

A Study of CO2 and WAG Injection Induced Asphaltene Precipitaion

by

Ong Sheau Hun

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

MAY 2012

Universiti Teknologi PETRONAS Bandar Seri Iskandar 31750 Tronoh Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

A Study of CO2 and WAG Injection Induced Asphaltene Precipitation

by

Ong Sheau Hun

A project dissertation submitted to the Petroleum Engineering Programme Universiti Teknologi PETRONAS in partial fulfilment of the requirement for the BACHELOR OF ENGINEERING (Hons) (PETROLEUM ENGINEERING)

Approved by,

(Mr. Ali F. Mangi Alta'ee) Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

MAY 2012

CERTIFICATION OF ORIGINALITY

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

ONG SHEAU HUN

ABSTRACT

Asphaltene is high molecular weight component of crude oil that exists in the oil as colloidal suspension, and is peptized or stabilized by resin that absorbed on its surface. Asphaltene might loss its stability during different phases of production and specially during carbon dioxide flooding. The precipitation of asphaltene during CO2 injection might lead to formation damage, wellbore plugging and recovery reduction. Water-alternating-gas (WAG) injection is the mobility enhancement method of CO2 injection and it is believed that the presence of water could reduce the asphaltene precipitation.

In this work, dynamic core flooding experiments were conducted to study the effect of CO2 injection and WAG injection on the amount of asphaltene precipitated. Core properties after displacement were inspected for any porosity, permeability and wettability alteration to study the effect of asphlatene precipitation on rock properties. The recovered oil is collected over a time interval and the change in asphaltene content was reported against pore volume of injection. The reduction of the asphaltene content in the effluent oil indicates the amount of asphaltene precipitated inside the core.

The laboratory data had justified that WAG injection gives less asphaltene precipitation compared to CO2 injection. Higher porosity and permeability reduction were observed with CO2 injection. It was also found out that during CO2 injection, the presence of asphaltene would altered the rock wettability to more oil wet. However, in the presence of water film during WAG injection, the initial water wet condition of the rock remained and contributed to higher oil recovery. Overall, WAG injection gives less asphaltene precipitation, less formation damage, and higher oil recovery compare to CO2 injection.

ACKNOWLEDGEMENT

Greetings,

Thanks and praise God, the research entitled **"A Study of CO2 and WAG Injection Induced Asphaltene Precipitation"** has been completed successfully. This research took nearly 8 months to complete all the research works; literature reviews, experimental works, results discussions and documentations. The author would like to take this opportunity to convey her upmost gratitude to the following people.

• *FYP Supervisor; Mr. Ali F.Mangi Alta'ee* for his continuous guidance and advices since the first day of the project assigned. His dedication and constant caring and patience have taught the author so much about this research.

• *Lab Technologists; Mr. Shahrizal and Mr. Riduan* for their assistants in operating the equipments for data gathering and analysis for all of the experiments. Their technical knowledge and trouble-shooting skills have certainly enabled the experiments to run smoothly and made the research work more valuable.

• *Postgraduate Student; Ms. Sima Sh. Alian* for her time and willingness in sharing her knowledge and experience on experimental works. All the support, guidance, and feedbacks are truly appreciated.

Token of appreciation also goes to the author's family who have been giving the courage and moral support to complete this research successfully.

Thank you.

TABLE OF CONTENTS

CERTIFICATIONSi
ABSTRACTii
ACKNOWLEDGEMENTiv
TABLE OF CONTENTv
LIST OF FIGURES viii
LIST OF TABLESix
CHAPTER 1: INTRODUCTION
1.1 Project Background 1
1.2 Problem Statement 1
1.2.1 Problem Identification1
1.2.2 Significant Of The Project2
1.3 Objective 2
1.4 Scope Of Work
1.3 The relevancy of the Project
1.4 Feasibility of the project within the scope and time frame

CHAPTER 2: LITERATURE REVIEW

2.1 CO2 Injection and WAG Injection	4
2.2 Asphaltene	5
2.2.1 Colloidal Model	5
2.2.2 Asphaltene Fraction in Crude Oil	6
2.2.3 Mechanism of Asphaltene Precipitation	7

2.3 Asphaltene Destabilizes Factors	8
2.3.1 Temperature Drop	8
2.3.2 Pressure Drop	8
2.3.3 Compositional Change	9
2.4 Effect of CO2 Injection on Asphaltene Precipitation	10
2.5 Effect of WAG Injection on Asphaltene Precipitation	12
2.6 Effect of Asphaltene Precipitation on Formation Properties	13
2.7 Literature Summary	14

CHAPTER 3: METHODOLOGY

3.1 Research Methodology	15
3.1.1 Core Properties Measurement	16
3.1.2 Crude Oil Properties Measurement	17
3.1.3 Asphaltene Content Measurement	18
3.1.4 Core Flooding	19
3.1.5 Post-flooding Evaluation	21
3.1.6 Core Cleaning	22
3.2 Project Activities	23
3.3 Gantt Chart and Key Milestones	24
3.4 Tools, Material and Equipments	25
	 3.1 Research Methodology 3.1.1 Core Properties Measurement. 3.1.2 Crude Oil Properties Measurement

CHAPTER 4: RESULTS AND DISCUSSION

Reduction
4.4 Effect of Asphaltene Precipitation on Porosity and Permeability
4.3 CO2 and WAG Injection Induced Asphaltene Precipitation28
4.2 Core Displacement Test
4.1 Sample Properties

4.5 Effect of Asphaltene Precipitation on Rock Wettability	32
4.6 CO2 and WAG Injection Recovery Factor	33

CHAPTER 6:	CONCLUSION	
REFERENCES		
APPENDIXES		41
NOMENCLATI	URES	45

LIST OF FIGURES

Figure 1: Resin and Asphaltene in Crude Oil	6
Figure 2: Methodology Outline	16
Figure 3: Poro-Perm Measurement System	17
Figure 4: Densitometer	18
Figure 5: ASTM D3279-07 Standard Test Method for n-Heptane	19
Figure 6: Relative Permeability Test System	20
Figure 7: IFT 700 System	22
Figure 9: Soxhlet Extractor	23
Figure 9: Project Activities	24
Figure 10: Simple Schematic of Core Flooding Equipment	27
Figure 11: Asphaltene Content of the effluent versus Pore Volume of Injection	29
Figure 12: Asphaltene Precipitation inside the Core versus Pore Volume of Inject	ion
	30
Figure 13: Porosity Reduction during CO2 and WAG Injection	32
Figure 14: Permeability Reduction during CO2 and WAG Injection	32
Figure 15: Contact Angle Measurement for CO2 and WAG Injection Before and	
After Core Flooding	34
Figure 16: Recovery Factor of CO2 and WAG Injection	37

LIST OF TABLES

Table 1: Project Gantt Chart And Key Milestones	25
Table 2: List of Chemicals/ Materials Use In Project	26
Table 3: List of Equipment Use In Project	26
Table 4: Crude Oil Properties	27
Table 5: Core Samples Properties	27
Table 6: Core Displacement Test Parameters	28
Table 7: Core Properties Before and After Displacement Test	31
Table 8: Recovery Calculation from Displacement Test	36

LIST OF EQUATION

1.	Bulk Volume	17
2.	Porosity	18
3.	Weight Percentage of Asphaltene Content	19
4.	Initial Oil Saturation	21
5.	Residual Oil Saturation	21
6.	Oil Recovery Factor	21
7.	Oil Density Equation Line	44
8.	API Gravity	45
9.	Specific Gravity	

CHAPTER 1 INTRODUCTION

1.1 Project Background

Carbon dioxide injection is one of the efficient Enhanced Oil Recovery methods, but it may induce asphaltene precipitation problem. During CO2 gas injection, the miscibility of the CO2 gas with the reservoir oil will contribute to oil composition change which alters the asphaltene-to-resin ratio and favour the precipitation of asphaltene (Kokal & Sayegh, 1995; Hammami *et al.*, 2000; Oskui & Abuhaimed, 2009). The precipitated asphaltene might lead to formation damage, wellbore plugging and recovery reduction. (Sima et al., 2011; Ghedan, 2009; Srivastava et al., 1997

Water-alternating-gas (WAG) injection is the enhancement of CO2 injection in providing mobility control over fingering problem. A reduction in mobility would improve the sweep efficiency and leads to higher oil recovery (Caudle & Dynes, 1957). Okwen (2006), Sarma (2003), Walcot *et al.* (1989) and Srivastava *et al.*, (1997) are researchers who reported that the presence of water could minimize the asphaltene precipitation (Sarma, 2003; Srivastava *et al.*, 1997, Wolcott et al., 1989; Okwen, 2006). In this paper, the effect of CO2 and WAG injection on asphaltene precipitation was investigated to further determine the role of water in minimizes the amount of asphaltene precipitated.

