Prediction of Asphaltenes Behaviors in Reservoir during CO_2 Injection

by

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Supervised by

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

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CERTIFICATION OF APPROVAL

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Approved by;

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(AP Dr. Muhannad Talib Shuker)

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SUFIAN ABD HAMID

ABSTRACT

Asphaltenes study for its precipitation has been a regular study for a field which has its Enhanced Oil Recovery (EOR) by Water Alternating Gas (WAG) technique. This technique uses CO_2 gas injected into the reservoir alternately with injection water. This technique will results in better field ultimate recovery. Unfortunately, besides increasing the recovery factor of the hydrocarbon, the presence of CO_2 cause a slight change in the oil composition, this change destabilizes the asphaltenes in the crude oil. As the asphaltenes is no longer stable in the crude oil, it will precipitate. This Asphaltenes precipitation creates major problems to the production performance of particular reservoir. Problems encountered as the results of asphaltenes precipitation are it can plug the wells and causes separation difficulties at the separation facilities. For a long time in the industry, remedial approach for this problem has been practiced by the operator instead of preventive approach from the beginning of well life.

Asphaltenes Onset Pressure (AOP) is the very important in understanding the asphaltenes behavior in the reservoir [2]. AOP are mostly conducted using a mixture of reservoir fluid and the injection gas. However this approach only shows the static behavior of asphaltenes in reservoir. AOP will be measured using Solid Detection System, (SDS) using Near InfraRed (NIR) technique. Besides of experimental study, AOP can be predicted by mathematical modeling. This numerical method of finding AOP has been incorporated in the simulation software. In addition some simulation software can calculate the possible amount of asphaltenes precipitate. In some case of the cases shows that results from the static analysis of asphaltenes behavior is inconsistent with the real field fact, there is occurrence of asphaltenes precipitation at the region where no precipitation estimated using static asphaltenes behavior of asphaltenes precipitation envelope.

For better understanding of asphaltenes precipitation, dynamic behavior of the asphaltenes in the reservoir needs to be understood for a realistic risk evaluation. This research is to investigate the behavior of asphaltenes in the reservoir by developing the Asphaltenes Precipitation Envelope (APE), calculate the amount asphaltenes precipitate and also determine the AOP of the crude oil. By

understanding all these parameters, further strategies to prevent the occurrence of asphaltenes precipitation can be modeled effectively.

ACKNOWLEDGEMENT

In the name of God,

I am sincerely thankful to my Supervisor, AP Dr. Muhannad Talib Shuker, my co-supervisor Mr Muhammad Ali Buriro, whose have provided me with courage, complete guidance and continuous support upon completing this project. This project would not have been possible without their constructive ideas and knowledge that have been taught to me.

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CHAPTER 1

1. INTRODUCTION

1.1. Project Background

Problems related to asphaltenes has become common for a reservoir in Malaysia which having Water Alternating Gas (WAG) to increase the ultimate recovery of the reservoirs. This technique is the popular method practiced in Malaysia [1]. Even though this technique was chosen because its increase the ultimate recovery of crude oil in Malaysia better than other technique, it is also come with their own problems.

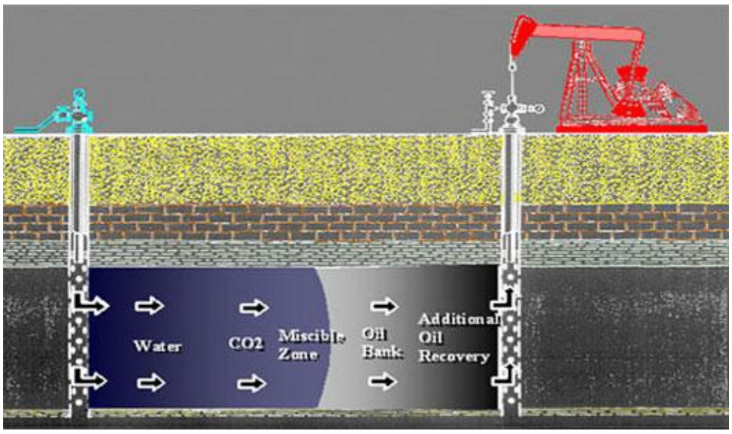


Figure 1-1 : WAG Process

WAG techniques injecting CO_2 gas alternately with the water into the reservoir. However, CO_2 injected into the reservoir cause the crude oil composition changed and this changed destabilizes the asphaltenes in the crude oil. Study of the unstable asphaltenes that cause precipitation is a regular menu for the producing reservoir, unfortunately the studies are only concentrated to the static behavior of the asphaltenes in reservoir. As the CO_2 injected into the reservoir at the condition precipitation pre-predicted not to occur, the field results is vice versa as what predicted from the static study, asphaltenes precipitation occurred. This show the dynamic behavior of the asphaltenes has not well understood. It is crucial to fully understand the dynamic of asphaltenes to correctly predict the possibility of asphaltenes precipitation realistically

1.2. Problem statements

Injection of CO_2 creates problems caused by the precipitation of asphaltenes. CO_2 caused composition changed in the crude oil, this leads to the instability towards the asphaltenes. Instability of asphaltenes can form a separate phase from the crude oil, this is called precipitation. This asphaltenes precipitate will cause fouling in the reservoir, wells, pipelines and oil production and processing facilities. In addition asphaltenes precipitation also causes severe permeability and porosity reduction and wettability alteration towards the reservoir properties. In some severe cases, asphaltenes can cause plugging the wellbore and surface facilities. Plus the results from the static asphaltenes study don't accurately predict the occurrence of the precipitation.

1.3. Objective and Scope of Study

This research is to study the dynamic properties of the asphaltenes inside the reservoir. By knowing this aspect, a better understanding and prediction of the possible asphaltenes precipitation and deposition can be obtained.

The objectives of this study are:

i) To determine the AOP of a light crude with and without gas injections.
ii) To correctly predict the asphaltenes precipitation behavior for the life of the reservoir using mathematical models.
iii) Developing the Asphaltenes Precipitation Envelope (APE) that very useful in predicting the occurrence of asphaltenes precipitation.

CHAPTER 2

2. LITERATURE REVIEW

2.1. Asphaltenes Definition

Asphaltenes definition has never been very clear despite all of the various study done. For asphaltenes, the definition of it is defined based on its solution properties [3]. Asphaltenes is the component of the crude oil. One of the definition for asphaltenes is solubility class of petroleum that is insoluble in light alkanes such as n-heptane or n-pentane but soluble in tuolene or dichloromethane [4]. The cause of the asphaltenes deposition is the instability of asphaltenes in the crude oil. The stability of the asphaltenes is unrelated to the composition of the asphaltenes in the crude, but it is related to the quality of the asphaltenes solvent in the crude oil.

2.2. Asphaltenes's Structure

Many intensive study has been made to confirmly defined the exact chemical structure of asphaltenes. Due to the complex structure of the asphaltenes, the exact chemical structure is still on debate [3]. So far there are two recognized structure of the asphaltenes, (1) the Continental Structure and (2) Archipelago model. For continental the basis of the structure is large central aromatic region with small alkyl chains on the periphery and for the archipelago model, smaller aromatic regions linked by bridging alkanes [5].

Asphaltenes are not crystallized, not pure and not identical molecules, it cannot be separated into its individual component. Asphaltenes are polar, polyaromatic and have high molecular weight hydrocarbon fraction of crude oil [6,7]. So this makes asphaltenes as the heaviest component in the crude oil. The carbon number of asphaltenes would be around 40-80 [1].

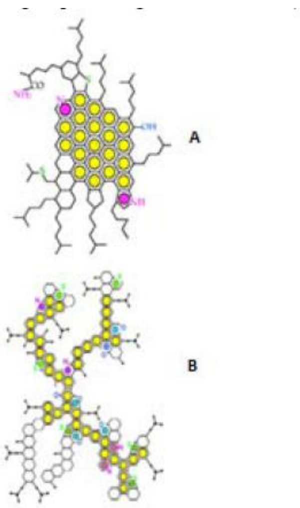


Figure 2-1 : Asphaltenes Model Molecules: A) Continental B) Archipelago

Figure 2-2: Appearance of Asphaltenes

2.3. Characteristics of asphaltenes

There are several factors that contribute to the amount of asphaltenes in the crude oil. Some of the factors are source, depth of burial, and also the API gravity of the crude oil. To know the characteristics of asphaltenes precipitated, the amount and type of solvent added into the crude oil is crucial. Asphaltenes will precipitate with a present of n-alkanes, asphaltenes are insoluble in n-alkane with the ration of 40:1 (40 parts n-alkanes to 1 part of crude oil). Short n-alkanes yield tacky and sticky asphaltenes, longer n-paraffins produce powdery and dry asphaltenes [1]. As for the effect of size of the n-alkanes molecules, the smaller the n-alkanes molecules size, the amount of precipitated increase sharply [8]. Most of the insoluble asphaltenes are precipitated by n-heptane and heavier solvents [1]. Short/light alkanes widely known tend to co-precipitated resins along with the asphaltenes.

2.4. State of asphaltenes in the crude oil

Two approaches of the asphaltenes models in the crude oil are solubility or real solution and colloidal solution.

- Solubility or Real solution

  - This model considers asphaltenes dissolved in the crude oil completely and in a true liquid state than form a uniform solution

  - The model of this type can be sub grouped into two, regular solution model and polymer solution model.

  - For the regular solution model, asphaltenes dissolves in the crude oil like any other smaller hydrocarbon molecules and for the polymer solution model, asphaltenes dissolves as large molecules like polymer dissolved in the water [9].

- Colloidal model

  - Asphaltenes are considered to be solid particles which are suspended colloidally in the crude oil and are stabilized by large resin molecules [10,7]. Resins in the crude oil act as a peptizing agent of the asphaltenes particles thus resin maintain asphaltenes in colloidal dispersion [1]. The precipitation of asphaltenes are not completely reversible [11]. Crude oil with high amount of resins are relatively stable.

