INVESTIGATION ON ASPHALTENE PRECIPITATION DURING CARBON DIOXIDE FLOODING FOR OIL RECOVERY

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We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy of Science in Industrial Chemistry.

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I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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EDICATIO

This work is dedicated to:

Soul of my mother and to all my family,
who have been supporting me,
my supervisor,
who guided me to this day,
my friends,
who have always been on my side,

Thank you for everything

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In the name of Allah, the most gracious and merciful;

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ABSTRACT

Asphaltene precipitation is one of the serious problems during the secondary and tertiary oil recovery in light oil reservoirs using carbon dioxide injection. Asphaltene precipitation leads to significant problem in production system such as wellbore plugging, permeability reduction and porosity alteration. In this work, light crude oil was chosen to predict the effect of carbon dioxide injection and its interaction with oil. Saturate aromatic, resin and asphaltene (SARA) analysis was conducted to know the propensity of the light crude oil to precipitate. Later, the laboratory study was conducted to analyse the behaviour of asphaltene and carbon dioxide with different gas oil ratios (GOR). Different pressure volume temperature (PVT) experiments were conducted to know the asphaltene precipitation behaviour. The results from the PVT test showed that asphaltene precipitation was found significant at GOR 310 scf/st and the bubble point pressure of 2100 Psig. Dynamic core flooding study with various carbon dioxide concentrations and flow rates were conducted to measure asphaltene precipitation induced by carbon dioxide. Before running the core flooding, the minimum miscibility pressure was determined and it was found to be 1500 Psi. Three Berea sandstone cores were used as formation reservoir to determine the asphaltene precipitation and to study the effect of carbon dioxide injection. The parameters for three cores were kept constant at the pressure of 2000 Psi and temperature of 100°C while varying the injection flow rates. The three flow rates of 0.4 cc/min, 0.6 cc/min and 0.8 cc/min were set for three core flooding runs, i.e. Core 1, 2 and 3 respectively. As the pore volume of gas injected increased, there was a decreased in the asphaltene content in the recovered oil and thus the amount of asphaltene recovered in the core is increased. At pore volume 1.00 cc, the asphaltene precipitation from the dynamic core flooding tests for Core 1, 2 and 3 were found to be 0.13% wt, 0.18% wt, and 0.19% wt respectively. From the study, it was found that at higher pore volume of gas injected, it will lead to more asphaltene precipitation in the core and lesser amount of asphaltene inside the oil recovered. It can be concluded that high injection of pore volume fluid in the sample core can change the resin, asphaltene ratio and precipitate higher amount of asphaltene particles. The injection flow rate of 0.8 cc/min showed the highest amount of asphaltene precipitated in the core.

ABSTRAK

Asfaltena adalah pecahan pepejal minyak mentah yang boleh termendap di ruang liang takungan. Minyak mentah dengan kandungan asfaltena rendah mempunyai kemungkinan yang lebih tinggi menghadapi masalah pemendakan. Oleh itu, adalah penting untuk menjalankan kajian mengenai pemendakan asfaltena minyak mentah ringan yang disebabkan oleh suntikan CO_2 dan pengaruhnya ke atas sifat-sifat minyak. Dalam kajian ini, minyak mentah ringan telah dipilih untuk meramalkan kesan suntikan karbon dioksida dan interaksinya dengan minyak. Di peringkat awal, analisis SARA telah dijalankan untuk mengetahui kecenderungan minyak mentah ringan untuk termendak. Seterusnya, kajian makmal telah dijalankan untuk menganalisis kelakuan asfaltena dan karbon dioksida dengan nisbah gas minyak yang berbeza. Pelbagai eksperimen PVT telah dijalankan untuk mengetahui sifat-sifat mendakan asfaltena. Hasil keputusan daripada ujian PVT menunjukkan bahawa mendakan asfaltena didapati signifikan pada GOR 310 scf/st dan tekanan takat gelembung 2100 Psig. Kajian pembanjiran teras dinamik dengan berbagai kepekatan karbon dioksida dan kadar aliran yang berbeza telah dijalankan untuk mengukur mendakan asfaltena yang disebabkan oleh penusukan karbon dioksida. Sebelum menjalankan pembanjiran teras, nilai kebolehcampuran minimum yang ditentukan adalah 1500 Psi. Tiga batu pasir Berea digunakan sebagai pembentukan takungan untuk menentukan mendakan asfaltena dan untuk mengkaji kesan penusukan karbon dioksida. Parameter untuk ketiga-tiga teras banjir telah dimalarkan pada tekanan 2000 Psi dan pada suhu 100°C disamping mempelbagaikan kadar aliran suntikan. Tiga kadar aliran 0.4cc/min, 0.6 cc/min dan 0.8 cc/min telah digunakan pada tiga laluan pembanjiran teras, iaitu teras 1, 2 dan 3. Apabila isi padu liang gas yang disuntik ditingkatkan, terdapat penurunan dalam kandungan asfaltena dalam minyak pulih justeru menyebabkan jumlah asfaltena pulih dalam teras meningkat. Keputusan daripada ujian pembanjiran teras dinamik diperhatikan di teras 1, 2, 3 pada isipadu liang 1.00 mendapati mendakan asfaltena diperolehi masing-masing pada 0.13% wt, 0.18% wt, dan 0.19%. Eksperimen ini menunjukkan bahawa apabila lebih banyak isipadu liang disuntik dalam teras, semakin kurang asfaltena yang dipulihkan daripada alur keluar dan lebih asfaltena termendak di dalam sampel teras. Kesimpulannya, nilai isipadu suntikan cecair yang tinggi ke dalam teras boleh menjejaskan kestabilan dan memendakkan jumlah zarah asfaltena yang lebih tinggi. Kadar aliran suntikan pada 0.8 cc/min membuktikan jumlah tertinggi mendakan asfaltena di dalam teras.

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%	Percentage
EOR	Enhanced Oil Recovery
PVT	Pressure Volume Temperature
CO_2	Carbon dioxide
° C	Degree Celsius
N_2	Nitrogen
OOIP	Original Oil In Place
ASTM	American Society For Testing and material
GOR	Gas Oil Ratio
mol	Mole
D	Diameter
cm	Centimeter
SARA	Saturate,Aromatic,Resin,Asphaltene
Ø	Porosity
K_∞	Corrected Permeability for Klinkenberg Effect
CII	Colloidal Instability Index
M	Molar
g	Gram
S_{or}	Residual Oil Saturation
S_{wi}	Water Oil Saturation
Kair	Air Permeability
V_p	Pore volume
HPLC	High Pressure Liquid Chromatograph
SCF	Standard Cubic Feet
STB	Stock Tank Barrel
MMP	Minimum Miscibility pressure
cc/min	Cubic Centimeter Per Minute
L	Liter
m	Meter
min	Minutes
mL	Milliliter
mL/min	Milliliter per minute
v/v	Volume per volume
Wt%	Weight percentage
API	American Petroleum Institute
UV	Ultraviolet spectrometry
IR	Infrared
Soxhelt	Solvent semi-continuous extraction
et al	And others

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CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACK GROUND

In the life of reservoirs, there are always three (3) stages of oil field development, which are primary, secondary and tertiary recovery. For tertiary recovery, it is also known as Enhanced Oil Recovery (EOR). The demand for petroleum products are increasing continuously while worldwide petroleum productions are steadily declining. This has created a new technical development called Enhanced Oil Recovery (EOR). It is a collection of general methods, each of them having their own capability to extract most oil in the selected reservoirs where it has been investigated both from theoretical and laboratory perspective as well as in the field. Usually, the availability of this tertiary recovery process contributes to the increase in production when compared to the production by primary and secondary recovery. EOR is classified in two (2) types, which are thermal and non-thermal (Kokal and Sayegh, 1995).

In the primary recovery stage, the production of crude oil depends upon the energy from reservoir itself. The typical oil production using the primary drive mechanism is 20-40% of original oil in place (OOIP) (Hammer et al., 1983). The energy can be derived from drive mechanisms in the reservoir namely water drive, gas cap drive, gravity drive, compaction drive or solution gas drive. The drive mechanism can either be solely from single drive or a combination. After the reservoir pressure depleted and production of hydrocarbon decreased, secondary recovery takes place by placing injectors inside the reservoir to maintain its pressure and to squeeze out hydrocarbon from the reservoir. One of secondary recovery example is waterflooding. Prior to it, injector wells are drilled in a pattern to displace the remaining oil.

During waterflooding, water displaces the greatest at the bottommost and slightest at the topmost due to gravity segregation until water breakthrough. After water production had reached 80 percent of the total fluid production, the waterflooding stops and EOR will start.

Tertiary recovery is an essential stage in improving total production. Approximately, 40 percent of global average recovery factor for a typical oil field is from primary recovery until secondary recovery. The large amount of hydrocarbon left behind is the main driver behind EOR schemes that have been practiced around the world. Although the cost to cover EOR process is quite expensive, it can improve the production of crude oil up to 75 percent recovery. The main objective of EOR process is to change the properties of hydrocarbon such as surface tension, viscosities, and pH value which illuminate further the EOR process from secondary recovery method. There are three main types of EOR process, namely chemical flooding, gas injection and thermal recovery.

The rest of the crude oil is recovered using various techniques of enhanced oil recovery methods (Muhannad et al., 2012). Gas injection and thermal recovery techniques are the most popular and effective to produce the remaining oil. Recently, the use of non-hydrocarbon gases such as nitrogen (N_2) and carbon dioxide (CO_2) are becoming commonly applied to enhance the gas injection in EOR (Taber et al., 1997). Carbon dioxide flooding in particular, is the second most common enhanced oil recovery process, usually next to steam flooding which has resulted in significant recovery worldwide (Milind, 2002). In Malaysia, water alternating gas injection (WAG) has a greater attention for future enhanced oil recovery method. Carbon dioxide is used as an injection gas for water alternating gas process due to its high amount of availability and its well recognized solubility in oil.

Carbon dioxide (CO_2) injection is one of the efficacious Enhanced Oil Recovery (EOR) methods to improve oil recovery but it has the potential to cause asphaltene precipitation. As gas is injected into the reservoir, the miscibility of the carbon dioxide will disrupt asphaltene-resin ratio and cause asphaltene precipitation (Kokal and Sayegh, 1995). During water alternating gas injection process, the gas tends to contact with the oil and causes changes in the composition of reservoir fluid and its equilibrium. This sudden change in behaviour leads to asphaltene precipitation if the reservoir oil has unstable asphaltene content. The composition change means the injection of gas into reservoir either in miscible or immiscible state may lower the resin ratio or reduce the amount of the peptizing agent absorbed on asphaltene surface (Mohammed et al., 1998). When the resin ratio drops to a point where the absorbed amount was not enough to cover the asphaltene, the asphaltene particles will deposit. It is also reported that the increase of alkane carbon number decreases the amount of asphaltene precipitate (Chukwudeme and Hamouda, 2009).

Therefore, asphaltene precipitation and deposition are the most common problems in the carbon dioxide water alternating gas flooding method. Injection of gas should be treated as a separate subject for reservoirs having unstable asphaltene content (Kokal and Sayegh, 1995). Precipitation of asphaltene could plug near-wellbore formation and cause reduced recovery efficiency and formation damage. It may also precipitate at surface facilities especially in well tubing, well head and separator, which can cause high maintenance cost problem (Kokal and Sayegh, 1995).

1.2 PROBLEM STATEMENT

The problem of asphaltene precipitation during CO_2 injection in light oil reservoirs is one of the serious problems faced in the oil production. Low asphaltene content favours for higher possibility of having asphaltene precipitation problems thus it is relevant to conduct a study on the asphaltene precipitation of the light oil due to CO_2 injection and its influence on oil properties as researches have consistently showed that asphaltene precipitation always occur during CO_2 injection. The asphaltene precipitation can cause recovery reduction and problem in well inflow formation damage. Asphaltene can be removed via reservoir condition manipulation, mechanical cleaning or chemical cleaning. However, the cost of cleaning the asphaltene is very expensive that can affect the production process until it becomes economically ineffective (Kokal and Sayegh, 1995). Besides, the mechanism of asphaltene precipitation is the least understood and the most complex one too. This is because even minor changes in the reservoir properties or reservoir fluids such as temperature, pressure or composition may trigger asphaltene precipitation. It is important to understand the right conditions of asphaltene precipitation when the asphaltene content is low and it is also significant to identify the minimum conditions for GOR concentration of CO_2. The distance between the asphaltene particle and surrounding fluid is large and for that reason, the asphaltene precipitation typically occurred at lower asphaltene pressure. Furthermore, it is necessary to understand the rate of CO_2 that cause asphaltene precipitation. Researchers have work on asphaltene precipitation with high injection pressures, low flow rate and low gas oil ratio. Therefore in the present work, the research will be focusing on increasing the gas oil ratio other than having another approach that can be carried out to deal with asphaltene precipitation problem, which is to study the effect of pore volume and high flow rate conditions.

1.3 OBJECTIVES OF THE RESEARCH

There are three objectives of this research, which are:

1. To investigate the potential of asphaltene precipitation in stabilization of crude oil composition.
2. To investigate the effect of the pressure of CO_2 gas concentration on asphaltene precipitation of laboratory scale.
3. To optimize the process parameters of CO_2 injection on asphaltene precipitation in the cores

1.4 SCOPES OF THE RESEARCH

This study is based on the laboratory investigations of asphaltene precipitation under CO_2 injection. The research includes basic characterization of the crude oil, PVT experiments and the core flooding experiments. Asphaltene stability is evaluated in a number of ways. Saturated aromatic, resin and asphaltene (SARA) analysis and PVT experiments were done in this work. Furthermore, this work is focusing to predict the asphaltene onset pressure at which the asphaltene precipitation problem starts. PVT experiments were also conducted to measure the phase behaviour and asphaltene onset pressure. The core flood experiments were then conducted using Berea sandstone cores samples where three of it were used as formation representatives. A light crude oil sample with API and Asphaltene content were also used.

1.5 SIGNIFICANCE AND CONTRIBUTION OF THE RESEARCH

The findings in this research are significant in support to investigate asphaltene precipitation in terms of stabilization and minimization. Further findings will provide more data on the amount of asphaltene precipitation which is induced by CO_2 injection

1.6 LAYOUT OF THE THESIS

Chapter 1 describes the introductory information of the research problem addressed in this work. The chapter starts with the introduction of CO_2 flooding and its effect on asphaltene particles. Then, it further describes the problems caused by asphaltene precipitation and the scope of study is defined. Later, the objectives are set for the proposed study. Chapter 2 gives the basic background literature that is required to conduct this study. The chapter starts with the characterization and SARA analysis of crude oil. The chapter then discusses the PVT experiments and phase behaviour predictions. In the end, the core flooding experiments are discussed in details. Chapter 3 gives information about the laboratory procedures to conduct the experiments such as the information of the tools and equipment used in this study. The experimental methodology to conduct SARA analysis, PVT experiments, minimum miscibility pressure and core floods under CO_2 injection are described in this chapter. Chapter 4 gives the results for the experiments conducted for the experimental investigation of asphaltene precipitation. It starts with SARA analysis and also covers the onset pressure and constant composition test to predict the asphaltene behaviour in the reservoir. Finally, the effect of carbon dioxide on asphaltene particles is discussed in details. This chapter describes the conclusion based on the study conducted on asphaltene precipitation. Additionally, this chapter gives the recommendations for future study

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter covers comprehensive knowledge on each topic related to the project. The literature review starts with the discussion on Enhanced Oil Recovery (EOR), carbon dioxide injection and its implication on asphaltene precipitation, Saturated Aromatic, resin, asphaltene (SARA) analysis, phase behaviour and PVT experiments. This chapter also discusses on carbon dioxide injection induce in asphaltene precipitation.

2.2 ENHANCED OIL RECOVERY

In the last decades, there are many demands for energy all over the world and therefore, a great attention has been required for oil production. These demands increased continuously for petroleum products though worldwide oil productions are steadily decline. Petroleum reservoirs usually consist of three stages in the oil field, which are primary, secondary and tertiary techniques that are also called Enhanced Oil Recovery (EOR). EOR methods are illustrated below in figure 2.1.

Primary recovery techniques are mostly applied at first stage in production phase by using the reservoir natural forces to drive the oil to flow from the well up to the surface. Pumps are implemented to maintain the flow when the reservoir drive is declining. Primary recovery is completed once the pressure is too low, when the production rate is no more economical and the water-to-oil or gas-to-oil ratio is too high. The recovery oil at primary stage is only 5-25% of its original oil in place (OOIP) (Thomas 2008). Secondary recovery techniques are used once the primary method is no longer effective or economical. In this method, the typical water as fluid besides other gases and liquids can be employed. For this type of operations, recovery factor depends on reservoir and oil characteristics. The range of recovering is usually from 6-30 % of OOIP (Thomas 2008).

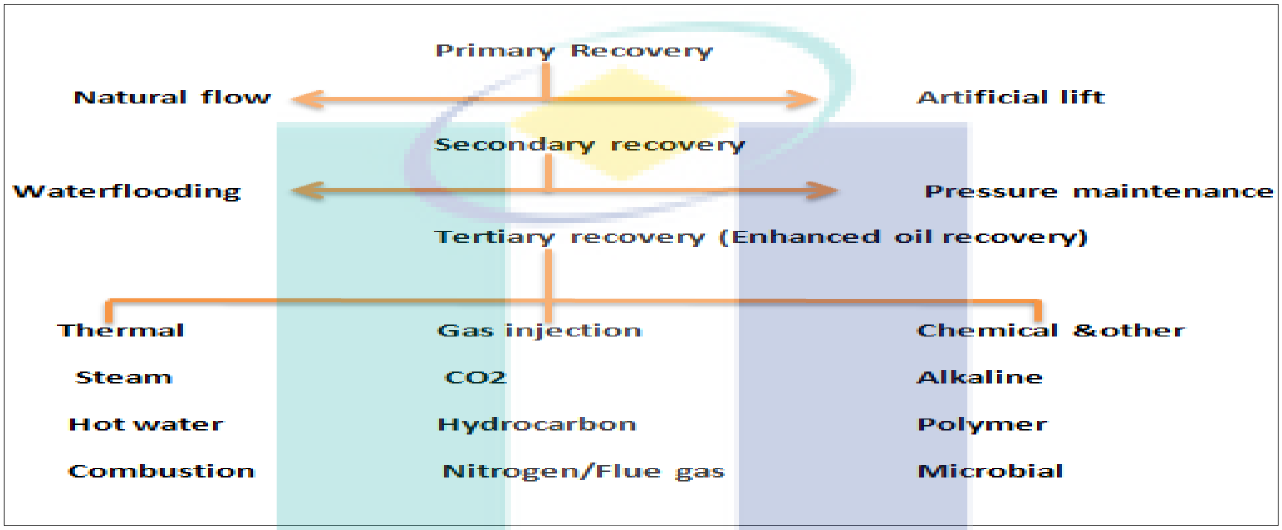


Figure 2.1: Oil recovery stages

Tertiary recovery technique is generally known as Enhanced Oil Recovery (EOR) and this technology is usually applied when the oil field comes to the end of their life and usage of this method may improve the oil flow capacity in reservoirs. However, it may be a suitable production for light or medium oil reservoir ranging from 45-60% of OOIP and one of the distinct methods is EOR with CO_2 injection (Thomas 2008). EOR processes are categorised in two types, namely thermal and non-thermal recovery. The thermal recovery is divided into hot water flooding, in-situ combustion and steam injection while the non-thermal technique consists of three sub categories namely waterflood, gas drive chemical flood and Microbial (AI-Anazi, 2007).

The EOR screening criteria is given in Table 2.1. The good criteria is based on CO_2 flooding where pore volume is greater than 20%, the formation is sandstone or carbonate and the injection pressure should be more than minimum miscibility pressure (MMP). The main purpose of EOR is to improve displacement of oil mobility by increasing viscosity for oil and water and reducing the interfacial tension between oil and water. Thermal recovery has the greatest attraction of success and being implemented at 70% of EOR all over the world. It showed high efficiency in recovering with low cost. However, in chemical recovery, the cost and technical problems have excluded them from mainstream application (Larry et al., 1992).