1.2 Problem Statement

1.2.1 Problem Identification

Asphaltene precipitation is a common problem during natural depletion, and especially during CO2 injection. The precipitation of asphaltene might lead to formation damage, wellbore plugging and recovery reduction. In dealing with the asphaltene problem, most studies were focus

on determining the optimum CO2 injection condition which could minimizes the asphaltene precipitation. For example, the concentration of CO2 gas, injection pressure, injection rate and etc.

Another approach that can be carrying out to deal with asphaltene precipitation problem is by investigating the role of water in minimizing asphaltene precipitation. It is believed that the presence of water could minimize the asphaltene precipitation. Thus, it is inquisitive to determine if WAG injection could give less asphaltene precipitation, less formation damage, and higher oil recovery compare to CO2 injection.

1.2.2 Significant of the project

The findings from this research are significant in support of the role of water in reducing asphaltene precipitation. This will further highlight the beneficial of WAG injection over CO2 injection in providing mobility control, giving higher sweep efficiency, higher oil recovery and lower asphaltene precipitation. The findings would further provide the data on the amount of asphaltene precipitation and the formation damage induced by WAG and CO2 injection.

1.3 Objectives

- 1. To investigate and compare the asphaltene precipitation induced by CO2 injection and Water-Alternating-CO2 (WAG) injection.
- To investigate the effects of asphaltene precipitation during CO2 and WAG injection on rock properties.

1.4 Scope of Work

In this project, two Barea sandstone core were used as formation representative. A light crude oil sample with API gravity of 36° and asphaltene

content of 0.12% were used. Dynamic core flooding test were taken out with two runs, one with continuous CO2 injection and another one with WAG injection under 1:1 WAG ratio. Both runs of experiments were fixed under 3000 Psi and 100oC with an injection rate of 0.2cc/min and 2000 Psi injection pressure.

Both CO2 and WAG injection were injected as tertiary oil recovery after water flooding. With known initial asphaltene content, the effluent oil was collected every 25 minutes and the asphaltene content changes were determined and studied. The effect of asphaltene precipitation on formation properties were only focused on effective porosity, absolute permeability and wettability. From the results, the changes of formation properties after the precipitation of asphaltene were related to the type of injection scheme and the amount of asphaltene precipitation. Lastly, the amount of oil recovery was obtained and study.

1.5 The relevancy of the project

The study on CO2 injection and WAG injection is relevant because miscible hydrocarbon and CO2 WAG injection is the most favourable process in Malaysia field as presented by Hamdan *et al.* (2005) in their report. Malaysia field are having oil with low asphaltene content which have higher possibility of having asphaltene precipitation problems (Khanifar *et al.*, 2011). Thus, it is relevant to have a study on the asphaltene induced by light oil in Malaysia using CO2 and WAG injection.

1.6 Feasibility of the project within the scope and time frame

With careful planning and full dedication in conducting this research, all the experimental works will be manage to complete in time. All the materials and equipments needs to conduct the experiments were readily available; and with the assistance of the technicians in operating the equipments, this research will be successfully conduct and all the objectives set for this research will be achieve.

CHAPTER 2 LITERATURE REVIEW

2.1 CO2 INJECTION AND WAG INJECTION

CO2 (Carbon dioxide gas injection) and WAG (Water-Alternating-Gas injection) are one of the efficient Enhanced Oil Recovery (EOR) methods. EOR is refers to processes that could increase the amount of oil removed from a reservoir, typically by injecting a liquid (e.g., water, surfactant) or gas (e.g., nitrogen, carbon dioxide) (Green & Willhite, 1998). Most of the fields in Malaysia have entered mature state for primary or secondary recovery. The declining production and increasing water cut and gas oil ratio (GOR) trend have give rise to the need for timely implementation of EOR. The Dulang field is the first pilot EOR development project in Malaysia implementing immiscible WAG recovery. EOR Screening study on 72 wells in Malaysia by PETRONAS on year 2000 stated that miscible hydrocarbon and CO2 WAG injection is the most favourable process (Hamdan *et al.*, 2005). Malaysia field are having oil with low asphaltene content which have higher possibility of having asphaltene precipitation problems (Khanifar *et al.*, 2011).

CO2 injection can be classified as miscible or immiscible and are applicable in both secondary and tertiary recovery. CO2 miscible flooding improves oil recovery through gas drive, oil swelling and viscosity reduction (Sima *et al.*, 2011; Ghedan, 2009; Srivastava *et al.*, 1999; Al-Qasim, 2011). However, miscibility of the CO2 gas with the reservoir oil will contribute to compositional change, and alter the asphaltene resin ratio which favors the precipitation of asphaltenes (Ghedan, 2009; Kokal & Sayegh, 1995).

WAG injection is the mobility enhancement method for CO2 injection. During CO2 injection, as gas injected is less viscous than the reservoir oil, the gas will tend to displace the oil causing instability in the displacement front. The instability will then induce an initially sharp displacement front which will further convolute and develop "fingers" which will cause undesired early breakthrough (Green & Willhite, 1998).Water alternating gas injection has been used as mobility control methods which result in sweep efficiency improvement and oil recovery increment (Ghedan, 2009; Berenblyum et al., 2009; Sarma, 2003; Green & Willhite, 1998). The presence of water in WAG injection is believed to reduce the asphaltene precipitation. (Al-Qasim, 2011; Sarma, 2003; Srivastava *et al.*, 1997, Walcot *et al.*, 1989; Shedid *et al.*, 2008),

2.2 ASPHALTENE

Asphaltenes is non-volatile, polar and high molecular weight faction of crude oil that is insoluble in n-alkenes. Asphaltene is insoluble in nonpolar solvent with a surface tension lower than 25 dynes/cm at 25°C (77F) such as methane, ethane and propane and have no defined melting point (Alta'ee *et al.*, 2010). The definition of asphaltene is quite controversial as different solvents and extraction method used producing different asphaltene. Thus, the asphaltene should defined based on its solubility class rather than molecular structure (Sima *et al.*, 2011; Khanifar *et al.*, 2011).

2.2.1 Colloidal Model

Asphaltene is believed to exist as colloidal suspension in oil phase and is stabilized by a protective layer formed by the peptized of highly polar resin on its surface. The combination of these resin and asphaltenes are called micelles. Micelles would not flocculate due to the presence of repulsive force in between the resin molecules absorbed on asphaltene surface. (Thou et al., 2002) The concept of asphaltene stabilization by resin is well recognized; however, the exact mechanism in behind still remains not well known for light oil reservoir (Alta'ee *et al.*, 2010; Srivastava *et al.*, 1999). Figure 1 shows the illustration of resin and asphaltene in crude oil. Resin and asphaltene have similar molecular structure but resins are less polar, less aromatic and lower molecular mass compared to asphaltene.



Figure 1: Resin and Asphaltene in Crude Oil (Miftachul, 2010).

2.2.2 Asphaltene fraction in Crude Oil

SARA analysis is a laboratory method used to quantify the asphaltene fraction in the crude oil. This analysis separates the crude oil into SARA (Saturates, Aromatics, Resin, and Asphaltene). The amount of asphaltene in crude oil is varies with sources, depth of burial, API gravity of the crude oil (Thou *et al.*, 2002; Khanifar *et al.*, 2011).