2.5. Mechanism of asphaltenes precipitation and deposition

Asphaltenes in the crude must be unstable for precipitating yet deposition. Asphaltenes started to precipitated as it reach its onset point of asphaltenes. The onset point of asphaltenes is the point where the asphaltenes lose its stability in term of pressure, temperature and composition.

A few stages included for the whole process of asphaltenes aggregation from its natural behavior, the stages are precipitation, flocculation and deposition. Flocculation occurs after the stage of precipitation, after the precipitation, it may flocculates to form much larger molecules but they are still suspended into the solution [12]. Flocculation can be suspended in the oil as they become so large and cannot be carried by the liquid thus settle out on the formation and cause the formation damage. Deposition means the settling of the asphaltenes flocculated particles onto the rock surfaces. Precipitation is necessary, but not the sufficient condition for deposition to occur.

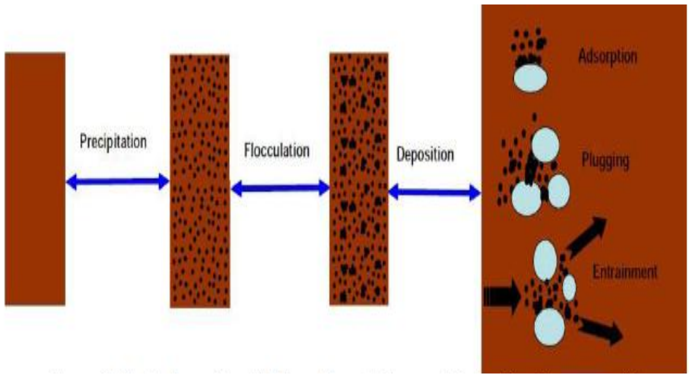


Figure 2-3 : Asphaltenes Precipitation and Deposition

One other theory of mechanism of asphaltenes precipitation is explain by Thou *et al*, (2002). The mechanism consists of four effects- Solubility, Colloidal, Aggregation and Electro kinetic effects. Two main steps occur due to the solubility are micellization and precipitation. Micellization is due to the increasing of aromaticity of the crude composition and the addition of light parafinic compound results in the asphaltenes precipitation. Figure 5 below shows how the mechanism works

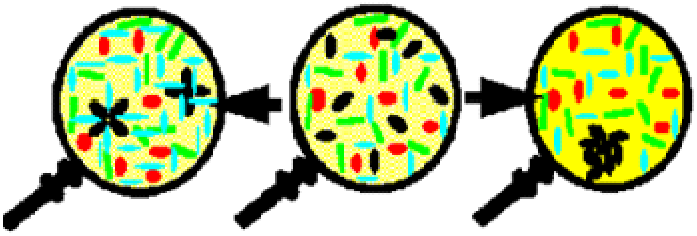


Figure 2-4 : Asphaltenes Micellization (left), Precipitaion (right)

For colloidal effect, peptization caused by resins in the crude oil holds the asphaltene inside the crude oil, in form of micelles. Increasing of the light paraffinic compound in the oil composition results of resins leaving the asphaltenes surface thus breaks the bonds of asphaltenes-resin. Concentration variation occurs in terms of additional light saturates alter the

chemical potential balance between asphaltenes-resins. Figure 2-5 below illustrates the colloidal effect,

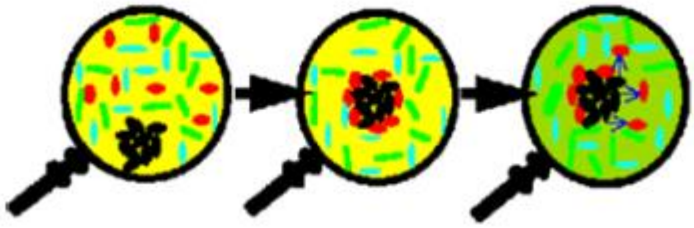


Figure 2-5 : Peptization by Resins (centre), Change in chemical potential balance (right)

For the effect of aggregation, it is mainly due to the insufficient amount of resins that hold the asphlatene surface. This insufficiency leads to the unstable asphaltenes in the crude oil. Instability cause asphaltenes to start flocculate due to their polarity (Buckley et al., 2007). For the elect kinetic effect, it is related during the flowing of fluid in the porous medium, it is due to the electrical potential difference during the motion of the fluid charged.

2.6. Factors contributing to asphaltenes precipitation

Below are the factors that influence the precipitation of asphaltenes (but not limited to)

- The crude composition
- Pressure
- Temperature of the crude

The change of crude composition and pressure give more significant effect as compared to the temperature changed.

2.6.1. Pressure

Pressure creates instability for the asphaltenes when the occurrence of the respressure depletion. Asphaltenes oftenly creates problems in the real field after the oil fields have produced over a period of time. The life of the reservoir production cause the reservoir pressure depletion, this initiate the asphaltenes problems and this is caused by the compressibility different between light ends and the heavy component of hydrocarbon of the under saturated oil (Afshari et al., 2010: Hammami and Ratulowski, 2007; Gholoum et al., 2003). In the real oil production field, problems caused by the asphaltenes are at maximum at the region near the wellbore and along the production line up until at the surface. Pressure drop at this region is at the maximum and the oil started to become more saturated (Hammami and Ratulowski, 2007; Thou *et al.,* 2002; Hammami *et al.,*2000; Kokal and Sayegh, 1995;)

2.6.2. Compositional Change

According to Sarma, 2003, changes occurred to the composition of the crude oil include increase in aromaticity, addition in light paraffinic compounds, as well as change in gas-oil-ratio (GOR), ratio of high to low molecular weight component, asphaltenes-resin ratio, gas injection scheme, etc. (Sarma, 2003). According to Hammami and Ratulowski, (2007), asphaltenes precipitation can also occur in-situ during miscible flooding, mixing of incompatible hydrocarbon fluids, CO2 flooding, and other solvent injection operations that can cause compositional change to the crude oil

2.7. Precipitation in Light Oil

Even though light oil contains much smaller amount of asphaltene, precipitation of asphaltene is much more easier to happen in light oil as compared to heavy oil though heavy oil contain much more asphaltenes content (Kokal and Sayegh, 1995, Sarma, 2003, Akbarzadeh et al.,2007; Alta'ee et al., 2010). Heavier oil consists of higher intermediate components 12 with more resins and aromatics which make it becomes a good solvent to dissolve the asphaltenes. Meanwhile lighter oil contains higher fraction of light hydrocarbon ends which have limited solubility on asphaltenes thus cause asphaltenes to become less stable.

The solubility of the asphaltenes in the reservoir fluids in can be altered by the addition of the light paraffinic compounds (Hammami et al., 2000). In accordance to the colloidal model of asphaltenes behavior, resin molecules tend to de absorb from the surface of the asphaltenes and thus breaking the micelles bond, in respond to the addition of light hydrocarbon fraction to reservoir fluids in order to reestablish thermodynamic equilibrium.

2.8. Effect of Asphaltenes Content

According to the review based from the field experience, the asphaltene content of a crude oil is not an important characteristics that will further defined the possible asphaltenes precipitation (Kokal and Sayegh, 1995; Akbarzadeh, 2007). Light oil is oftenly related to be having asphaltene related problem as compared to the heavy oil, even though light oil containing small portion of asphaltene. The reservoir conditions for this light oil which experiencing asphaltene precipitation is at the reservoir pressure above the bubble point.

To prove this statement, two fields are taken as the example, which first is The Venezuelan Boscan with 17.2 wt% asphaltenes that producing with nearly trouble free. Another field is light oil field in Algeria that only contain 0.15 wt% of asphaltene yet having a problematic production mainly due to the asphaltene precipitation. According to Alta'ee et al, problems of asphaltene precipitation is usually related to the light oil that having a minor portion of asphaltenes rather than heavy oil that having much higher asphaltenes content.

2.9. CO_2 Injection

Based from the field data that CO2 gas injection is implemented to increase the recovery, gas injection tends to boost the occurrence of asphaltenes precipitation and depositions, light oil reservoir is the common candidates to be having gas injection (Srivastava and Huang, 1997; 13 Sarma, 2003).

Miscible solvents have the highest potential to cause asphaltene precipitation, and according to Gholoum et al., (2003), CO2 is the most asphaltene precipitant as compared to alkanes (C1 to C7)

During the CO2 injection, the miscibility of CO2 and the crude oil cause major compositional change to the crude oil. This compositional change favors the occurrence of asphaltene flocculation.

As the CO2 injected into the reservoir, it will in become in contact with the reservoir fluid, followed by the Vaporizing Gas Drive (VGD) that vaporizes the light and intermediate components to the gas phase (Green and Willhite, 1998). In addition, the resins that hold the asphaltenes vaporized to the CO2 phase. These process causes the reservoir fluid contain less amount of resins. Resins are the main solvent of asphaltenes in the crude oil. This loss of resins causes the change of the fluids behavior and equilibrium condition of the crude oil. This will cause instability of asphaltene, and thus leads to the asphaltene precipitation (Kokal and Sayegh, 1995; Sarma, 2003; Srivastava and Huang, 1997).

Based from the study did by Alta'ee et al., (2010), Srivastava and Huang, (1997), during isothermal depressurization experiments with different concentration of CO2 injected into the crude oil, the results shows that as the concentration of CO2 injected increase, the amount of asphaltenes precipitated is also increasing. Besides the results also showed that as CO2 concentration of injected gas increase, the saturation pressure is also increasing

According to the research did by Gholum et al., (2003) and Sarma, (2003) , addition of CO2 mole percentage will increase the Power of Transmitted Light up until certain CO2 concentration

2.10. WAG Operations in Malaysia

The need for implementing EOR techniques towards the mature reservoir in Malaysia is inevitable. Most of the mature fields in Malaysia like Dulang have been water flooded until recent and the recovery factor for Dulang is approximately 20%. Prompting initiatives to increase the recovery EOR techniques should be implemented to increase the recovery thus increase the production of hydrocarbon in Malaysia.

After several studies towards the options of EOR technique that suitable for the Malaysian oil field that mostly operated offshore, its found that CO_2WAG are the most suitable technique to be implemented [12]. Below are several fields in Malaysia that have been implemented by WAG to increase its recovery.