Table 2.1: Enhanced oil recovery screening criteria (Taber et al., 2005)

EOR	**Oil (saturation % pore volume)**	**Type of Formation**	**Permeability (mD)**	**Depth (m)**	**Temperature (^{o}C)**
Steam flooding	> 40	High porosity and permeability sandstone	> 200	< 1500	Not critical
In-situ combustion	> 50	Sandstone with high porosity	> 40	< 3833	> 60
Gel treatment polymer flooding	> 50	Sandstone preferred can also use for carbonate	> 40	< 3000	< 90
Alkali surfactant polymer, Alkali flooding	> 35	Sandstone preferred	> 40	< 3000	< 90
CO_2 flooding	> 20	Sandstone, carbonate	Not critical if sufficient injection rate can be maintained	Appropriate to allow injection pressure>than MMP, which increase with temperature	
Hydrocarbon	> 30	Sandstone, carbonate with minimum fractures	Critical if uniform	> 1333	Temperature can have significant effect on MMP
N_2,flue gas	> 40	Sandstone, carbonate with few fractures	Not critical	> 2000	Not critical

It is particularly important to note that EOR technique is more than challenging in offshore operation compared to onshore field (Bondar et al., 2005), which means it is necessary to finalize the study economically with high consideration of offshore environment (Thomas et al., 2010). The primary and secondary operations are left with two third of the oil in place in the reservoir and the only recovery is one third of the oil in place. This situation will put the life of a well in a high cost of production to prices paid for the barrel in the market. Because of that, about 70% of the oil is still left behind and become a reason for the well to be abandoned (Larry et al., 1992). Oil companies and authorities are having major concern for mature field as to increase the oil production from aging resources.

New discoveries in recent decades are steadily decline and the rate of replacement for the oil production reserves is substantially reduced. At present, most of the oil production comes from mature fields where the major concerns for oil companies and authorities are to increase the rate of oil recovery from the aging resources. It is also steadily decline over the rate of replacement for the produced reserves with the rate of new discoveries. This is where EOR is supposed to be effectively implemented in order to increase recovery factor in mature fields (Alvarado, 2010). Schlumberger Oilfield Glossary (2010) reported that Enhanced Oil Recovery (EOR) is a technology to enhance oil recovery using sophisticated technique, which is by altering the original oil properties. It is ranked to be the third stage and was carried out after the secondary recovery. Moreover, EOR benefits are not only to restore formation pressure but also to increase fluid flow and oil efficiency displacement in the mature reservoir.

2.3 CARBON DIOXIDE FLOODING

Since 1952, CO_2 has been used for oil recovery and can also be used for both miscible displacement (Stalkup, 1978) and immiscible displacement (Kumar and Von Gonten, 1973) besides maintenance of reservoir pressure (Holm and Josendal, 1974), well stimulation (Stright et al., 1977), and etc. The purity of CO_2 at more than 95% of the overall composition would give advantage to release oil from rock surface by providing easy swelling and lighter condition. To make miscibility of CO_2 is achieved, it should be put under particular conditions and these combined terms are oil chemical composition, injected gas composition, reservoir pressure and reservoir temperature (Melzer and Midland. 2012).

Carbon dioxide is a non-flammable gas and relatively non-toxic (Mohamed, 2009). It has a pressure of 7.3 MPa and temperature of 30.9 $^{\circ}$C respectively with its triple point is at -56.558 $^{\circ}$C and 517.15 MPa (Span & Wagner, 1994). Figure 2.2 illustrates the pressure-temperature property of carbon dioxide. It is obvious that carbon dioxide would exist in different phases depending on its pressure and temperature conditions.

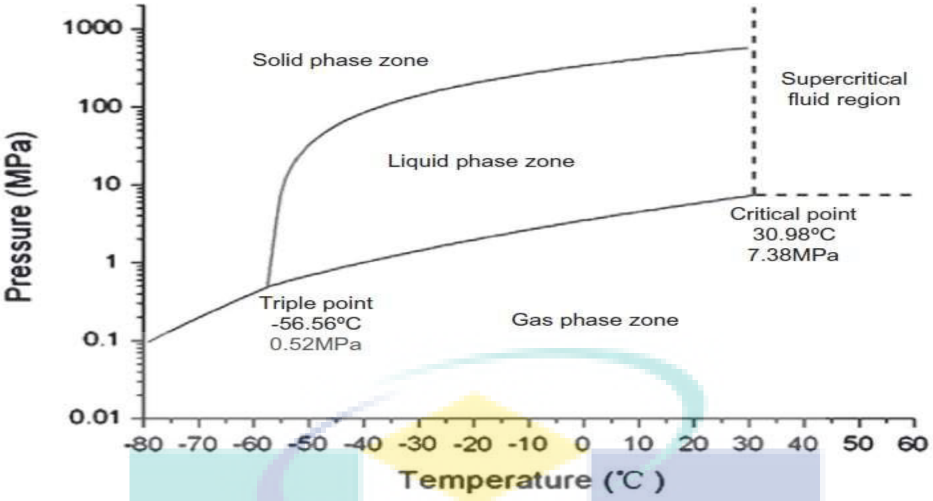


Figure 2.2: Pure carbon dioxide phase diagram (Zhang et al., 2012)

Gas flooding is one of the oldest methods used for the application of EOR (David and Taber, 1992) and it is widely used in light, condensate and volatile reservoirs (Alvarado et al 2010). There are two major types of gas injection, which are miscible and immiscible. The miscible injection mechanism process occurs when the reservoir fluid and gas are having a homogenous phase with new physicochemical properties are formed. The act of continuous injection for the gas will make the oil flow through the miscible front towards the production well (Lindley, 2011). After the injection of CO_2 in a particular reservoir, it will create a permanent storage of CO_2 in geological formation, and about 80 projects of CO_2 in the world are located at onshore operations (Gozalpour, 2005). Practically in US, carbon dioxide is the fastest growing method of EOR for gas flooding.

Since 1970s, the CO_2 process has been used to compute commercial techniques for enhanced oil recovery. Furthermore, 80% of oil reservoirs over the world are favourable for CO_2 injection depending on the criteria for oil recovery. The main reservoir formations in order to apply CO_2 process are carbonate and sandstone formations with different porosity, thickness and permeability of hydrocarbon (Sangeetha and Pasala, 2010). David and Taber (1992) described that the methods involved for gas flooding are both miscible and immiscible, but more favourable mechanism is miscible flooding because it may recover more production capacity for residual oil rather than immiscible process. The highest solubility between oil and CO_2 usually creates low interfacial tension between the two phases. Carbon dioxide can create ease of flow with crude, which increases oil production.

Khanifar et al., (2011) has reported that during the primary and secondary oil recovery, the Gas Oil Ratio (GOR) and water cut are increasing and then the oil production will decline and it may raise by time the demands of implementing EOR techniques. Some light oil fields that have oil with low asphaltene content, is induced to have the possibility of asphaltene deposition. Carbon dioxide flooding is the most popular and productive method in EOR but it may lead to asphaltene precipitation problem. In the recent study by Harvey et al,.(1980); Abdassah, ; Siregar. and Kristan (2000), carbon dioxide flooding has been known widely as the mosteffective enhanced oil recovery methods in the oil field and it becomes the real option to obtain high recovery. EOR technique can increase oil recovery by increasing oil swelling and lowering in oil viscosity

Studies conducted by Okwen, (2006); Kokal and Sayegh, (1995); Hammami et al., (2000); Sima et al., (2011); Ghedan, (2009); and Srivastava et al., (1997) stated that CO_2 flooding can increase the oil recovery, yet it may create asphaltene precipitation and deposition problems which lead to plug the wellbore, formation damage, recovery reduction and suffer in the oil production system at high concentration level. CO_2 flooding either miscible or immiscible is usable in both techniques, namely secondary and tertiary. CO_2 miscible increases the oil production by reducing viscosity and oil swelling through gas drive (Sima et al., 2011; Ghedan, 2009; Srivastava et al., 1999; Al-Qasim, 2011). However, CO_2 gas miscibility with oil will due to change in reservoir compositions, resin asphaltene ratio and causes asphaltenes precipitation (Ghedan, 2009; Kokal and Sayegh, 1995).

2.4 MISCIBLE FLOODING

Miscible flooding is considered when miscible gases are injected into the reservoir. Once the gases are injected, it will reduce *interfacial tension* between oil and gas injected and also maintain the reservoir pressure that lead to develop the recovery (Schlumberger Limited, 2013). To achieve the same miscibility, many miscible gasses might be injected to reservoir, thus, selection of gas should consider the availability and cost issues. Currently, few gases are being used such as propane, methane, other light hydrocarbon, carbon dioxide and nitrogen. However, carbon dioxide remained as the gas used for miscibility flooding because of its costs and its ability to reduce the oil viscosity compared to liquefied petroleum gas (LPG) (Schlumberger, 2013).

Green and Willhite, (1998) reported that miscible process as being illustrated in Figure 2.3 showed an achievement in multiple contact miscible (MCM). Pure CO_2 is injected to displace residual oil and mobilization. During multiple contacts of miscibility between CO_2 and crude oil, intermediate and higher molecular weight hydrocarbons are extracted into the CO_2-rich phase. In certain condition where CO_2 is in rich phase, it will react with the composition, which is miscible with oil reservoir. Starting from this point, the near miscible or miscible at the displacing front interface will exist.

This miscibility condition rapidly reaches its ideal condition in the reservoir. Throughout the CO_2 injection, the CO_2 miscibility will take part to change oil compositions of the crude oil likewise the resin asphaltene ratio, which is convenient for asphaltene precipitation. When CO_2 reacts with oil, it tends to displace oil and cause non-stability and displaced in the first stage. This action of non-stability will lead to initial abrupt displacement, which due to promote "fingers" and obtain early breakthrough that is undesirable during the early stage (Green & Willhite, 1998).

The initial distance of the established multiple contacts compared with the distance between wells is commonly negligible. During the injection process, CO_2 volumes are normally about 25% of the pore volume. The CO_2 critical temperature is 78.7 ° F and therefore injection is mostly performed to the fluid above its critical temperature. At injection condition, the viscosity of CO_2 is small, which is about 0.06 to 0.10 cp, depending on its pressure and temperature of reservoir (Green and Willhite 1998).

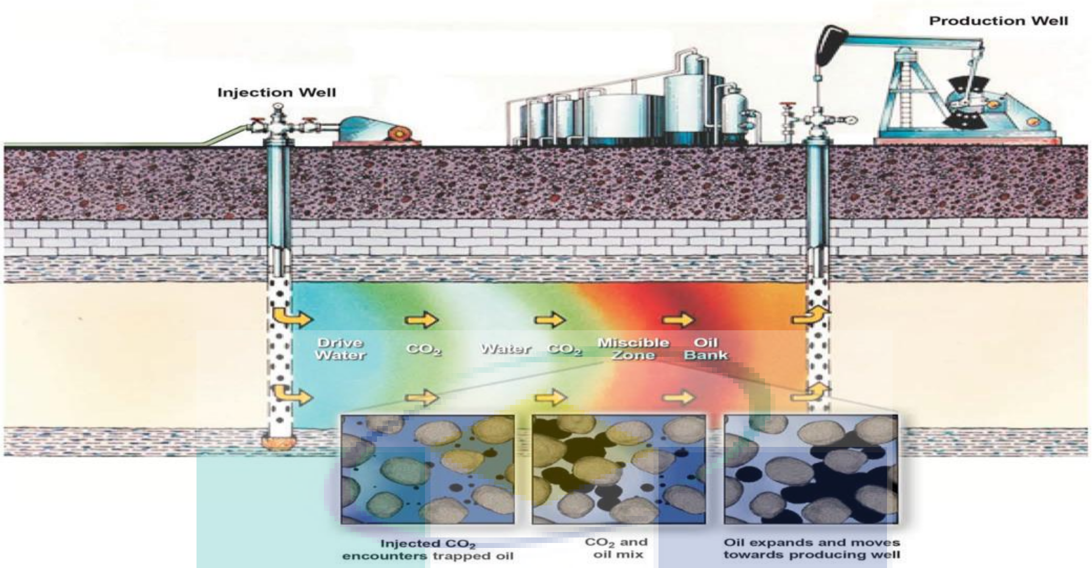


Figure 2.3: Carbon dioxide miscible process (Green and Willhite, 1998)

2.4.1 Effect of Carbon Dioxide Concentration on Asphaltene Precipitation

Asphaltene particles when it exist in crude oil can be destabilize due to various mechanisms. One of the mechanisms is injection of carbon dioxide in the reservoir. Moghadasi *et al*. (2006) had conducted an experimental study to investigate the influence of carbon dioxide injection on asphaltene precipitation. The asphaltene in the said experimental study was only 0.59% wt, which was considered quite low. The minimum pressure for carbon dioxide with the oil was 5300 Psig. The study indicated that the asphaltene started to precipitate at as low as 0.54 mole percent of carbon dioxide concentration. The asphaltene precipitation was highest at the bubble point. It was concluded that asphaltene precipitation is dependent on carbon dioxide gas concentration and rapidly increase from one critical value.

Another study was conducted by Yang et al., (2006), which indicated that the increasing injection of carbon dioxide also lead to an increase in precipitated asphaltene mass percent. With 10 mole percent carbon dioxide injection, the maximum asphaltene precipitation observed was 0.23 mass percent, while with 30 mole percent carbon dioxide injection, the maximum amount was 0.44 mass percent. With 50 mole percent carbon dioxide injection, the maximum amount is

0.52 mass percent and, with 60 mole percent carbon dioxide injection, the maximum asphaltene precipitation is 0.67 mass percent.

In 1999, Srivastava *et al*. had conducted a study on the asphaltene precipitation and it was observed that asphaltene precipitation at 42 mole percent of carbon dioxide concentration displayed a linear increase in asphaltene flocculation with carbon dioxide concentration after that. In many reservoirs, the miscibility of carbon dioxide with the oil is oscillatory. When the injected carbon dioxide and reservoir oil are mixed in any ratio from a single phase, they are said to be first contact miscible while due to the high pressure and temperature conditions requirement, the carbon dioxide is not always miscible in the reservoir. Carbon dioxide is greatly soluble in oil with lesser extent in water. To improve the efficiency in oil recovery, carbon dioxide can eliminate the interfacial tension and capillary forces. Under specific pressure and temperature conditions, and specific oil compositions, carbon dioxide can develop miscibility through multiple contacts (Parra-Ramirez et al., 2001).

Parra-Ramirez et al. (2001) had conducted an experimental study and the produced result is showed in Figure 2.4. They evaluated the effect of first contact and multiple contact miscibility. It was determined that most asphaltene precipitation on first-contact miscibility is negligible while at multiple contact miscibility, the amount of asphaltene precipitation was 3 to 5 times higher than the first contact miscibility. Oil sample growth changes in oil composition after the increase of contact with CO_2 concentration. The result of these changes will create instability in structures of micelles for resins and asphaltene fractions and the oil composition change gives instability in resins-asphaltene phases which lead to precipitation to occur (Dehghani et al, 2008). Report on studies by Chukwudeme and Hamouda, (2009); Al-Qasim, (2011); Alta'ee et al., (2010); and Khosravi et al., (2009) using light oil is to predicate asphaltene precipitation by means of static, dynamic test at constant pressure, temperature and effect of CO_2 concentration. From their studies, it is found that asphaltene precipitation were observed at high amount of injected CO_2 concentration, and increased rapidly near the bubble point pressure. Their suggestions for high oil recovery were obtained if CO_2 gas concentration is below the critical contact point of CO_2.

Based on experimental results conducted by Sima et al. (2011) on the effect of CO_2 injection on asphaltene precipitation, the injection of CO_2 into the core changed the oil composition by altering the resin asphaltene ratio of the residual oil. The asphaltene started to precipitate at 0.43 pore volume. Furthermore, the content of asphaltene increased from 0.11 wt% to 0.31 wt% till the end of the flooding operation. At low asphaltene pressure, the distance between the surrounding fluid and asphaltene particle is large and hence more precipitation occurred. It also indicated that asphaltene precipitation was 0.23 wt% at 1.26 pore volume of 2300 psi. However, at 2600 psi, the asphaltene precipitation was 0.19 wt% at 1.27 pore volume (Sima et al., 2011).

In the experimental studies presented by Alta'ee et al., (2012) to investigate the effect of CO_2 injection on asphaltene precipitation, it had indicated that the asphaltene precipitation at pore volume 0.33 was 0.024 wt%. Then, once the CO_2 reached 0.66 pore volume, the precipitated asphaltene was 0.056 wt%. Finally, the asphaltene precipitation had reached to a final value of 0.078 wt% at 1.66 pore volume. Other researchers like Kokal and Sayegh (1995); Sarma, (2003) and Srivastava and Huang, (1997) have stated in their studies that by increasing the CO_2 concentration contacted with the oil sample during the injection will lead to high asphaltene precipitation. The injection of CO_2 is the reason to changes in fluid behaviour and equilibrium conditions, which drive to asphaltene precipitation.

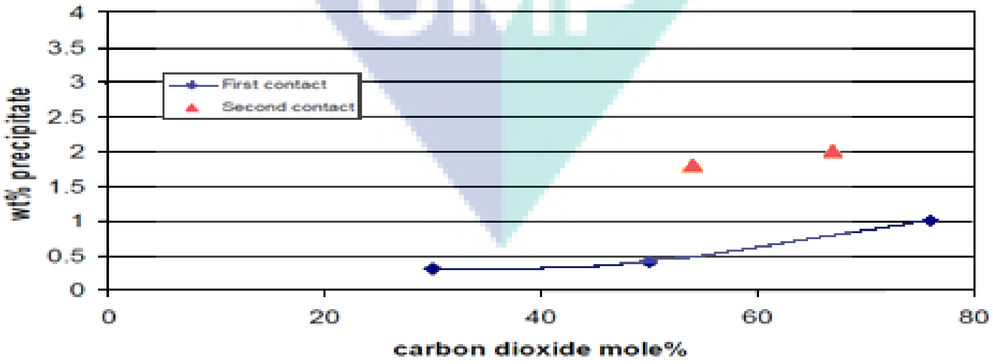


Figure 2.4: Comparison on the amount of carbon dioxide induced precipitation with the first and multiple contacts (Parra-Ramirez et al., 2001)

2.4.2 Minimum Miscibility Pressure

The minimum miscibility pressure (MMP) is the lowest pressure that can achieve miscibility through a multi contact between carbon dioxide and crude oil. A number of experimental methods to measure MMP are classified as rising-bubble apparatus (RBA) and slim-tube method vanishing interfacial tension (VIT) technique (Nobakht *et al.*, 2008). The slim-tube method is commonly applied as a standard technique in petroleum industry for measuring MMP between a crude oil and CO_2 especially when the density difference between the injected solvent and the crude oil is small (Stalkup Jr.F.I, 1983., Elsharkawy et al, 1992).

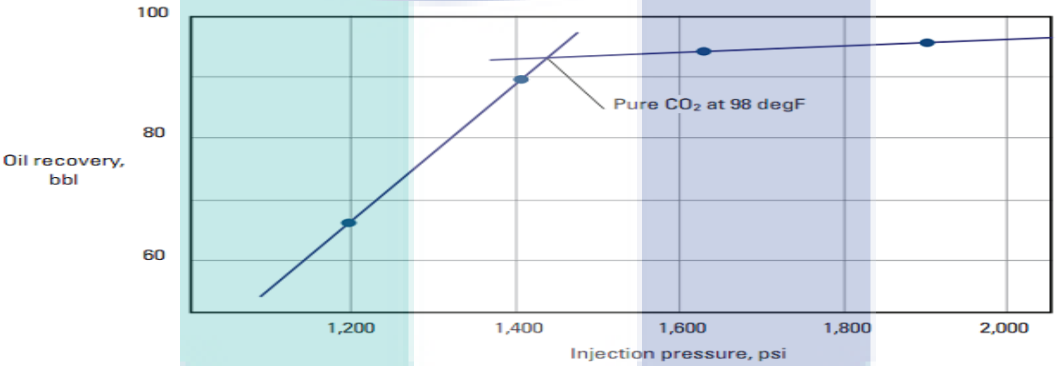


Figure 2.5: Determining MMP using slim-tube test (Green and Willhite, 1998)

Nevertheless, to obtain MMP displacement test conducted at different pressure, the rest of parameters such as injection rate and temperature are kept constant, as presented in Figure 2.5. The figure indicated oil recoveries as a function of displacement test. The MMP is assumed to be the pressure, which resulted between breaking the two lines

2.5 ASPHALTENE PRECIPITATION

Asphaltene stands for the solid fraction of crude oil, which normally soluble in toluene and insoluble in n-heptane or n-hexane. Asphaltene term is credited to a French scientist named Boussingault, who in 1837 had expressed the constituents of ashalts in that period in Eastern France and in Peru (Mansoori, 2005). Schumberger Oil Field defined asphaltene as a material that is insoluble in the n-pentane or n-heptanes at the dilution ratio of forty parts alkanes to one part crude oil and resolves in toluene. However, asphaltene particles are not well understood until today; therefore it is defined in the solubility class as asphaltene deposition and precipitation as shown in Figure 2.6.

