convection effect of the fluid flow (indicated by relative permeability in a Darcy-scale simulator) that continuously carries the gas phase away from the numerical grid, a pseudo-single phase method by gassy-liquid assumption was also tested to study the solvent dissolution and exsolution behavior. As mentioned in the previous section (b) CCF tests (non-gassy-liquid setup), since the system was under two-phase condition, in a Darcy-scale simulator, the fluid flow behavior is dependent on the relative permeability curves. In a fracture-like relative permeability regime, the capability for both gas and liquid phase to flow through the porous media is high. Compared to liquid, gas has higher mobility, which enables the channeling and fast escape from the grid towards the direction of pressure gradient. By defining the foamy oil as a pseudo single-phase elastic fluid, the dispersed gas component is treated as part of the foamy oil which mainly controls the volume of the entire pseudo phase. Hence, with only one phase presented in the numerical simulation, the stability of the fluid phase can be easily represented by a single reversible kinetic reaction frequency factor.

The following figures show the history matching of vapor volume fraction and system average pressure by gassy-liquid setup.
Figure 6.61 Dynamic history matching of vapor volume fraction in CCF tests by gassy-liquid setup (Sub-figures (a) to (e): 900kPa at 0.001mL/min, 700kPa at 0.001mL/min, 700kPa at 0.006mL/min, 500kPa at 0.006mL/min, 300kPa at 0.01mL/min)
Figure 6.62 Dynamic history matching of pressure in CCF tests by gassy-liquid setup
(Sub-figures (a) to (e): 900kPa at 0.001mL/min, 700kPa at 0.001mL/min, 700kPa at 0.006mL/min, 500kPa at 0.006mL/min, 300kPa at 0.01mL/min)
Figure 6.63 Optimized kinetic reaction frequency factor of gassy-liquid setup simulation
It can be seen from figure 6.61 to 6.62, that the history matching quality for vapor volume fraction under gassy-liquid setup was satisfactory even though no true gas component existed in the simulation process. In terms of system pressure history matching, under gassy-liquid setup, the trend was more “bouncier” which was closer to the actual recorded system pressure due to the high compressibility of the oil phase.

Figure 6.63 has plotted the RRF values laterally in time scale to each other for a convenient comparison between different pressure and injection rate conditions. It can be seen that the RRF mainly fluctuates up and down in Y axis. This indicates a process of the dynamic phase change between SG and BB component, which corresponded to the actual fluctuations of vapor phase volume fraction in the porous media under convective condition. When the sign is negative (-), BB became SG, and the dispersed content in the oil phase shrunk, and vice versa. As the foamy oil flowing velocity increased, even though there was a pressure differential from saturation pressure, the stability of foamy oil increased. This is observable as the fluctuations of the RRF values were getting smaller and closer to zero, indicating a balance between the flow velocity and the RRF. From the simulation of a gassy-liquid setup, it can be seen that RRF was not affected by the existence of relative permeability curve as there was only one active phase in the simulation.

6.2.5 Solvent Diffusion Tests in Micromodel

In this section, solvent diffusion tests were simulated in effective porous media. Effective diffusion coefficients and kinetic solvent dissolution reaction frequency factors were achieved by history matching the pressure decay curves. Totally, both CMOST self-defined formula module and a MATLAB-controlled reservoir simulator were used to
extract the kinetic reaction frequency factors to indicate the solvent non-equilibrium dissolution behavior.

6.2.5.1 CMOST Formula Module

In this section, solvent dissolution process simulation in CMG CMOST module by self-defined formula was tested for one of the diffusion tests in micromodel as described in section 5.1. An effective porous media was numerically built with a porosity of 56% and a permeability of 18 Darcy according to the experimental measurement of passing water through the model at various injection rate. Since there was excessive tubing for dead volume gas, and therefore, when those dead volume of gas chamber was measured and accounted for in the whole mass balance calculation, the whole geometry was expanded to the same volume with a rectangular shape geometry instead of a tubing shape to form an integrity of the domain. Also, due to the fluid properties of gas phase, the pressure propagation and flow path patterns would not affect the flowing behavior of gas in a static system under high permeability. Therefore, it is reasonable to set up such a numerical geometry for gas phase chamber. Figure 6.50 (a) shows the numerical geometry for the simulation. In the figure, the red arrow indicates the oil bearing are of the micromodel, and the orange arrow indicates the whole micromodel geometry with uniform porosity and permeability. The green arrow indicates the dead volume gas chamber that was also accounted for in the total mass balance calculation.