Less aspahaltene fraction in crude oil did not indicate less possibility of having less asphaltene precipitate problem (Sima *et al.*, 2011; Alta'ee *et al.*, 2010). Field observation indicate that lower asphaltene content in crude oil contribute to higher possibility of asphaltene destabilization. For example, the Boscan field in Venezula with 17wt% asphaltene was observed to have no asphaltene problem but the Hassi-Masoud in Algeria with only 0.15wt% asphaltene have asphaltene problem (Khanifar *et al.*, 2011; Sima *et al.*, 2011; Alta'ee *et al.*, 2010).

Many field and laboratory data have justified that the lighter oil which consists largely of paraffinic materials, have lower asphaltene solubility (Sima *et al.*, 2011). On the other hand, the heavier oil contains plenty of intermediate components which are good asphaltene solvents (Khanifar *et al.*, 2011). The stability of asphaltene is influenced by the ratio of aromatics to saturates and the ratio of resin to asphaltene. This ratio reduction of these will

lead to higher asphaltene precipitation possibility (Donnez, 2007; Kamath *et al.*, 1993).

2.2.3 Mechanism of Asphaltene Precipitation

Asphaltene itself is not problematic but the asphaltene precipitation is the major operational concern (Sima *et al.*, 2011). The precipitation and deposition of asphaltene can cause severe reservoir and production problems arises from permeability and porosity reduction, wettability alteration, plugging of wellbore and surface facilities (Ghedan, 2009; Srivastava *et al.*, 1999).

The terminologies for both precipitation and deposition are different (Miftachul, 2010; Hammami & Ratulowski, 2007). The asphaltene precipitation involved three steps, which are precipitation, flocuration, and deposition. Precipitation is defined as the solid phase (solid particle) comingout from the liquid phase. The flocculation is when the fines particles aggregate into larger particles. Deposition is a point at which the particles are too large to be supported by the liquid and therefore settle out on the solid surfaces or absorb onto rock surface (Khanifar *et al.*, 2011; Alta'ee *et al.*, 2010). Figure 2 shows the process of asphaltene precipitation, flocculation and deposition.

Asphaltene precipitation problems are usually firstly observed in production facilities, and then tubing move towards formation (Sima *et al.*, 2011; Ghedan, 2009; Srivastava *et al.*, 1999; Kokal & Sayegh, 1995). The asphaltene precipitation induced formation damage would start from the wellbore and extend over large distance from the origin. This is in contrast with the reservoir damage induced by organic deposit which is normally restricted to the wellbore zone only (Khanifar *et al.*, 2011).

2.3 ASPHALTENE DESTABILIZES FACTORS

The asphaltene stabilized by resin, remain in thermodynamics equilibrium under colloidal state at normal reservoir condition. Asphaltene will loss it stability when the initial equilibrium state disturbed. Asphaltene stability depends on a number of factors including pressure and temperature alteration, changes in chemical composition, asphaltene and resin content in reservoir oil and the nature of injected fluids. The composition and pressure are believed to have greater effect on asphaltene precipitation than temperature (Kokal & Sayegh, 1995; Hammami *et al.*, 2000; Oskui & Abuhaimed, 2009).

2.3.1 Temperature Drop

The studies conducted by Verdier *et al.* (2005) on pressure and temperature effect on asphaltene stability indicate that asphaltene less stable when temperature decreases; however, in the presence of CO2, asphaltene more stable when temperature decreases (Verdier *et al.*, 2005). Under low temperature, the asphaltene is unstable due to the energy difference between asphaltene and crude oil molecules. The temperature may alter the solubility of maltenes and resin. Temperature drop may cause the precipitation of paraffin that traps some asphaltene during solidification (Verdier *et al.*, 2005; Mohammed *et al.*, 1998).

2.3.2 Pressure Drop

Pressure effect is likely to be the major reason in destabilizing asphaltene. It is believed that the lower the reservoir pressure, the lower is the asphaltene solubility (Verdier et al., 2005; Sima et al., 2011; Khosravi *et al.*, 2009). The effect of pressure on asphaltene precipitation is more intense when the crude oil is rich in light ends just above bubble point pressure. Laboratory data indicated that the maximum asphaltene precipitation occurred at bubble point (Alta'ee et al., 2010; Khanifar, et al., 2011).

When pressure is depleting from above bubble point, the crude oil density reduce while the molar mass increases. The minimum asphaltene solubility occurred at bubble point when there is a maximum difference in molar mass between asphaltene and bulk oil (Hammami *et al.*, 2000; Oskui & Abuhaimed, 2009). With the lighter hydrocarbon increasing with pressure drop, the solubility parameter between resin and lighter ends decreases, which induces resin solve constantly causing asphaltene to precipitate (Alta'ee *et al.*, 2010; Kokal & Sayegh, 1995; Mohammed *et al.*, 1998).

With further pressure drop below the bubble point, some lighter hydrocarbons vaporize from reservoir fluid leaving the heavier reservoir fluid with higher resin fraction and the resin reestablishes some of its lost asphaltene stability. This is shown by Ventura field, Hassi-Messaoud Field and Lake Maracaibo where the asphaltene problem diminished after bottom hole pressure drop below bubble point (Kokal & Sayegh, 1995).

2.3.3 Compositional Change

The addition of compound may alter the existing resin-asphaltene solubility parameter and phase equilibrium in crude oil (Ghedan, 2009; Kokal & Sayegh, 1995; Sima et al., 2011; Khosravi *et al.*, 2009). For example mixing of hydrocarbon fluids, miscible flooding, CO2 injection, gas lift operation using gases and/or acidizing jobs (Hammami & Ratulowski, 2007).

The injection of gas into reservoir either in miscible or immiscible may lower the resin ratio or reduce the amount of the peptizing agent absorb on asphaltene surface (Mohammed *et al.*, 1998). When the resin ratio drops to a point which the absorbed amount were not enough to cover the asphaltene, the asphaltene particles will deposit. It is also reported that the increase of alkane carbon number decrease the amount of asphaltene precipitate (Chukwudeme & Hamouda, 2009). Most miscible solvents have the potential to cause asphaltene instability. Gholoum *et al.* (2003) reported that the CO2

is the most effective asphaltene precipitant followed by alkanes (C1 to C7) (Gholoum *et al.*, 2003: Shedid & Zekri, 2004).

2.4 EFFECT OF CO2 INJECTION ON ASPHALTENE PRECIPITATION

During gas flooding of CO2, the miscibility between the CO2 gas with the reservoir oil will contributes to the change of phase behaviour and compositional, which cause asphaltene to precipitate (Ghedan, 2009; Kokal & Sayegh, 1995; Sima et al., 2011; Khosravi et al., 2009; Mousavi Dehghani et al., 2007).

CO2 gas and the crude can be miscible through first contact or multiple contacts (Alta'ee et al., 2010; Srivastava et al., 1999). In the experimental studies presented by Srivastava *et al.* (1999) on the effect of operating pressure effects on asphaltene precipitation, they indicated that the asphaltene precipitated form multiple contact miscibility were more than the first contact miscibility. The vapor-liquid separation during the miscible injection process strips away the light components which increase the asphaltene precipitation (Srivastava et al., 1999).

Based on the experimental investigation conducted by Sima *et al.* (2011) on the effect of CO2 injection on asphaltene precipitation, more pore volume of CO2 gas injected would cause more asphaltene to precipitate. At pressure of 2000 Psi, the asphaltene start to precipitate at 0.43 pore volume. Then, the asphaltene content is increases from 0.11 wt% to 0.31 wt% until the end of the flooding process. However, as the injected pressure increase, the asphaltene precipitation decreases due to lower asphaltene solubility at low pressure. At lower pressure, the distance between the asphaltene particle and the surrounding fluid is large therefore causing more precipitation. Observation from their studies indicated that at pressure 2300 Psi, the asphaltene precipitation at 1.26 pore volume is 0.23 wt%; while at 2600 Psi, the asphaltene precipitation at 1.27 pore volume is 0.19 wt% (Sima *et al.*, 2011).