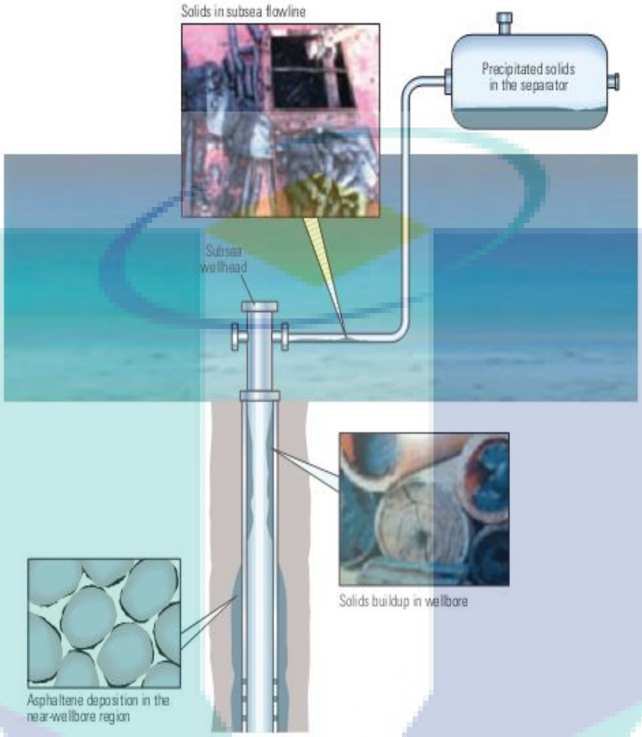


Figure Error! No text of specified style in document.**.6:** Asphaltene precipitation and deposition (Schumberger, 2007)

The asphaltene fraction is complicated because it consists of thousands of species which may exhibit similar solubility behaviour but different chemical structure size and shape. The elemental composition of the asphaltene particle was reported by Andersen et al. (2001). Figure 2.7 indicated some examples of asphaltene content all over the world such as from Boscan field in Venezuela with 17 wt% asphaltene was observed without asphaltene problem but Hassi-Masoud in Algeria is facing asphaltene problem though only 0.15wt% asphaltene was observed (Khanifar et al., 2011; Sima et al., 2011; Alta’ee et al., 2010; Cassani et al., 1992 and Chang, et al.,1996).

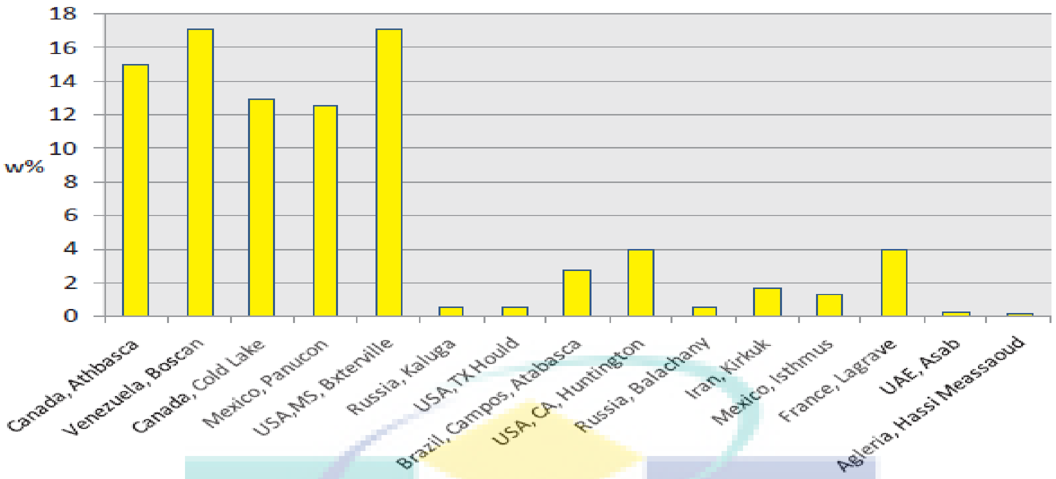


Figure 2.7: Asphaltene content in worldwide oil field (Ferworn, 1995)

Asphaltene particles can be deposited in the reservoir pore space, which can clog the porous matrix that leads to formation damage. Asphaltene deposits in the reservoir pore space may resulted in the reversal of the rock wettability to oil wet, which will lead to lower recovery factor. Unstable asphaltene poses a great threat to reservoir and production system. It can damage the reservoir by causing the wettability alterations and plugging of pore spaces. Asphaltene particles can aggregate in the wells and pipelines causing threat to flow assurance and reduce the capacity of oil production (Negahban, et al., 2003). Asphaltene precipitation process can be affected by sudden change in composition, pressure drop, asphaltene to resin ratio, temperature and PH concentration (Pereira et al., 2007).

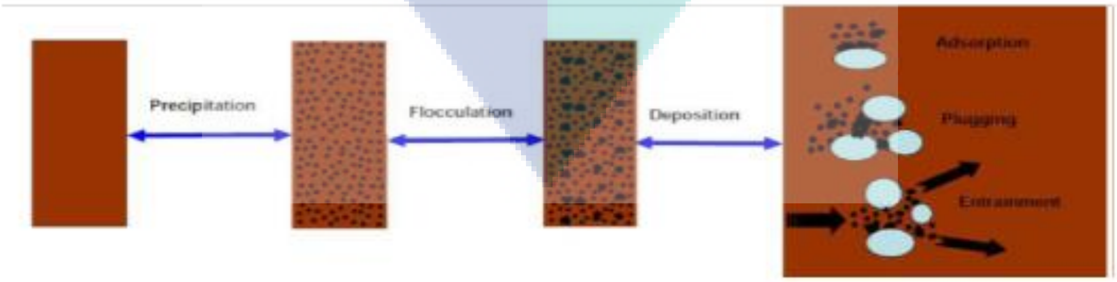


Figure Error! No text of specified style in document.**.8:** Asphaltene precipitation problem (Thawer., et al., 1990)

Asphaltene precipitation and deposition consist of a three step process. Initially, asphaltene particles are well dispersed in the crude oil. In the first step as shown in Figure 2.8, due to sudden composition or pressure change, the asphaltene particles started to aggregate forming the larger particles called floculates. These floculates as ilussteried in Figure 2.9 are then transported and can be deposited in the rock or well and pipelines. It is important to note that a sudden change in composition and pressure drop will be the main causes of asphaltene precipitation problem (Pereira et al., 2007). The asphaltene is a complex solid fraction corresponding to the solubility class rather than chemical behaviour. It is precipitated in the laboratory by the addition of liquid paraffinic hydrocarbon such as n-heptane and n-hexane. It is normally defined as a solid fraction that is insoluble in n-pentane or n-heptane at a dilution ratio of forty parts of alkane to one part of crude oil (Pereira et al 2007). Asphaltene extraction method from crude oil has been documented. The standard ASTM procedure to extract the asphaltene particle is D-3279, 1997ASTM if it is extracted using n-pentane in the laboratory.

Figure 2.9: Appearance of asphaltene fraction (Thawer.et al., 1990)

2.6 ASPHALTENE BASEIC CHARACTERISTICS

Figure 2.10 shows the illustration of resin and asphaltene in crude oil and therefore, many researchers have found that under reservoir conditions, asphaltene to resin ratio plays an important role (Miftachul, 2010). There is a chance in the resin to asphaltene ratio that can lead to unwanted phenomena called asphaltene precipitation and deposition. The ratio can be destabilized mainly by the change in crude oil compositional chances or pressure chances (Andersen et al., 2001). When gas is added in the reservoir or paraffinic solvents, the composition will change. This could happen during conventional field operations or during the application of any enhanced oil recovery methods. For example, the stimulation of acidizing jobs which involve the use of lighter hydrocarbons or gases (Andersen et al., 2001). In the heavy oil, the addition of gas will lower its viscosity, which causes asphaltene precipitation (Escobedo et al., 1995, Leontaritis, 1998).

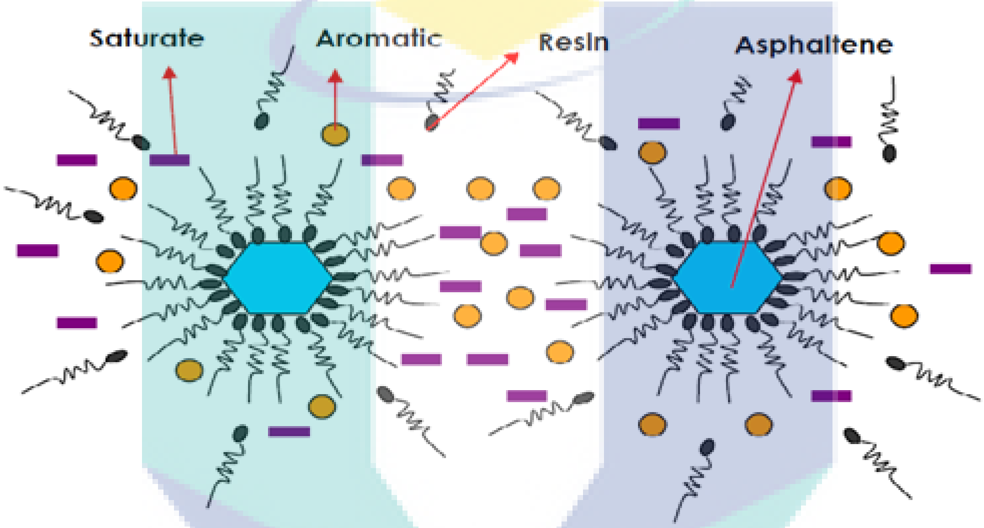


Figure 2.10: Resin and asphaltene in crude oil (Miftachul, 2010)

Pressure reduction can also destabilize the asphaltene particles. As the pressure reduces, the dissolved gas comes out of oil and hence the composition changes. This is very crucial if the reservoir is at under saturated conditions that have high concentration of light paraffinic compounds and high concentration of gas. When the pressure decreases, the gas comes out of solution and gets heavier and liquid components come closer that consequently causes asphaltene precipitation. The point at which the pressure starts to precipitate is called as asphaltene onset pressure (Negahban et al., 2003). Many researchers have concluded that asphaltene precipitation is more severe near the bubble point. After the bubble point, lighter components are separated and become a better solvent and asphaltene tends to be dispersed in that situation (Jamaluddin et al., 2001). On overall, it is concluded that pressure and composition played important role in asphaltene precipitation while temperature has only minor effect (Mullins et al., 2007).

It is observed that asphaltene precipitation and deposition are two different mechanisms. Precipitation occurred when nano particles come out of solution and form a separate distinguished phase and when these particles formed a separate phase sticking the surface, it is called the asphaltene deposition**.** The precipitation leads to deposition yet not all do the same but it can be said that deposition is affected by precipitation. These particles when deposited on the rock pore space can plug the pore throat and can cause formation damage.

2.7 SATURATED, AROMATICS, RESINES AND ASPHALTENE (SARA)

As indicated in Figure 2.11, crude oil composition can be classified based on SARA term, which stands for Saturates, Aromatics, Resins and Asphaltene (Fan et al., 2002). The SARA fractions are used widely to predict the asphaltene colloidal stability. The term saturates stands for non-polar material including linear and branched hydrocarbon. Aromatics are polarizable since they contain one or more rings. The remaining fraction of resin and asphaltene has polar constituents and their ratio plays an important role in asphaltene stability. The difference between asphaltene and resin fraction is that asphaltene is insoluble in n-petane or heptanes while resins are soluble. To conduct SARA analysis, the asphaltene part is first extracted using the addition of n-hexane with 1 gram of oil to 40 ml of hexane ration. Saturates, aromatics and resins later can be extracted through standard method using high pressure liquid chromatography from the de-asphalted oil (ASTM D6560 (IP 143/01, 2000). There are two ways to measure asphaltene stability and the most common method is using colloidal instability index, which can be measured using the following formulae (Bennet et al., 2006).

$$\mathrm{CII} = \frac{\mathrm{Asphaltene+saturates}}{\mathrm{Aromatics+Resins}} \qquad (2.1)$$

Index of 0.9 or more indicates that the particles are unstable while values below 0.7 indicate the stability of asphaltene particle. The mid value in between 0.7 to 0.9 suggests the uncertainty of asphaltene destabilization.

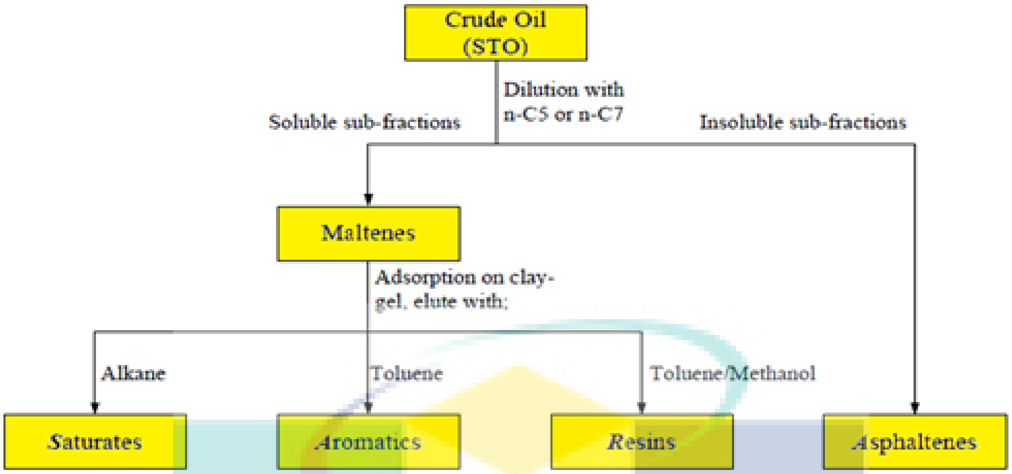


Figure 2.11: Crude oil solubility classification into SARA frication (Taher et al., 2002)

2.7.1 Asphaltene Stability Evaluation

Based on the field experiences by Cassani et al., (1992) and Chang et al., (1996), it is concluded that the asphaltene problem is severe in light crude oils than heavy crude oil. The heavy oil has more tendencies to dissolve asphaltene particles. The asphaltene de-stability is independent in the amount of asphaltene content. For example, the Venezuelan Boscan crude with 17.2wt% asphaltene was produced with nearly no trouble while Hassi Messaoud in Algeria has numerous production problems with as low as 0.15 weight percent (Cassani et al., 1992). In fact, the most common used method to evaluate the colloidal stability is SARA analysis or PVT analysis of the reservoir fluid. The PVT equipment with solid detection system is used in the laboratory. However, the quicker way to predict asphaltene precipitation is by using SARA analysis. The evaluation method started with the work of Jewel et al (1972) and is recognized as the proven evaluation methods (Fan et al., 2002). According to Jewel, each of the fractions in SARA analysis play roles in the asphaltene stability.

2.7.2 Asphaltene Onset Pressure

In the reservoir, when the pressure or composition of asphaltene particle started to precipitate, the critical point at which asphaltene starts to precipitate and loses its stability is termed asphaltene onset pressure (Negahban et al., 2003). It is very important to determine the onset conditions of asphaltene precipitation before carbon dioxide injection. Several methods have been reported that can identify the onset asphaltene pressure including measurement of electrical conductivity, oil viscosity, light transmission, interfacial tension, and the visual method (Reichert et al., 1986; Fotland et al., 1993; Fuhr et al., 1991; Burke et al., 1990 and Buckley, 1996). The most common method to obtain asphaltene onset pressure in the laboratory is using PVT equipment with the solid detection system at reservoir pressure and temperature. However, for easier way and in atmospheric conditions, the titration technique is used.

Experiments have been conducted by Muhammad et al. (2013) for different gas oil ratio (GOR) used in light crude oil located at offshore field in Malaysia. Asphaltene content found was only 0.3 wt%. The isothermal depressurization test using solid detection system was used with 40% and 60% addition of gas. Results showed that the increase in gas concentration in the reservoir has made asphaltene to be unstable. Asphaltene precipitation was observed at 1600 Psi and 100 ^{o}C for 40% increment of gas. When gas oil ratio is increased to 60% at 100 ^{o}C, the pressure was at 2250 Psi. In this technique, the solvent and oil are mixed and stirred. Later, optical microscope is used to check the asphaltene precipitation. The amount of solvent required is then noted. Solid detection system is based on light scattering technique and it is also the standard method used by the industry. Solid detection system is a special equipment designed for the industry for asphaltene measurement. (Idem et al., 2002).

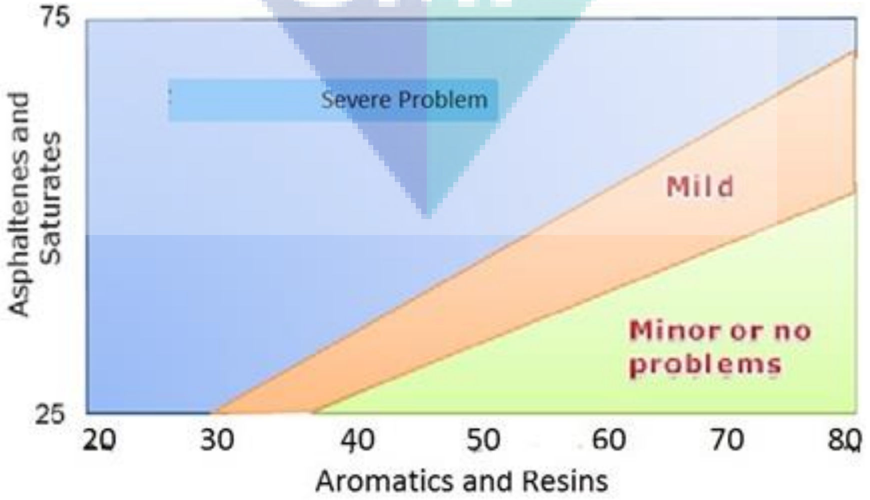


Figure Error! No text of specified style in document.**.12:** Stability index (De Boer et al., 1995)

Figure 2.12 shows the stability index chart. This chart displays the relationship of asphaltene and saturates versus aromatics and resins. It is divided into three regions: severe problem, mild and minor or no problems. The method is only a preliminary analysis. It is recommended that the laboratory investigations should be carried out to predict the asphaltene precipitation.

2.8 PREDICTION OF ASPHALTENE PRCIPITATION BEHAVIOUR

When one inject carbon dioxide in the reservoir, the changes in the composition are dynamic and are difficult to simulate in the laboratory at every point. However, static experiment with the fixed carbon dioxide concentration can be done in the laboratory environment using PVT equipment (Yarranton et al 2007). Asphaltene onset pressure, which is described as the critical point at which the asphaltene starts to precipitate is the most important factor in understanding the asphaltene behaviour. To predict asphaltene stability, phase behaviour and reliable model are required (Yarranton et al 2007). Solid detection system along with PVT equipment is used to measure asphaltene onset pressure. The study will measure asphaltene precipitation induced by carbon dioxide concentration and pressure changes. Different concentrations of reservoir fluid and carbon dioxide should be evaluated in the lab since the conditions in reservoir are quite dynamic. However, such laboratory experiments would only provide the static behaviour (Yarranton et al 2007: Muhammad Ali Buriro et al 2013).

When carbon dioxide with its miscibility is injected in the reservoir, the gas is mixed with the reservoir fluid causing composition changes. The lighter component mixed with the gas ultimately will change the composition of the reservoir fluid (Yarranton et al 2007). The reservoir can also be divided into three regions, namely early time late time. Once the gas is injected into the reservoir, it contacts the early region of it. Some of the gas is left behind and some of the gas is mixed with the middle region fluid. When another stream of gas is injected, it again contacted the fluid and the previous remaining gas in early time region and therefore, increasing the concentration of gas in that region. This process is known as “Vaporizing Gas Drive” mechanism (hereafter addressed as “VGD”), which is shown in Figure 2.13 (Hideharu Yonibayashi et al., 2011). The experiments in the laboratory can only simulate the static behaviour of fluid and injection. Hence, more dynamic experiments should be performed in the laboratory to simulate the reservoir conditions (Hideharu Yonibayashi et al., 2011). The correct equation of state is also important to predict asphaltene precipitation, which can account for its behaviour. Various thermodynamic models are available in the literature to predict the phase behaviour along with asphaltene particles.

Recently, some models have proposed the associated terms to predict the asphaltene phase behaviour. Cubic plus associated is the reliable equation of state that can be used to account for asphaltene phase behaviour (Yarranton et al., 2007). Cubic plus associated equation of state is composed of two parts: Physical part which is Soave Redlich Kowang equation of state and the association part, which is based on first order Wrtheim theory. The specific site–site interact-tions due to hydrogen bonding between like molecules (self-asso-ciation) and unlike molecules (cross-association or solvation) are considered in the association term. The activity of each bonding site is also assumed as independent of the other bonding sites on the same molecule (Yarranton et al., 2007).