Unlike pressure depletion tests, the system pressure of a diffusion process in a fixed volume chamber will always decline as long as a concentration gradient occurs. Allowing for molecular diffusion. Therefore, since the system pressure was depleting at a continuous $dP/dt$ until equilibrium pressure, the solvent dissolution behavior achieved from Chapter
4.2.4 was applied in the CMOST self-defined formula module to indicate the solvent dissolution into the oil phase. The actual physics was first, the gaseous solvent would condense on the interface of the gas and oil, and second, under the concentration gradient, the dissolved solvent at the interface would penetrate into the bulk oil phase until the concentration profile in the bulk oil phase was equal to the concentration of solvent at the gas-oil interface. Therefore, the pressure decay due to the mass transfer of gas into oil phase was mainly controlled by the condensation rate on the interface and the effective diffusion coefficient of gas in the oil phase. In the history matching of the vertical test 1 in chapter 5.1.2.1, the effective diffusion coefficient was not chosen as the adjustment object, instead, it was chosen at a fixed value as $0.005 \text{cm}^2/\text{min} = (8.33 \times 10^{-9} \text{m}^2/\text{s})$ and only the kinetic reaction rates of both CO$_2$ and C$_3$H$_8$ were adjusted in the history matching. From figure 6.50 (b), we can see the example of history matching of the pressure decay curve in micromodel diffusion vertical test 1. Since the history matching was one-time running, there was no chance to adjust the parameters in the middle of the simulation. One has to wait for the end of simulation in order to judge the history matching quality and optimize the parameters for the next trial. In this case, since the pressure decay curve is at a very high dropping rate at the first 200~300 minutes, indicating a very fast solvent condensation and high molecular diffusivity of solvent into oil phase. Unless in self-defined formula, two separate exponential relationships between kinetic reaction rate and pressure was set up for the time period before and after, say 200 minutes, respectively to achieve a sound match, or it will be quite hard to find the one set of an optimized combination of kinetic reaction rates to fit whole pressure decay curve. In this way, either by adjusting each kinetic reaction frequency factors at each prevailing pressure in the run
all together as one large optimization parameter set will work or by segmentally history matching the pressure decay curve and achieving the relationship of the optimized parameters with prevailing reservoir condition, i.e., pressure, temperature, component concentration in grid cells, etc.

In order to understand the dynamic variation of the optimization object data, a segmental history matching technique will be the most suitable technique to investigate the real-time evolution of the optimized parameters against prevailing reservoir condition. Therefore, in section 6.2.5.2, two different boundary conditions plus segmental history matching by MATLAB-controlled reservoir simulator were applied to simulate the diffusion processes in an effective porous media with the same porosity and permeability of the actual glass micromodel.
Figure 6.64 (a) Numerical model setup for diffusion test in micromodel (red arrow: oil bearing area in the micromodel; orange arrow: micromodel part; green arrow: dead volume of the gas chamber in the tubing connections) (b) An example of pressure decay curve history matching by CMOST
Figure 6.65 Optimized RRF value from CMOST simulation

\[ y = 4E^{-24e^{0.0445x}} \]

\[ R^2 = 1 \]
6.2.5.2 MATLAB-Controlled Reservoir Simulator

In order to understand the dynamic behavior and extract the reaction frequency factors’ relationship with prevailing reservoir condition and time, similar technique by combining MATLAB and CMG for mutual alternation was developed to study the effective diffusion coefficients of mixture solvent inside the porous media by MATLAB-controlled CMG STARS reservoir simulator.

Many researches have been done on achieving diffusion coefficients through pressure decay method by solving Fick’s 2nd Law with a finite domain. The governing equation is the list as equation in section 6.3.2.1. Unlike section 6.3.2.1 for determining CO₂ effective diffusion coefficient in bulk phase, in this section, the boundary conditions that creates and controls the concentration gradient not only will include equilibrium boundary condition as in 6.3.2.1, but also, a dynamic phase change rate will be incorporated to describe the process of solvent condensation on the gas-oil interface before diffusing into the bulk oil phase.

Other than using vapor-liquid-equilibrium (VLE) K value, the condensation of solvent on the gas-oil interface is expressed by the interphase mass transfer term to indicate the phase change of the system.

The target tests for pressure decay curve history matching were vertical micromodel diffusion tests in Chapter 5.1.2.1. Although the system was positioned vertically, the numerical grid was set to be one-dimensional. The aim is to achieve an effective diffusion coefficient of solvent through porous media. After each set of pressure depletion, the gas and oil saturation of the micromodel was quantified by image processing as described in
Chapter 5.1.2.2. Then instead of conducting a pressure depletion simulation after each cycle of diffusion, the saturation profile of each numerical grid was re-defined for each set of diffusion simulation, by assuming a complete exsolution of solvent from the oil phase at the end of each cycle of pressure depletion test where ambient pressure and temperature was reached.