Srivastava *et al.* (1999) studied on the effect of oil properties and CO2 gas concentration on asphaltene precipitation by means of static and dynamic test. Their studies on asphaltene onset pressure have indicated that the amount of asphaltene precipitation at bubble point was maximum. They also concluded that the asphaltene

precipitation is dependent on the concentration and pore volume of CO2 gas injected. CO2 gasconcentration is the most important parameter which affects the asphaltene precipitation (Srivastava *et al.*, 1999). This is agreed by Chukwudeme & Hamouda (2009) who reported that the asphaltene deposition is proportional to the injected CO2 concentration, and will rise rapidly when the injected CO2 gas exceed it critical value. They suggested that higher recovery may be obtained if the injected CO2 gas is remained below the critical content point (Chukwudeme & Hamouda, 2009; Al-Qasim, 2011; Alta'ee *et al.*, 2010; Khosravi *et al.*, 2009).

Khosravi *et al.* (2009) reported in his studies that the presence of CO2 gas increases the oil density through withdrawing the light components, but asphaltene precipitation decreases the oil density. A reduction in oil density and viscosity are favoured in oil recovery19. The mass transfer which takes place during miscibility development would enhance the asphaltene precipition (Khosravi *et al.*, 2009).

According to Bagheri (2011), who investigated the effect of injection rate on asphaltene precipitation under natural depletion. The observations from the studies show that the increase of flow rate will increase asphaltene precipitation due to larger pressure drop along the core. They concluded that the increase of production rate from the wells causes more serious formation damage problems far from the well (Bagheri *et al.*, 2011). This is also supported by Shedid & Zekri (2004) who reported that the increase of flow rate will increase the formation damage due to more asphaltene deposited (Shedid & Zekri, 2004).

2.5 EFFECT OF WAG INJECTION ON ASPHALTENE PRECIPITATION

Based on the studies by Srivastava *et al.* (1999) on the effect of brine on asphaltene flocculation, it is observed that the effect of the brine on asphaltene flocculation seemed to be negligible. However, an increase in the brine concentration appears to reduce the asphaltene precipitation (Srivastava *et al.*, 1999). This finding is further supported by Wolcot *et al.* (1989) who presented that the presence of brine could reduce the deposition but could not eliminate it at all (Wolcot *et al.*, 1989).

According to Okwen (2006), the formation water would act as a CO2 buffer during CO2 injection. When the injected CO2 gas concentration reduces, the amount of asphaltene precipitation reduces too. Other than this, the laboratory data indicated that the presence of water film on rock surface in water wet rock can reduce or delay the asphaltene deposition process as asphaltene are preferentially deposited on the less water wet surface than the water surface. Water is believed to act as a shield to rock surface which shield it from direct interaction with asphaltene. This explains why there are more asphaltene deposited on sandstone core than limestone core which is more water wet (Mousavi Dehghani *et al.*, 2007; Okwen, 2006). This paper also recommended further researches to be carried out on the optimum concentrations of CO2 and formation water which can minimize the asphaltene deposition (Okwen, 2006).

Wang & Civan (2005) conducted investigation on water injection scheme for prevention of asphaltene deposition by means of simulation. This paper concluded that the application of water injection can increases the oil recovery through asphaltene deposition prevention ^(Wang & Civan, 2005). The issue of the role of brine on the precipitation and its effect on asphaltene precipitation has been raised up by Sarma (2003) too (Sarma, 2003),

2.6 EFFECT OF ASPHALTENE PRECIPITATION ON FORMATION PROPERTIES

Hayashi & Okabe (2010) performed experimental investigation on asphaltene induced permeability reduction and the results indicate a 20% permeability reduction during CO2 injection due to asphaltene precipitation. The permeability reduction is presented as a function of asphaltene precipitation increment (Hayashi & Okabe, 2010). The effect of asphaltene precipitation on porosity and permeability reduction are depends on few factors. For instant, the pore size distribution, the degree of asphaltene deposition and the intial permeability of the formation (Kamath *et al.*, 1993).

Some researchers reported that core with lower permeability show more intense formation damage effect than the core with higher permeability (Zekri *et al.*, 2007; Shedid & Zekri, 2004). The reduction of injection flow rate may decrease the formation damage due to less asphaltene precipitate (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). The permeability reduction is consider to due to the larger size asphaltene particles block the smaller pore throat or the smaller size asphaltene accumulate or absorb in large pore throat causing reduction in pore throat radii (Kamath *et al.*, 1993).

Asphaltene precipitation is the major cause of the wettability change in oil reservoir. The understanding of role of asphaltene in wettability reversal will help in more efficient enhanced oil recovery planning (Kim & Mansoori., 1990; Yeh & Emanuel, 1992). The wettability change of the core is due to the potential of asphaltene adsorb onto high energy mineral surface (Al-Maamari & Buckley, 2000; Kamath *et al.*, 1993). Huang and Holm (1988) used asphaltene dissolved in toluene to effect reverse the rock wettability. This indicates the role of asphaltene in wettability alteration (Huang & Holm, 1988). However, Al-Maarmari and Buckley (2000) reported that in the presence of stable water film, the water wet rock will remain water wet (Al-Maarmari & Buckley, 2000). When wettability change from

water wet to oil wet, it can cause a higher water cut profile which my possibly reduce oil recovery (Al-Qasim, 2011).

Another possible effect from asphaltene precipitation is the flow diversion effect, where when the high permeability zone plugged; the fluid will flow to the low permeability zone. This may be a positive result from asphaltene precipitation as improved sweep efficiency may be obtained. Other than this, the increase in asphaltene precipitation can lead to an increase in water breakthrough time (Kamath *et al.*, 1993).

2.7 LITERATURE SUMMARY

Light oil is having higher possibility of having asphaltene precipitation than heavy oil. The common factors causing asphaltene precipitation are pressure drop, temperature drop and compositional change. The composition and pressure have higher effect on asphaltene precipitation than temperature. The asphaltenes precipitated could cause reservoir damage, change of wettability of the rock matrix and affect the flood performance.

The addition of CO2 gas can destabilizes the asphaltene colloidal model and possibly causes the asphaltene to precipitate, flocculate and deposit. The amount of asphaltene precipitated during CO2 injection are depending on the injected CO2 concentration and pore volume, injection pressure, flowrate, and miscibility development. The maximum asphaltene precipitation is believed to occur at bubble point.

The presence of water is believed could reduce the asphaltene precipitation. Water is act as a CO2 buffer in CO2 injection and an increase in the brine concentration appears to reduce the asphaltene precipitation. The investigations of the optimum conditions that could reduce or avoid the asphaltene to precipitate are one of the good efforts in dealing with asphaltene precipitation problem. There are further researches require in investigate the optimum concentration of brine and CO2 gas in WAG injection that can reduce the asphaltene precipitation.

CHAPTER 3 METHODOLOGY

3.1 Research Methodology

Core flooding experiment was conducted under operation conditions of 3000 Psi and 100° C. Berea sandstone cores were used as formation representative. Below are the outlines of the works.



Figure 2: Methodology Outline

- The core sample properties such as porosity and permeability were measured. The density of crude oil was measured at 100°C.
- The core was saturated with 5000ppm brine follow by oil to restore the irreducible water saturation. Water flooding is conducted to restore the residual oil saturation in core.
- The displaced oil in core outlet was collected over a 25 minutes time interval. The oil recovery was calculated.
- The asphaltene content of the oil before and after the core flooding were measured according to ASTM standard D3279-07.
- The change of the rock properties after the precipitation of asphaltene were measured, these including the change in effective porosity, absolute permeability and wettability. (In order to retain the asphaltene inside core while only remove residual oil, the cores are treated with n-heptane after core displacement.)

3.1.1 Core Properties Measurement

Poro-Perm System is a permeameter and porosimeter used in determine the properties of core samples at ambient confining pressure.

Chemical and Apparatus

Oven, Poro-Perm System,



Figure 3: Poro-Perm System

Procedure:

Nitrogen Gas

- The core samples were cleaned using toluene and dry in oven before loaded into the core holder.
- The length and diameter of samples were measured with digital caper and subsequently bulk volume was determined automatically from system.
- Nitrogen gas was filled into core chamber to fully saturate the samples.
- Using suitable confining pressure of 300 Psia, the effective porosity and gas absolute permeability can be obtained.
- The Klinkenberg gas slippage effect is corrected using the build in klinkenberg correction software.