As this research is to study the asphaltenes behavior during gas injection, the oil samples collected from these fields are highly recommended to be analyzed by the similar way as presented in this report.

2.10.1. Dulang Oilfield

Dulang oilfield is a multi stacked sandstone reservoir located in the offshore of the Peninsular Malaysia. This oilfield has been operated for almost 19 years. Initially water flooding has been chosen as the supplementary drive mechanisms for the field and the recovery factor result from aid of water injection is approximately 20% [12]. By the needs to increase the recovery, WAG of CO_2 EOR technique has been implemented to this oilfield. Based from the results from the pilot test that encouraging, immiscible WAG techniques has been implemented to this whole field. The expected field's oil recovery after implementing WAG process is 49% of STOIIP [12].

Dulang's Reservoir Description

The major sand package of this field is E10/14 reservoir, and these reservoirs were deposited in a tidal environment and capped by coal throughout the field separating it from the upper E6/8 sands [12]. Eventually the horizontal permeability is higher in the horizontal direction and the permeability of the E14 sand are generally higher than E10/13 sands. In addition to the routine PV analysis, phase behavior of CO_2/Dulang oil mixture was also studied and the MMP(Minimum Miscible Pressure) for this mixture was evaluated to be 2875 psig [12]. The proposed composition of injection gas is produced gas with only 60% of CO_2, then the MMP is expected to be higher. Thus the miscibility will not be occurred between the CO_2 and the reservoir oil since the initial reservoir pressure is much below than MMP which is 1800psia [12].

2.10.2. Tapis and Guntong Field

Tapis and Guntong Field are located in the Malay Basin, offshore Peninsular Malaysia, These fields contains approximately 1 billion barrels OOIP [13].Tapis started its production in 1078 and Guntong started since 1985. Both these fields are the two largest water flooded fields operated by ExxonMobil Malaysia. Both fields have been water flooded since the early life of its production and have taken 25 years of water flooding technique. Until recent, Tapis and Guntong have achieved approximately 40% recovery factor to the OIIP [13]. However, both fields have produced almost 90% of their anticipated water flood reserves date [13], means that, there is a need for further EOR technique implemented to lift its recovery percentage. Based from the reservoir properties and location, studies show that WAG is the most suitable EOR technique to be implemented

Tapis and Guntong Reservoir Descriptions [13]

Both reservoirs are made up of stacked sandstone reservoirs of the lower Miocene Group J and Group I respectively. And both reservoir also are made of marginal marine to fluivial deposits. The Tapis J are approximately have the average permeability between 50mD and 300mD, while Guntong I have average permeability of 100mD to 500mD [13]. For the initial reservoir pressures, it is around the range of 1500 to 2500 psia. For the properties of the crude oil in both reservoir, both reservoir contain saturated, light crude oil with 45 degree of API gravity [13]. Initial gas caps were also presents in all reservoirs varying in size. For Tapis, the MMP for mixture of CO2 with reservoir fluids is higher than the current reservoir pressure. Thus Immiscible WAG is the most suitable for Tapis. The MMP for CO_2 and reservoir fluids is 3400 psia [13].

CHAPTER 3

3. METHODOLOGY

The main objective of this research is to study the behavior of the asphaltenes in the reservoir during CO_2 injection. The methods to study the behavior of asphaltenes consists of determining the Asphaltenes Onset Pressure (AOP) of crude oil with and without gas injection, predict and determine the possible amount of asphaltenes to be precipitated and to develop Asphaltenes Precipitation Envelope. Initially, this project is planned to consist of experimental work and simulation work. The experimental work is to determine the AOP measurement experiment. This experiment require PVT lab cell, but unfortunately due to unexpected breakdown of the PVT lab cell, major change in project research approach has to be done.

After discussion, the decision made is to proceed the research without experimental work, only simulation. The main objective of this project is to develop Asphaltenes Precipitation Envelope for an oil sample (without CO_2) and APE for mixture of CO_2 and oil. and below are steps taken to achieved this objective.

3.1. Data Gathering

The first step for this research is to find the reliable input data for the simulation activities. The desired data should insufficient to be inserted into the simulator software. After literature studies done, the data found to be an oil sample from carbonate reservoir of Arabian Gulf (Yanebashi *et al.*, 2011) [1]. Important data needed for the simulation provided by the literature.

3.2. Simulation Modeling (Multiflash 3.7)

The development of APE for original oil and mixture of oil and CO_2 for different composition are developed by using Multiflash ver 3.7 (Infochem Ltd).

3.2.1. Input Data

The important input data to continue the simulation study are:

- Oil composition
- Fluid Properties (MW, GOR, Bubble Point Pressure, SG)
- SARA Analysis Data
- Results of Asphaltenes Onset Pressure (AOP) measurement test
- Reservoir Conditions (pressure and temperature)

3.2.2. Pseudo Component

The pseudo component of the oil composition started at the C7+, and the splitting of pseudocomponents is 4.

3.2.3. PVT Matching

PVT analysis feature provided by the software enable phase envelope of the oil composition to be developed. The Equation of State (EOS) for this simulation is PR (Peng-Robinson) equation of state. The matching parameter for this PVT analysis is saturation pressure, P_b oil density and viscosity.

3.2.4. Asphaltenes modeling

Asphaltenes model has to be set first in order to developed the APE for original oil and various gas and oil mixture. For this experiment, 5 combination of mixture are used for the study which is reservoir fluid mixed with the 0, 25, 40, and 50 mol% of CO_2.

3.2.5. APE prediction

After asphaltenes model has been set, development of the APE for all the combinations of mixture is developed.

3.3. Simulation Modelling (CMG, WinProp)

To determine the AOP and the amount of asphaltenes precipitated for this crude sample, WinProp package of CMG simulation software is used. To calculate these parameters, asphaltenes precipitation model is developed by using the WinProp.

The main steps required to develop this precipitation model consists of

- Fluid characterization
- Distributions models
- Regression
- Asphaltenes model selection
- Prediction of the asphaltenes prediction

3.3.1. Fluid Characterization

The main input data for this fluid characterization is the components of the crude oil, mole%, and molecular weight and Std. density of each of the components of the crude oil. Saturation pressure is needed for the resgression purposes.

The most important things in developing asphaltenes precipitation model is to split the heaviest organic component of the crude oil to the precipitating and the non precipitating component. Both these components have the similar critical properties and its acentric factors but different interaction coefficient with the light components. Precipitating components has larger value of interaction coefficient with the light components. The increase of the amount of the light components in the crude oil will increase the amount of precipitating components.

To split the precipitating and non-precipitating, spliiting function in the WinProp is used. The C7+ components are split into 4 Single Carbon Number (SCN).

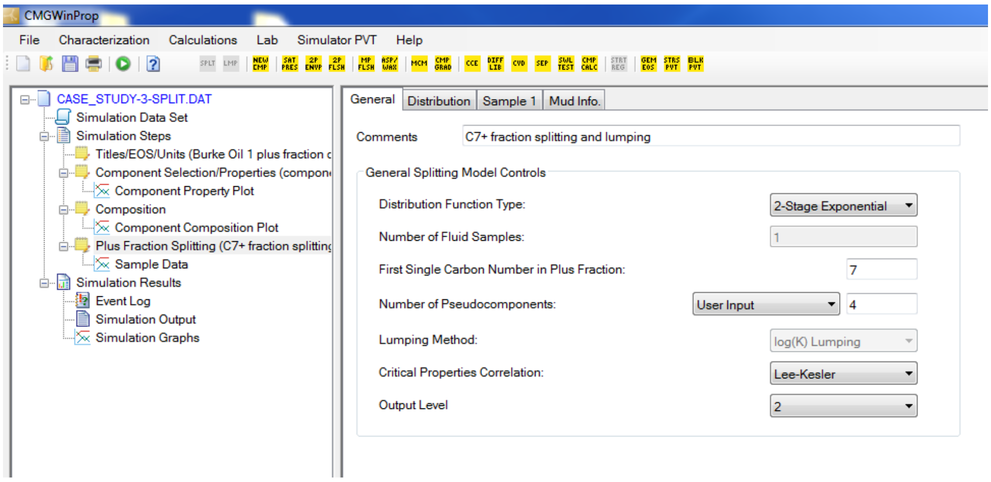


Figure 3-1 : C7+ splitting function

The properties for each of the SCN are calculated based on the empirical correlations. After updating the components after splitting, 4 pseudocomponents of SCN are produced in the set list of the oil components. Noted that after splitting, the mole fraction for asphaltenes and C31+ shares the same value. Next is to calculate the mole fraction of C31+ and asphaltenes, the formula to calculate is as below

$$Mole\% \ of \ Asphaltene \ = \ Weight\% \ of \ Asphaltene * \frac{MW_{oil}}{MW_{Asphaltene}}$$

Output file from the simulation provides the molecular weight of the asphaltenes component. Use the MW of asphaltenes generated to calculate the mole fraction of the asphaltenes.

Component	Primary	Secondary
CO2	0.000000E+000	0.0
H2S	0.7596849147	0.0
N2	0.1044566793	0.0
C1	28.2681928	0.0
C2	7.046868951	0.0
C3	5.343117263	0.0
IC4	1.130822692	0.0
NC4	3.132117578	0.0
IC5	1.39196439	0.0
NC5	1.987842186	0.0
FC6	2.87493258	0.0
C07-C15	19.65888686	0.0
C16-C25	12.55131391	0.0
C26-C30	4.000532272	0.0
C31+	10.38002553	0.0
asph	1.36924139	0.0
Sum	99.999999996	0.000000E+000

Figure 3-2 : Components updated after splitting

Update the mole fraction for each compositions in the compositions tab. Figure 3-2 above is the component window after have been updated.