For the first boundary condition on gas-oil interface, or rather, a numerical grid with both the saturation of oil and gas, similar condition was used as mentioned in section 6.2.2.1 equation 6.13. Under this condition, the grid containing two-phase flow will always be under equilibrium state. Only effective diffusion coefficient of solvent in oil phase should be adjusted for pressure decay curve history matching.

For the second type of boundary condition, unlike quasi-equilibrium or non-equilibrium boundary conditions, solvent condensation on the gas-oil interface was not in instant equilibrium in one numerical grid, but instead, a similar technique by using kinetic reaction was applied to describe the transient behavior of vapor phase solvent condensation into liquid solvent and diffusion inside the oil phase. In total, 3 components were defined: heavy oil phase, solution gas in liquid form, and solvent in vapor form. By this, the number of components were reduced for an easier simulation to ensure a proper mass balance. The diffusion processes underwent two steps:

1. free gas solvent → liquid solvent: solvent condensation process by kinetic reaction rate;

2. liquid solvent diffusion inside oil phase: molecular diffusion process by the existing concentration gradient.

Similar governing equations can be found in section 6.2.2 and 6.2.4.
An example schematic of the numerical diffusion test is plotted as figure 6.66. Grid 2 indicates the solvent condensation, and grid 3 indicates the molecular diffusion.

1. Quasi-equilibrium

\[ x_{SGCO_2} = \frac{y_{SGCO_2}}{K} \]

2. Non-equilibrium

\[ n_{SGCO_2}^{t_1} = n_{SGCO_2}^{t_0} + \frac{\partial n_{FGCO_2 \rightarrow SGCO_2}}{\partial t} \Delta t \]

\[ x_{SGCO_2} = \frac{n_{SGCO_2}^{t_1}}{n_{SGCO_2}^{t_1} + n_{Oil}^{t_1}} \]

Figure 6.66 Schematics of a numerical diffusion test (orange arrow: liquid condensation on the interface; red arrow: molecular diffusion under concentration gradient)
Quasi-Equilibrium Condition (Adjustment of Effective Diffusion Coefficient):

Figure 6.67 An exemplification of pressure decay curve history matching by quasi-equilibrium condition (a) dynamic history matching (b) final result
Figure 6.68 Transient effective diffusion coefficient of each cycle (a) vertical (b) horizontal
Figure 6.69 Optimized coefficients (a) average effective diffusion coefficient (b) maximum value among the transient effective diffusion coefficients
Using quasi-equilibrium condition, the equilibrium was instantly reached in numerical grid with both the existence of oil and gas phase as shown in figure 6.66 grid 2. Hence, the only parameter to measure the solvent dissolution rate was utilizing effective diffusion coefficient. By adjusting the effective diffusion coefficient, the rate of mass transfer of solution gas (SGCO₂ in figure 6.66 for instance) inside the oil phase was altered, and hence, the grid containing both free gas, solution gas and oil would re-equilibrate under prevailing pressure and temperature. Thus, a new molar fraction of solution gas in grid 2 would present, and diffusion process went on under new concentration gradient. Due to the fact that the equilibrium K value at each pressure and temperature was a fixed value, only the real-time adjustment of effective diffusion coefficient D can describe the solvent dissolution behavior, hence, to history match the pressure decay curves.

Figure 6.67 shows an example of dynamic adjustment of effective diffusion coefficient to history match the pressure decay curves. During the simulation, since the effective diffusion coefficient was adjusted at a real-time basis, and it was found out from figure 6.68 that the most intense pressure decay period for all cycles of diffusion processes was at the beginning when the system pressure was re-pressurized to the pre-specified injection pressure. Then, the pressure decay curve gradually flattened. It is also seen from the figure 6.67 that the initial effective diffusion coefficient for the starting period of each cycle of diffusion test increased with cycle number then decreased. This corresponded to the gas-oil distribution in the micromodel after each set of pressure depletion. The higher gas-oil interfacial area after pressure depletion stage contributed to the ease of interphase mass transfer.
Figure 6.69 shows the comparison of the effective diffusion coefficient between vertical and horizontal diffusion tests. For both the average and the maximum value of the optimized effective diffusion coefficients, it can be seen that under the effect of gravity, the numeric value was always higher for vertical tests. This was mainly due to the more exposed interfacial area of oil with solvent under the gravity drainage. This was also reflected in the variation of effective diffusion coefficient where as the cycle number went on, oil was in a more dispersed form in the micromodel, enhancing the solvent diffusion.
Non-Equilibrium Condition (Adjustment of effective diffusion coefficient and kinetic reaction rate frequency factor of FGCO₂ → SGCO₂):

(a)

(b)

