STUDY ON THE CHANGE OF ASPHALTENE CONTENT OF THE RECOVERED OIL DURING CO_2 INJECTION FOR LIGHT OIL

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Study on the Change of Asphaltene Content of the Recovered Oil during CO_2 Injection for Light Oil

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CERTIFICATION OF ORIGINALITY

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

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ABSTRACT

Gas injection is one of the oldest and widely known methods in the Enhanced Oil Recovery (EOR) process. Injection of CO_2 resulted in the increasing of oil recovery and created a permanent storage of CO_2 in geological formation when it was injected in a particular reservoir conditions. Unfortunately, when the CO_2 was injected to the light oil reservoir, it will cause severe asphaltene problems especially in light oil reservoir which contained low percentage of asphaltene content. Asphaltene will precipitate and deposited in the reservoir, well bore, tubing as well as surface facilities. Presence of asphaltene may reduce the permeability of the reservoir, changing the wettability of reservoir and plugging the wellbore and tubing which cause of loss in production. This project studied the changes of asphaltene content (weight %) in recovered oil during CO_2 injection using Dulang crude oil at three (3) different injection pressures. Recovered oil was collected every 4 cc of pore volume has been injected with CO_2 during core flooding at 3 different injection pressure which are 2000, 2300 and 2600 psig. Asphaltene content in the recovered oil was measured using ASTM (D3279-07) standard test method. Results showed the decreasing trend of asphaltene content in the recovered oil for all the three (3) injection pressures. As the injection pressure decreased, the asphaltene precipitation in the porous media increased as well decrease the oil that can be recovered during the CO2 injection.

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CHAPTER 1

1. INTRODUCTION

1.1. Enhanced Oil Recovery

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 known as Enhanced Oil Recovery (EOR). The demand for petroleum products increased continuously while worldwide petroleum productions are steadily decline. This created the 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 increasing in production when compared to the production by primary and secondary recovery. EOR consists of two (2) types which are thermal and non-thermal. (Al-Anazi, 2007) Important to note that EOR is more challenging in offshore environment compared with onshore field. (Bondor *et al,* 2005) It must be economically feasible which fall within the high cost offshore environment. (Thomas *et al.*, 2010)

1.2. Gas Injection: CO_2 Injection

Gas injection is one of the non-thermal types of EOR. It is widely used in light, condensate and volatile reservoirs (Alvarado *et al.*, 2010). Injection of CO_2 resulted in the increasing of oil recovery. It will also create permanent storage of CO_2 in geological formation after the injection of CO_2 in a particular reservoir conditions. There are about 80 CO_2 projects in the world where all of them located in onshore operations (Gozalpour, 2005). In U.S, CO_2 injection is the fastest growing method of EOR for gas injection. It involves two (2) processes which are immiscible and miscible. But the most preferable mechanism is miscible because it helps to recover more residual oil compared to immiscible. High solubility between CO_2 and crude oil help to create low interfacial tension between those two (2) phases. As a result, CO_2 and crude oil can easily flow together and increase the production (David & Taber, 1992).

1.3. Asphaltene Precipitation and Deposition Problems

Asphaltene is defined as the fraction separated from crude oil or petroleum products upon addition of hydrocarbon solvents such as n-heptane (Speight, 1999). Asphaltene has a colloidal system (Speight, 1984) which carries intrinsic charge and will migrate to the opposite charge of electrode when placed in the electric field (Lichaa, 1977). Highly polar resins will be adsorbed and attracted by asphaltene to form a protective layer. When asphaltenes and resins are together they can be called as micelle (Leontaritis *et al.*, 1987).

However, when light oil reservoirs are considered for miscible gas injection processes especially using CO_2, it will create a potential of asphaltene precipitation and deposition problems. This matter is usually has been overlooked and not been anticipated by the operator of the field. It is due to the small weight percent of asphaltene content in the light reservoirs and the reservoir has no experience of asphaltene problems occurred during the previous production. Based on the results from field and laboratory data, it is confirmed that the lighter the oil, the lower the asphaltene stability, thus it will precipitate more easily from light oil than from heavy oil even though heavy oil has higher weight percent of asphaltene content (Sarma, 2003).