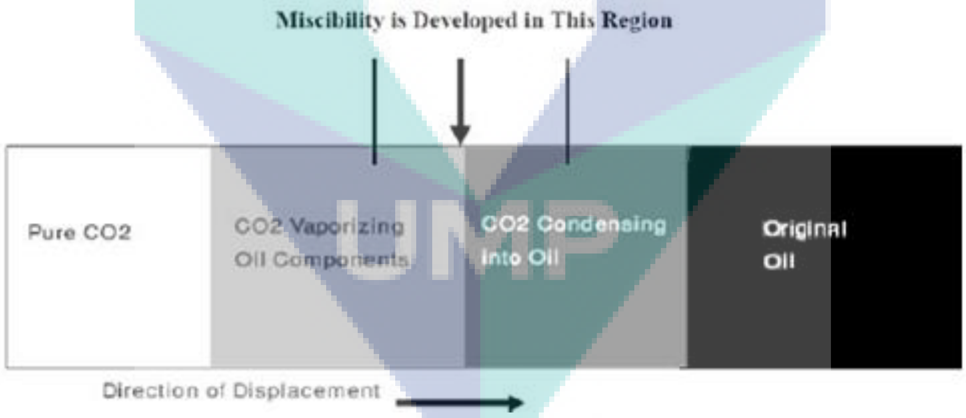


Figure: 2.13: Schematic of CO_2 miscible flooding process (Holm and Josend, 1974)

2.9 FORMATION DAMAGE DUE TO ASPHALTENE PRCIPITATION

The formation damage prevention, assessment, control and removal of asphaltene particles are the important issues of asphaltenic oil production (Civan, 2000). Any enhanced oil recovery method can change the flow and phase behaviour of the reservoir fluid which may lead to formation damage caused by asphaltene precipitation. Usually, the deposition takes place nearby the wellbore zone but the precipitation extends over larger distance from the vicinity of wellbore (Groffe et al., 1995). Asphaltene particles can cause formation damage by impairing the permeability through plugging the pore throat. The asphaltene particle can also cause wettability alteration through adsorption of negatively charged particles. The alteration of wettability can change from water wet to mix wet (oil-water wet) and plugging of the wellbore (Kamath et al., 1993 ; Kokal and Sayegh, 1995).

It should be emphasized that alteration of wettability from water to oil wet is not necessary to cause formation damage. Sometimes it can be favourable for oil recovery depending on the nature of oil. It may improve the displacement performance and efficiency. In 1993, Kamath et .al, had studied the effect of asphaltene deposition on one core Berea sandstone and two unconsolidated sand pack. The result showed that asphaltene deposition may cause permeability reduction but it improved the oil relative permeability. In conclusion, asphaltene precipitation may or may not be favourable for reservoir (Al-Maamari et al., 2000). A proper investigation should be conducted for each crude oil with its reservoir core samples so that the genuine relationship could be observed.

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

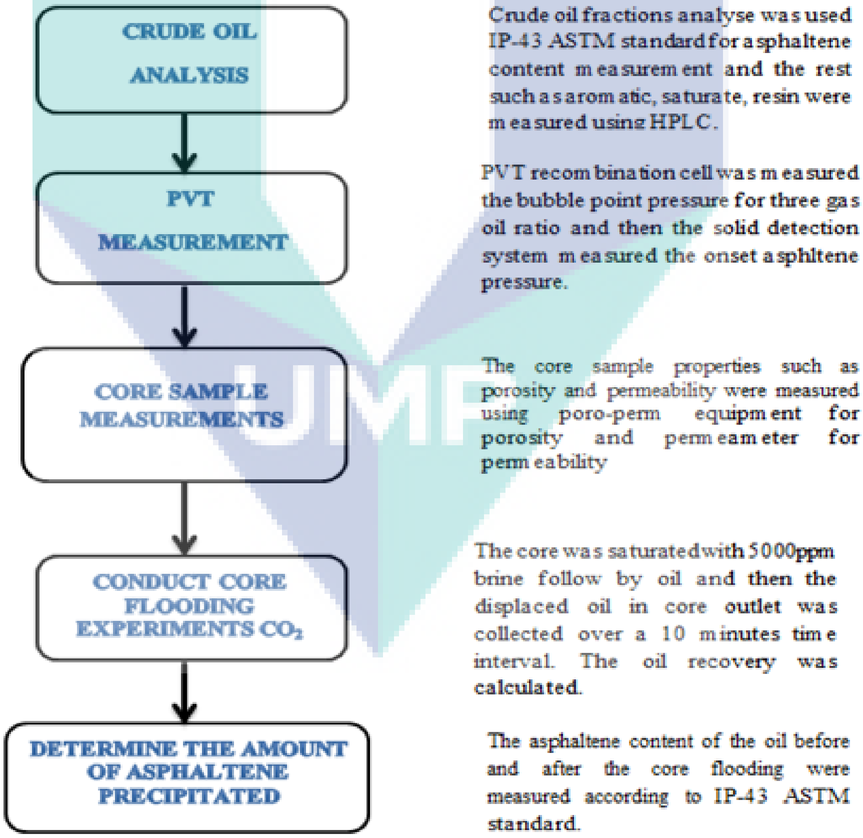
This chapter describes the experimental work conducted and the materials used during this study, which consist of N-Heptane, N-Hexane $CH_3(CH_2)_4CH_3$, (HPLC Grade), HPLC Standards and filter papers for Saturates, Aromatic, Resin, and asphaltene (SARA) analysis. Mix composition Gas (CO_2+C_1), Malaysian crude oil, and Berea core samples used to investigate the effect of carbon dioxide on asphaltene precipitation are also among considered materials. The main experimental apparatus employed in the study are High Pressure Liquid Chromatograph, Poro-perm Instrument, Manual Saturator, Digital Balance Magnetic Stirrer, Pressure Volume Temperature (PVT) equipment, Solid Detection System (SDS), Core Cutter Machine, High Pressure High Temperature core flooding equipment and Drying Oven.

3.2 CRUDE OIL SPECIFICATION

Dulang crude oil was used during the study where the oil has been identified as having unstable asphaltene content since the Colloidal Index is less than 0.7%. The basic properties of the crude oil were taken from the laboratory. Asphaltene content was measured using ASTM standard IP-143 method, which will be future detailed in Section 3.10. The properties of the crude oil were determined and it was found that the API is 37.5 and asphaltene content is 3% wt.

3.3 FLOW CHART OF THE RESERCH

Figure 3.1 illustrated the outline of this work, the research methodology started with determining the API for the crude oil and then the amount of asphaltene content was measured according to IP-43ASTM standard and the rest of solid frication was measured used HPLC. Later, the crude oil was charged into PVT recombination cell to detect the saturation pressure with different gas oil ratio and then Solid detection System (SDS) is used to measure the onset asphaltene pressure. Next, the second part started with the sandstone cores properties such as porosity and permeability that were measured and then saturated with 1000ppm brine to get it prepared for core flooding. After that, the core was conducted to core flooding and the oil displace from the core outlet was collected over 10 minute time interval and the recovery was calculated. Finally, the asphaltene content after the core flooding were measured according to IP-43ASTM standard.



Crude oil fractions analyse was used IP-43 ASTM standard for asphaltene content measurement and the rest such as aromatic, saturate, resin were measured using HPLC.

PVT recombination cell was measured the bubble point pressure for three gas oil ratio and then the solid detection system measured the onset asphltene pressure.

The core sample properties such as porosity and permeability were measured using poro-perm equipment for porosity and permeameter for permeability

The core was saturated with 5000ppm brine follow by oil and then the displaced oil in core outlet was collected over a 10 minutes time interval. The oil recovery was calculated.

The asphaltene content of the oil before and after the core flooding were measured according to IP-43 ASTM standard.

Figure 3.1: Methodology outline

3.4 PROCEDURE FOR SARA FRACTION

SARA Fraction is a three step process. To begin, the asphaltene content is removed from the crude oil using hexane, which was used as mobile phase in HPLC. Hexane based maltene fracture is then pumped using high pressure mobile phase inside the HPLC and column to detect saturates and aromatics. NH_2 bonded columns were used in series while the adopted temperature was a room temperature. In order to appropriately detect the signals, a 254 nm wave length was used. The flow rate of injection was raised to 1.5ml/min from crude oil and the pressure was stabilized at around 98 bars. The following section provides details of procedures adopted.

3.4.1 Asphaltene Content Measurement

IP 143/01 D6560 methods were used to separate and measure the asphaltene content. In this method, firstly, the sample is mixed well with the precipitant and the one used in our method is heptane. The mixture is then heated using reflux. Once the mixture is heated, the asphaltene particle will have separate phase in the crude oil. The mixture is then filtered using filter paper to separate the inorganic material. Wax content is removed by washing the filter paper with warm n-heptane in the extractor. The remaining mixture is then mixed with toluene as the asphaltene content is soluble in it. The new solvent is then heated again. The extracted solvent is then evaporated, and the asphaltene is weighed. The procedure, according to IP 143/01 D6560 is 1 gram of sample crude oil is mixed with 30 ml of n-heptane and stirred for 10 minutes using magnetic stirrer. The mixture is then boiled at 60±5 minutes using reflux. The flask containing sample is then allowed to cool and placed in a dark room for approximately 2 hours. Whatman filter paper no. 42 is placed in a filter funnel and the sample residue is filtered using a filter paper in another flask with successive quantities of hot n-heptane. Remaining residue in the flask is rinsed well with hot n-heptane and is filtered through the filter paper. After that, the flask is kept in the safe place without washing

The filter paper containing inorganic material is removed from the funnel and placed in the reflux extractor. Next, the extraction is done with n-heptane at the rate of 2-4 drops/ second for 60 minutes until the heptane leaves no residue at the bottom of the flask. Later on, 30-60 ml toluene is put in a new flask and filter paper is then washed with toluene so that all the asphaltene content becomes soluble in toluene. Toluene containing asphaltene is then transferred to the pre-weight evaporating vessel. The toluene is removed using evaporation process in the boiling water bath. Dish and content are then allowed to dry in an oven and then allowed to cool. Finally, the difference between the weight before and after the evaporation is taken as the amount of asphaltene content being measured.

Asphaltene content measurement in 1 gm of crude oil was weighed and mixed with 40 ml of HPLC grade hexane in a beaker. Aluminium foil was used to make the beaker air tight. The beaker was then kept in air tight condition in dark place for 48 hours. After 48 hours, 5 cc syringe with 0.2 mm PTFE syringe filter was used to withdraw the maltene fraction. Roughly 0.5 ml sample of matlene/hexane were prepared to be injected into HPLC. Filter paper with the size of 0.22mm was used to separate asphaltene from the oil and finally the filter paper is then dried and weighed.

3.4.2 High Pressure Liquid Chromatograph

Chromatographic technique using high pressure liquid chromatograph was adopted to conduct the SARA analysis. Asphaltene was first filtered using an IP-143 ASTM D6560 (IP 143/01) method. Later on, the HPLC was used to disintegrate and quantify the aromatics, resins and saturates. Figure 3.2 shows the high pressure liquid chromatograph used in this study. The process of HPLC is based on a mass transfer using the columns. The columns used in HPLC have the sorbent inside it and the adsorption process is used to quantify the compounds. The pressure pumps are used to inject the fluid through the column filled with sorbents.

General sorbents used are polymer based or silica based and their size varies from 2-50 micrometres. Aromatics, saturates and resins are adsorbed using NH_2 columns. Prepared mixture of sample is passed through NH_2 based columns where the compounds are separated due to degree of different interaction with the sorbent. The column dimension for SARA analysis could range from 2.1-4.6 mm in diameter and 30-250 mm in length. The sorbent particle size is around

2-5 micrometre. The temperature also influences the interaction between the mixture and sorbent.

To pressurize the compounds mixture into the column, a mobile phase is used in HPLC. In our case, Hexane was used as a mobile phase (Tianguang *et al.,* 2002). HPLC operation involves the use of detector, pump and sampler. The sample compound is sent through the column using the pressurized mobile phase at a certain flow rate and pressure. The parameters are assigned using the pump. The detector then generates the signal, which is proportional to the amount of sample component emerging in the column. Based on Tianguang *et al.,* (2002), SARA Fractionation procedure uses NH_2 bonded columns in series. The Mixture of N-Decane (C_{10}), N-Tridecane, n-pentadecane and n-octadecane was injected in the column with the hexane as a mobile phase. This mixture eluted as a single peak in the results. Additionally, the mixture of toluene and 1, 3-diisopropylbenzene (DIPB) was injected in HPLC column. This mixture had also eluted as a single peak. Then, the mixture of 1,3-diisopropylbenzene and 1-Methylnepthalene was also injected in the column, which eluted as two peaks. After that, the mixture of 1, 3-diisopropylbenzene, 1-methylnaphthalene, and n-pentadecane was injected into HPLC and eluted as three well resolved peaks. Finally, it was clear from the column test that the column was appropriately functioned and the system is ready to receive maltene samples.

Figure 3.2: High pressure liquid chromatograph

3.4.3 Maltenes Separation

According to Tianguag et. al. (2002) the prepared maltene aliquots were placed in the chamber of HPLC. The programmed computer software then starts taking the aliquots from the vial and inject them into column. The Hexane was used as mobile phase for the injection into column. The computer monitor shows the live graphs of maltene separation. Saturates were supposed to be eluted first using the RI detector response. Aromatic components are then eluted from the column as seen by the decrease in UV detector response. Aromatic components are eluted almost after 50 minutes of saturates. The amounts of saturates and aromatics were calculated from peak areas using calibration factors and measured for known compounds.

A different procedure is required for resin component as they do not elute using hexane phase. Then, the column was refreshed and cleaned by flushing it with H- hexane. To extract the resin content from maltene fraction, a 30% (v/v) of dichloromethance/haxane backflush was used to extract the resin fraction. A sufficient amount of maltene fraction should be injected in the backflush so that the enough resin can be accumulated for the gravimetric quantification. Saturates are clearly seen as a sharp peak on the RI-detector, while the aromatic and resin fractions are seen in UV-detector response.

3.5 PVT INSTRUMENT

Pressure volume temperature (PVT) equipment as shown in Figure 3.3 was used for the evaluation of thermodynamic properties and phase behaviour studies of the fluids. The high pressure high temperature PVT is used to conduct the fluid studies for any kind of reservoir fluids. The equipment main part is PVT cell and the configuration of the PVT cell depends on the type of cell. For example, the liquid head is used for oil studies. This cell is enclosed in the chamber. It has the piston on one side and the cell head on the other side. Magnetic stirrer is placed with the piston. The purpose of the magnetic stirrer is to mix and homogenize the fluid inside the cell. The complete system comprises of the embedded pump, PVT cell, air bath and rocking system. The rocking system is used to homogenize the oil and gas components. The PVT equipment can be rotated 360 degree using the rocking system.

The high pressure glass sight is also located on the stainless steel cap. The glass is used to see the condition of fluid and to observe the saturation pressure. PVT equipment along with recombination cell and solid detection system were used to conduct the asphaltene precipitation study for the Malaysian crude oil. Asphaltene onset pressure measurement was done for different concentration of mixed gas and oil composition. Recombination cell as discussed earlier is used to homogenize the dead oil and gas composition in order to prepare live oil, which is the representation of reservoir stream. In our case, reservoir temperature is 100ºF and current reservoir pressure is around 1850 Psi. Three different gas oil ratio were used. A calculated amount of injection gas along with oil was charged in the recombination cell at reservoir temperature and pressure. For each case, the injected oil and gas streams were stabilized and homogenized to create an under saturated condition.

Figure 3.3: PVT System

3.5.1 RECOMBINATION CELL

It has the heating metal for temperature control and magnetic stirrer to mix the fluid together. It also has the rocking system to provide agitation for heavy oil samples. The cell also has a glass to observe the saturation pressure. Figure 3.4 below shows the recombination cell where the separated gas and oil are specified by the user before recombination operation using the field and laboratory data. The recombination calculation for our case is mentioned in Appendix C.

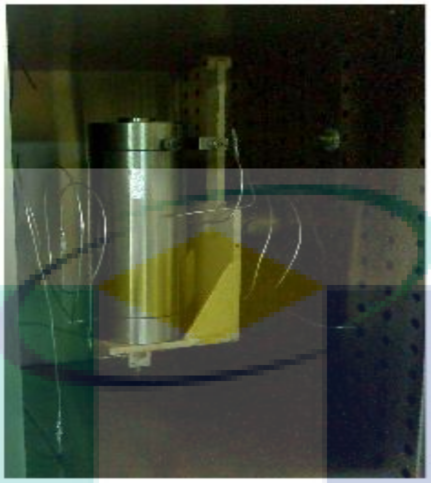


Figure 3.4: Recombination cell (Vinci Technologies France)

Mix composition was obtained to represent the real reservoir gas concentration or closer to reservoir conditions. The reservoir is assumed to have CO_2 and C_1 to represent a reservoir. The mixed composition gas used in our experiments has only 60% of CO_2 and 40% of C_1. The recombination was done based on the past and present reservoir conditions and was based on the matching of gas to oil ratio. The original gas to oil ratio for the reservoir was assumed at 180 scf/stb. To evaluate the effect of increased concentration of gas, the GOR was increased to 250 scf/stb and 310 scf/stb with the addition of gas. The additional gas was injected in the PVT cell using booster pump, which increases the pressure and temperature of gas before injection. Firstly, the 0.00030 stb dead crude oil was injected in the high pressure PVT cell at 2000 Psi and 100°C. Then, the gas of 0.054 scf was injected at the same pressure and temperature using booster pump. The rocking system was later used to agitate the sample after every 15 minutes for few times. Later on, the PVT system was left overnight to stabilize and homogenize the fluid sample. The process was repeated for GOR 250 and 310 scf/stb. For GOR 250 scf/stb, the 0.0030 stb of dead crude oil and 0.075 scf of gas was injected and for GOR 310, the dead crude oil was 0.00030 stb and 0.093 scf of gas was added. The temperature and pressure for both fluid was kept the same when mixing. The step by step procedure following the PVT manual is given below:-

The cell was first cleaned properly before the injection of fluids in it. Then, dead crude oil and mix composition gas were charged in the PVT cell at 100°C and 2000 Psi. The pressure was then raised to 3000 psi. The oil was later allowed to equilibrate for 12 hours. The reservoir fluid was then depressurized until the bubble point in discreet steps. Each discreet step of depressurization was 200 Psig and at each step, the fluid was allowed to stabilize for 10 minutes. After equilibration at each step, the volume of fluid and the cell pressure was noted from the system. The measured total volume of fluid was plotted against the fluid pressure at each discrete step. The intersection of straight-line-fits for both single and two phase regions provide an estimation of the saturation pressure. The procedure was repeated for other GOR conditions.

3.5.2 Solid detection System

The solid detection is part of the PVT equipment. It is designed to detect solid deposits and its stability in crude oil. It is also used to determine the critical point at which solid starts to form separate phase. The solid detection system is based on the light scattering technique. A laser source beam is generated, which is guided and passed through optical fibre and throughout the fluid inside the PVT cell. The amount of transmitted light is measured by a power meter. The power meter has a precision near infrared measurements in the solid detection system. Figure 3.5 shows the transmittance of light in solid detection system.

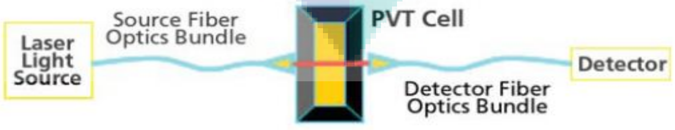


Figure 3.5: Transmittance of light

The system pressure, temperature, flow rate and power of transmitted light can be monitored concurrently in the computer software databank that is attached to the system pressure curve versus the power of the transmitted light being generated using computer software attached to the equipment. It detects the upper asphaltene onset pressure. The laser transmittance is passed through the oil phase. The detector is then used to measure the transmitter through the oil. Reservoir oil with no asphaltene content shows minimum light scattering due to homogeneous fluid. Partial light transmittance is observed at pressure higher than onset pressure. From the upper onset pressure, the light transmittance is decreased until the bubble point at which total scattering takes place. At lower onset pressure, the light transmittance starts increasing again due to the re-dissolution of dispersed asphaltene particles. Light transmittance depends on the reservoir oil fluid density and the presence of solid phase. Light transmittance is inversely proportional to the density. If the density is decreased, the light transmittance is increased. For the single phase live oil, density is proportional to the pressure. If the pressure decreases, the light transmittance increases. Light transmittance is inversely proportional to the size of particles. If the solid size increases, the light transmittance decreases.