3.3.2. Distribution Model

There are several types of oil, hence it is vital to have a specific models that describe the molar distribution as a function of molecular weight for each type. Below are the type of distributions model available in the WinProp,

- Exponential (gas condensate and light fluids)
- Two-Stage exponential (for simulating black oil)
- Gamma (for all types of fluids)

Meanwhile, 3 correlations to calculate the critical properties of the pseudo component, which are

- Kesler and Lee (1975)
- Riazi and Daubert (1980)
- Twu (1984)

For this research, Two-Stage exponential distribution model and Kesler and Lee correlation is used for the simulation, this can be seen in the Figure 3-1.

3.3.3. Regression

After the splitting of the heavy component, the model can be tuned to any PVT data by using the regression. The main objective of performing iterative regression is to obtain a closer result value to the experimental data. WinProp uses the regression procedure proposed by Agrawal *et al* (1987). The regression parameters chosen for this simulation is the saturation pressure and Stock tank API gravity. The convergence tolerance for the regression is 1*10^5.

Figure below is showing the regression control tab of the regression main window. The calculation of the EOS model depends solely to the results from the regression. Thus it is important to make sure the results from the regression is still within the acceptable limit

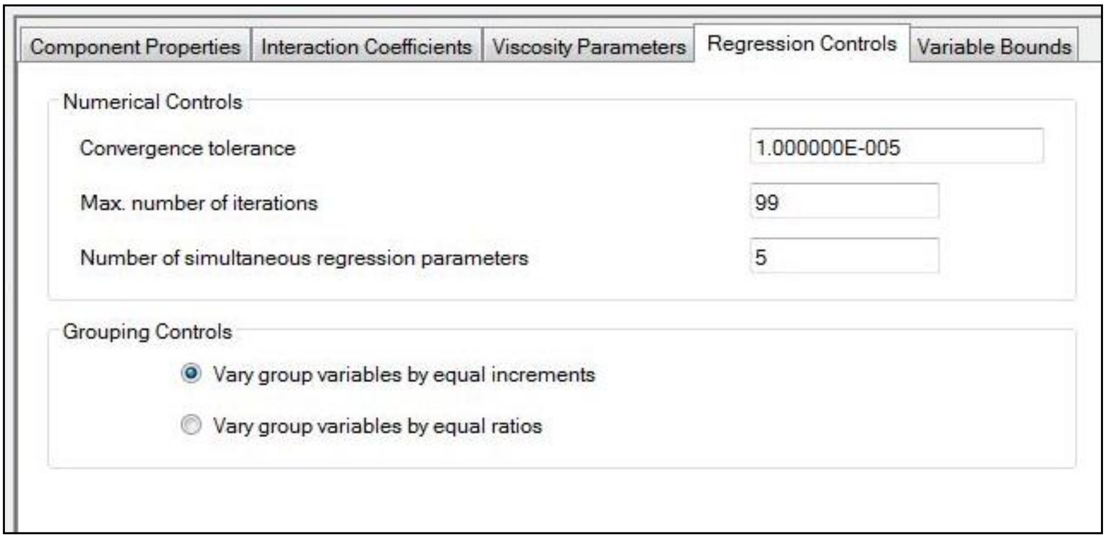


Figure 3-3 : Regression control tab

3.3.4. Asphaltenes model selection

For the case of WinProp, it uses the solid precipitation model, that assumes asphaltenes precipitation is reversible. This assumption has been proved experimentally. The maximum precipitation of asphaltenes occurs at a condition near or at the bubble point pressure. The process of reversibility of asphaltenes precipitation is mainly due to the liberated gas from the oil changed the solubility of the crude oil, thus inducing the re-dissolution of the precipitated asphaltenes.

Two main factors that determine and control the behavior of asphaltenes precipitation is solid molar volume and the interaction parameter. Increasing the solid molar volume will increase the maximum amount of the possible precipitated.

Meanwhile, increasing the binary interaction coefficient between heavy components (asphaltenes) and the light hydrocarbon will induce the conditions for re dissolution of the precipitated asphaltenes.

Select the asphaltenes/wax modeling at the 'calculation' tab in the WinProp. Then enter the AOP and the temperature in degF.

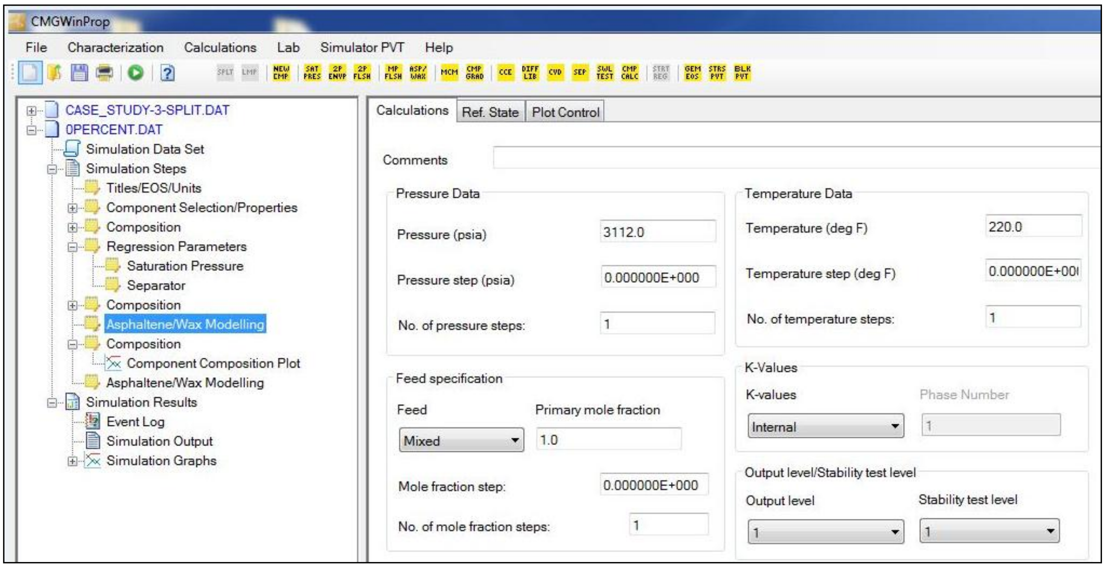


Figure 3-4 : Asphaltenes/wax modeling window

The value of the solid molar volume should be chosen carefully in order to get the maximum amount of precipitation desired. If there is no experimental data available, 1 L/mol would gave a good results.

Below is the window to manipulate the solid molar volume in the WinProp.

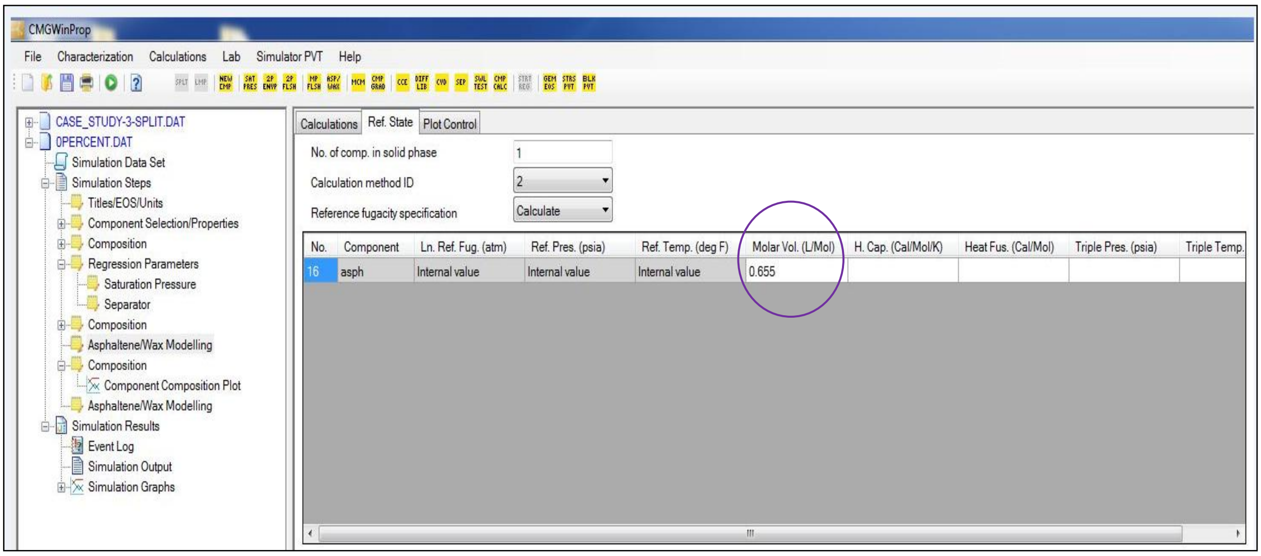


Figure 3-5 : Window to manipulate solid molar volume

3.3.5. Prediction of Asphaltenes precipitation

The best method to calculate the AOP is by conducting experimental study using SDS. The amount of asphaltenes in the crude oil from SARA analysis is 0.71wt%. Then to calculate the AOP using WinProp, run the first trial by clicking 'Run simulation ' button. The desired shape of the generated plot should have 'bell shape' look. this shape able us to determine the AOP, maximum amount of asphaltenes precipitate and also approximate saturation pressure.

As mention earlier, two main parameters that control and determine the shape of the plot generated is solid molar volume and also interaction coefficient between asphaltenes and the light hydrocarbons. The interaction coefficient is tuned until the desired graph is generated. Below is the figure of a window to change the interaction coefficient. To open this window, click the "component selection/properties" in the tree view, then click the 'Int Coef' tab.