Several changes in pressure, temperature and composition of reservoir fluids may alter the thermodynamic equilibrium of asphaltene-resins micelles which is induced to the precipitation of asphaltene (Alta'ee *et al.*, 2010). The precipitation of asphaltene will lead to the losses in production, reduced efficiencies (Sim *et. al.*, 2005), reduces permeability of reservoirs near the wellbore region and able to plug the wellbores and well tubings due to the deposition of asphaltene on the solid surfaces (Sarma, 2003).

Some of field conditions that contribute to the presence of asphaltene are normal pressure depletion, acid simulation, gas-lift operations, and miscible flooding. During the operations of enhanced oil recovery by miscible displacement, the process is highly sensitive to the complex phase behavior of crude oil where the organic will be induced to deposit (Nikookar *etal,* 2005). Thus, the efforts of investigating the precipitation phenomena and problems are very pertinent.

1.4. Problem Statement

1.4.1. Problem Identification

CO_2 injection in light oil reservoirs has influenced the precipitation and deposition of asphaltenes. It is induced by the thermodynamic changes occurred in the reservoir. They are pressure drawdown, temperature changes and the most important factor is the change in oil composition. The deposition of asphaltenes created several problems to the reservoir, well and tubing. Presence of asphaltene may reduce the permeability of the reservoir, changing the wettability of reservoir and plugging the wellbore and tubing which cause of reduction in production.

1.4.2. Significant of the Project

This project is very important in order to support the occurrence of asphaltene precipitation and deposition during CO_2 injection in light oil reservoirs. The changes of asphaltene content in the recovered oil will be measured throughout the experiment process. This project may help to raise a concerned on the asphaltene precipitation and deposition problem for light oil reservoirs. When the awareness of the problem has increased, this will increased the effectiveness of CO_2 injection for EOR applications by an increment in production of the field. Finally, this project will help to strengthen the available statement and information on CO_2 injection in the light oil reservoir induced asphaltene precipitation and deposition.

1.5. Objectives

The objectives of this project are:

1. To measure the relationship of changes in asphaltene content with the injection pore volume.
2. To determine the changes of asphaltene in recovered oil during CO_2 injection for light crude oil at three (3) different injection pressures.

1.6. Scope of Study

For the purpose of this project, the scope of study would be about Enhanced Oil Recovery (EOR). A detail understanding about EOR helped to understand about this project better. On the other hand, a good knowledge about gas injection which is specifically about CO_2 injection must be a part of the research. One must know the impact of CO_2 injection to improve the production, the mechanism and the conditions of reservoir during injection which affect and create the problems. Besides the others, the most important thing to be curious about is asphaltene. It is the best if can understand on the nature of asphaltene and its precipitation and deposition process since asphaltene is a complex nature. An extensive and a detail research about it would be good to understand the results of experiment, later.

CHAPTER 2

2. LITERATURE REVIEW

2.1. Enhanced Oil Recovery (EOR)

Primary and secondary production methods typically recover only one third of oil in place and left with two third of the oil in place in the reservoir. This is where the life of a well is located in a situation where the cost of production is higher than the price that market will pay for that barrel. It will cause the well to be abandoned where about 70% of the oil is still left behind (Larry *et al.*, 1992).

Currently, most of the oil production comes from mature fields where is the major concern for oil companies and authorities to increase oil recovery from the aging resources. Since the last decades, it is a steadily decline on the rate of replacement of the produced reserves by new discoveries. This is where the EOR comes into account to effectively increase the recovery factor of the mature fields (Alvarado, 2010).

From Schlumberger Oilfield Glossary, Enhanced Oil Recovery (EOR) is an oil recovery enhancement method using sophisticated techniques that alter the original properties of oil. It has been ranked as third stage of oil recovery that was carried out after secondary recovery. It has a purpose not only to restore formation pressure but also to improve oil displacement or fluid flow in the reservoir.

EOR has the potential to reclassify unrecoverable and contingent reserves. It is viable because there are lots of mature technologies. The implementation of EOR also does not require drilling and completion cost and most of the existing infrastructure can be used. The design and implementation of an EOR project require a systematic integration from a multidisciplinary team (Bai, 2010).