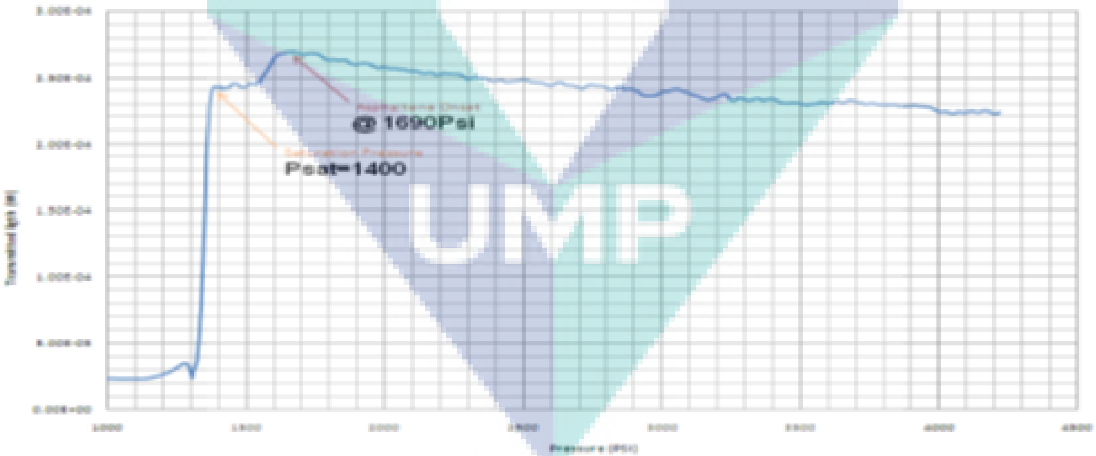


Figure 3.6: Precipitation curve of unstable asphaltenic crude oil (Muhammad et al., 2013)

Figure 3.6 illustrates a study conducted by Muhammad Ali Buriro *et al*., (2013) that is used to show the precipitation curve for unstable asphaltenic crude oil. It is observed that the transmittance of light signal increase from 4300 Psi to 1690 Psi. At 1690 Psi, the signal reaches the maximum. The sudden decrease in pressure is then observed from 1600 Psi to 1500 Psi. This is due to the agglomeration of asphaltene particles. At the bubble point, the signal falls down. In this figure, the bubble point is at 1400 Psi. Table 3.1 defines oil compositions which have been given from laboratory.

Table 3.1: Malaysian oil composition

Component	**Mole Percent**	**MolecularWeight**
CO_2	0.00	44
CH_4	0.000	16
C_5H_{12}	0.004005	72.15
C_6H_{14}	1.863993	86.17
C_7H_{16}	7.713000	100.2
C_8H_{18}	5.996991	114.2
C_9H_{20}	3.674989	128.3
$C_{10}H_{22}$	4.678996	142.3
C_{11+}	76.068026	213.35
CO_2	0.00	44
CH_4	0.000	16
C_5H_{12}	0.004005	72.15
Total	100.0000	189.85

3.5.3 Asphaltene Onset Pressure Measurement

The asphaltene onset pressure is the pressure where the asphaltene starts to precipitate the dead crude oil and mixed composition gas was used to create a live oil. The live oil was charged into the system at 2000 Psig and 100°C with the assumption that the initial reservoir condition we are dealing with has 2000 Psig and 100°C. In actual, we dealt with Dulang reservoir and these initial conditions are prescribed for this crude oil. The pressure of the cell was then raised to 3500 Psig. The near infrared light transmittance is observed in the computer. At under saturated conditions, the base line is stable (Oskui et al., 2006). The live crude oil is then depressurized in discreet steps of 2000 Psig until the bubble point pressure. During the depressurization, the light transmittance through the live oil is monitored and noted. The light transmittance was recorded as the function of pressure. The onset pressure is then measured by observing the NIR light transmittance signal. The process was repeated for all prepared live oil of different GOR (Hideharu Yonebayashi et al., 2010). The results are discussed in Chapter 4 and 5.

3.6 OPERATION EQUIPMENT FOR MMP

To simulate reservoir temperature, the extractor vessels are filled with core saturated and inserted inside the oven through the mountings brackets, which was set to 98.9°C as shown in Figure 3.7. For extraction process, CO_2 was delivered through external cylinder into the extractor vessel at the desired system pressure. Within 30 minutes, the gas was injected at the planned pressure. Then, the inlet valves were closed. To let the extracted oil to be collected through the control and collection module as indicated in Figure 3.8, the outlet valves and vent were opened. Therefore, it will be easier for collection of residues into collection tubes via outlet valves (Orr et al., 1982).

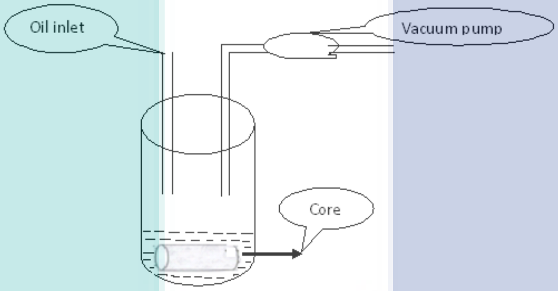


Figure 3.7: Setup for saturation process

The oil extracted was collected within 5 minutes. Similarly, the extraction process was repeated from the pressure of 1000 Psi to1900 Psi with the pressure interval of 1500 Psi. The collection tubes were weighed before and after collection to determine the net weight of the extracted oil. The schematic diagram below shows the layout of Spe-ed SFE. (Orr *et al.*, 1982).

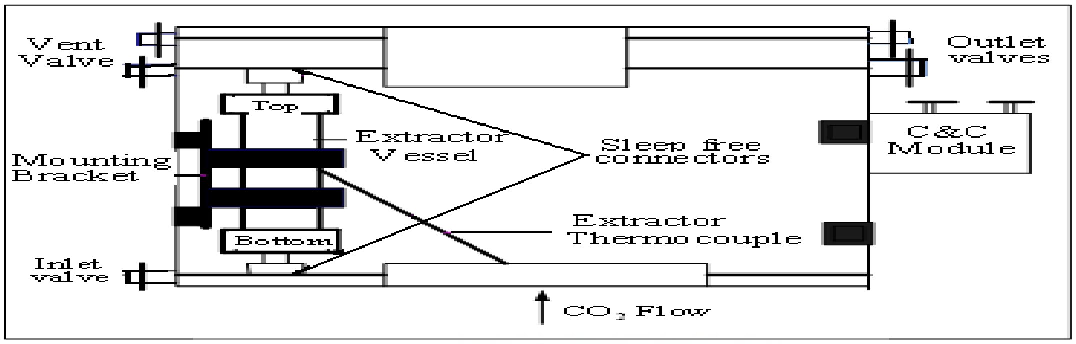


Figure 3.8: Schematic diagram spe-ed SFE

3.7 CORE SAMPLE PRPARATION

The one feet long core was cut into four pieces using core cutter machine. Figure 3.9 shows the core and cutter machine for it. As shown, the diamond impregnated radial blade is utilized to slab core samples into pieces. The standard machine has a work table, blade guard, motor to power the saw and a core clamping assembly. The recirculation coolant system is also available. The one feet core was cut into three inches per piece. It is labelled as Core-1, Core-2 and Core -3. The one, one-feet long and 1 inch in diameter core samples were used for this study. The porosity and permeability data for Core-1, Core -2 and Core -3 are described in Table 3.1.

Figure 3.9: Core and cutter core machine

3.8 POROSITY AND PERMEABILITY MEASUREMENTS

Porosity and the permeability of the core sample are the important factors to be evaluated. The porosity of the core sample can be measured by measuring the bulk pore volumes or grain volume. The bulk volume can be calculated using the dimensions of the core sample. Permeability was described as the property of the porous medium and it is measured of its ability to transmit fluids. Permeability measurements are conducted using permeameter equipment. In this equipment operation, the core is loaded through it. The flow of air is passing appropriate calculation as to obtain air permeability and could be conducted by changing inlet pressure and keeping out the pressure as zero. Further tests were conducted by flowing the same amount of volume from core 500 cc at different inlet pressure (10 Psi, 14 Psi, 18 Psi, 22 Psi, and 26 Psi) to acquire different points or air permeability. Afterwards, these points could be plotted into Klinkenbergs effect graph to find out slope and liquid permeability. Figure 3.10 shows the poro-perm used in this study.

Figure 3.10: Poro-perm system

The porosity of the core sample is measured during the core saturation using the equipment. The values of the core bulk volumes are computed from the dimensions of the core sample. The values of pore volume are calculated from the difference between the dry and wet weights of rock samples and brine density. Core flooding experiments were conducted to measure the effect of carbon dioxide being induced by asphaltene precipitation. The pore volume, bulk volume, porosity and absolute permeability are the important properties that need to be measured before the core flooding experiments.

$$BV \quad = \frac{\pi}{4}(D)^2(L) \tag{3.1}$$

Where
B_V is the bulk volume of core plug samples, cm^3
D is the core plug diameter, cm
L is the core plug length, cm
The porosity of the core plug can be calculated by considering the ratio of pore volume of core plug sample to bulk volume of core.

$$\emptyset \quad = \frac{PV}{BV}\, X\, 100 = \frac{(BV - GV)}{BV}\, X\, 100 \tag{3.2}$$

Where
Ø is the porosity in percentage
PV is pore volume, cm^3
G_V is grain volume,

Poro-perm device was used to measure the basic properties to calculate porosity. The dry weights of core plug samples are carefully measured by digital balance before stating any measurements. The Boyle-Mariotte's law is used to determine the grain and pore volume for the expansion of a known mass of helium into the matrix cup in poro-perm experiments. The pore volume can be computed based on the difference between dry weight and wet weight of core plug sample and identifying the density of saturated fluid during saturation method. Therefore, after saturating the core plug samples with brine water, it is necessary to measure the weight of the core samples. The pore volume of core plug samples is calculated according to the formulae given below (Nnaemek, 2011).

$$PV \quad = \frac{W_{sat} - W_{dry}}{\rho_{Brine}} \tag{3.3}$$

Where

W_{sat} is weight of wet and saturated core, gr

W_{dry} is weight of dry core, gr

ρ_{brine} is the brine density, gr/Cm$_3$.

3.9 METHODOLOGY FOR CORE FLOODING EXPERIMENT

Core saturation with brine water is the first step in conducting core flood experiments. The manual saturator apparatus was used to saturate the core with brine water. The apparatus is shown in Figure 3.11. This apparatus permits the sequence of saturation cycles and vacuum on different core plug sizes. The standard apparatus includes plug sized core cell, a vacuum pump, a hand operated valves and plumbing. A larger capacity cell to accommodate full size core sample is also available. Any kind of fluid can be used to saturate the core by this apparatus. It could be distilled water, brine or oil.

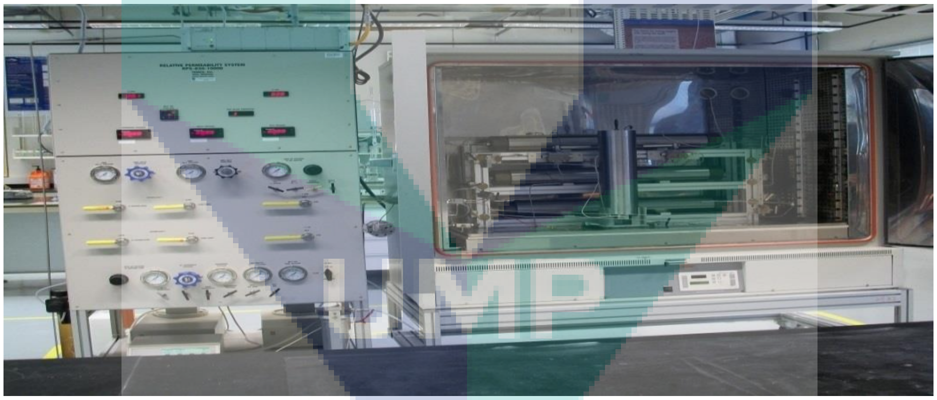


Figure 3.11: Relative permeability test system

The core saturation process starts after the bulk volume of core is measured from the dimensions of core sample and weighing the dry core samples. Later on, the core sample is placed inside the core holder. Then, half of the core sample is filled with brine of 10,000 ppm sodium chloride concentration, which is needed for core sample saturation. The injection pressure was made constant at 2000 Psig for three cores with the flow rates were various at 0.4 cc/min, 0.6 cc/min, and 0.8 cc/min respectively. The core sample is connected to two valves and two pressure gauges. One of the valve and pressure gauge is connected to the vacuum pump and the other side is connected to the core cell. This controls the cell pressure and brine water level. Vacuum valve is opened initially; the saturation process is then started by extracting the air inside the sample and replacing the void spaces of the sample with prepared water brine. The step takes around half an hour. Figure 3.12 indicated the core plug inside core holder.

Figure 3.12: Core plug inside the core holder

Vacuum valve is then turned off. The other valve is opened and the core cell is filled with brine water in the container using hand operated pressure pump. The step is continued until the water has come out of the valve. When the pressure becomes 2000 Psig, the hand pump is stopped. The core cell is kept for two days and the pressure is maintained at around 2000 Psi. After two days, the pressure is released and the saturated core sample is taken out from the cell. The previous step was repeated with Core 2 and Core 3 respectively. Core sample weight has been measured again after the saturation. The core sample is immersed inside the brine water in the beaker to keep the initial brine saturation condition.

3.9.1 Basic Core Properties Evaluation

The bulk volume of the core sample was calculated using the dimensions of the core and the dry core sample was also weighed. The brine of 10,000 ppm sodium chloride concentration was used to saturate the core with the saturation procedure is described earlier in this chapter. The rock porosity was also measured along with saturating the core. After that, the saturated core sample is inserted into the rubber sleeve and carefully tighten in the core holder to ensure direct contact between the core sample and core holder sleeves. The three accumulators are fully filled by the crude oil sample, brine water and n-heptane. The core flooding system temperature was increased to 100 °C. The overburden pressure is applied on the rubber sleeve, which is always 500 Psi over the injection pressure. The core flooding system pressure was kept at 2000 Psi and the overburden pressure was later mentioned at 2500 Psi.

3.9.2 Absolute Permeability, Irreducible Water and Initial Oil Saturation

The brine is injected into the core at a constant flow rate of 1.0 cc/min until the pressure drop across the core is stabilized and a steady state condition is achieved. The absolute core permeability is calculated using Darcy’s Law and the stabilized pressure drop. Then, the oil is injected into the core at the same injection pressure condition to displace the brine water at 0.4 cc/min, until the pressure drop is again stabilized and no more water could be displaced from the core. Total amount of brine production is recorded during the oil injection process. The stabilized pressure drop is used to calculate the effective oil permeability at irreducible water saturation using Darcy’s Law. This is considered to be original effective oil permeability without the asphaltene effects at irreducible water saturation. The irreducible water saturation and initial oil saturation are then determined using volumetric material balance.

3.9.3 In-Situ Asphaltene Precipitation and Deposition

The oil injection is stopped after the core is fully saturated with the oil at irreducible water saturation. Gas injection displace is then conducted. In this study, a mix composition of gas was used to displace the oil. For this purpose, after draining out all the brine from brine accumulator, the mixed composition gas is transferred carefully from high pressure cylinder into accumulator at pressure less than 2000 Psi. After heating up the gas system up to temperature at around 100°C, the accumulator pressure had reached 2000 Psi. In this experiment, the gas injection pressure was adjusted around 2000 Psi that is similar to oil injection pressure. The gas is injected through setting with three different flow rates at 0.4 cc/min, 0.6 cc/min, and 0.8 cc/min for three different cores for injection pump. The gas rate during gas injection should represent the typical reservoir gas velocities and pressure drop of 1 to 5 Psi/ft.

For this purpose, after stopping the oil injection and when the core is fully saturated with oil at irreducible water saturation, gas injection is started to displace the oil out at 0.4 cc per minute. The pore volume, pressure drop across the core, and oil and gas production are measured continuously until pressure drop is again stabilized and no more oil could be displaced from the core. Effective gas permeability at irreducible liquid saturation is again calculated based on stabilized pressure drop and using Darcy’s Law.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter presents the results of the experimental work conducted during this study. The results are discussed in details and their interpretation is given. SARA analysis was conducted to characterize the crude oil and to conduct the colloidal stability test. PVT experiments are then discussed in details. Later, the asphaltene onset pressure is measured and its significance is given. Finally, the chapter discusses the core flooding experiments and their results in details. The effect of carbon dioxide on asphaltene precipitation was measured by conducting the core flooding experiments.

4.2 ASPHALTENE CONTENT MEASUREMENTS

The Malaysian crude oil was used in our analysis. The basic properties of the crude oil were obtained along with the crude oil employed from Malacca refinery. Asphaltene was measured using standard IP-143 method. The details of the experimental procedure were given in Chapter 3. The evaluation of colloidal stability was done for Malaysian crude oil in different ways. The preliminary analysis to know the stability of crude oil can be obtained by SARA analysis. Stability analysis at high pressure high temperature was then done using PVT equipment and experiments.

4.3 SARA ANALYSIS

SARA analysis started with Jewel et al., (1972) work. To begin with, saturates, aromatics, resins and asphaltene content for the Malaysian crude oil were measured. Asphaltene was measured using IP-143 method while saturates, aromatics and resin content were measured using the high pressure liquid chromatograph. Table 4.1 indicated SARA fractions obtained for the Malaysian crude oil, which are saturates at 74.7%, aromatics at 14.9%, resins at 8.11% and asphaltene at 3%. Colloidal Instability Index (CII) was measured using the formula given below (Bennet et al., 2006). The index of 0.9 or more indicates that the asphaltene particles are unstable while value below 0.7 indicates that the crude oil has stable asphaltene, and the value in between 0.7 to 0.9 means that the asphaltene stability is uncertain. The calculations suggest that the asphaltene stability index is 3.37 and the result proposes that the asphaltene particles in Malaysian crude oil are highly unstable and it can cause damage to the reservoir and may cause problems upon precipitation. Since this was the preliminary analysis and was at ambient temperature, high pressure high temperature onset pressure measurement was then required to know at what condition the asphaltene started to precipitate. Solid detection system was used to measure these conditions and will be described in the next sections.

Table 4.1: Crude oil properties

Sample Name	Malaysian Light Oil
API	37.5
Saturates	74.7%,
Aromatics	14.9%
Resins	8.11%
Asphaltene Content (wt%)	3%

4.4 ASPHALTENE ONSET PRESSURE MEASUREMENTS

Live oil is a high pressure high temperature oil containing gas and therefore, three different live oil were selected to check its propensity to precipitate. Table 4.2 describes the GOR of the original Malaysian oil as well as increased gas to oil ratio details. The reservoir temperature and pressure were assumed to be 100°C and 2000 Psi at current conditions. According to the literature, recombination procedure is done in PVT equipment to achieve this.

Recombination composition of dead oil and live oil is given in Table 4.3 where the recombined sample composition was calculated using molar balance equation and the details of the calculation is given in Appendix B.

Table 4.2: GOR for Original crude oil

Oil name	**GOR (scf/stb)**
Malaysian oil	180
Malaysian oil	250
Malaysian oil	310

Table 4.3: Malaysian live oil composition

Component	**Mole Percent at GOR 180 scf/stb**	**Mole Percent at GOR 250 scf/stb**	**Mole Percent at GOR 310 scf/stb**
CO_2	18.44132	25.61295	31.76005
CH_4	12.29421	17.0753	21.17337
C_5H_{12}	0.002774	0.002295	0.001885
C_6H_{14}	1.291085	1.068287	0.877318
C_7H_{16}	5.342368	4.420456	3.630245
C_8H_{18}	4.153783	3.43698	2.822578
C_9H_{20}	2.545461	2.106201	1.729692
$C_{10}H_{22}$	3.240877	2.681611	2.20224
C_{11+}	52.68811	43.59592	35.80262
Total	100	100	100

4.4.1 Bubble Pressure Measurements

The asphaltene precipitation problem is more severe near to bubble point pressure and it is necessary to know it in order to investigate the onset asphaltene pressure. The constant composition test was performed for different gas to oil ratio. Figure 4.1 shows the pressure volume curve for the gas to oil ratio of 180 scf/stb. The intersection of the two lines on the pressure volume curve suggests that the bubble point for the Malaysian oil at 180 scf/stb is 1300 Psig and it can be observed that the saturation pressure was low when gas oil ratio is low.