Figure 6.70 An exemplification of pressure decay curve history matching by non-equilibrium condition (a) dynamic history matching (b) final result
Unlike quasi-equilibrium condition, in non-equilibrium condition, the molar fraction of solution gas in figure 6.6 grid 2 was a transient value. The change of molar fraction was controlled by the non-equilibrium mass transfer term defining the phase change of free gas → solution gas, that is, \( FGCO_2 \rightarrow SGCO_2 \) shown in figure 6.6. Due to the fact that the direct compositional measurement of the oil phase in the diffusion test was not feasible, and hence, the main mechanism that the free gas chamber pressure decay was mainly caused by the condensation of vapor phase into liquid phase solvent at the gas-oil contact interface. The main parameters to be tuned in solvent dissolution simulation under non-equilibrium condition were diffusion coefficient and kinetic reaction rate frequency factor. However, in order to make the adjustment of the RRFs more prominent, the tuning of diffusion coefficient was undergoing a procedure: first, the D and RRFs were tuned together; second, the average value of the optimized transient D was taken to be a non-varying value; third, only the RRFs were adjusted under a fixed D. By this way, the main factor contributing to the pressure decay of the system was shifted to the tuning of RRFs. In real experiments, in order to yield a perfectly accurate diffusion coefficient, a real-time compositional analysis of the oil phase should be tracked, and the actual concentration profile should also be one of the constraints in the optimization of the diffusion coefficient. However, the real-time measurement of the solvent concentration field in heavy oil was highly unfeasible, and hence, the optimized diffusion coefficient was only numerically correct, but not necessarily experimentally correct. Due to the fact that diffusion process of solvent in heavy oil is a very slow process, hence, under non-equilibrium condition, it is justified that the main factor contributing to pressure decay is the rate of vapor solvent condensation into liquid phase.
Figure 6.70 shows the exemplification of the history matching process by tuning the kinetic reaction rate frequency factors. In order to investigate the actual rate of the solvent vapor condensation, one example here shows a very refined time stepping in the history matching. With a more refined time step, the RRFs value can be smoother if regressed against time and pressure. As it is observed from figure 6.70 (b), the history matching was almost perfect. Under such circumstance, the RRFs vs. pressure can be more accurate and this regression was compared with the CMOST optimization where a pre-specified mathematical relationship was given, so as to see if the segmental history matching could yield resembling relationship to describe the solvent condensation behavior. Figure 6.71 shows the optimized transient RRFs against time. It can be seen that from figure 6.72 when the model was positional vertically to the ground, gravity drainage would help enhance the ease of mass transfer by creating more contact interfacial area between solvent and oil phase. Hence, the kinetic reaction rate frequency factors of vertical tests Similar to the behavior of the effective diffusion coefficients, the most intense stage of solvent condensation occurred at the beginning of the pressure decay, and the RRFs can be correlated with time using a 2-term exponential function, $y=a*exp(bx)+c*exp(dx)$. Since under pressure decay method in a closed system, the pressure was continuously decreasing as the mass transfer of solvent into oil phase went on. Therefore, the RRFs can be plotted against prevailing pressure to investigate the intensive parameter effect on the kinetic rate of solvent condensation.
Figure 6.71 Transient kinetic reaction rate frequency factors of each cycle (a) vertical (b) horizontal
Figure 6.72 Optimized RRFs (a) average RRFs (b) maximum value among the transient RRFs
Figure 6.73 Comparison of vertical test 1 between (a) CMOST optimization, and, (b) MATLAB-controlled-CMG history matching.
Figure 6.74 Refined time-stepping optimization of RRFs
Figure 6.73 has shown the comparison of vertical diffusion test 1 between the history matching results of CMOST self-defined formula module and the MATLAB-controlled reservoir simulator. In CMOST self-defined formula module, the exponential relationship between RRFs and pressure was pre-specified in the java script programming box in CMOST. In the MATLAB-controlled reservoir simulator, the relationship between RRFs and pressure was not pre-specified, and after the segmental history matching, the optimized RRFs in each time/pressure segment would be extracted and plotted against pressure to examine if the exponential relationship held. It turned out that both the pre-specified CMOST formula module as well as the MATLAB-controlled reservoir simulator have yielded very close results at the same order of magnitude. This can be indicated from figure 6.73. Since the history matching was segmental for MATLAB-controlled reservoir simulator, hence, in order to satisfy the objective function in equation 6.18 in section 6.2.2.1. In figure 6.70, a refined time-stepping of RRFs adjustment was conducted for one set of tests in order to see if the optimized RRFs followed an exponential relationship with prevailing pressure. Figure 6.74 shows the optimized RRFs value of refined time-stepping, which was in an exponential relationship against prevailing pressure. In addition, from the single bubble dissolution analysis in section 4.2.4, it can be seen that all the RRFs value was behaving like the Taylor bubble dissolution behavior in the order of magnitude. The bubble dissolution behavior in a pore-scale can be upscaled to Darcy-scale by the implement of an exponential function. By knowing the injection pressure (initial pressure) as well as the potential final pressure at the end of the soaking period, an exponential relationship could be incorporated into reservoir simulator to predict the pressure decay rate of the reservoir so as to roughly determine the amount of solvent that was/would be
diffused into the oil phase in an effective porous media. As discussed above, to achieve the true effective diffusion coefficient of solvent into oil phase in porous media, one should measure not only the pressure decay in the free gas chamber to determine total mass of solvent condensation, but also, the actual concentration profile of solvent inside the bulk oil phase so as to determine the true solvent diffusion penetration depth. To sum up, in the simulation using quasi-equilibrium condition for gas-oil interface concentration, the main mechanism was to adjust the effective diffusion coefficient in the porous media. In this case, it can be comprehended as the adjustment of the dynamic effective dispersion coefficient (same unit in [L²T⁻¹]) in the effective porous media under static condition, and hence, effective diffusion coefficient which indicated a static molecular diffusion. This parameter controls the mass transfer rate of solvent inside the oil phase (oil-bearing grids), and hence, the pressure in the free gas chamber according to the real-gas law. While, under non-equilibrium condition, the gas-oil interface concentration was no longer controlled by VLE K value. Instead, a transient sink term was applied to the continuity equation of the gas phase in the effective porous media. By adjusting the kinetic rate of the sink term, the mass loss of gas phase could be considered as the mass gain of oil phase. Under real-gas law, mass loss of gas chamber in a closed and fixed-volume system could only result in a pressure decay of the system. Considering a relatively low value of diffusion coefficient at 0.00162~0.002cm²/min (2.7~3.3333×10⁻⁹m²/s) used in non-equilibrium condition simulation, the mass transfer rate of solvent inside the oil phase should be very slow, and hence, the pressure decay should be mainly attributed to solvent condensation rate. Similar to the adjustment of the effective dispersion/diffusion coefficient, the kinetic rate of solvent was adjusted to history match pressure decay curves.
CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