Bulk Volume:

$$V_b = \pi r^2 L \tag{1}$$

r = radius of the core

L= length of the core

Porosity:

$$\emptyset = \frac{v_p}{v_b} \times 100\% \tag{2}$$

Vb = bulk volume of the core

Vp = pore volume of the core

3.1.2 Crude Oil Properties Measurement

Density Measurement



- About 3 ml of crude oil sample was drawn into a syringe and injected into the air tube.
- The crude oil was injected continuously and slowly to decrease the possibility of having air bubble forming inside the air tube.
- The injected crude oil was then heated up from 40 $^{\circ}$ C to 89 $^{\circ}$ C.
- Then the option to start recording the density was selected. The equipment provided the density value once the reading had stabilized.
- The results were then extrapolated to obtain the density at temperature of $100 \,^{\circ}$ C.

3.1.3 Asphaltene Content Measurement

ASTM D3279-07 Standard Test Method for n-Heptane Insoluble is used to measure the mass percent of asphaltene in crude oil sample. This test determines the mass percent of asphaltene as defined by insolubility of asphaltene in normal heptane solvent.

Chemical and Apparatus

Gooch Crucible, n-Heptane, Filter Paper, Heating Flask, Suction Flask, Reflux Condenser, Hot Plate, Magnetic Stirrer, Desiccator, Hood, Oven



Figure 5: ASTM D3279-07 Standard Test Method for n-Heptane

- The sample was weighted to the nearest 1.0 g (B) and 100 ml of solvent per 1.0 g of sample was added into the heating flask.
- With the magnetic stirrer added, the flask was heated on the hot plate at 70 °C under the reflux condenser for about 20 minutes and cool down.
- The filter paper was placed into the gooch crucible and put into oven at about 107 °C for 15 minutes. The gooch crucible was allowed to cool down in desiccator and the weight was measured.
- The gooch crucible was pre-filtered with n-heptane and the mixture in the heating flask was poured into the suction flask through the gooch crucible.
- The gooch crucible was put into oven at about 107 °C for 15 minutes. The gooch crucible was then allowed to cool down in desiccator and the weight was measured. The amount of insoluble inside is denoted as (A).
- The weight percentage of asphaltene content, $wt\% = \frac{A}{B} \times 100\%$ (3)

3.1.4 Core Flooding

Relative Permeability Test System is used to conduct core flooding experiment. Brine, oil and CO2 gas are injected simultaneously into the core sample for CO2 injection and WAG injection experiment.

Chemical and Apparatus

Relative Permeability System, Brine water (5000 ppm), 99.99% Pure CO2 Gas, Crude Oil Sample



Figure 6: Relative Permeability Test System

- The core sample was flooded with brine follow by dead oil for irreducible water saturation restoration.
- It was assuming that the core was 100% saturated with water, where the initial volume of water should be equal to the pore volume. The original oil in place was determined through the amount of water dispersed.
- The core was then flooded with brine and the amount of produced oil was measured to obtain the residual oil saturation. The process was conducted until a stable residual oil was established. This is when only water is being produced at the outlet.
- To determine the CO2 gas effect on the asphaltene precipitation, CO2 gas is injected into the core 2 cc/min injection rate. The amount effluent oil were collected every 25 minutes to obtain the recovery factor and phase saturation change.
- The above step was repeated for WAG injection (1:1 ratio) under same injection rate. The injection length for brine and CO2 gas injected were 10 minutes each.

Initial Oil Saturation:

The amount of brine displaced by oil from the brine saturated core is the volume of oil saturated in the core. Initial oil saturation was determined by dividing the amount of brine produced to the pore volume of the core.

$$S_{oi} = \frac{V_o}{V_p} \tag{4}$$

Soi = initial oil saturation

Vo = volume of oil

Vp =pore volume of the core

Residual Oil Saturation:

The amount of oil remains in the core after water flooding over the pore volume of the core.

$$S_{or} = \frac{V_{oi} - V_o}{V_p} \tag{5}$$

Sor = residual oil saturation

Voi = Initial oil volume in the core

Vo = volume of oil produced from water flooding

Vp = pore volume of the core

Oil Recovery Factor:

Oil Recovery can be estimated from the amount of oil recovered by amount of residual oil after water flood.

$$0il\,recovery\,factor = \frac{V_o}{V_{or}} \tag{6}$$

Vo = volume of oil produced

Sor = residual oil saturation

3.1.5 Post Flooding Evaluation

IFT Measurement

In determining the effect of asphaltene precipitation on wettability alteration, Sessil Drop method is applied using IFT 700 equipment.

Chemical and Apparatus

IFT 700 Equipment, Core Sample, Crude Oil Sample, Brine water (5% NaCl)



Figure 7: IFT 700 System

- A degreaser and air-blower were used to clean the chamber cell to remove any impurities.
- A small piece of core sample was inserted into the sample holder and load into the chamber cell.
- The cell was then pressurized to 3000 Psi at constant temperature of 100°C to resemble the core flooding conditions.
- By slowly controlling the inlet/ outlet pressure of the oil tank, a single droplet of oil was injected into the pressure cell.
- The oil droplet image adhere on the core surface was observed from the computer through the microscopic camera.
- The position and the resolution of camera were adjusted to give clear image.
- The results with low contact angle (0 to 90°C) indicate water wet properties while the large contact angle (90 °C to 180 °C) represent oil wet properties.

3.1.6 Core Cleaning

Cores were cleaned using toluene before displacement test. After the displacement test, cores were cleaned using n-heptane to dissolve and extract oil and brine from core sample with core flooding apparatus. The use of n-heptane enables the asphaltene precipitated to retain inside the cores for porosity and permeability reduction analysis.



- Core to clean was inserted into the core chamber. The solvent was filled in the boiling flask and the condenser was connected to water supply source.
- Upon heating the boiling flask, the solvent will vaporized and then cool in the condenser and flow back into the core chamber.
- The cleaned solvent filled the chamber and soaked the core sample.
- When the chamber was full, the condensed solvent was abosorb back into the boiling flask and was redistilled.
- The colour of the solvent was observed from the siphons to determine the cleanliness of the core sample.
- The core sample was dry in the oven to make sure it is clear from any impurities.

3.2 Project Activities



Figure 9: Project Activities

3.3 Gantt Chart and Key Milestones

Final Year Project I															
Details/Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14
Topic Selection &															
Confirmation															
Preliminary Research															
Work							ak								
Preliminary Report							re								
submission							L B								
Proposal Defense							ste								
(Oral Presentation)							me								
Project Work							Sei								
Continues							id								
Interim Draft Report							N								
submission															
Submission of Interim															
Report															

Table 1: Project Gantt Chart and Key Milestones

Key Milestones

Final Year Project II															
Details/Week	1	2	3	4	5	6		7	8	9	10	11	12	13	14
Materials Preparation &															
Lab Booking															
Pre-test Analysis															
1 st Project Run															
Progress Report															
Submission							ak								
2 nd Project Run							Bre								
Post-test Analysis							er								
Pre-EDX							lest								
Draft Report Submission							Sen								
Dissertation Submission							id								
(Softbound)							M								
Technical Paper															
Submission															
Oral Presentation															
Dissertation Submission (Hardbound)															

3.4 Tools, Material and Equipment

Below is the summary of tools and equipment that used throughout the project.

Chemicals/ Materials	Experiment
Sample core plug	Core flooding
Sample crude oil	Core flooding
99.99% pure CO2 gas	CO2 & WAG injection
Brine	Core restoration/ WAG injection
Toulene	Core cleaning
n-heptanes	Core cleaning, Asphaltnene content measurement
Distilled water	Brine preparation

Table 2: List of Chemicals/ Materials Use in Project

Table 3: List of Equipments Use in Project

Equipments	Experiment
Soxhlet Extractor	Core cleaning
Drying oven	Core cleaning, Asphaltnene content measurement
Poro-perm system	Core properties measurement
Dessicator	Asphaltnene content measurement
Densitometer	Crude oil density measurement
IFT 700	Interfacial Tension measurement

CHAPTER 4 RESULTS AND DISCUSSION

Below are the summaries of results obtained from each experimental phases. Details results from each experiment are presented in Appendix for reference.