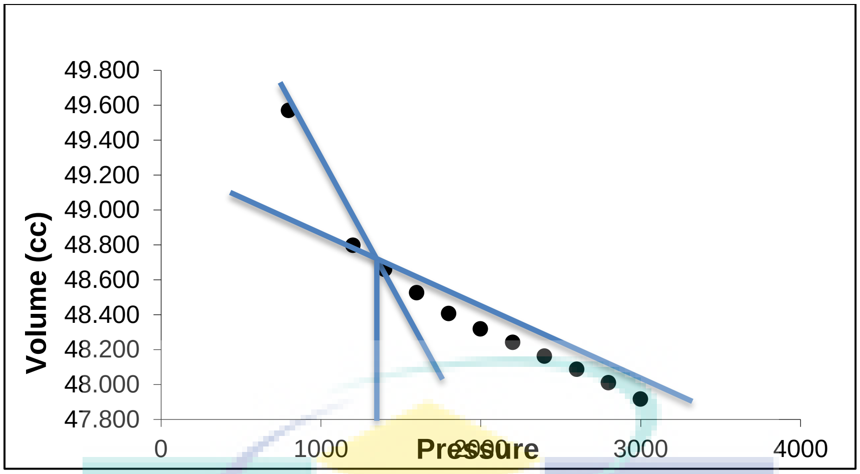


Figure: 4.1: Pressure volume curve at GOR of 180 scf/stb

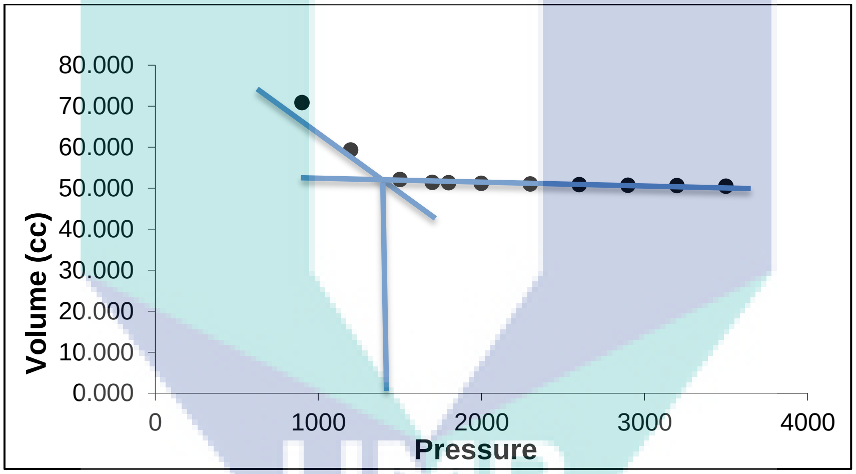


Figure: 4.2: Pressure volume curve for the gas oil ratio of 250 scf /stb

Figure 4.2 shows the pressure volume curve for gas oil ratio of 250 scf/stb. Once the GOR is increased, the saturation pressure value increased as well because of more interaction between the gas and oil and the intersection of the lines at the pressure volume curve suggests that the bubble point pressure for 250 scf/stb gas to oil ratio is 1500 Psig.

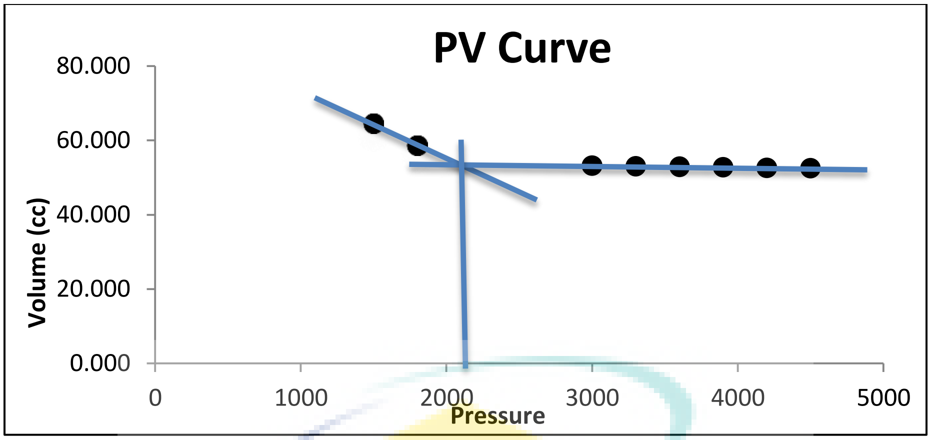


Figure: 4.3: Pressure volume curve for GOR of 310 scf/stb

Figure 4.3 shows the pressure volume curve for gas to oil ratio of 310 scf /stb and it can be declared that the value of saturation pressure had raised since the GOR amount is increased to 310 scf/stb. The intersection of two lines in Figure 4.3 suggests that the bubble point pressure at GOR of 310 scf/stb is 2100 Psig.

4.4.2 Asphaltene Onset Pressure Measurements

Malaysian crude oil was recombined with the mixed composition gas to make it a live oil. The live oil was placed in the PVT system and solid detection system was used to measure asphaltene onset pressure. The complete procedure to measure onset pressure is described in section 3.6.3. Malaysian crude oil of different gas to oil ratio was investigated for its propensity to precipitate. Figure 4.4 shows the isothermal depressurization of original composition in crude oil. The original gas oil ratio was kept at 180 scf/stb.

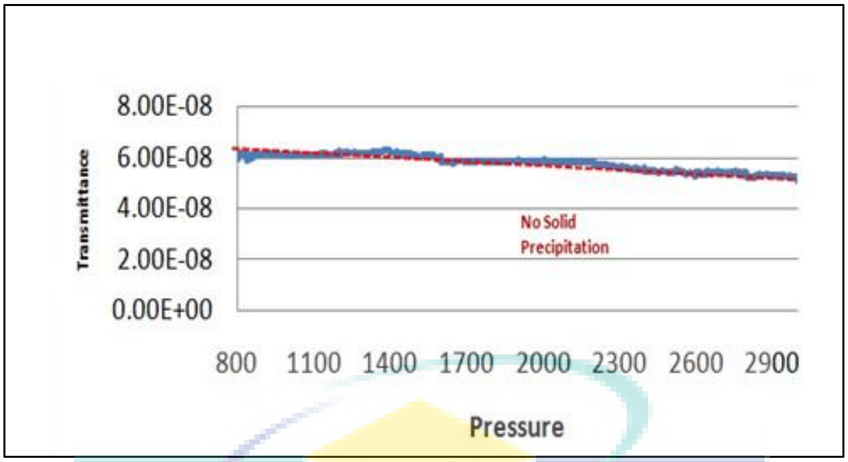


Figure 4.4: Solid detection system at GOR of 180 scf/stb

Figure 4.4 shows the transmittance of laser light through oil sample versus pressure. The result shows that as the pressure decreases, the transmittance of light increases. During isothermal depressurization, no drop of light transmittance is observed even at the bubble point. The bubble point for the original crude oil composition was 1300 Psig. The increase in light transmittance observed is due to the decrease in density as the pressure is decreased. The result of solid detection experiment indicated that asphaltene particles are stable in the crude oil before any additional gas injection.

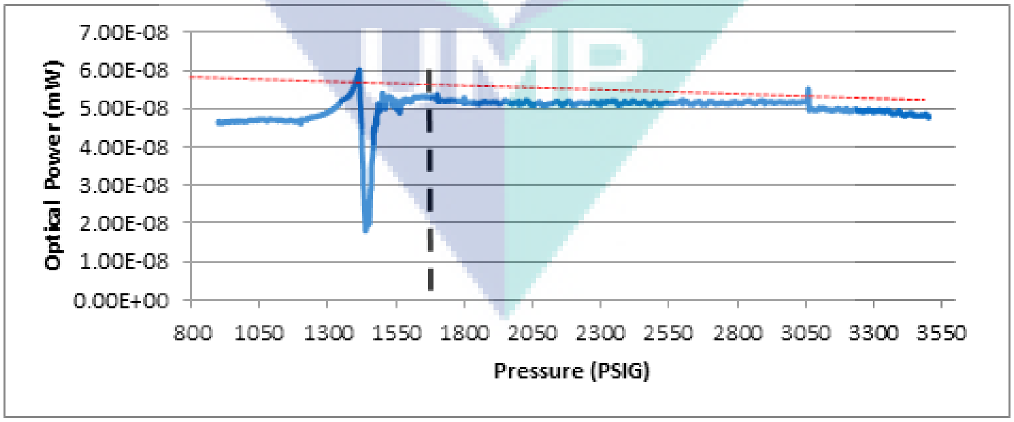


Figure 4.5: Onset Pressure measurement at 250 scf/stb

The GOR of the original crude oil was increased to 250 scf/ stb. This oil was placed in the PVT cell for isothermal depressurization and solid detection test. The isothermal depressurization test started at 3500 Psig until 800 Psig. The bubble point pressure was measured at 1500 Psig. As shown in Figure 4.5, with the decrease in pressure from 3000 Psig to 1600 Psig, the light transmittance was increased. It shows that there was no asphaltene precipitation. Sudden decrease in the transmittance and high scattering in the signal from 1650 Psig to 1500 Psig is due to the agglomeration or growth of solid particles. The light transmittance falls down at 1500 Psig. The result shows that the fluid loses its equilibrium condition at this pressure and the gas started to liberate and asphaltene particles are precipitated. The sudden increase of light transmittance after the bubble point pressure was observed due to loss of equilibrium and the light transmittance is then stabilized and trending downward. Asphaltene particles are unstable due to CO_2 injection program even though its content is only 0.3 weight percent.

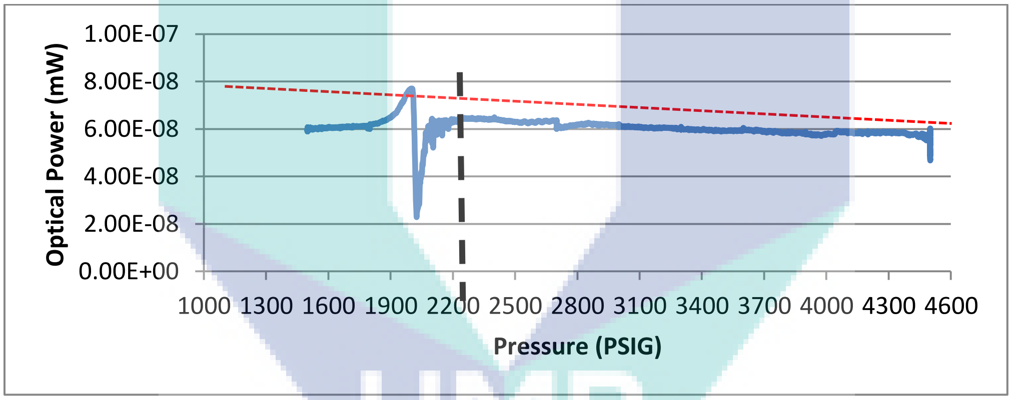


Figure 4.6: Onset Pressure Measurement At 310 scf/stb

GOR for Malaysian crude oil was increased to 310 scf/stb. Figure 4.6 represents the isothermal depressurization test using solid detection system at 310 gas to oil ratio. The isothermal depressurization test was started at 4500 Psig until 1400 Psig. It was observed that there is an increase in the light transmittance from 4500 Psig to 2300 Psig. However, after 2300 Psig, the light transmittance started scattering and the highest is observed at 2200 Psig. This sudden decrease in the transmittance is due to asphaltene agglomeration. At 2100 Psig, the fluid equilibrium is lost due to bubble point pressure and asphaltene precipitation. Unstable transmittance curve leading to maximum light transmittance at the bubble point pressure was observed due to loss of equilibrium (Muhammad et al., 2013).

4.5 DETERMINATION OF MMP

The graph obtained is shown in Figure 4.6. The oil recovery volumes grow gradually first to the values of 1000-1400 psi where they form a kind of step and secondly to the break over point, which according to a definition made by Orr et al., (1982) is a criterion for MMP determination. Above the break over point, the volume of extracted oil does not change significantly with the increasing pressure. Such type of correlation is typical for slim tube experiment. Based on such similarity, MMP at 98.9^{o}C for the oil in this investigation was 1500 Psi.

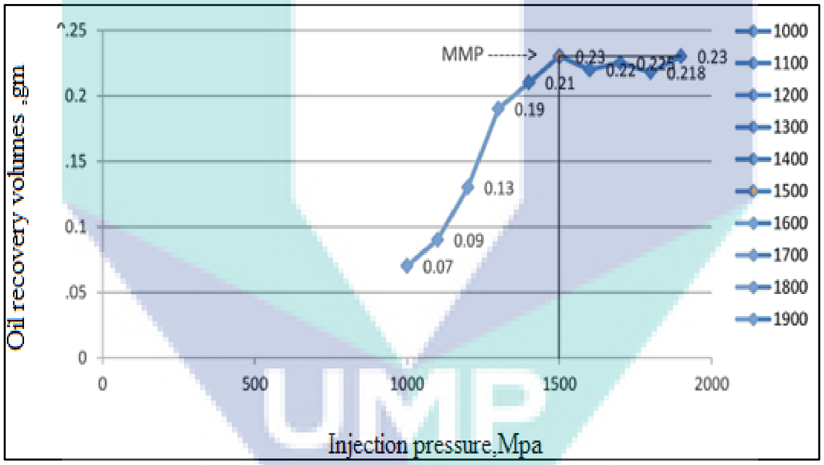


Figure 4.7: Determination of minimum miscibility pressure (MMP)

4.6 ORIGINAL CORE SAMPLES PROPERTIES

Core properties such as porosity, permeability and bulk volume are determined before running the core flooding test. The basic core properties and porosity of three core samples used in this study are mentioned in Table 4.4.

Table 4.4: Basic core properties

Sample ID	V_{grain} cc	V_{bulk} cc	W g	PV cc	Ø $_{grain}$ g/cc	L cm	D cm	A Sq.cm	Ø %
Core- 1	67.430	82.790	117.96	15. 36	2.64	7.3	3.8	11.3411	18.55
Core -2	9.738	85.626	184.12	15. 89	2.64	7.55	3. 8	11.3411	18.55
Core -3	72.036	88. 400	190.05	16.36	2.64	7.4	3.9	11.9459	18. 51

$V_{grain:}$ Grain volume; $V_{bulk:}$ Bulk volume; W: wight; PV: Pore volume; Ø $_{grain:}$ Grain density; L: Leanth; D: Ø: Porosity

Table 4.5: Liquid permeability of core samples

Sample Name	**Flowing fluid**	**Absolute permeability K_L**
Core-1	Air	38.77
Core-2	Air	41.56
Core-3	Air	40.11

Table 4.5 indicated absolute permeability for 3 cores and some researchers reported that core with lower permeability shows more intense formation damage effect than the core with higher permeability (Shedid & Zekri, 2004). The reduction of injection flow rate may decrease the formation damage due to less asphaltene precipitation (Shedid & Zekri, 2004). A study of asphaltene induced formation damage by Sima *et al.*, (2011) has demonstrated that the porosity and permeability reduction is more intense at lower injection pressure due to more asphaltene deposited (Sima *et al.*, 2011).

4.6.1 Asphaltene Content in Recovered Oil for Core 1, 2, and 3

Tables 4.6, 4.7 and 4.8 show the result for core flooding test. Total pore volume of 15.36 cc was used in the first core flooding experiment. This is the prepared volume that was injected into the core. The amount is set based on the core sample size and the capacity of core flooding equipment in order to handle the volume. The flow rate was kept at 0.4 cc/min and the initial asphaltene content was 3%. The inlet pressure was kept at 2000 Psig. When 0.25 percent pore volume was injected, 0.29% of asphaltene was recovered from the crude oil.

Table 4.6: Core flooding data for core-1

Pore volume of gas injected (PV)	**Asphaltene content in the recovered oil (wt %)**	**Asphaltene content precipitated in the core (wt %)**
0.25	0.29	0.01
0.50	0.25	0.05
0.75	0.20	0.1
1.0	0.17	0.13

Table 4.7: Core flooding data for core-2

Pore volume of gas injected (PV)	**Asphaltene content in the recovered oil (wt %)**	**Asphaltene content precipitated in the core (wt %)**
0.25	0.24	0.06
0.50	0.21	0.09
0.75	0.16	0.14
1.00	0.12	0.18

Table 4.8: Core flooding data for core-3

Pore volume of gas injected (PV)	**Asphaltene content in the recovered oil (wt %)**	**Asphaltene content precipitated in the core (wt %)**
0.25	0.22	0.08
0.50	0.18	0.12
0.75	0.13	0.17
1.00	0.11	0.19

Mixed gas was used in PVT experiments. It is a mixed gas plus the crude oil in order to determine asphaltene precipitation in the crude oil. It was observed from the experiment that the higher pore volume was injected in the core, the lesser asphaltene was recovered from the outlet and more asphaltene was precipitated inside the core. The procedure to conduct the experiment was described in Chapter 3. Figure 4.8 shows the injected pore volume versus asphaltene recovered from the crude oil for Core 1, 2 and 3.

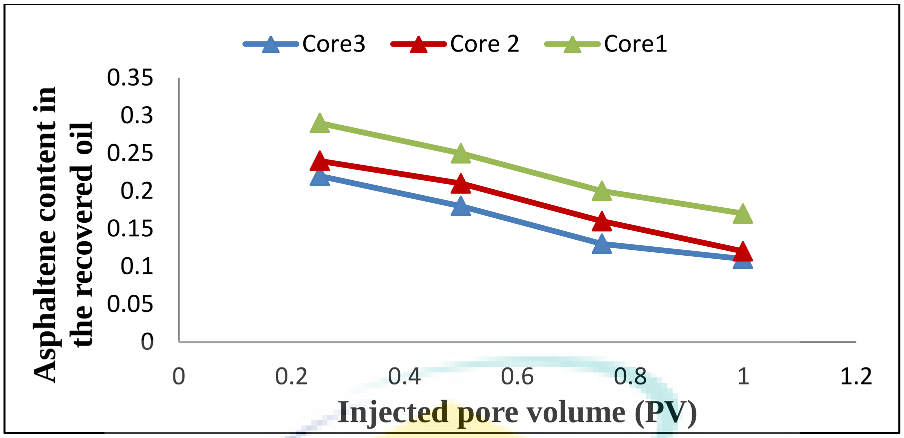


Figure 4.8: Asphaltene Content in the recovered oil for three cores

For Core 1, the graph shows the pore volume injection versus asphaltene particles in the recovered oil. It is observed in Figure 4.8 that the more fluid was injected into the core, the lesser asphaltene was recovered from the oil. It can be concluded that with the increase in pore volume, the higher weight percent of asphaltene was precipitated in the core. It proved that asphaltene particles are highly unstable in Malaysian crude oil and triggered asphaltene precipitation in the reservoir. However, in core flooding experiment that was conducted in Core 2, the inlet and outlet pressure was kept similar at 2000 Psig and the flow rate was changed to 0.6 cc/min and the asphaltene content remained similar at 3 wt%. From the graph, it was observed that at 0.25 pore volume, the asphaltene recovered at the outlet was around 0.24% wt. Once the pore volume is increased to 1.00 cc, the asphaltene content is also increased to 0.12% wt

For Core 3 graphs, the injected pore volume versus recovered asphaltene content in the crude oil was at the flow rate of 0.8 cc/min. It was observed from Figure 4.8 that when the pore volume of injection was 0.25cc, the amount of asphaltene content in the recovered oil was 0.22% wt while at injected pore volume of 1cc, the amount of recovered asphaltene content was 0.11% wt. It gives the same consistent results like other core flooding experiments that higher amount of asphaltene was precipitated inside the core when higher pore volume was injected. It can be concluded that with the increase in the pore volume, the higher weight percent of asphaltene was precipitated in the core.

4.6.2 Asphaltene Content Precipitated In Core 1, 2, and 3

Figure 4.9 shows asphaltene content precipitated in the core versus the pore volume injected for three cores: 1, 2, and 3 and for Core 1, the flow rate was set at 0.4 cc/min. The graph shows that at 0.25 pore volume of injection, the asphaltene precipitated inside the core was 0.01% wt while at the injection of pore volume 1, the asphaltene precipitation inside the core was 0.13% wt. The total asphaltene content in the fluid was 3% wt. It should be noted that lower volume of fluid injection will cause less damage to the core sample while higher pore volume of the CO_2 injection in the core causes higher damage to the core due to asphaltene precipitation. Then, it was found that with the increase in pore volume injection, the amount of asphaltene precipitation also increases. Furthermore, the flow rate also has the effect on the amount of asphaltene precipitation. It was observed that the three flow rates of 0.4cc/min, 0.6cc/min and 0.8cc/min have a different trend of asphaltene precipitation and the amount of asphaltene precipitation increased with more flow rate. Additionally, when the fluid injection volume is increased, more asphaltene precipitation will occur.

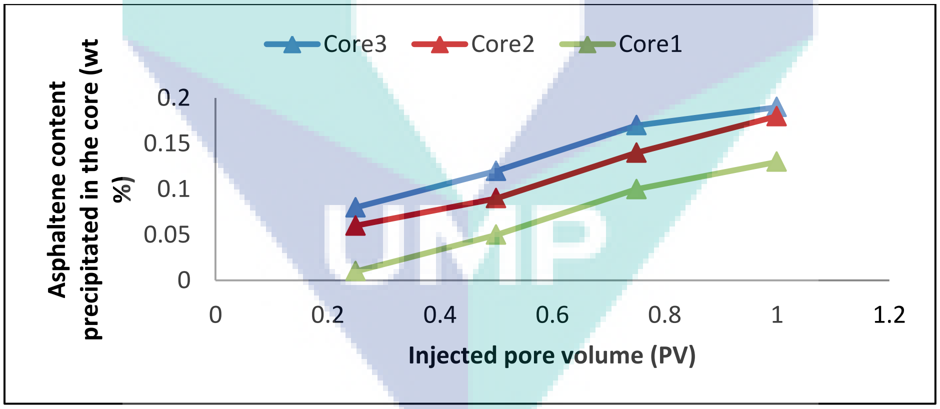


Figure 4.9: Asphaltene content precipitated in the three core

Compared to Core 2, the same total pore volume of 15.89cc is used, but the flow rate was increased to 0.6 cc/min. The graph shows that at 0.25 pore volume of injection, the amount of precipitated asphaltene in the core was 0.06 wt %. At the injected pore volume 1, the amount of precipitated asphaltene was increased to 0.18 wt %. The result indicates that by increasing the amount of pore volume injection, more asphaltene was precipitated and the more damage will be to asphaltene precipitation. According to Alta'ee et al., (2012) results indicated that asphaltene precipitated at pore volume 0.33 was 0.024 wt %. Once the CO_2 reached 0.66 pore volume, the precipitated asphaltene was 0.056 wt %. Then, the asphaltene precipitation had reached to a final value of 0.078 wt % at 1.66 pore volume. Similarly indicated by Sima et al., (2011), asphaltene precipitation was 0.23 wt % at 1.26 pore volume of 2300 Psi. However at 2600 Psi, the asphaltene precipitation was 0.19 wt % with 1.27 pore volume.