In this research, experimental study of solvent non-equilibrium dissolution and exsolution behavior in a heavy oil system have been conducted in both bulk phase and porous media by visualization techniques. Subsequently, numerical simulations and history matching of the experimental data for the parameters’ optimization were conducted and validated by the newly developed MATLAB-controlled reservoir simulator with real-time optimization module. Solvent non-equilibrium dissolution and exsolution behavior were both experimentally and numerically validated. The major conclusions of this research are listed as the following:

Experimentally, the following major conclusions have been drawn:

*Live oil differential liberation tests:*

1. live oil equilibrium properties tests were conducted, and a comprehensive set of live oil properties such as saturation pressure, live oil density, live oil viscosity, system vapor/liquid mole/volume fraction, individual component fraction in vapor/liquid phase etc., have been meticulously measured for CO₂- and CO₂-C₃H₈-heavy oil system using the newly developed Differential Liberation method. It was suggested that DL tests can be experimentally fulfilled under a non-visual system. Live oil two-phase flash and liquid-phase properties at each saturation pressure under isothermal condition (@20°C) were input into equation-of-state regression and calculation for equilibrium plot as a comparison to non-equilibrium plot.
**CO₂ dissolution and exsolution in bulk phase visual cell**

2. CO₂ solubility increased under higher injection pressure in a pressure decay test. Foamy oil stability was experimentally suggested to increase with higher initial GOR, higher pressure depletion rate, higher pressure drawdown level and longer solvent-heavy oil contact time. The feasibility of a Hele-Shaw-like high-pressure visual cell on solvent dissolution and exsolution behavior was proved and the experimental methodology can be further applied in similar tests in the future.