4.1 Sample properties

Table 4 presents the initial asphaltene content and the density of sample used. Knowing the initial asphaltene content of the oil sample used enables us to study the variation in amount of asphaltene precipitation during CO2 and WAG injection.

Asphaltene content (wt %)	0.12
Density @ 100°C (g/cc)	0.7939
API gravity	36.04

Table 4: Crude Oil Properties

Before running the core flooding test, the core properties such as porosity, permeability and bulk volume are determined. Table 5 shows the initial core properties before the displacement test measured using Poroperm System.

Parameter	Core 1 (CO2 injection)	Core 2 (WAG injection)
Diameter (mm)	37.01	36.94
Length (mm)	77.18	77.76
Weight (g)	180.43	182.55
Bulk volume (cc)	80.03	83.337
Pore volume (cc)	15.087	15.473
Kair (mD)	89.148	95.762
K∞ (mD)	78.028	80.359
Porosity (%)	18.170	18.566

Table 5: Original Core Samples Properties

4.2 Core Displacement Test

Dynamic displacement experiments were conducted to determine the effect of CO2 and WAG injection on asphaltene precipitation. Table 6 shows the parameters used in the displacement. Operation condition of the equipment was fixed at 3000 Psi and 100 °C with an injection rate of 0.2 cc/min under 2000 Psi injection pressure. The WAG injection was conducted with 10 minute injection length for gas followed by water continuously until no oil production was obtained. In order to measure the change of asphaltene content, the effluent were collected every 25 minutes interval for both CO2 and WAG injection. The simple schematic of the core flooding equipment is illustrated in figure 10.

Injection rate (cc/min)	0.2
Inlet Pressure (Psia)	2000
Confining Pressure (Psia)	3000
Temperature (°C)	100
CO2 injection length	continuous
WAG injection length	
Water injection length (min)	10
Gas injection length (min)	10
Effluent collection interval (min)	25
Brine concentration (ppm)	5000

Table 6: Core Displacement Test Parameters



Figure 10: Simple Schematic of Core Flooding Equipment

4.3 CO2 and WAG Injection Induced Asphaltene Precipitation

During CO2 and WAG injection, the injected gas might dissolves into the oil during the displacement process. The change of oil composition would further alter the asphaltene-resin ratio which favors the precipitation of asphaltene. Asphaltene would start to flocculate when the fraction of resin drops to a concentration where it absorbed amount is insufficient in covering the entire surface of asphaltene particles. The flocculation of asphaltene particle may follow by precipitation and deposition.



Figure 11: Asphaltene Content of the effluent versus Pore Volume of Injection

Figure 11 shows the asphaltene content of the effluent oil during CO2 and WAG injection over the pore volume of injection. The weight percentage of asphaltene in the effluent oil were measured based on ASTM D3279-07 Standard Test Method. The original asphaltene content of the oil is 0.12%. At the end of the displacement test where oil production stopped, the asphaltene content of the effluent oil from CO2 injection is 0.042%, while for WAG injection is 0.055%. The reduction of the asphaltene content in the effluent oil indicates the precipitation of asphaltene inside the core. The results show that the asphaltene content of the effluent oil from CO2 injection is lower than WAG injection.



Figure 12: Asphaltene Precipitation inside the core versus Pore Volume of Injection

Figure 12 shows the weight percentage of asphaltene deposited inside the core during CO2 and WAG injection. In run 1 of core flooding using CO2 injection, the amount of asphaltene precipitate inside the core at 0.33 pore volumes was 0.024 wt%. When the CO2 injection reaches 0.66 pore volume, the asphaltene precipitated was 0.056 wt%. At 0.99 pore volumes, the amount of asphaltene precipitation was 0.074 wt%. After that, the asphaltene precipitated inside the core was continued to increase as the injected pore volume increase. It reaches to a final value of 0.078 wt% at 1.66 pore volumes.

In run 2 of using WAG injection, the asphaltene precipitation was 0.009 wt% at 0.33 pore volumes of injection. In compare with the same pore volumes of injection from previous run, the asphaltene precipitation from the CO2 injection is much higher. At 0.65 pore volumes of injection, the asphaltene precipitation was 0.05 wt% and then the asphaltene precipitation continue to increase and rise to 0.065 wt% at 0.97 pore volume of injection.

Figure 12 clearly shows that asphaltene precipitation is a function of pore volume of injection. As pore volume of gas injected increasea, the asphaltene precipitated inside the core increase. Based on the results, it is also observed that the asphaltene precipitatiwd from CO2 injection is more than that of WAG injection. This is due to the fact that CO2 is soluble in both water and crude oil. During WAG

injection, CO2 gas will dissolve in brine and reduces its concentration. The reduction in CO2 available to precipitate the asphaltene had minimizes the asphaltene precipitation.

4.4 Effect of Asphaltene Precipitation on porosity and permeability

Once asphaltene is destabilizes, it may flow as suspended particles and may deposit on the rock surface causing changes to the rock properties. The effects of asphaltene precipitation on rock sample are indicated by the porosity and permeability reduction. In order to indicate the change of rock properties due to the presence of asphaltene, each core was treated with n-heptane after displacement test. The n-heptane will removes the residual oil while only leave asphaltene fraction inside the core. Table 7 present the original core properties and properties after the asphaltene precipitate. The change of the porosity and permeability from the original indicate the extent of asphaltene precipitation induced formation damage.

		Porosity	Difference	Permeability	Difference	Pore
		(%)	%	(mD)	%	Volume
						(cc)
Run 1	Before					
(CO2)	Displacement	18.170		78.028		15.087
	After		7.01		75.85	
	Displacement	16.896		17.753		13.469
Run 2	Before					
(WAG)	Displacement	18.566		80.359		15.473
	After		6.66		71.92	
	Displacement	17.330		22.560		13.679

Table 7: Core Properties Before and After Displacement Test

Figure 13 and 14 shows the percentage of porosity and permeability reduction during CO2 and WAG injection. Results show an obvious reduction in porosity and permeability for both runs. It is justified that the precipitation of asphaltene would cause reduction in porosity and permeability. The permeability reduction is considered to due to the larger size asphaltene particles block the smaller pore throat

or the smaller size asphaltene accumulate or absorb in large pore throat causing reduction in pore throat radii.



Figure 13: Porosity Reduction during CO2 and WAG Injection



Figure 14: Permeability Reduction during CO2 and WAG Injection

A larger reduction in porosity and permeability are observed with core undergo CO2 flooding. In CO2 injection, permeability decline of 75.85% and porosity reduction of 7.01% was detected. In WAG injection, the permeability decline was 71.91% while porosity reduction is 6.66%. It is observed that the degree of porosity and permeability reduction is a function of the degree of asphaltene precipitation. This can explained why the permeability reduction of core undergo CO2 injection is more than WAG injection. As discussed in the precious section, asphaltene precipitation is increases with the time the CO2 gas contacted the oil. Thus, with time, it is anticipated that the porosity and permeability reduction would be getting higher. More asphaltene may continue to deposit and accumulate resulting in severe core plugging problem. The effect of asphaltene precipitation on porosity and permeability reduction are depends on few factors. For instant, the pore size distribution, the degree of asphaltene deposition and the initial permeability of the formation.

4.5 Effect of Asphaltene Precipitation on Rock Wettability

Once the asphaltene are destabilized, the highly polar and surface active asphaltene particles would adhere onto rock surface and change its wettability. The core wettability is determined through contact angle measurement using sessile drop method. The angle of the denser fluid (brine) to the rock surface of less than 90^{0} indicate a water wet condition while an angle of more than 90^{0} indicated oil wet condition as illustrated in figure 15.

For run 1, the CO2 gas injected changed the rock wettability from water wet (25^{0}) toward more oil wet condition (70^{0}) . This signifies the role of asphaltene precipitation on wettability alteration to more oil wet. These findings should be placed high concern as wettability alteration governs the relative permeability curve, end point saturation and oil recovery. The change of rock oil wet may cause higher water cut that reduce the amount of oil recovered.