In Core 3 flooding experiment, the total pore volume of 16.36 cc was used. The flow rate was increased to 0.8 cc/min and initial asphaltene content was 3% wt. The inlet pressure was kept at 2000 Psig. It was observed that with the injection of CO_2 0.25 PV, the asphaltene content precipitated in the core was around 0.08% wt. With the increasing amount of pore volume injected to 1.00 cc, it leads to higher amount of asphaltene particles precipitated in the core that reach the maximum of 0.19 wt %.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION

Based on the results of this study, the physical and chemical factors were significantly involved in asphaltene stability. From SARA analysis, the following composition were found; The saturates, aromatics, resins and asphaltene were 74.7%, 14.9%, 8.11% and 3% respectively. This research was then further extended by PVT experiments. The bubble point pressure of the Malaysian live oil at different gas to oil ratio of 180 scf/stb, 250 scf/stb and 310 scf/stb were measured. It was found that the asphaltene problem mostly occurred close to the bubble point pressure of 1500 Psig for GOR 250 scf/stb and 2100 Psig for GOR 310 scf/stb but there is no presence of precipitation at 1200 Psig for GOR 180 scf/stb. It can also be concluded from the investigation of carbon dioxide effect and flow rate that the results of core flood had indicated that with the increase in pore volume of CO_2 injected to 1 cc, asphaltene precipitation has reached the highest amount of precipitation, which is 0.19 % for Core 3 with the injection flow rate of 0.8 cc/min

5.2 RECOMMENDATIONS FOR FURTHER WORK

It is recommended that wettability changes due to asphaltene precipitation should be evaluated in the core sample. Other than that, it is recommended to investigate the adsorption of asphaltene particle on rock sample besides the impact of asphaltene precipitation on relative permeability of the fluid. It should also be investigated on how the benefit of wettability alteration was caused by asphaltene precipitation.

REFRENCES

Abubakar, E.M. 2010. Antibacterial potential of crude leaf extracts of *Eucalyptus camaldulensis* against some pathogenic bacteria. *African Journal of Plant Science*. **4**(6): 202-209.

Akpan, U.G., Jimoh, A. and Mohammed, A.D. 2006. Extraction, characterization and modificationof *Castor* seed oil. *Leonardo Journal of Sciences*. **8**: 43-52.

Ali, M.A., Sayeed, M.A., Islam, M.S., Yeasmin, M.S., Khan, M.A. and Muhamad Ida, I. 2011. Physicochemical and antimicrobial properties of *Trichosanthes anguina* and *Swietenia mahogani* seeds. *Bull. Bulletin of the chemical Society of Ethiopia*. **25**(3): 427-436.

Anup, M., Subhash, C.M. and Saikat, D. 2007. *In vivo* evaluation of antidiarrhoeal activity of the seed of *Swietenia macrophylla* king (*meliaceae*). *Tropical Journal of Pharmaceutical Research.* **6**(2): 711-716.

AOCS, 1993. Official methods and recommended practices of the American Oil Chemists' Society, AOCS. Press. Washington, DC.

Abdassah, D., Siregar, S. and Kristanto, D. 2000. The potential of carbon dioxide gas injection application in improving oil recovery. International oil and gas Conference, Beijing, China, 7-10. *http://dx.doi.org/10.2118/64730-MS.*

Aladasani, A. and Bai, B. 2010. Recent developments and updated screening criteria of enhanced oil recovery techniques. International oil and gas Conference. Beijing, China. Society of Petroleum Engineers.

Al-Anazi, B.D. 2007.Enhanced oil recovery techniques and nitrogen injection. CSEG Recorder, pp. 29-33.

Al-Maamari, R.S.H. and Buckley, J.S. 2000. Asphaltene precipitation and alteration of wetting: can wettability change during oil production? SPE/DOE improved oil recovery symposium, Tulsa, Oklahoma, Society of Petroleum Engineering.

Al-Qasim, A.S. 2011 Simulation of Asphaltene deposition during CO_2 flooding, The University of Texas, Austin, August.

Alta'ee, A.F., Saaid, I.M. and Masoudi, R. 2010. Carbon dioxide injection and asphaltene precipitation in light oil reservoirs. Eleventh mediterranean petroleum conference and exhibition, Libya.

Alta'ee, A.F., Ong, S.H, Sima, S.A. and Ismail, M.S. 2010. Experimental investigation on effect of CO_2 and WAG injecation on permeability reduction induced by asphaltene precipitation in light oil. *International journal of chemical science and engineering*. **6**(12): 1203-1208.

Alvarado, V. and Manrique, M. 2010. Enhanced oil recovery: An update review, Energies. **3**(9): 1529-1575.

Andersen, S.I. and Speight, J.G. 2001. Petroleum resins: Separation, character, and role in petroleum. Petroleum science and technology. **19**(1): 1-34.

ASTM, D6560 (IP 143/01). 2000. Standard test method for determination of asphaltenes (heptane insolubles) in crude petroleum and petroleum products.

ASTM, D3279. 1997. Standard test method for n-heptane insolubles, annual book of ASTM standards.

Bennet, C.A., Appleyard, S., Gough, M., Hohmann, P.R. and Joshi, M.H. 2006. Industry recommended procedures for experimental crude oil preheat fouling research. *Heat Transfer Eng*. **27**: 28-35.

Buckley, J.S. 1996. Microscopic investigation of the onset of asphaltene precipitation. *Fuel Sci. Technol. Int*. **14** (1 and 2): 55-74.

Burke, N.E., Hobbs, R.E. and Kashou, S.F. 1990. Measurement and modeling of asphaltene precipitation. *JPT*. 1440-1447.

Cassani, F., Ortega, P., Davila, A., Rodriguez, W., Lagoven, S.A. and Seranno, J. 1992. Evaluation of foam inhibitors a the jusepin oil/gas separation plant, El Furrial field, eastern Venezuela. Second latin american petroleum engineering conference. Caracus, Venezuela.

Chang, C.L. and Fogler, H.S. 1996. Peptization and coagulation of asphaltenes in apolar media using oil-soluble polymers. *Fuel Sci. Technol. Intl*. **14** (1and 2): 75-100.

Chukwudeme, E.A. and Hamouda, A.A. 2009 .Enhanced oil recovery (EOR) by miscible CO_2 and water flooding of asphaltenic and non-asphaltenic Oils. Department of Petroleum Engineering, University of Stavanger, Norway.

Civan, F .2000. Reservoir formation damage."University of Oklahoma, Houston, Texas" book.

De Boer, B. and Leerlooyer, L. 1995. Screening of crude oils for asphalt precipitation: theory, practice and the selection of inhibitors. Paper SPE-24987-PA.

Dehghani, A.K., Gholami, V., Moghadasi, J. and Abdi, R. 2008. Formation damage through asphaltene precipitation resulting from CO_2 gas injection. *Iranian carbonate reservoir. SPE production and operations*. 210-214.

Escobedo, J. and Mansoori. 1995. G. A. Asphaltene and other heavy-organic particle deposition during transfer and production operations, in SPE. Annual technical conference and exhibition. Society of petroleum engineers. Dallas, USA.

Fan, T. and Wang .J. 2002. Evaluating crude oil by SARA analysis, paper SPE-75228 presented at improved oil recovery symposium.

Ferworn, K.A. 1995. *Thermodynamic and kinetic modeling of asphalteneprecipitation from heavy oils and bitumens.* Ph. D. dissertation. University of Calgary.

Fotland P., Anfindsen H. and Fadnes, F.H. 1993. Detection of asphaltene precipitation and amounts precipitated by measurement of electrical conductivity. *Fluid phase equilibria*. **82**(2): 157-164.

Elsharkawy, A.M., Poettmann, F.H. and Christiansen, R.L. 1992. Measuring minimum miscibihty pressure: Slim-tube or rising-bubble method?. SPE 24114, SPE/DOE symposium on improved oil recovery, Tulsa, UK. 22-24.

Fred, I. and Stalkup, J. 1992. Miscible displacement, SPE monograph series.

Fuhr, B.J., Cathrea, L., Coates, H., Kalra, H. and Majeed, A.I. 1991. Properties of asphaltenes from a waxy crude. *Fuel*. **70**(11): 1293-1297.

Gozalpour, F., Ren S.R. and Tohidi, B. 2005. CO_2 EOR and storage in oil reservoirs. *Oil and gas science technology*. **60**(3): 537-546

Gray, M.R. 2003. Consistency of asphaltene chemical structures with pyrolysis and coking behavior. Energy fuels. **17**(6): 1566-1569.

Green, D.W. and Willhite, G.P. 1998. Enhanced oil recovery. Society of petroleum engineers. Richardson. Texas, USA.

Groffe, P., Volle. J.L. and Ziada. 1995. Application of chemicals in prevention and treatment of asphaltene precipitation in crude oils. European formation damage conference. the Hague, Netherlands. 15-16.

Hammer, S. and Kuuskraa, L. 1983. Recovery efficiency of enhanced oil recovery methods: A review of significant field tests. Annual technical conference and exhibition. San Francisco, USA. 5-8.

Harvey, M.T.J., Shelton, J.L. and Kelm, C.H. 1977. Field injectivity experiences with miscible recovery projects using alternate rich-gas and water injection. JPT 105.

Hideharu, Y. and Ali A. 2011. Dynamic asphaltene behaviour for gas injection risk analysis, Iptc Conference. Doha, Qatar.

Holm, L.W. and Josendel, V.A. 1974. Mechanisms of oil displacement by carbon dioxide. *Journal of petroleum technology*. **26**(12): 1427-1436.

Idem, R.O. and Ibrahim, H.H. 2002. Kinetics of CO_2-induced asphaltene precipitation from various saskatchewan crude oils during CO_2 miscible flooding". *J. Pet. Sci. Eng.* **35**(3-4): 233-246.

Jamaluddin, A.K.M., Nighswander, J. and Joshi, N. 2001. A systematic approach in deepwater flow assurance fluid characterization. Annual technical conference and exhibition. New Orleans, Louisiana.

Jewel, D.M., Weber, J.H., Bunger J.W., Plancher, H. and Latham, D.R. 1972. Ion-exchange, coordination and adsorption chromatographic separation of heavy-end petroleum distillates. Analytical Chemistry. 44(8): 1391-1395.

Kamath V.A., Yang, J. and Sharma, G.D. 1993. Effect of asphaltene deposition on dynamic displacements of oil by water. SPE Western regional meeting anchorage, Alaska.

Khanifar, A., Alian.S,S., Demiral, B. and Darman, N. 2011. Study of asphaltene precipitation and deposition phenomenon during wag application. Enhanced oil recovery conference. Kuala Lumpur, Malaysia. 19-21.

Khosravi, M., Rostami, B. and Nghiem, L. 2009. Influence of CO_2 dissolution and asphaltene precipitation on oil PVT and recovery enhanced oil recovery. *Iranian chemical engineering journal*. **8**(43): 54-61.

Kokal, S.L., Sayegh, S.G. and Asphaltenes. 1995. The Cholesterol of petroleum, in middle east oil show. Society of petroleum engineers, Inc. Manama, Bahrain.

Kumar, N.A. and Von Gonten, W.T. 1973. An Investigation of oil recovery by Injecting CO_2 and LPG mixtures. Fall meeting of the society of petroleum engineers of AIME. Las Vegas, Nevada.

Leontaritis, K.J. and Asphaltene. 1998. Near-wellbore formation damage modeling in SPE. Formation damage control conference.Society of petroleum engineers, Inc. Lafayette, Louisiana.

Leontaritis, K.J. and Mansoori G.A. 1987. Asphaltene flocculation during oil production and processing: A thermodynamic collodial model, in SPE International Symposium on Oilfield Chemistry. Society of petroleum engineers, Inc. San Antonio, Texas.

Lindley, J.R. 2011. Exploration and production technologies exploration technologies-EOR process drawings. Retrieved from the energy Lab. *http://www.netl.doe.gov/technologies/oilgas/publications/eordrawings/BW/bwnf.PDF*

Mansoori, G.A. 2005. Nanoscale structures of asphaltene molecule, asphaltene steric colloid and asphaltene micelles and vehichles. *http://tigger.uic.edu/~mansoori/Asphaltene.Molecule_html.*

Melzer, L.S. and Midland, T. 2012. Carbon dioxide enhanced oil recovery (CO_2 EOR): Factors involved in adding carbon capture, utilization and storage (CCUS) to enhanced, oil,recovery. *http://neori.org/Melzer_CO2EOR_CCUS_Feb2012.pdf.*

Miftachul, C. 2010. *Study of CO_2 effect on asphaltene precipitation and compositional simulation of asphaltenic oil reservoir*. University of Stavenger.

Milind, D.D. 2002. *Enhanced the effectiveness of carbon dioxide flooding by managing asphaltene precipitation*. University of Utah, final report.

Mohammed, S.A., Arisaka, K. and Kumazaki, Y. 1998 .Integrated analysis of asphaltene deposition from field production data and laboratory experiments. Abu Dhabi International petroleum exhibition and conference. 11-14.

Mohammed, A.A. 2009. *Measurement of the interfacial tension of CO_2/brine mixtures and estimantion of the CO_2 storage capacity in deep saline aquifers*. Dalhousie University Halifax.

Moghadasi, J., Kalantari-Dahaghi, V. and Gholami, R.A. 2006. Formation damage due to asphaltene precipitation resulting form CO_2 gas injection in Iranian carbonate reservoirs. Europec/EAGE annual conference and exhibition. Vienna, Austria. 12-15.

Muhannad Talib Shuker, Muhammad Ali Buriro, Malik Muhammad Hamza. 2012 .Enhanced oil recovery: the future of Pakistan" SPE 163124-MS, presented at Annual Technical Conference, Islamabad, Pakistan.

Muhammad, A.B. and Muhannad, T.S. 2012. Asphaltene prediction and prevention: A strategy to control asphaltene precipitation. Annual technical conference. Islamabad, Pakistan.

Muhammad, A.B. and Muhannad, T.S. 2013. Minimizing asphaltene precipitation in Malaysian reservoir. Annual technical symposium and exhibition. Khobar, Saudi Arabia.

Mullins, O.C. 2007. Asphaltenes, heavy oils, and petroleomics. New York, USA.

Mungan, N. 1979. A Review and evaluation of carbon dioxide flooding applications report. AR-5, Petroleum Recovery Institute.

Mungan and Necmettin. 1982. Carbon dioxide flooding EM dash fundamentals. *Journal of canadian petroleum technology*.

Negahban, S. and Joshio, N. 2003. A systematic spproach for experimental study of asphaltene deposition for an Abu Dhabi reservoir under WAG development Plan. Chemistry Symposium. Texas, USA.

Nobakht, M.M. 2008. *Interactions between crude oil and CO_2 under reservoir conditions.* Master's Thesis. Department of Petroleum Systems Engineering, University of Regina.

Orr, F.M. and Silva. M.K. 1982. Equilibrium Phase compositions of CO_2-Hydrocarbon mixtures: Measurement by a continuous multiple contact experiment. Third joint symposium on enhanced oil recovery, Tulsa.

Oskui, G.P., Salman, M., Gholoum, E.F. and Rashed, A. 2006. Laboratory technique for screeningasphaltene inhibitors for Kuwaiti reservoirs. Technical symposium of Saudi Arabia, Dahran.

Pereira, J.C., López, I., Salas, R., Silva, F., Fernández, C., Urbina, C., López, J.C. 2007. Energy and Fuels. 21, 1317.

Pereira, J.C. and Lopez. 2007. Resins: The molecules responsible for the stability/instability phenomena of asphaltene. *Energy and Fuels*. 2**1**: 1317-1321.

Parra-Ramirez., Pertson, B. and Deo, D. 2001. Comparsion of first and multiple contact carbon dioxide induced asphaltene precipitation. Symposium on oil field chemistry. Houston-Texas.

Recombination Cell Apparatus (Rca 1000), User Manual V1.10, Vinci Technologies France

Reichert, C., Fuhr, B.J. and Klein, L. 1986. Measurement of asphaltene flocculation in bitumen solutions. *J. Can. Pet. Technol*. **25**(5): 33-37.

Sima, S.A., Omar, A.A., Alta'ee, A.F. and Hani, I. 2011. Study of asphaltene precipitation induced formation damage during CO_2 injection for Malaysian light oil. World academy of science, engineering and technology.

Sarma, H.K. 2003 .Can we ignore asphaltene in a gas injection project for light-oils? International improved oil recovery conference. Kuala Lumpur. Malaysia. 20-21.

Schlumberger oil field review Summer. 2007. Asphaltenes-problematic but rich and potential.

Schlumberge oil field glossary:http://www.glossary oilfield.slb.com/Display.cfm? Term= enchanced %20oil%20recover,Retrieved on(1November,2010).

Schlumberger. 2013. Interfacial tension. Retrieved from schlumberger oilfield glossary: *http://www.glossary.oilfield.slb.com/en/Terms/i/interfacial_tension.aspx*

Schlumberger. 2013. Miscible displacement. Retrieved from schlumberger oilfield glossary: *http://www.glossary.oilfield.slb.com/en/Terms/m/miscible_displacement.aspx*

Schlumberger Limited. 2013. Miscible displacement. Retrieved from Schlumberger oilfield glossary: *http://www.glossary.oilfield.slb.com/en/Terms/m/miscible_displacement.aspx*

Sclumberger Limited. 2013. Oil swelling. Retrievedfrom oilfield glossary: *http://www.glossary.oilfield.slb.com/en/Terms.aspx?LookIn=term%20name&filter=oil%20swelling*

Shedid, S.A. and Zekri, A.Y. 2004. Formation damage caused by simultaneous sulfur and asphaltene deposition. International symposium and exhibition on formation damage control. Lafayette, Louisana. 18-20.

Span, R. and Wagner, W. 1994. A new equation of state for carbon dioxide covering the fluid region from triple-point temperature to 1100 K at pressures up to 800 MPa. 1509-1594.

Srivastava, R.K., Huang, S.S. and Dong, M. 1997. Asphaltne deposition during CO_2 flooding. Production operations symposium. Oklama City, Oklahoma.

Srivastava, R.K., Huang, S.S. and Mingzhe, D. 1999. Asphaltene deposition during CO_2 Flooding. *Production and facilities Journal*. **14**(4): 235-245.

Stalkup, F.L. 1978. Carbon dioxide miscible flooding: Past, present and outlook for the future. Journal of petroleum technology. 30(8): 1102-1112.

Stalkup, F.L. 1983. Status of miscible displacement. *Journal of petroleum technology*. 35(4): 815-826.

Stright J., Aziz, K.U. and Settari, A.S. 1977. Carbon dioxide injection into bottom-water, undersaturated viscous oil reservoirs. *Journal of petroleum technology*. 29(10): 1248-1258.

Taher, A., Al-Sahhaf. Mohammed, A.F. 2002. Retardation of asphaltene precipitation by addition of toluene, resins, deasphalted oil and surfactants. *Fluid phase equilbria*. **194**(1): 1045-1057.

Taber J.J., Martin, F.D. and Seright R.S. 1997. EOR screening criteria revisited-part. 2: Applications and impact of oil prices, SPE Reservoir Engineering, August.

Tianguang, F. and Jianxin, W. 2002. Evaluating crude oils by SARA analysis Improved oil recovery symposium. Tulsa, Oklahoma.

Thawer. R., Nicoll, D.C.A., Dick, G. 1990. Asphaltene deposition in production facilities, SPE Production Engineering.

Thomas, B., Lliyas, A., Johansen, T., Hawboldt, K. and Khan, F.T. 2010. Sustainable and environmentally friendly enhanced oil recovery in offshore new foundllan. Offshore Technology confernce. Houston, Texas, USA.

Thomas, S. 2008. Enhanced oil recovery. An overview, oil and gas. *Science and technology*. **63**(1): 9-19.

Yang, X.L. and Lu, W.Z. 2006. Study on interfacial properties of asphaltenes and resins from Liaohe crude. *Acta Petrolei Sinica* (*Petroleum Processing Section*) **30**: 1-6

Yarranton, H. W. 2005. Asphaltene self-association. *J. Disp. Sci. Tech*. **26** (1): 5-8.