Component | Int. Coef. | Viscosity | Aqueous Phase

HC Int. Coef. Exp. HcIntCoefExp - 1(1.2)

Component	CO2	H2S	N2	C1(HC)	C2(HC)	C3(HC)	IC4(HC)	NC4(HC)	IC5(HC)	NC5(HC)	FC6(HC)
CO2	zero	0.096	-0.02	0.103	0.13	0.135	0.13	0.13	0.125	0.125	0.15
H2S	0.096	zero	0.176	0.08	0.07	0.07	0.06	0.06	0.06	0.06	0.000000E+000
N2	-0.02	0.176	zero	0.031	0.042	0.091	0.095	0.095	0.095	0.095	0.12
C1(HC)	0.103	0.08	0.031	zero							
C2(HC)	0.13	0.07	0.042		zero						
C3(HC)	0.135	0.07	0.091			zero					
IC4(HC)	0.13	0.06	0.095				zero				
NC4(HC)	0.13	0.06	0.095					zero			
IC5(HC)	0.125	0.06	0.095						zero		
NC5(HC)	0.125	0.06	0.095							zero	
FC6(HC)	0.15	0.000000E+000	0.12								zero
C07-C15(HC)	0.15	0.000000E+000	0.12								
C16-C25(HC)	0.15	0.000000E+000	0.12								
C26-C30(HC)	0.15	0.000000E+000	0.12								
C31+(HC)	0.15	0.000000E+000	0.12								
asph	0.15	0.000000E+000	0.12	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.08977292912

Figure 3-6 : Interaction Coefficients window

Before tuning these two parameter, the graph generated is not showing the desired results. Figure below is the plot that shows the desired bell shape look, after tuning has been done.

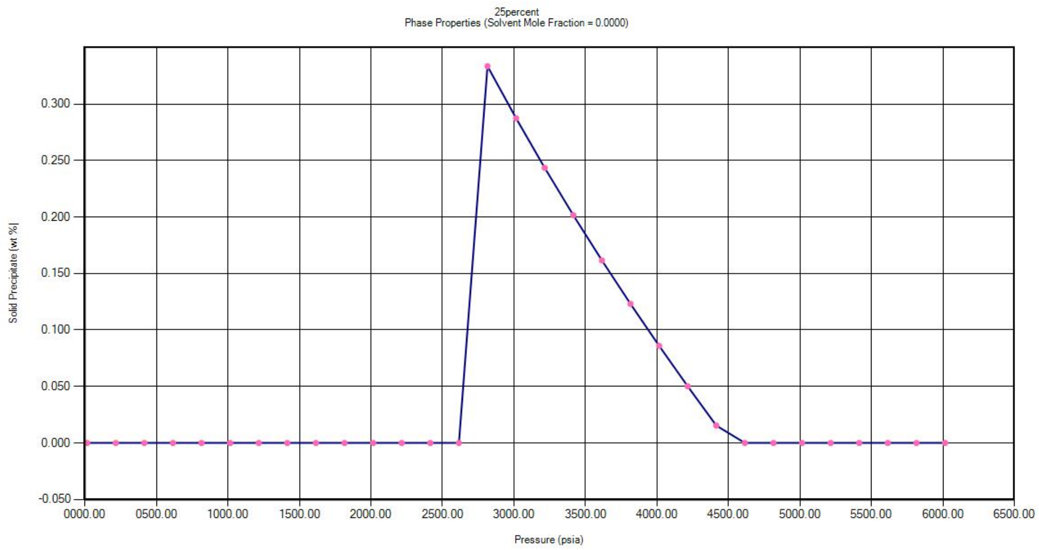
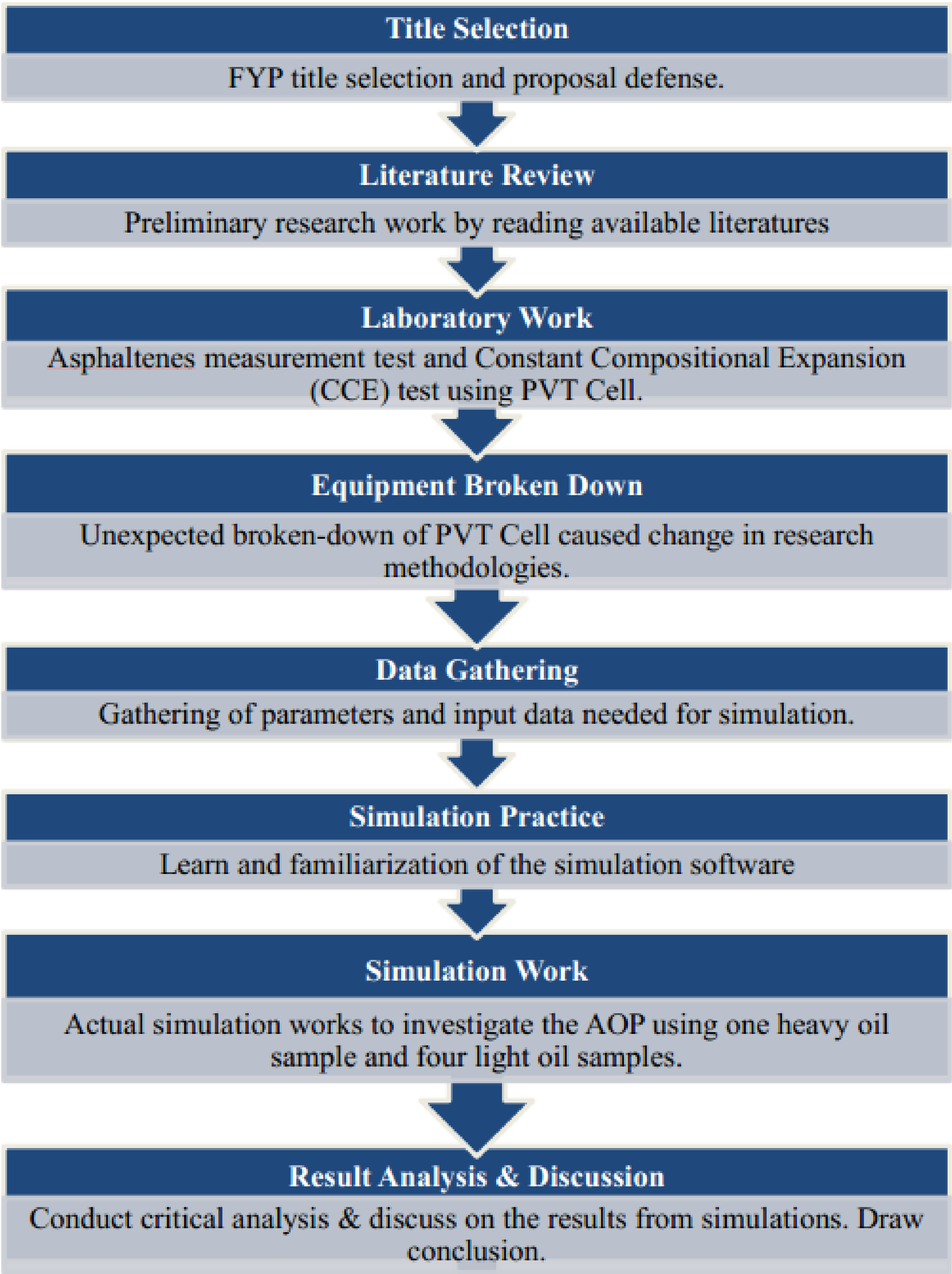


Figure 3-7 : Graph generated after tuning

3.4. Project Activities



3.5. Key Milestones

3.5.1. Key Milestones for FYP 1

Milestone	Planned Timescale	Progress
Selection of FYP topic	Week 2	Completed
Prelim research work	Week 2 - Week 5	Completed
Submit Proposal Defense Report	Week 4	Completed
Project Work (Literature Review)	Week 2 - Week 8	Completed
Proposal Defence Oral Presentation	Week 8 - Week 9	Completed
Project Work continues	Week 8 - Week 12	Completed
Fix Methodology	Week 9	Completed
Start Pre-Lab Preparation	Week 10 - Week 14	Completed
Submit Interim Report Final Draft	Week 12	Completed

3.5.2. Key Milestones for FYP 2

Milestone	Planned Timescale	Progress
Briefing & Update on students progress	Week 2	Completed
Project Work continues	Week 1 - Week 8	Completed
Submit Progress Report	7-11-2012	Completed
Project Work continues	Week 9 - Week 10	
Pre-EDX (Seminar/Poster Exhibition)	Week 11	
Submit Final Report (CD & soft bound)		
Final Oral Presentation		
Submit Dissertation (hard bound)		

3.6. Gantt Charts

3.6.1. Gantt Chart for FYP 1

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Topic Selection / Proposal														
2	Preliminary Research Work														
3	Submission of Proposal Defense Report						*								
4	Proposal Defense (Oral Presentation)							Sem break							
5	Project Work Continues														
6	Submission of Interim Draft Report												*		
7	Submission of Interim Report													*	

3.6.2. Gantt Chart for FYP 2

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	Project Work Continues							Sem break									
2	Submission of Progress Report								*								
3	Project Work Continues																
4	Pre-EDX (Seminar/Poster)											*					
5	Submission of Dissertation (soft bound)													*			
6	Final Oral Presentation														*		
7	Submission of Dissertation (hard bound)																*

3.7. Tools Required

- To develop the APE for this oil sample, Mutiflash ver. 3.7 (Infochem Ltd) is used. All the simulation done is by using this software. The license is named under UTP and available at the computer laboratory.
- To predict the AOP and the possible amount of asphaltenes to be precipitated, WinProp of CMG software is used. WinProp is one of the features available under CMG simulation software package.

Figure 3-8 : Multiflash software

Figure 3-9 : CMG software

CHAPTER 4

4. RESULTS AND DISCUSSION

An oil sample data obtained from the literature has been chosen for this study. This oil sample is taken from a carbonate reservoir of Arabian Gulf. For the APE development, four APE will be generated based from four different mixture combinations. The mixture is between oil sample and CO_2 acted as injected gas. The data gathering, results analysis and discussion will be shown in this section.

4.1. Data Gathering

After unexpected broke down of the PVT cell, research approach has to be changed to only consist of simulation works. After some literature review done, it is decided to select the data from the paper produced by Yanebashi *et al.*, 2011 [1]. The oil sample investigated from the carbonate reservoir of the Arabian Gulf.