EOR can be divided into two major types of techniques which are thermal and non-thermal recovery. For thermal, it consists of steam injection, hot waterflooding and in situ combustion. While for non-thermal recovery, it can be divided into three (3) types which are chemical flood, waterflood and gas drive (Al-Anazi, 2007). The objectives of EOR are to increase the mobility of the displacement medium by increasing the viscosity of the either oil or water or it can be both, extract the oil with a solvent and reduce the interfacial tension between oil and water. Thermal processes having the greatest certainty of success and have been apply at about 70% of EOR worldwide. It gives the highest recovery with the lowest costs. While for chemical processes, the cost and technical problems have excluded them from mainstream application (Larry *et al.*, 1992).

.1.1. Gas Injection – CO_2 Injection

On the other hand, gas injection is one of the oldest methods used for application of EOR (David & Taber, 1992). There are two major types of gas injection which are miscible and immiscible. In miscible gas injection, the gas is injected at or above minimum miscibility pressure (MMP) which causes the gas to be miscible with the oil. While for immiscible gas injection, flooding by the gas is conducted below MMP. This is due to maintain reservoir pressure in order to prevent production cut-off as well as directly increase the rate of production. Gas injection processes can be divided into several techniques which are liquefied petroleum gas miscible slug, enriched gas miscible process, high pressure lean gas miscible process and carbon dioxide process (Al-Anazi, 2007).

While CO_2 injection is one of the methods available in gas injection which appeared in 1930's and has been frequently used since 1970's. It has been the leading enhanced oil recovery technique for light and medium oils. Usually, it helps to prolong the production lives of light or medium oil fields nearing depletion under waterflood by 15 to 20 years. It will also recover 15% to 25% of the original oil in place. CO_2 is usually been used in light crude oil reservoirs. However, several immiscible CO_2 displacements are presently being conducted in reservoirs containing heavier oils. In a lighter oil systems, at relatively high pressures (>17 MPa), an extremely efficient process can be established with CO_2 is vaporizing type multicontact miscibility. And for heavier oils where reservoir pressure is very low and cannot be increased due to economic or technical reasons, CO2 can be used effectively in the immiscible mode. CO2 is a diatomic molecule and have high solubility in both aqueous and hydrocarbon solutions. This is the contribution where CO_2 has a potential used as an enhanced recovery agent (Bennion, 1993).

The advantages of CO_2 are the availability of being an inert, non flammable gas which is non-toxic to humans and easily can be transported in a liquid form at relatively low pressures. It contains a much greater viscosity and higher density than other gas injection agents. It helps to reduce problems associated with gravity override and viscous fingering effects. On the other hand, there are still few disadvantageous of the usage of CO_2. There is limited availability in some areas of the world, corrosion problems and a propensity for some oil systems to precipitate asphaltenes and other high molecular weight insoluble solids when contacted by CO_2 (Bennion, 1993).

However, several researches have emphasized that miscible process able to recover more oil than immiscible process (Stalkup, 1983). But, regardless of how it is applied in the field, either miscible or immiscible, there are the same mechanisms which play a role in increasing the oil recovery by CO_2 injection which are reduction of oil viscosity, swelling of oil, vaporization of oil, miscibility effects, reduction of interfacial tension, solution gas drive during blow-down, and increase in injectivity. They are more or less important depending on whether the CO_2 displacement is miscible or immiscible. From an experiment result, it showed that, CO_2 is miscible with light oil and immiscible with heavy oil. However, the highest recovery of CO_2 flooding achieved with the lightest oil, due to maximum oil swelling and minimum viscosity value attained saturation of this oil with CO_2. This greater efficiency of CO_2 flooding is due mostly to the fourfold reduction in the oil viscosity. But there are also because of 35% swelling of the oil (Mungan, 1991).

Minimum miscibility pressure (MMP) is the lowest pressure at which a solvent, CO_2 or hydrocarbon fluid, will become miscible with a reservoir crude oil at reservoir temperature. It is important to know the value of MMP if want to achieve miscibility during a flood (Mungan, 1991). MMP is the pressure where miscible displacement of reservoir oil by CO_2 occurs is dependent on the reservoir temperature and the composition of the oil. It is also can be defined as the lowest temperature where at a given temperature, 95% of the contacted oil is recovered. If the displacement pressure is lower than MMP, this will cause the value of oil recovery would be lower because immiscible displacement is less efficient. Besides that, the immiscible oil recovery enhancement has the mechanism of reduction in viscosity and swelling of oil where it helps to release of residual oil, particularly high gravity oils. The applications of immiscible CO_2 process usually in low gravity, high viscosity crudes where the viscosity reduction effect dominates (Holm, 1987).