For run 2 under WAG injection, the original water wet condition (25^{0}) of the rock remained, in which the wettability of the rock moving towards more water wet (27^{0}) after displacement test. The presence of water film on the rock surface is believed to shield the rock surface from interaction with the asphaltene particles. This is also explained why during WAG injection, the asphaltene precipitation is less and the original wettability moving to more water wet. Table 8 summarizes the findings on the change of rock wettability before and after core displacement.



Figure 15: Contact Angle Measurement for CO2 and WAG Injection Before and After Core Flooding

4.6 CO2 and WAG injection Oil Recovery Factor

Table 8 presents the oil recovery factor for CO2 and WAG injection. During CO2 injection, 17.18% of the original oil in place was displaced, while for WAG injection, a total of 24.72 % of water was produced. The results indicated that both CO2 and WAG injection can improve the oil recovery after water flooding. It can be obviously distinguish that WAG injection shows a better performance in oil recovery. The residual oil saturation after CO2 injection is 0.63, which is less than that of 0.39 after WAG injection. Detailed calculation of oil recovery factor is stated in the Appendix.

	Water Flooding (%OOIP)	EOR (%OOIP)
Run 1		
(CO2 flooding)	17.18	18.92
Run 2		
(WAG flooding)	24.72	47.05

Table 8: Recovery Calculation from Displacement Test

From the results, it is justified that gas injection during tertiary oil recovery can significantly increase oil recovery. The mechanisms behind the oil recovery increment are oil swelling, reduction of the reservoir fluid viscosity and interfacial tension (IFT). However, one problem encounters with CO2 flooding is the gas fingering problem. Gas fingering problem may cause early breakthrough and sweep efficiency reduction. As gas injected is less viscous than the reservoir oil, the gas will tend to displace the oil causing instability in the displacement front. The instability will then induce an initially sharp displacement front which will further convolute and develop "fingers" which will cause undesired early breakthrough.

WAG injection can be used as a main mobility control scenario for the fingering problem. It is working on the principle of decreasing the mobility behind the flood front to increase the sweep efficiency. Thus, the presence of water has reduces the relative permeability to gas, lower the mobility, and reduce the fingering phenomena which resulted in higher oil recovery.

Figure 16 illustrates the recovery factor of CO2 and WAG injection. Based on the results, WAG injection gave a recovery of about 47.05 % of residual oil in place (OOIP) while CO2 injection only gave a recovery of about 18.92% OOIP. During CO2 injection, the change of wettability to more oil may cause the increased of irreducible oil saturation, resulted in lower oil recovery which is not favorable in oil recovery.

It is also observed that during CO2 injection, the change of wettability to oil wet increases othe irreducible oil saturation. However, during WAG injection, the water wet condition of the rock retained. The presence of water film on rock surface had maintained the water wet condition of the rock, leaded to less amount of

asphaltene precipitated. The retention of rock initial water wet condition would increases the relative permeability to oil and increase oil recovery.



Figure 16: Recovery Factor of CO2 and WAG Injection

CHAPTER 5 CONCLUSION AND RECOMMENDATION

Both CO2 and WAG injection would cause asphaltene instability. The precipitation of asphaltene may lead to reduction in porosity, permeability and alter the rock wettability. A smaller reduction in amount of asphaltene precipitation is observed with WAG injection. It is due to the tendency of CO2 gas to dissolves in water, which reduces its concentration and minimizes the asphaltene precipitation. The porosity and permeability reduction is higher during CO2 injection due to more asphaltene precipitated. Other than that, the presence of asphaltene was observed to alter the rock wettability to more oil wet. However, in the presence of water film, the initially water wet condition of the rock remains. This retention of water wet condition of the core during WAG injection has contributed to higher oil recovery.

Overall, it is justified that CO2 injection causes more asphaltene problem than WAG injection in term of the amount of asphaltene precipitated, porosity and permeability reduction and wettability change. This research have further highlight the beneficial of WAG injection over CO2 injection in providing mobility control, giving higher sweep efficiency, higher oil recovery and lower asphaltene precipitation.

Other than focusing on determining the optimum condition of CO2 injection, it is recommended to place the research focus on WAG injection too. Further studies are suggested in determining the optimum concentration of CO2 and brine, which can give less asphaltene precipitation. More studies are also recommended on optimum WAG ratio to have a better understanding of the role of water in reducing asphaltene precipitation.

REFERENCES

- Al-Maamari R.S.H., Buckley J.S., "Asphaltene Precipitation and Alteration of Wetting: The potential for Wettability Change During Oil Production", SPE paper 84938 presented at SPE/DOE Improved Oil Recovery Symposium, Tulsa, 3-5 April, 2000.
- Al-Qasim, A.S. "Simulation of Asphaltene Deposition During CO2 Flooding", The University of Texas, Austin, August 2011.
- Alta'ee, A.F., Saaid, I.M., Masoudi, R., "Carbon Dioxide Injection and Asphaltene Precipitation in Light Oil Reservoirs", paper presented at the Eleventh Mediterranean Petroleum Conference and Exhibition, Tripoli – Libya, 23-25 February, 2010.
- Bagheri, M.B., Kharrat, R. & Ghotby, C. "Experimental Investigation of the Asphaltene Deposition Process during Different Production Schemes", Oil & Gas Science and Technology – Rev. IFP Energy nouvelles, 2011.
- Caudle, B.H., Dynes, A.B. "Improving Miscible Displacement by Gas-Water Injection", SPE paper 911-G presented at 32nd Annual Fall Meeting of Society Petroleum Engineers, Dallas, Tex., 6-9 October, 1957.
- Chukwudeme, E.A., Hamouda, A.A. "Enhanced Oil Recovery (EOR) by Miscible CO2 and Water Flooding of Asphaltenic and Non-Asphaltenic Oils", Department of Petroleum Engineering, University of Stavanger, Norway, 2009.
- Ghedan, S. "Global Laboratory Experience of CO2-EOR Flooding", SPE paper 125581 presented at 2009 SPE/EAGE Reservoir Characterization and Simulation Conference, Abu Dhabi 19-21 October, 2009.
- Gholoum E.F., Oskui G.P. & Salman M. "Investigation of Asphaltene Precipitation Onset Conditions for Kuwaiti Reservoirs", SPE Paper 81571 presented at SPE 13th Middle East Oil Show & Conference, Bahrain, 5-8 April, 2003.

- Hammami, A. & Ratulowski J. "Precipitation and deposition of asphaltene in production systems: a flow assurance overview", Asphaltene, Heavy Oils, and Petroleomics 23: 617-660.
- Hammami, A., Phelps, H. & Little, T.M. "Asphaltene Precipitation from Live Oils: An Experimental Investigation of the Onset Conditions and Reversibility", *Energy & Fuels 2000 14: 14-18.*
- Hayashi, Y. & Okabe, H. "Experimental Investigation of Asphaltene Induced Permeability Reduction", SPE paper 129271 presented at SPE EOR Conference at Oil & Gas West Asia, Muscat, Oman, 11-13 April, 2010.
- Huang, T.S. & Holm L.W. "Effect of WAG Injection and Rock Wettability on Oil Recovery During CO2 flooding", SPE paper 15491, SPE Reservoir Engineering, February, 1988.
- Kamath, V.A., Yang, J., & Sharma, G.D. "Effect of Asphaltene Deposition on Dynamic Displacement of Oil by Water", SPE paper 26046 presented at Western Regional Meeting, Anchorage, Alaska, 26-28 May 1993.
- Khanifar, A., S.Alian, S., Demiral, B. & Darman, N. "Study of Asphaltene Precipitation and Deposition Phenomenon during WAG Application", SPE Paper 143488 presented at SPE Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia, 19-21 July, 2011.
- Khosravi, M., Rostami, B. & Nghiem, L., "Influence of CO2 Dissolution and Asphaltene Precipitation on Oil PVT and Recovery", *Enhanced oil recovery – Iranian Chemical Engineering Journal (Special Issue) – Vol.8 – No.43, 2009.*
- Kim, S.T. & Mansoori G.A. "The Role of Asphaltene in Wettability Reversal", SPE paper 20700 presented AT 65th Annual Technical Conference and Exhibition of Society of Petroleum Engineers, New Orleans, LA, 23-26 September, 1990.
- Kokal, S.L. & Sayegh, G. "Asphaltene: The Cholesterol of Petroleum", SPE paper 29787 presented at SPE Middle East Oil Show, Behrain,, 11-14 March, 1995.