Some of the important input data needed for the simulation is available in the literature. Table 4-1, below is the summary of the fluid sample data (0% gas, original oil) without injection gas

Table 4-1: Summary of fluid sample data

Summary of fluid sample data	
Compositions	Moles
NItrogen	0.132
H_2S	0.96
CO_2	0
Methane	35.722
Ethane	8.905
Propane	6.752
Iso-butane	1.429
n-Butane	3.958
Iso-pentane	1.759
n-Pentane	2.512
C_6	3.633
C_{7+}	34.237
Molecular Weight	91.14
GOR, scf/bbl	897
Density, g/cm-$^{-3}$	0.833
°API	38.3
SARA content, wt%	
Saturate	71.54
Aromatics	20.62
Resin	7.11
Asphaltene	0.71

The bubble point for this oil sample based form the Constant Composition test is 2547 psia. This value is obtained at the reservoir temperature which is 220°F.

Viscosity of the oil at reservoir pressure is 0.322 cp and at bubble point pressure is 2547 psi cp. SARA analysis is to determine the saturates, aromatics, resins and asphaltenes content in the reservoir.

As the gas injected into the oil, it will change the composition of the original oil, the composition of each mixture is an important data to develop the APE, different composition will have a different APE size and shape. Below is the table that represents the composition of the mixtures

Table 4-2 : Composition of the mixtures

	Mixture of Oil Sample and Injection Gas			
Injection gas added, mol%	25	40	45	50
Component				
NItrogen	0.204	0.24	0.258	0.276
CO2	0.048	0.072	0.084	0.096
H2S	1.336	1.524	1.618	1.713
Methane	45.964	51.085	53.645	56.206
Ethane	10.076	10.661	10.954	11.246
Propane	6.412	6.242	6.157	6.072
Iso-butane	1.175	1.048	0.984	0.921
n-Butane	3.144	2.736	2.533	2.329
Iso-pentane	1.337	1.126	1.02	0.915
n-Pentane	1.899	1.593	1.439	1.286
C_6	2.727	2.274	2.048	1.822
C_{7+}	25.679	21.399	19.259	17.119

4.2. Results and Discussion

Base Case Modeling (0% CO_2)

The base case model for this research is for the original oil, without any injection gas (0% gas). The Pressure-Temperature graph of the base case shows the phase envelope of the original fluid sample. The phase envelope below is developed base on the bubble point data and matching with the GOR of the fluid.

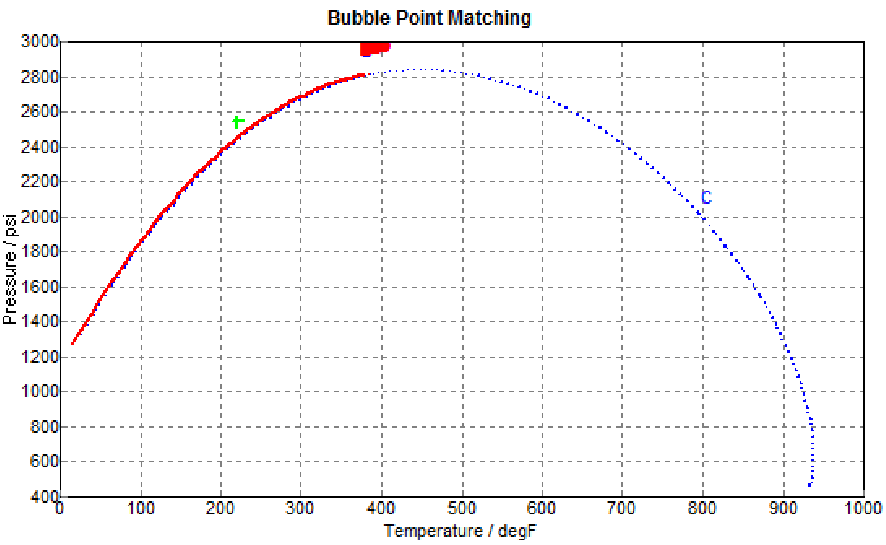


Figure 4-1 : Phase envelope of the base case

Simulation from the Multiflash is to generate the APE for every cases, below is the APE for the base case model (0 mol% injection gas), The envelope is plotted pressure against temperature. The isothermal depressurization test is at the reservoir temperature, 220°F from 8000 psia to 14.7 psia. The pressure within the depressurization test range that first intersect the APE is the AOP for the crude oil.

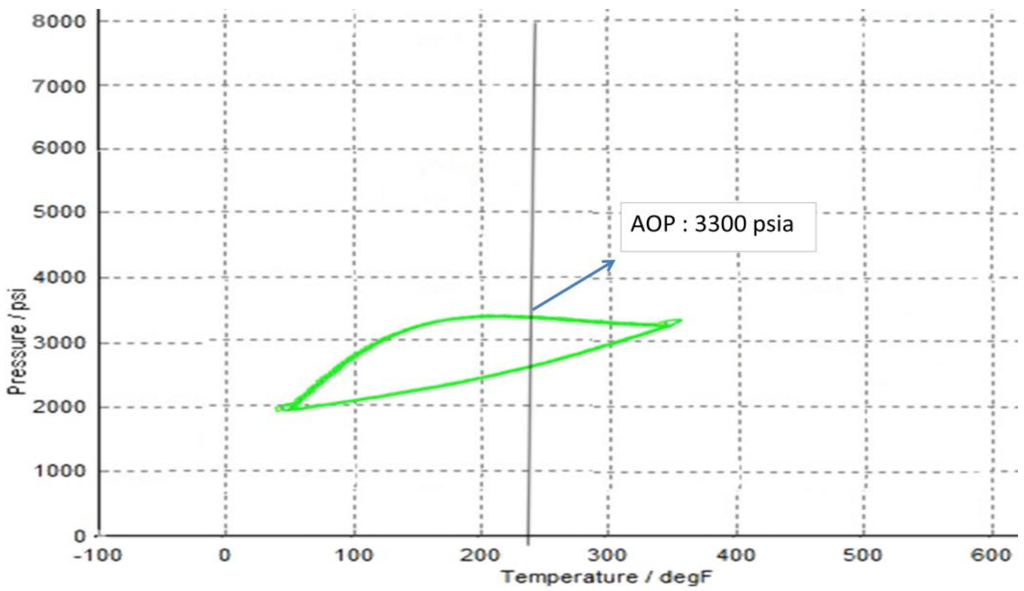


Figure 4-2 : APE for base case

WinProp generates asphaltenes precipitates wt% vs pressure. Below is the plot generated by the WinProp.

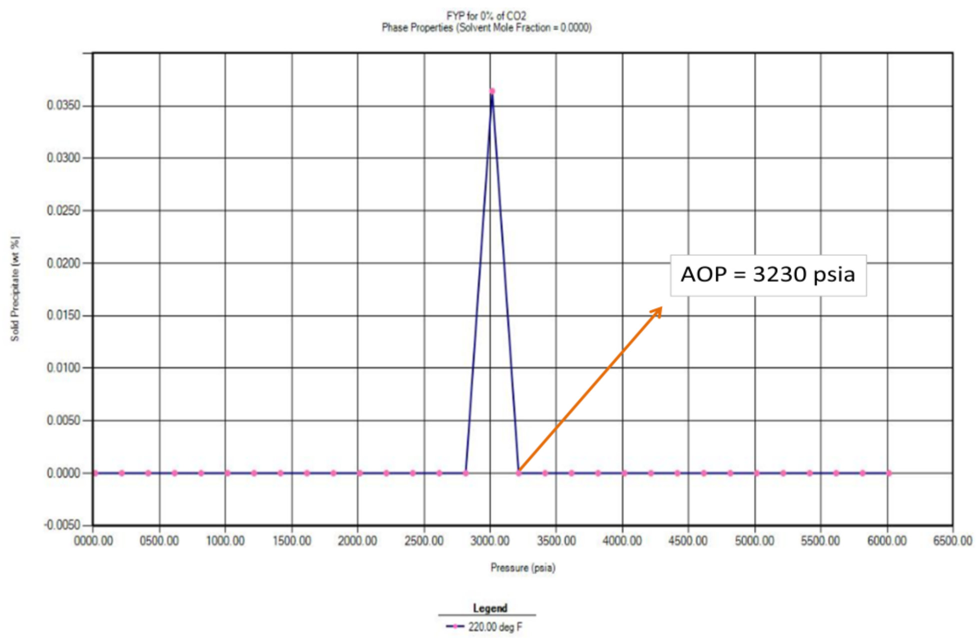


Figure 4-3 : Asphaltenes precipitated wt% vs Pressure (developed by WinProp)

The pressure at which the amount of asphaltenes starts to increase from the zero value is the AOP of the oil sample. AOP is the point which the asphaltenes become unstable and starts to form solid out of the crude oil.

Based from the results obtained from Multiflash and WinProp, the AOP of this crude oil can be clearly determine, for the case of the APE by Multiflash, based from the isothermal depressurization test, , the AOP of this crude oil is about 3300 psia. For the case of the plot generated by WinProp, the estimated AOP is about 3230 psia. The estimations of AOP from both simulator give a reasonable and consistent results.

This result is also showing, at the condition of the reservoir temperature, with only original crude oil, without any gas injection, the risk and possibility for the case of asphaltenes precipitation is high. Meanwhile, for the conditions of the low risk of possible asphaltenes problem are at the condition of, at the reservoir temperature depressurization test range does not intersect the APE of the crude oil. This is showing AOP is not detected due to no possible precipitation at the isothermal pressure depletion range.

Simulation for the AOP prediction for the cases of mixture of oil and injection gas also has been done, both simulator consistently produce reliable and consistent value of AOP. The table below shows the comparison of the AOP estimation generated by both software.