**CO₂-C₃H₈-heavy oil system CCE tests in bulk phase visual cell**

3. Constant Composition Expansion tests under different pressure depletion schemes were carried out in bulk phase visual cell system to determine the non-equilibrium regimes of CO₂-C₃H₈-heavy oil system. The most important factor determining the extent of non-equilibrium in the visual system during pressure depletion was directly quantified, namely, the vapor/liquid phase volume fraction. The non-equilibrium regimes can be found by comparing non-equilibrium phase volume ratio and equilibrium phase volume ratio. By knowing the vapor/liquid phase volume fraction during pressure depletion process, the non-equilibrium K value against prevailing pressure can be calculated and compared with the equilibrium K value to define the non-equilibrium extent. This non-equilibrium K value shift was also beneficial for the history matching in numerical simulation study. This experimental methodology successfully captured the essential parameter to define the existence and extent of non-equilibrium, and can be further promoted to any other test conditions including different components, pressures, temperatures, etc.
The fill-up percentage of the visual cell can have a significant effect on inducing the non-equilibrium. The experimental methodologies to test solvent-heavy oil systems with either no gas cap or a pre-existing gas cap as the initial condition of the experiments were established, and the non-equilibrium regimes during pressure depletion were found. For tests conducted with 100% fill-up percentage, both lower and higher pressure depletion rates can effectively induce non-equilibrium phenomenon, by analyzing the phase volume ratio. For tests with half of the fill-up volume with a pre-existing gas cap in the system, it was found that a lower pressure depletion rate can induce obvious non-equilibrium, while for tests with higher pressure depletion rates, the non-equilibrium phenomenon was less prominent than lower pressure depletion rate tests. This is because under lower pressure depletion rate, a pre-existing gas cap can better maintain the pressure in the system to prevent a rapid pressure drop, hence, preventing dissolution gas from liberating too soon. While under a higher pressure depletion rate, this is due to the existence of a large interfacial area between vapor and liquid phase for dissolution to “exit”, as well as a much too rapid gas cap escaping from the system that cannot properly maintain system pressure, and hence, dissolution gas would liberate faster to approach equilibrium state. By using pre-existing gas cap as pressure propagation medium based upon the experimental methodologies, the same function of a solid piston inside a traditional PVT cell can be fulfilled in visualization system where a solid piston cannot be incorporated. In field application, the pressure depletion rate will be much slower compared to the experimental study, also, in a real post-CHOPS reservoir, both free gas and live oil will be presented together. Hence, the real field condition resembles to the non-
equilibrium tests with a pre-existing gas cap in this thesis. By the proposed experimental methodology, the optimum operation schemes to maintain non-equilibrium state as long as possible can be easily fulfilled for various components, pressures and temperatures.

5. Single bubble nucleation and growth behavior from a nucleation site and single bubble dissolution behavior were studied by a customized bulk phase microfluidics pattern. In these two series of tests, a relationship between the bubble exsolution rate w.r.t prevailing pressure and bubble dissolution rate w.r.t prevailing pressure, respectively, were found. In the single bubble exsolution behavior test, the exsolution rate/pressure relationship was in power function, and in the single bubble dissolution behavior tests, both spherical bubble and Taylor bubble showed a dissolution rate/pressure relationship to be an exponential function. These relationships were successfully applied as the input formula expression to simulate solvent dissolution and exsolution behavior in the history matching. The direct upscaling of solvent non-equilibrium dissolution and exsolution behavior from a micro-bubble-scale characterization to lab-scale characterization was ascertained.

**Solvent diffusion and post-diffusion pressure depletion tests in micromodel system**

6. Solvent diffusion and post-diffusion pressure depletion tests were conducted in glass micromodel. Solvent diffusion tests were aimed to study solvent solubility under the effect of residual oil distribution and gravity drainage. Post-diffusion pressure depletion tests were aimed to study how effectively pressure depletion can alter the residual oil distribution and boost the advancement of residual oil towards the higher pressure gradient direction. Pressure decay method was used for both a horizontally
and a vertically position micromodel. It was found that for both model positioning orientations, the solvent mass transfer was significantly affected by the residual oil distribution and very possibly the light component extraction from each cycle of pressure depletion. In terms of gravitational effect, it was found that a vertically positioned micromodel would benefit the solvent dissolution due to the gravity drainage of the gas-oil contact front with lower viscosity, and would help expose more deeper oil to allow for solvent dissolution.

**Static Constant Composition Expansion (SCCE) tests and Continuously Convective Flowing (CCF) tests in micromodel system**

7. Visualization of dynamic foamy oil stability in a porous media have been realized experimentally by using glass micromodel, including static Constant Composition Expansion (SCCE) tests and continuously convective flowing (CCF) tests. The former was aimed to study how foamy oil state deviates from the vapor-liquid equilibrium (VLE) statically and the latter was mainly aimed to investigate how non-equilibrium foamy oil behaves under a dynamic condition. It was found that under static condition, non-equilibrium phenomenon would always be presented in the porous media under pressure depletion, and it was observed that in a segmented pressure depletion tests, it would still take a significantly longer time for the system to attempt to re-reach equilibrium than CCE tests conducted in a bulk phase visual cell. This can be attributed to the confined space of porous media in which the growth rate of gas bubbles would be hindered by the geometry of the domain. For the CCF tests, the vapor phase volume ratio during the whole processes was low due to the existence of continuous flow. As shear effect (higher injection rate) increased, larger gas clusters
would be shredded to smaller gas bubbles. The highest deviation of from equilibrium vapor phase volume ratio can be up to 65% as observed in the experiments. Foamy oil stability was indicated to be higher under CCF tests than that of SCCE tests, as the background flow field would enhance the shredding effect of bubbles into smaller bubbles, which were more easily dissolved back into liquid phase by Ostwald Ripening.