- Miftachul, C. "Study of CO2 Effect on Asphaltene Precipitation and Compositional Simulation of Asphaltenic Oil Reservoir", *University of Stavenger, 30 June, 2010.*
- Mohammed, S., A., Arisaka, K. & Kumazaki, Y. "Integrated Analysis of Asphaltene Deposition from Field Production Data and Laboratory Experiments", SPE Paper 49501 presented at 8th Abu Dhabi International Petroleum Exhibition and Conference (ADIPEC), 11-14 October, 1998.
- Mousavi Dehghani, S.A., Vafaie Sefti, M.M.B. & Fasih, M., "Experimental Investigation on Asphaltene Depositon in Porous Media During Miscible Gas Injection", *Iran.J. Chem. Chem. Eng. Vol. 26, No 4, 2007.*
- Okwen, R.T. "Formation Damage by CO2-Induced Asphaltene Precipitation", SPE paper 98180 presented at SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, LA, 15-17 February, 2006.
- Oskui, G. P. & Abuhaimed W. A. " Laboratory Investigation of Asphaltene Precipitation Problems During CO2/Hydraocarbon Injection Project for EOR Application in Kuwait Reservoirs", *SPE paper 126267 presented at Kuwait International Petroleum Conference and Exhibition, Kuwait City, Kuwait, 14-16 December, 2009.*
- Sarma, H.K. "Can We Ignore Asphaltene in a Gas Injection Project for Light-Oils?", SPE paper 84877 presented on SPE International Improved Oil Recovery conference in Asia Pacific, Kuala Lumpur, Malaysia, 20-21 October, 2003.
- Shedid, S.A. & Zekri, A.Y. "Formation Damage Caused by Simultaneous sulfur and Asphaltene Depositon", SPE paper 86553 presented at SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, Louisana, 18-20 February, 2004.
- Sima, S.A., Omar, A.A., Alta'ee, A.F. & Hani, I. "Study of Asphaltene Precipitation induced formation Damage during CO2 injection for a Malaysian light oil", *Paper presented at World Academy of Science, Engineering and Technology* 78, 2011.

- Srivastava, R.K., Huang, S.S. & Dong, M. "Asphaltne Deposition During CO2 Flooding", SPE paper 59092 presented at SPE Production Operations Symposium, Oklama City, Oklahoma, 9-11 March, 1997.
- Thou, S., Ruthammer, G., Potsch, K. "Dectection of Asphaltene Flocculation Onset in a Gas Condensate System", *SPE Paper 78321 presented at 13th European Petroleum Conference, Arberdeen, Scotland, U.K., 29-31 October, 2002.*
- Verdier, S., Carrier, H., Anderson, S. I. & Daridon, J. "Study of pressure and temperature effects on asphaltene stability in presence of CO2", *Energy & Fuel* 2006, 20, 1584-1590
- Wang, S. & Civan, F. "Preventing Asphaltene Deposition in oil Reservoir by Early Water Injection", SPE paper 94268 presented at SPE Production and Operation Symposium, Oklahoma City, U.S.S., 17-19 April, 2005.
- Wolcott, J. M., Monger, T. G., Sassen, R. & Chinn E.W. "The Effect of CO2 Flooding on Reservoir Mineral Properties", SPE paper 18467 presented at SPE International Symposium on Oilfield Chemistry, Houston, TX, February 8-10, 1989.
- Yeh S.W., Ehrlich, R., Emanuel, A.S. "Miscible-Gasflood-Induced Wettability Alteration: Experimental Observations and Oil Recovery Implication", SPE paper 20186-PA, SPE Formation Evaluation, June 1992.
- Zekri, A.Y., Shedid, S.A. & Almehaideb R.A. "An Experimental Investigation of interactions between supercritical CO2 Asphaltenic Crude Oil and Reservoir Brine in Carbonate Cores", SPE paper 104750 presented at SPE International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A., 28 February-2March, 2007.

APPENDIXES

Appendix 1: Core Flooding Results

Parameters	CO2 Flooding	WAG Flooding
Pore Volume (ml)	15.087	15.473
Initial Oil Volume (ml)	11.47	7.97
Initial Oil Saturation	0.76	0.52
Initial Water Volume (ml)	3.617	7.503
Initial Water Saturation	0.24	0.48
Water Flooding		
Oil Produced (ml)	1.97	1.97
Residual Oil Volume (ml)	9.50	6.00
Residual Oil Saturation	0.63	0.39
Residual Water Volume (ml)	5.587	9.473
Residual Water Saturation	0.37	0.61
Oil Recovery Factor	17.18 %	24.72 %

Appendix 2: Oil Recovery Factor

	CO2 Flooding		WA	G Flooding
Time (min)	Vp of injection	Oil Produced (ml)	Vp of injection	Oil Produced (ml)
25	0.33	0.70	0.33	3.05
50	0.66	0.32	0.65	0.40
75	0.99	0.20	0.97	0.30
100	1.32	0.10	1.29	-
125	1.66	0.40	1.62	-
150	1.99	0.45	1.95	-
Total Oil Produced		2.17		3.75
Oil Recovery Factor (OOIP)		18.92 %		47.05 %

Appendix 3: Oil Sample Density

Temperature (⁰ C)	Density (g/cc)
40	0.82940
60	0.8191
70	0.8126
80	0.8061
85	0.8031
89	0.8005



Given the above line equation Y = 0.0006 x + 0.8539 (7)

The density (Y) of crude at temperature (X) of 100 $^{\circ}$ C is as below:

Y = -0.0006 (100) + 0.8539= 0.7939 g/cc

Appendix 4: Oil Sample API Gravity

$$API \ Gravity = \frac{141.5}{SG} - 131.5 \tag{8}$$

SG = Specific Gravity

Equation to obtain the oil specific gravity,

$$SG = \frac{\rho \ oil}{\rho \ H20} \tag{9}$$

p oil = Density of oil

 ρ H20 = Density of water

* The above equation is applied with reference to density of water at 15.55 $^{\circ}$ C or 60 $^{\circ}$ F, which is 1.0g/cc.

The density of oil sample at 15.55 $^{\circ}$ C is obtained from the line equation (7) in Appendix 3. The density (Y) of crude at temperature (X) of 15.55 $^{\circ}$ C is as below:

$$Y = -0.0006 (15.55) + 0.8539$$
$$= 0.84457 \text{ g/cc}$$

Thus, the specific gravity,

$$SG = \frac{0.84457}{1.0} = 0.84457$$

The Oil API Gravity,

$$API \ Gravity = \frac{141.5}{0.84457} - 131.5 = 36.04$$

Appendix 5: Asphaltene Content Measurement

Below is the asphaltene content (wt%) of the effluent oil measured after the core displacement experiment:

	Pore Volume of Injection	Asphaltene content (%)
	0	0.12
Run 1	0.33	0.096
(CO2)	0.66	0.064
	0.99	0.046
	1.66	0.042
Run 2	0	0.12
(WAG)	0.33	0.111
	0.65	0.070
	0.97	0.055

NOMENCLATURES

- EOR Enhanced Oil Recovery
- CO2 Carbon Dioxide
- WAG Water-Alternating-Gas
- wt % -Weight Percentage Percent
- ASTM American Society for Testing and Materials
- Voi Initial Oil Volume
- Vo Produced Oil Volume
- Vb-Bulk Volume
- Vp Pore Volume
- r Radius of the core
- L Length of Core Sample
- Soi Initial Oil Saturation
- Sor Residual Oil Saturation
- Kair Air Permeability
- Kon Corrected Permeability for Klinkenberg Effect
- $\theta Porosity$
- OOIP Original Oil in Place