Table 4-3 : AOP generated by both simulator

	Results from WinProp			Results from Multiflash	
Co2 concentration	Upper AOP	Lower AOP	Max solid precipitated (wt%)	Upper AOP	Lower AOP
0	3215	2500	0.0364054	3300	2550
25	4615	2615	0.333449	4550	2800
40	4900	2615	0.562249	4900	2900
50	5815	2815	0.569466	5500	3300

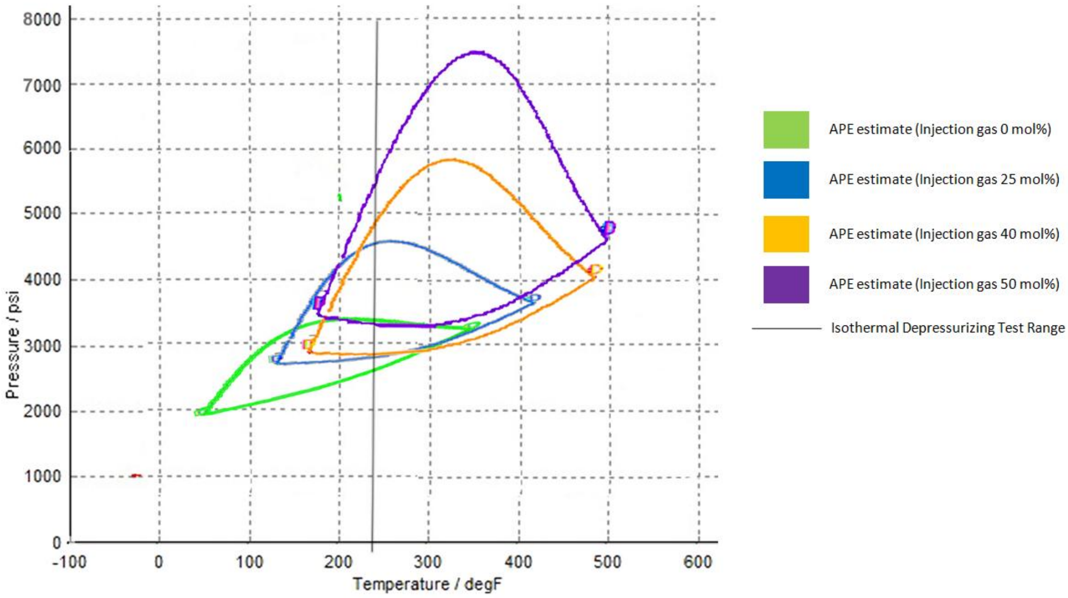


Figure 4-4 : APE for all cases

APE for all combination of mixtures are generated and plotted on a same plot area, this is aim to be able to see the trend of the APE changing with the increasing concentration of injection gas. This is also aim to identify the APE shifting area during CO_2 gas injection.

Prediction of the APE generated by the Multiflash for every cases is shown in the Figure 4-5. Based from the results obtained, the APE is shifting to the higher pressure and temperature region as the concentration of the CO_2 injection gas increases. The area covered by the APE or the size of the APE is gradually increasing as the concentration of the injection gas increased. As the size of the APE expanding, this is showing the risk of asphaltenes related problem is also increasing.

This is due to the compositional change caused by the gas injection process. Injection of CO_2 gas causes the injected gas in contact with the intermediate component induce a vaporizing gas drive process. CO_2 vaporizes the intermediate component as well as the resin in the crude oil (Green and Wilhite,1998)[15]. Reducing amount of resins in the crude oil cause the instability of asphaltenes, due to the fact of resins is the stabilizing agent for asphaltenes phase in the crude oil. Increase the concentration of the injection gas will cause higher loss of the resins in the crude oil, thus causes the higher amount of asphaltenes to be precipitated.

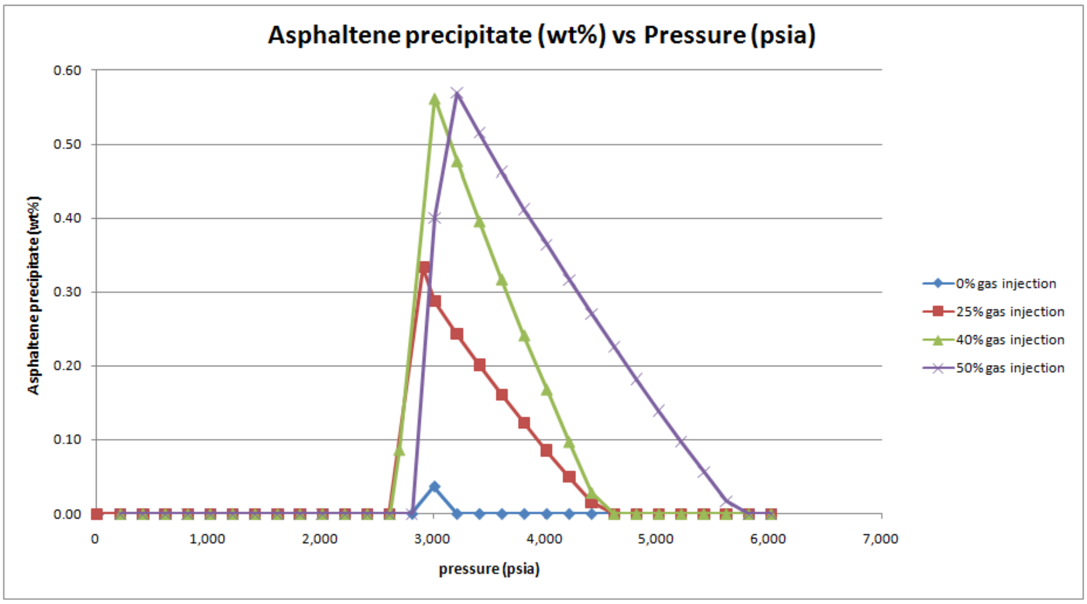


Figure 4-5 : Asphaltenes precipitate vs pressure

Figure 4-5 is generated from WinProp, it shows the amount of asphaltenes precipitated is increasing as the concentration of the injection gas increased. This results also represents that gas injection cause compositional change, thus increase the risk of the asphaltenes related problems.

Figure 4-5 also showing that the increasing concentration of injection expand the asphaltenes precipitation region. This results generated by WinProp is giving a tally and consistent with the APE developed from Multiflash. If the reservoir pressure is located within the asphaltenes precipitation region, it is most likely to encounter asphaltenes deposition even before the gas injection campaign and the asphaltenes problems will occur up until 50 mol% of injection gas.

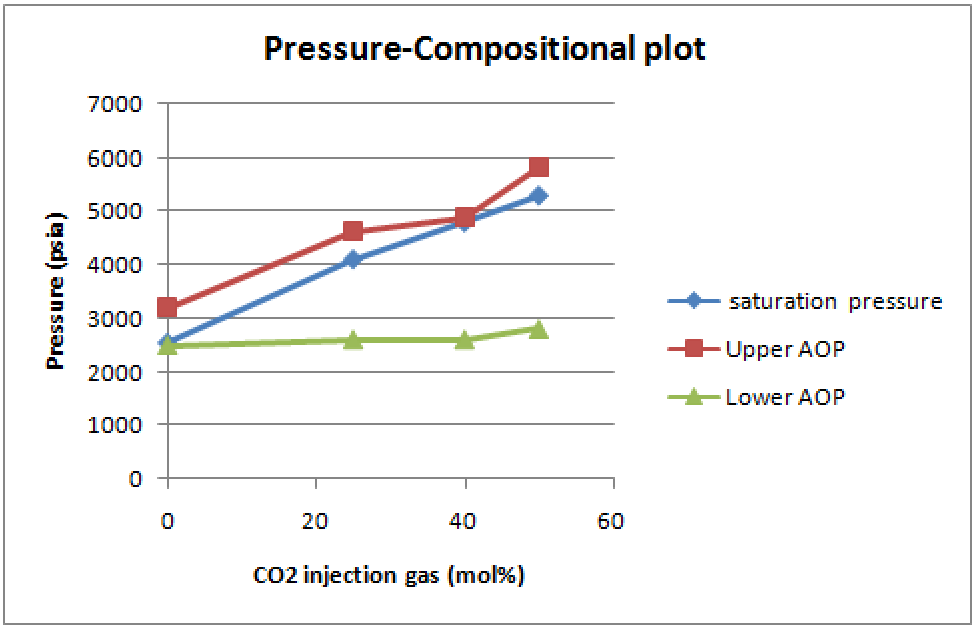


Figure 4-6 : Pressure-Compositional Plot

Figure 4-6 is showing the bubble point is bounded within the upper and lower AOP. This figure also shows that increasing amount of the injection gas concentration increase the saturation pressure of the oil. This is due to the fact of injection gas liberates the light and intermediate components of the oil, thus increasing the heavy components of the oil. Increasing heavy component cause less gas contained in the crude oil thus it is difficult to reach the bubble point and increase the bubble point pressure.

Lower AOP is also known as the offset AOP, which pressure at where asphaltenes re dissolve into the oil. From this figure, the area between the upper and lower AOP is the area of the asphaltenes precipitation. This figure shows increasing concentration of the injection gas increase the area in between lower and upper AOP. This result is consistent with the APEs developed by the Multiflash.

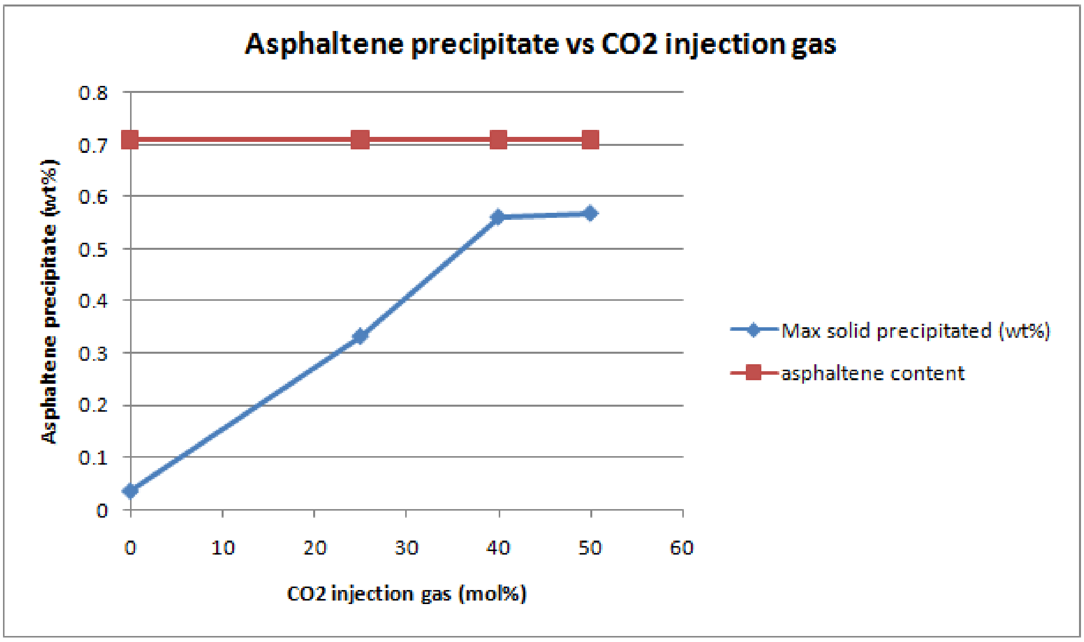


Figure 4-7 : Asphaltenes precipitate vs CO2 injection gas concentration

Figure 4-7 is showing that at original oil without injection gas, the precipitation has already occurred within the depressurization-testing pressure range. Increase concentration of the injection, gradually increase the amount of asphaltenes precipitated. The maximum of the precipitation occurred at the 50 mol% gas injection.