**Solvent flooding and post-flooding pressure depletion tests in micromodel system**

8. Solvent flooding tests were conducted to observe the solvent distribution in the injection stage of a cyclic solvent injection processes. It was found that under higher capillary number, viscous force dominated more, and solvent fingering and breakthrough to the production port was faster. The repeatability of solvent flooding in the micromodel was high by properly setting up the initial saturation conditions. Due to the large viscosity contrast, even though the order of magnitude of the smallest and the largest capillary number was at a difference of $10^2$, viscous fingering still dominated the whole capillary number region shown in the experimental study, indicating capillary fingering was not in effect unless even smaller capillary number was applied. Post-flooding pressure depletion tests indicated that a longer-soaking time, a higher injection pressure, and an intermediate pressure depletion rate (-20kPa/min out of -5, -10, -20, -50kPa/min) can enhance the performance of recovery.

Above all, from the experimental point of view, the feasibility of visualization techniques based upon the concept of microfluidics to observe and quantify the solvent non-equilibrium dissolution and exsolution behavior in heavy oil system was proven.
Numerically, the following major conclusions have been drawn:

9. The concept of non-equilibrium K value was analyzed by 3 different scenarios as shown in figure 6.1 to 6.3. By such non-equilibrium K value concept, corresponding adjustment of K value in a reservoir simulation could efficiently fulfill the simulation of solvent non-equilibrium. In a reservoir simulator, it is suggested that, except for a tunable K value table at different pressures and temperatures, a tunable K value against time at a fixed pressure and temperature condition (good for continuous pressure depletion) can be added as a feature for the reservoir simulator to simulate non-equilibrium solvent exsolution behavior under a fixed pressure and temperature production.

10. The history matching of CO$_2$ non-equilibrium dissolution and exsolution behavior by the MATLAB-controlled reservoir simulator have shown satisfactory results. In CO$_2$ dissolution, a quasi-equilibrium condition was applied to simulate the gas-oil thermodynamic interaction in the numerical grid with the co-existence of the gas and oil phase, while dispersive (in this case, diffusive) mass flux was applied in the oil-bearing region to represent the molecular diffusion of CO$_2$ inside the bulk oil phase. Successful history matching was achieved for pressure decay curves and oil swelling factor curves. the effective diffusion coefficients ranged from $6.198 \times 10^{-9}$ to $25.333 \times 10^{-9}$ m$^2$/s for injection pressure from 1555 to 3320 kPa. Diffusion test simulation has proven the feasibility and superiority of Darcy-scale simulator over purely solving for a diffusion-advection equation set (Fick’s 2$^{nd}$ law) with certain boundary conditions (equilibrium, quasi-equilibrium, non-equilibrium). CO$_2$ exsolution behavior was simulated by kinetics-based mechanism. Solvent exsolution behavior was simulated
through defining multiple kinetic reactions. Kinetic reaction rate frequency factors (RRFs), which indicated the rate of multi-component inter-phase mass transfer, were achieved by history matching foamy oil volume under multiple operational schemes. By comparing various RRFs, foamy oil stability was found both experimentally and numerically to increase with higher initial GOR, higher pressure depletion rate, higher pressure drawdown level and longer solvent-heavy oil contact time.

11. Numerical simulation has been conducted on the solvent non-equilibrium exsolution behavior of CO$_2$-C$_3$H$_8$-heavy oil under pressure depletion. Two methodologies were used, first, the dynamic adjustment of K value; second, kinetics-based mechanism. By dynamically adjusting K value in the simulation, solvent exsolution behavior was successfully history matched, including total vapor/liquid phase volume ratio in the system, individual solvent component exsolution behavior, etc. The history matching has proven the feasibility of a deviated K value on describing the delayed solvent exsolution under a continuous pressure depletion condition. Kinetics-based mechanism was also applied in the simulation. By obtaining the relationship between single bubble exsolution rate versus a scaled pressure, the mathematical relationship was directly input in the self-defined formula section in the simulator. The input relationship obtained from single bubble exsolution test have successfully history matched the solvent non-equilibrium exsolution behavior. The optimized exsolution rate coefficient from the history matching was very close to the experimental value as well as in the same order of magnitude. The experimental and numerical characterization have been mutually validated.
12. SCCE tests and CCF tests have been numerically simulated to achieve the kinetic reaction rate frequency factors under static and dynamic condition. Foamy oil stability was investigated numerically by both non-gassy-liquid setup and gassy-liquid setup. It was found that under CCF tests, the optimized kinetics rate reaction frequency factors indicated a higher foamy oil stability than that of the SCCE tests. This has indicated that under the effect hydrodynamic instability, the thermodynamic coarsening of vapor phase will be affected, and the liquid phase of foamy oil mixture will always be compositional non-equilibrium. A proper balance between the differential pressure from live oil saturation pressure to induce gas exsolution and the bulk fluid flow rate can help better enhance foamy oil stability.