Yarranton, H.W., Fox, W.A. and Svrcek, W.Y. 2007. Effect of resins on asphaltene self-association and solubility. *Can. J. Chem. Eng*. **85**(5): 635-642.

Zhang, D., Wang, Z., Sun, J., Zhang, L. and Li, Z. 2012. Economic evaluation of CO_2 pipeline transport in China. Energy Conversion and Management.

APPENDICES

APPENDIX A

SARA ANALYSIS

To conduct SARA analysis, the asphaltene part is first extracted using the addition of n-hexane with 1 gram of oil to 40 ml of hexane ration. Saturates, aromatics and resins later can be extracted through the standard method using high pressure liquid chromatography from the de-asphalted oil (ASTM D6560 (IP 143/01). There are two ways to measure asphaltene stability. The most common method is using colloidal stability index, which can be measured using the following formulae:

$$BV \qquad = \frac{Asphaltene + saturate}{Aromtics + resins}$$

Index of 0.9 or more indicates that the particles are unstable while values below 0.7 indicate the stability of asphaltene particle. The mid value between 0.7 to 0.9 suggests the uncertainty of asphaltene destabilization

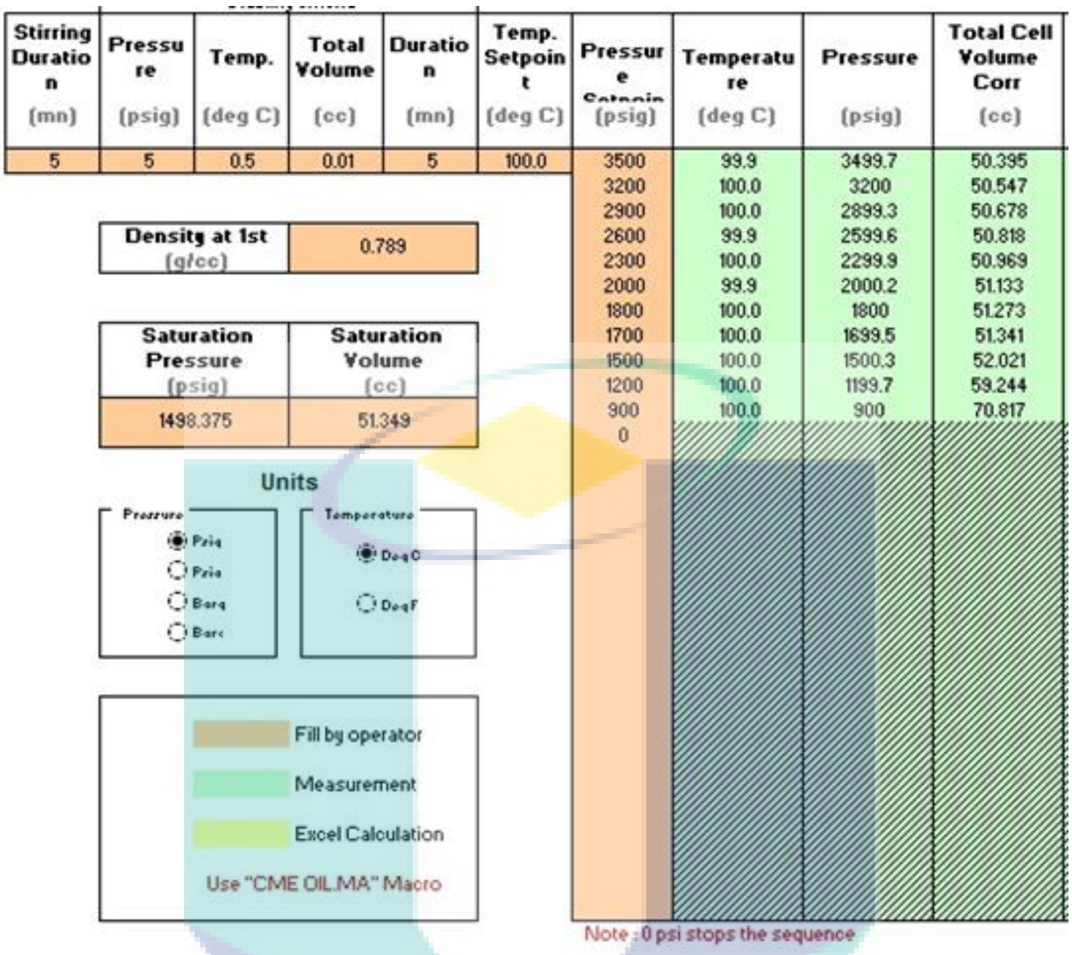
APPENDIX B

PVT TESTS

Appendix B covers the results of PVT tests. The tests conducted on PVT instrument are constant composition test and solid detection test. This appendix covers the results of both tests.

B.1 Constant Composition Test Result of Crude Oil With 40% Injection Gas

A sum of 52 cc of live crude oil sample was transferred from recombination cell into PVT cell at a pressure of 2000 Psi and 100°C temperature. The pressure was then raised to 3500 Psi. The sample was allowed to equilibrate for 24 hours. Isothermal depressurization was carried out and the pressure was reduced discretely from 300 Psi. Total volume of PVT cell was recorded at each step. The main window of the constant composition test with live sample of 53cc is shown in Figure B.1. The live sample was recombined with 45cc of dead crude oil and 18cc mixed composition injection gas.



Stirring Duration (mn)	Pressure (psig)	Temp. (deg C)	Total Volume (cc)	Duration (mn)	Temp. Setpoint (deg C)	Pressure Setpoin (psig)	Temperature (deg C)	Pressure (psig)	Total Cell Volume Corr (cc)
5	5	0.5	0.01	5	100.0	3500	99.9	3499.7	50.395
						3200	100.0	3200	50.547
						2900	100.0	2899.3	50.678
						2600	99.9	2599.6	50.818
						2300	100.0	2299.9	50.969
						2000	99.9	2000.2	51.133
						1800	100.0	1800	51.273
						1700	100.0	1699.5	51.341
						1500	100.0	1500.3	52.021
						1200	100.0	1199.7	59.244
						900	100.0	900	70.817
						0			

Density at 1st (g/cc)	0.789

Saturation Pressure (psig)	Saturation Volume (cc)
1498.375	51.349

Units

Pressure
● Psig
○ Psia
○ Barg
○ Bara

Temperature
● DegC
○ DegF

🟧	Fill by operator
🟩	Measurement
🟨	Excel Calculation

Use "CME OIL.MA" Macro

Note : 0 psi stops the sequence

Figure B. 1: Main window of CCE experiment for 40 % injection gas in oil

Bubble point pressure can be elicited from the sharp changes in total cell volume data versus pressure. Pressure volume curve for live crude oil with 40% injection gas is shown in Figure B.2. In addition, captured images on camera from the top of PVT cell can be visualized as an indication of bubble point pressure. According to both indications, the bubble point pressure of live oil is 1500 Psi at 100^{o}C temperature.

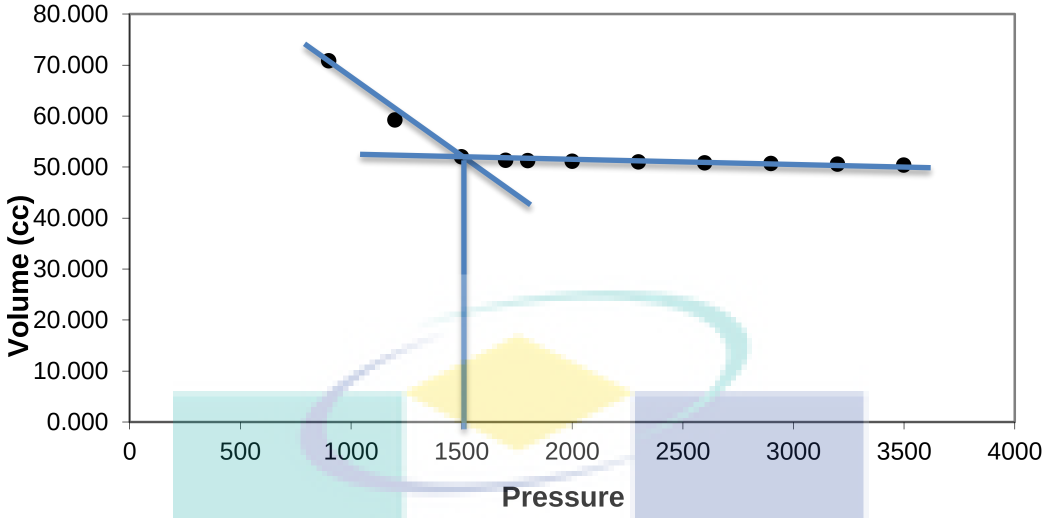
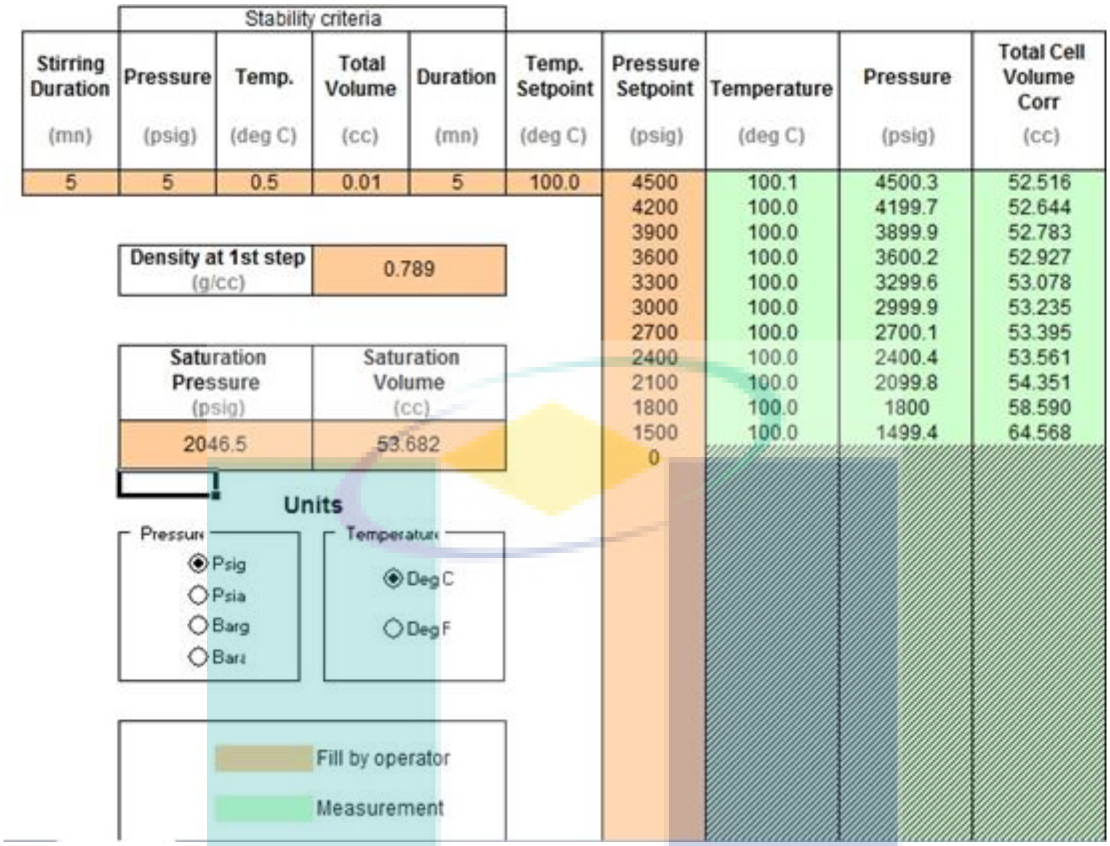


Figure B. 2: Pressure volume curve for oil with 40 % mixed composition gas

B.2 Constant Composition Test Result of Crude Oil With 60% Injection Gas

A sum of 55cc of live crude oil sample was transferred from the recombination cell into PVT cell at a pressure of 2000 Psi and 100^{o}C temperature. The pressure was then raised to 4500 Psi. The sample was then allowed to equilibrate for 24 hours and later, isothermal depressurization was carried out. 300 Psi was reduced in discreet steps and total volume of PVT cell was recorded at each step. The main window of the constant composition test with live sample of 55cc is shown in Figure B.3. The live sample was recombined with 45cc of dead crude oil and 27cc mixed composition injection gas.



	Stability criteria								
Stirring Duration (mn)	Pressure (psig)	Temp. (deg C)	Total Volume (cc)	Duration (mn)	Temp. Setpoint (deg C)	Pressure Setpoint (psig)	Temperature (deg C)	Pressure (psig)	Total Cell Volume Corr (cc)
5	5	0.5	0.01	5	100.0	4500	100.1	4500.3	52.516
						4200	100.0	4199.7	52.644
						3900	100.0	3899.9	52.783
						3600	100.0	3600.2	52.927
						3300	100.0	3299.6	53.078
						3000	100.0	2999.9	53.235
						2700	100.0	2700.1	53.395
						2400	100.0	2400.4	53.561
						2100	100.0	2099.8	54.351
						1800	100.0	1800	58.590
						1500	100.0	1499.4	64.568
						0			

Density at 1st step (g/cc)	0.789

Saturation Pressure (psig)	Saturation Volume (cc)
2046.5	53.682

Units

Pressure
● Psig
○ Psia
○ Barg
○ Bar

Temperature
● Deg C
○ Deg F

🟫 Fill by operator
🟩 Measurement

Figure B. 3: Main window of CCE experiment for 60% injection gas in oil

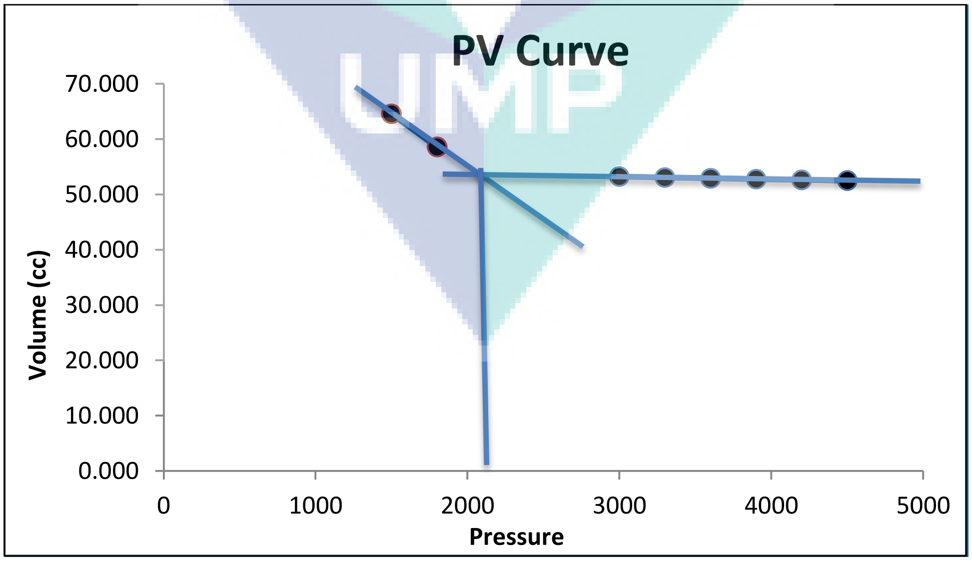


Figure B. 4: Pressure volume curve for oil with 60% mixed composition gas

Bubble point pressure can be elicited from the sharp changes in total cell volume data versus pressure. Pressure volume curve for live crude oil with 60% injection gas is shown in Figure B.4. In addition, captured images on camera from on top of the PVT cell can be visualized to indicate the bubble point pressure. According to both indications, the bubble point pressure of live oil is 2050 Psi at 100 ^{o}C.

APPENDIX C

FLUID RECOMBINATION

$$\frac{GOR_{ST}}{\mathrm{V_m^{id}}}\,[=]\,\frac{(\mathrm{scf/STB})}{(\mathrm{scf/lb\text{-}mole})}\,[=]\,\mathrm{lb\text{-}mole_{gas}/STO}$$

$$\frac{GOR_{SP}}{\mathrm{V_m^{id}}}\,[=]\,\frac{(\mathrm{scf/STB})}{(\mathrm{scf/lb\text{-}mole})}\,[=]\,\mathrm{lb\text{-}mole_{gas}/STO}$$

$$\mathrm{V_m^{id}} = 380.7\,\mathrm{scf/lb\text{-}mole}\ \text{(ideal gas molar volume)}$$

$$z_i = y_{iSP} f_{v_{SP}} + x_{iSP}\left(1 - f_{v_{SP}}\right)$$

$$x_{iSP} = y_{iST} f_{v_{ST}} + x_{iST}\left(1 - f_{v_{ST}}\right)$$

$$z_i = y_{iSP} f_{v_{SP}} + \left[y_{iST} f_{v_{ST}} + x_{iST}\left(1 - f_{v_{ST}}\right)\right]\left(1 - f_{v_{ST}}\right)$$

APPENDIX D

LABORATORY DATA FOR CORE 1

Pressures and Temperature

Inlet Pressure: 2000 Psi

Outlet/BPR Pressure: 2000 Psi

Pressure difference was unreadable and negligible due to high permeability.

Over Burdon/Confining Pressure: 2500 Psi

Flow Rate: 0.4 cc/min

Temperature: 100°C

Production Values

Brine Production: 13.5 cc, S_{wi} = 12.43%

Oil Production: 9.2 cc, S_{or} = 40.32%

CO_2 Breakthrough: 3 cc = 19.45%

Results for asphaltene content analysis during flow rate = 0.4 cc/min with initial asphaltene content = 3 wt %.

Example of calculations:

Brine Production = 13.5 cc, S_{wi} = 12.43%. When the core with oil flow together, the brine was produced from outlet and therefore it is a must to make sure that this production must go into graduate cylinder. The percentage of remaining Brine from this formula is as follows:

$$\text{Remaining Brine } (S_{wi}) = \text{Total Pore Volume} - \text{Brine Production}$$

$$S_{wi}\ \%\text{age} = \frac{\text{Remaining Brine Volume}}{\text{Total Pore Volume}} \times 100$$

Oil Production = 9.2 cc, S_{or} = 40.32%

When the core flows with CO_2, oil production was found from outlet and make sure that this production must go into graduate cylinder so that it will be able to measure the volume in the end and the percentage of the remaining oil from this formula.

$$\text{Remaining oil } (S_{or}) = \text{Total Pore Volume - Oil Production}$$

$$S_{or}\% = \frac{\text{Remaining Oil Volume}}{\text{Total Pore Volume}} \times 100$$

CO_2 Break Through: 3 cc = 19.45%

After sometime, the CO_2 will bypass the oil and the two phase production (oil and CO_2) together. This point is called CO_2 breakthrough. It is necessary to be noted that this is the single phase production volume of oil (oil production volume only with single phase) from outlet, and make sure that this production must go into graduate cylinder so it will be able to measure the volume in the middle. Afterwards, the percentage of the CO_2 breakthrough can be calculated from this formula.

$$CO_2 \text{ Breakthrough } \% = \frac{\text{Oil Production With Single Phase}}{\text{Total Pore Volume}} \times 100$$

LABORATORY DATA FOR CORE 2

Pressures and Temperature
Inlet Pressure: 2000 Psi
Outlet/BPR Pressure: 2000 Psi
Pressure difference was unreadable and negligible due to high permeability.
Over Burdon/Confining Pressure: 2500 Psi
Flow Rate: 0.6 cc/min
Temperature: 100°C
Production Values
Brine Production: 12.6 cc, S_{wi} = 15.639%
Oil Production: 9.05 cc, S_{or} = 39.40%
CO_2 Breakthrough: 2.65 cc = 17.74%
Results for asphaltene content analysis during Qinj = 0.6 cc/min with initial asphaltene content = 3 wt %.

LABORATORY DATA FOR CORE 3

Pressures and Temperature

Inlet Pressure: 2000 Psi

Outlet/BPR Pressure: 2000 Psi

Pressure difference was unreadable and negligible due to high permeability.

Over Burdon/Confining Pressure: 2500 Psi

Flow Rate: 0.8 cc/min

Temperature: 100°C

Production Values

Brine Production: 11.9 cc, , S_{wi} = 17.57%

Oil Production: 8.9 cc,S_{or} = 38.32%

CO_2 Breakthrough: 2.4 cc = 16.624%

Results for asphaltene content analysis during Qinj = 0.8 cc/min with initial asphaltene content = 3 wt %.

APPENDIX F

LIST OF PUBLICATIONS

Conference Paper

Abdalla. A.M Ali, Zulkefli Bin Yaacob, Abdurahman H. Nour.2014. Enhanced Oil Recovery Techniques. The 3th International Conference of Chemical Engineering and Industrial Biotechnology (ICCEIB) 28 August,2013.

Journal Paper

Abdalla. A.M Ali, Zulkefli Bin Yaacob, Abdurahman H. Nour.2014. Enhanced Oil Recovery Techniques Miscible And Immiscible Flooding. *Journal of Applied Science*. **14**:1016-1022.