Miscible process is good to recover more oil because CO_2 is very soluble with crude oils at reservoir pressures. The net oil volume will swells and reduce the viscosity of oil before achieving miscibility state by a vaporizing-gas-drive mechanism. After approaching the miscibility state, CO_2 and crude oil are able to flow together because of low interfacial tension between their two (2) phases. As a result, a good oil recovering is achieved at pressure below those required for the generation of miscibility. However, high pressures are still required to compress CO_2 to a density at which it can becomes a good solvent for the lighter hydrocarbon in the crude oils. CO_2 injection is normally carried on in the reservoir depth more than 2500 ft deep. By the way, oil composition also important to a performance of CO_2 injection. A high percentage of intermediate hydrocarbons (especially C5 to C12) are good. Based on the survey results, the API of more than 30^0 is presentable for the most active CO_2 floods (David & Taber and Taber, 1992).

The mechanism for CO_2 flooding or injection is the same as for hydrocarbon miscible floods, CO_2 will give better recoveries. This is due to the high solubility of CO_2 in water than hydrocarbon. This has allowed CO_2 to diffuse through the water phase to swell bypassed oil until the oil is mobile. And there are cases where the oil recoveries for some CO_2 field projects are exceeding the simulator predictions, while miscible hydrocarbon normally do not. For sources and supply of CO_2, miscible CO_2

flooding continues to expand and natural CO_2 is available from pipelines. Electricity and low cost CO_2 can be produced by efficient, gas fired cogeneration methods (David & Taber and Taber, 1992).

2.2. Asphaltene Precipitation and Deposition

Asphaltene precipitation from reservoir fluids during oil production is a serious problem. This is because it has cause plugging in formation, wellbores and production facilities (Nghiem *et al.*, 1993). Field conditions that induced to the precipitation of asphaltene include normal depletion and gas injection for Improved Oil Recovery (IOR) (Nghiem, 1999).

French scientist, Boussingault (1837) has been started to use the term "asphaltene". He used it to describe certain constituents during distillation of asphalts in eastern France and Peru. Because they are match in the appearance with parent asphalt, they are known as "asphaltenes" in order to stand for their origin. For easily understanding, asphaltene is a constituent of asphalt. Even after 166 years from Boussingault's qualitative definition of asphaltene, there are no correct definitions of asphaltene in terms of chemistry. This is due to the difficulties in the determination of asphaltene actual structure. (Boussingault, 1837)

However, there are many other definitions of asphaltene. It is a fraction insoluble in low boiling point paraffin hydrocarbons, but soluble in carbon tetrachloride and benzene by Nellensteyn (1924). Marcussan (1945) defined asphaltene as an insoluble fraction in light gasolines and petroleum ether while it is a fraction insoluble in n-heptane but soluble in toluene defined by Pfeiffer (1950) (Mansoori, 1997). Then, Mitchell and Speight (1973) have defined asphaltene as the part precipitated by addition of low boiling paraffin solvents such as n-heptane (Speight *et al*, 1973). The physical appearances of asphaltene are dark brown to black friable solids with no definite melting point, and they are decomposed on heating leaving a carbonaceous residue and volatile products (Sarma, 2003; Speight, 2004). The amount of asphaltene in petroleum varies with sources, depth of burial, API gravity of the crude oil, the sulphur content as well as the non-asphaltene sulphur (Koots and Speight, 1975).

Characteristics of the reservoir that experienced asphaltene precipitation in normal pressure depletion are the fluid in place is light to medium oil with small asphaltene content, the initial reservoir pressure is much larger than the saturation pressure where the fluid is highly undersaturated and maximum precipitation occurs around the saturation pressure (de Boer *et al.*, 1995). For heavier crudes where having a larger amount of asphaltene content, they have a very little asphaltene precipitation problems because heavier crudes can dissolve more asphaltene compare to the lighter crudes. There are few field cases with asphaltene precipitation problems during primary depletion. They are Venezuelan Boscan crude with 17 weight % asphaltene that was almost having nearly trouble free, while, Algerian Hassi Messaoud crude with 0.15 weight % asphaltene were having serious precipitation problem during production (Leontaritis and Mansoori, 1988).