13. Solvent diffusion tests in micromodel system were simulated and relevant parameters were optimized. Two different methods were applied to simulate the gas-oil thermodynamic interaction in gas-oil co-existing grid, namely, a quasi-equilibrium condition, and a non-equilibrium condition. In a quasi-equilibrium condition, the main parameter to be adjust to history match the diffusion pressure decay curves was the effective diffusion coefficient of solvent in oil phase. The optimized effective diffusion coefficients of vertical tests were higher than the horizontal tests, indicating that gravity drainage of the diluted oil on the gas-oil interface can help enhance the solvent solubility by exposing the oil phase in the deeper part of the micromodel to get in contact with the solvent. In a non-equilibrium condition, the solvent condensation on the gas-oil co-existing grid was represented by a transient sink (source) term in gas (oil) phase continuity equation. In order to investigate the effect of gas condensation rate on the pressure decay of the free gas chamber, the effective diffusion coefficient
of solvent in oil phase was chosen to be a relatively low value at 0.00162~0.002cm²/min (2.7~3.3333×10⁻⁹m²/s) to eliminate the pressure drop imposed by molecular diffusivity. The optimized kinetic reaction rate frequency factors of gas phase condensation indicated that gravitational effect can increase the rate of condensation, hence, a relatively faster pressure decay as observed in vertical tests than horizontal tests. In addition, the optimized kinetic reaction rate frequency factors of a micromodel-scale were in the same order of magnitude with the exsolution rate of the Taylor bubble in the single bubble dissolution tests. This has proven a direct upscaling of solvent non-equilibrium dissolution behavior from a micro-bubble-scale to lab-scale.

14. Solvent non-equilibrium dissolution and exsolution behavior in the above experimentations can be efficiently simulated by a Darcy-scale simulator, and the complexity of bubble morphing dynamics can be simplified into intra- and inter-phase mass transfer sour/sink terms of each component in each phase. This can be advantageous over the DNS methods in larger-scale simulations and predictions where the coupling of multiphysics into a full CFD equation set would be relatively more difficult and time-cost of computation is not efficient.

Above all, the feasibility of visualization techniques based upon the concept of microfluidics system to study solvent non-equilibrium dissolution and exsolution behavior was proven experimentally, and validated numerically.

7.2 Recommendations

In this series of solvent non-equilibrium dissolution and exsolution behavior studies, several recommendations are given below to further close the knowledge gap:
1. In order to understand solvent non-equilibrium dissolution and exsolution behaviour in a broader range of reservoir conditions, a wider pressure and temperature range can be tested based upon the experimental methodologies established in this thesis. More components can be considered, including other types of solvent, heavy oil with different viscosities, and aqueous solution such as reservoir brine, polymer, surfactant, alkaline, Nano-particle solution or any other feasible aqueous solutions. Also, since this thesis aims to deliver the feasibility of the experimental methodologies, the pressure depletion rates were set high to induce more prominent effects for a manner of efficient time-cost. In future study, a field-scale pressure depletion rate, which is generally lower than laboratory pressure depletion rate, can be tested to investigate the fluid interaction in a tip of the true reservoir.

2. In order to better define the foamy oil stability under flowing condition in porous media, which is the more realistic cases, foamy oil flowing tests under multiple flowing velocities, differential pressures, operating temperatures, co-existence of multiple components etc. can be carried out in a microfluidics device.

3. A moveable piston withstanding high pressure/temperature and chemical corrosion can be created inside a micromodel by polymerization technique to better create a closed system inside a microfluidics reservoir to reduce the measurement error. Meanwhile, a high-pressure/temperature sapphire visual cell with low volume and floating piston can also be an alternative to the usage of non-visual ISCO pump cylinder, so as to form a visual and closed system in microfluidics system for thermodynamic behavior study to achieve a better volume reading of the fluids that go outside of the microfluidics device.
4. Multiple microfluidics patterns can be used, including bulk pool, T-junction, flow focusing, co-flow, step emulsification, serpentine channel, dead-end pore, homogeneous pore pattern, heterogeneous pore pattern with permeability zone difference, real SEM scanned rock pore etc. Given the complex conditions of the real reservoir, the utilization of microfluidics system can minimize this scale-related effect and simplify the true complexity at a small and highly controllable scale. The microfluidics mimics the reservoir by using just a tip of the whole space, and gives reliable results.

5. Real-time concentration field measurement inside the liquid phase and a wider range of compositions’ analysis in the gas phase for a solvent-heavy oil-(aqueous) system is highly suggested to achieve an accurate diffusion coefficient and relevant kinetic solvent dissolution and exsolution rate.
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