As shown in the Figure 4-7, the ratio of the precipitated asphaltenes over the total asphaltenes content is very high. This is due to the nature of this oil as a light oil. By having API gravity of 39 API, light oil as compared to the heavy oil, has a smaller portion of asphaltenes content and low content asphaltenes-resin ratio. Resins acts as the stabilizing agents for the asphaltenes in the crude oil. Resins is a good asphaltenes solvent in the crude oil, it stabilizes asphaltenes in micelles form in the oil (Kokal and Sayegh, 1995[2]; Sarma, 2003[14]; Akbarzadeh et al, 2007[16]; Alta'ee et al, 2010[17]). Less amount of resins provide instability of the asphaltenes in the crude oil, thus have a higher risk of asphaltenes depositions to occur.

For the case of heavy oil, the ratio of the precipitated asphaltenes over the total contents of asphaltenes is extremely small and almost none. This is because heavy oil contains higher amount of asphaltenes-resins ratio. This provides a great asphaltenes stability in the crude oil, thus the risk of having a problematic asphaltenes depositions very low and almost problems free as like happening in Venezuela, production of heavy oil is asphaltenes deposition problems free. Thus even though the light oil contains a smaller amount of asphaltenes, it has a higher risk of asphaltenes deposition problems during the production life of the reservoir.

CHAPTER 5

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusion

Simulations to study the behavior of the asphaltenes in the crude oil have been carried out, the results shown a different asphaltenes behavior as the concentration of the injection gas is increasing. Findings that can be concluded based from the results obtained are as follows

- Bubble point pressure is located in between the upper and lower AOP, the region between upper and lower is the asphaltenes precipitation region, increase the injection gas concentration, will increase the saturation pressure as well as upper and lower AOP.
- Increasing injection gas concentration will increase the amount of asphaltenes precipitates
- Increasing injection gas concentration will move the APE to the region of higher pressure and temperature
- The ratio of the asphaltenes precipitates over the total asphaltenes contents for this light oil sample is high, this show light oil has a higher risk of asphaltenes problems

The findings from the simulations are showing that gas injection is creating a compositional change of the crude oil. The simulation done is based from depressurization test range, to determine the AOP, thus the results is showing that compositional change and pressure change do have a very significant effect towards the asphaltenes stability in the crude oil. The higher the level of asphaltenes's instability, the higher the risk for the asphaltenes depositions.

5.2. Recommendations

The study of the oil sample for this research is from Arabian Gulf oil field, it is better to have a study of asphaltenes prediction for oil samples of Malaysia's oil field. An experimental data of the Malaysia's oil sample can be brought further to the analysis. This steps could help in having a better preparations as some of the Malaysia's oil field is going for WAG as one of the EOR method to increase the recovery until maximum.

Secondly, most of the results obtained is based from the regression and EOS equation performed by the simulation software. The simulation results is better to be compared to the experimental results such as Solid Detection System (SDS). Experimental measurement detailed data is recommended to gain more accurate input data for the simulation study.

Based from the experimental results and study, not a complete reversibility of asphaltenes precipitation can be obtained. As for the WinProp, it assumes a complete reversibility of asphaltenes deposition, where all of the precipitated solid re dissolve back into the solution. Hence, author would like to suggest that the portion of the solid that is not re dissolve back into the solution should be taken into the calculations.

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APPENDICES

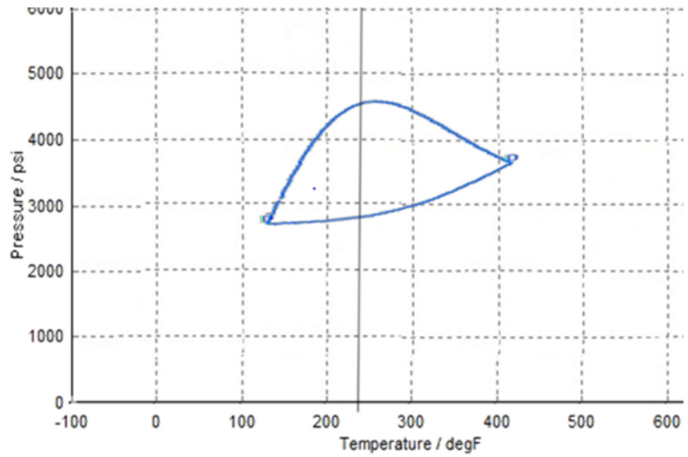
APPENDIX - A : Graph for 25 mol% CO_2 Injection Gas

APPENDIX - B : Graph for 40 mol% CO_2 Injection Gas

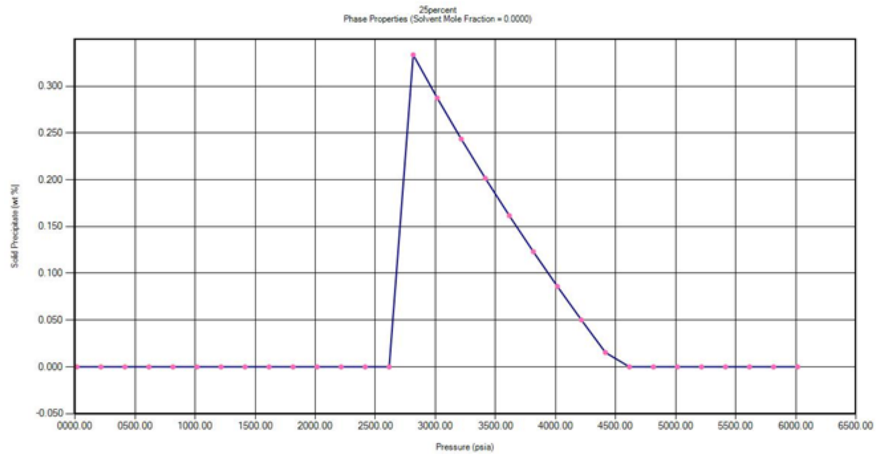
APPENDIX - C : Graph for 50 mol% CO_2 Injection Gas

APPENDIX - A

APE for 25 mol% CO_2

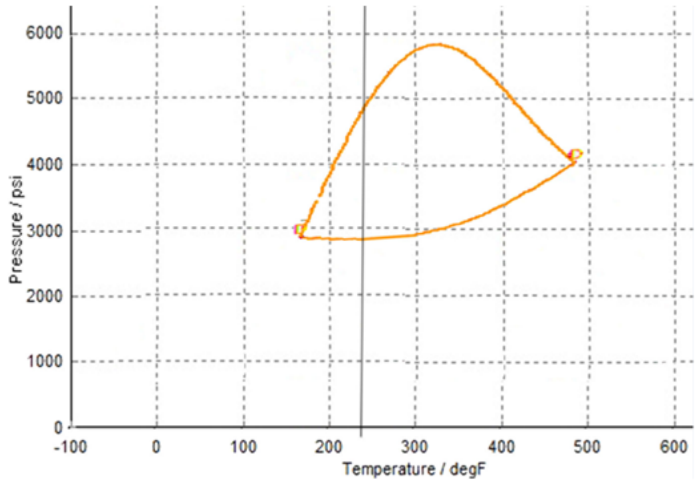


Solid Precipitate (wt%) vs Pressure (psia) of 25 mol% CO_2

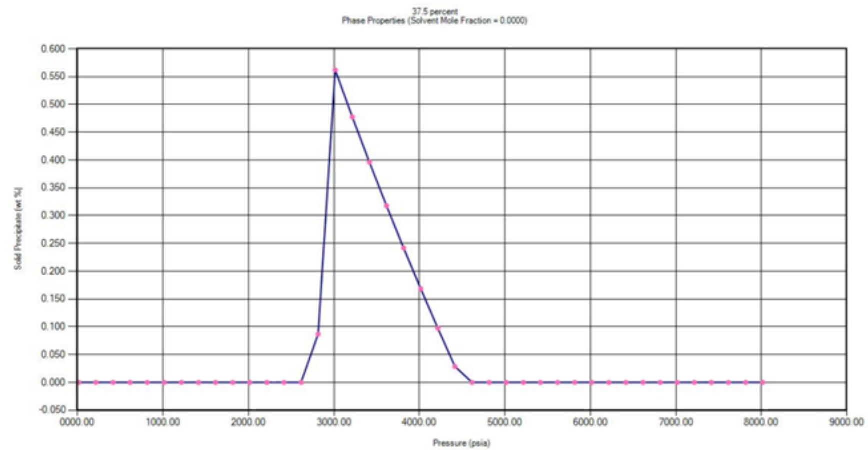


APPENDIX- B

APE for 40 mol% CO_2



Solid Precipitate (wt%) vs Pressure (psia) of 40 mol% CO_2



APE for 50 mol% CO2	Solid Precipitate (wt%) vs Pressure (psia) of 50 mol% CO2