Even though the subject of asphaltene has been studied for more than half century, there are still some disagreements among the researchers and investigators about the nature of the asphaltene in the crude oil. There are two different models to describe the nature of the asphaltene in the solution. First is a solubility model. This model considered the asphaltene to be dissolved in a true liquid state. Second is a colloidal model. It considered asphaltene to be solid particles which are suspended colloidally in the crude oil and are stabilized by large resin molecules. Solubility model describes asphaltene precipitation as a thermodynamically reversible process while in the colloidal model, precipitation of asphaltene is considered to be irreversible. The validity of the two models are depends on whether the precipitation process is reversible or not (Ashoori *et al.*, 2006). When asphaltenes and resins are together, they can be called as micelles (Leontaritis *et al.*, 1987; Leontaritis, 1989). It is subjected to any thermodynamic changes since it was separate molecular entities of the crude oil.

Resins are having a behavior of strong tendency to associate with asphaltene (Gonzalez *et al.*, 2004). Resins constituents have a role in the stability petroleum and prevent separation of the asphaltene constituents as a separate phase. The mole fraction of resins is always larger than asphaltenes. Thus micelles are expected to be richer in resins (Speight, 2004). There are experimental evidence suggested that for an oil mixture there is a critical concentration of resins. Below it, the flocculation asphaltene may precipitate and above which, they cannot precipitate. This is in the conditions with disregarded how much the oil mixture is agitated, heated, or pressurized, sort of changing its composition (Lichaa, 1977; Swanson, 1942).

Colloidal system is the best explanation when asphaltenes were in solution in the crude oil (Speight and Moschopedis, 1981; Speight *et al.*, 1984; Leontaritis and Mansoori 1987). Asphaltenes contain intrinsic charges where it can be positive or negative which rely on the oil composition. The available charges make it attracted to any opposite charges available in the surroundings(Lichaa, 1977; Lichaa and Harrera, 1975; Leontaritis and Mansoori, 1987). That is why for some reasons, highly polar resins are able to act as peptizing agent for asphaltenes and act as a protective layer when adsorbed by the asphaltenes(Leontaritis and Mansoori, 1987; Leontaritis, 1989).

When flocculation of asphaltene occurred inside reservoir matrix, it can be followed by its deposition and adsorption on the rock surfaces. However, flocculation and deposition are two different processes. Deposition can reduce permeability, cause formation damage and alter the wettability. There are factors that control adsorption of asphaltene and heavy ends of petroleum on mineral surface. They are chemical and structure nature of the surface mineralogy, the asphaltene and resins contents of the crude oil, brine pH and composition, pressure and temperature. Several studies have shown that rock wettability can be altered by treating a core with a solution of petroleum heavy ends. The wettability of the core can be shifted from water wet to intermediate water wet after treatment (Kokal and Sayegh, 1995).

Since the precipitated asphaltene can reduce porosity, permeability, alter rock wettability, affect well injectivity and productivity and cause plugging of wellbores, pipes and processing equipment (De Pedroza *et al.*, 1996; Minnssieux, 1997), it is valuable to know the factors that affect the precipitation of asphaltene inside a reservoir. They are nature, saturation and distribution of the reservoir fluids, the mineralogy and properties of the rock, the pressure and temperature, the nature of the injection fluids, the electrokinetic effects due to streaming potential generation due to reservoir fluid flow, the asphaltene and resin contents of the reservoir oil and the amount of formation brine and its composition (De Pedroza *et al.*, 1996; Minssieux, 1997; Gonzalez and Louvisse, 1991;Rayes *et al.*, 2003).

Asphaltene deposition can cause a serious problem. It occurs during the production and processing of oils. Many cases have shown that the deposits can be formed in the reservoir, in the well tubing, can be carried through the flow lines and into the separators and other downstream equipment. The cost of remediation of this problems is expensive and significantly affect the economics of a project (Kokal and Sayegh, 1995).

In the reservoir, there are three (3) important parameters that affect asphaltene deposition. First is changes in the composition of reservoir fluid. During the production, pressure deplete which cause the loss of lighter components in the oil. Thus this will reduce asphaltene flocculation since it always compete with the gas for solvency in the crude oil. Thus, as the field gets older, there will be less asphaltene problems since the oil is heavier. Second is the injection fluids. During gas flooding, miscible fluid is injected to the reservoir in order to displace the residual oil left after water flooding. This will also cause the precipitation of asphaltene inside the reservoir matrix and its deposition on the reservoir rock. The greater the amount of injected solvents, the tendency of asphaltene problem is greater. Third is electro-kinetic effects. The flow of oil through reservoir pores and well tubing created streaming potential which can assist in flocculating asphaltenes by electro-deposition. Near the wellbore where having high velocity of flow, the tendency of asphaltene problem is high. While in the wellbores and tubing, the asphaltene will deposits plug the wells and result in production losses. This will lead to the increase in well clean up cost and may also cause serious accidents to occur. For the processing equipment, the asphaltene will deposits in it and plug safety devices and safety relief valves in processing equipment. This may cause a disastrous effects (Lichaa, 1977; Lichaa and Harrera, 1975; Leontaritis and Mansoori, 1987; Leontaritis, 1989; Hirshberg *et al.*, 1984; Leontaritis and Mansoori, 1988; Tuttle, 1983; Hasket and Tartera, 1965).

The mechanism of asphaltenes precipitation is very complex and still has not fully understood. But, it is widely understand that the asphaltenes precipitation caused by changes in thermodynamic conditions of temperature, pressure and oil composition. There are also other operational that contribute to the precipitation and deposition of asphaltenes which are high pressure drawdown, synergistic changes in conditions of temperature and pressure, mixture of fluids with varying density within the production and transportation facilities, during acidizing and the most important one, during gas injection (Sarma, 2003).

The injection of hydrocarbon gases or CO_2 also induced asphaltene precipitation (Srivastava *et al.*, 1995). Precipitation occurred anywhere in the reservoir although it usually happened at the production wellbore at solvent breakthrough. It also occurred during solvent injection into heavy oil reservoir (Kokal and Sayegh, 1995).

2.2.1 Asphaltenes precipitation and deposition in a CO_2 injection project for light oil.

Overlooked of asphaltene precipitation and deposition problems by operators during gas injection in light oil reservoir are common. This may due to the low weight percents of asphaltene in light oil and the field has no experience in asphaltene precipitation during its primary production (Sarma, 2003). As a consequence, the fields will experiences several problems because the precipitation of asphaltene will cause severe permeability reduction and wettability alteration in reservoir which will decrease the production (Cuiec, 1984). Plugging of the well and surface facilities also are the potential problems to occur. It is well known that remedial measures for this problem are expensive and disruptive like chemical treatment.

Injected CO_2 when it is in contact with the crude oil, it can cause several changes in fluid behavior and equilibrium conditions which favor precipitation of asphaltene (Kokal and Sayegh, 1995; Sarma, 2003; Srivastava *et al.*, 1997). Alta'ee *et al.* (2009) have been reported about their study on asphaltene precipitation using light oil sample (41.5°) at constant pressure and temperature. They found that the asphaltene precipitation increases with increasing in the concentration of CO_2. From their study, they observed that asphaltene starts to precipitate at the concentration of 22mol% of CO_2 and increases slowly until 40mol% CO_2. And after 40mol% of CO_2 injection, the asphaltene precipitation starts to increase linearly.

Carbon dioxide is highly soluble in oil to a lesser extent in water. The existence of miscibility between CO_2 and crude oil could eliminates the appearance of interfacial tension and cappilary pressure. This may resulted to CO_2 is very good in recover almost all of the residual oil. When the injected CO_2 and crude oil mixed in any ratio, they are said to in a first contact miscible. However, the first contact miscibility only can be achieved by highly hydrocarbon rich gases, or at very high pressure for lean system. But CO_2 is not first contact miscibility with most of reservoir oils even at highly operating pressure. On the other hand, CO_2 can develop miscibility through multiple contacts under specific conditions of pressure and temperature and specific oil compositions (Jai Ying *et al.*, 2006). By Parra-Ramirez *et al.* (2001), they conducted an experimental study on the effect of first and multiple contact for 34° API crude oil from Rangely field, Colorado. The crude contained about 1.5wt% asphaltene and was determined that first contact precipitation at different CO_2 concentration were not exist. Multiple contact experiments showed that multiple contact precipitation amounts were 3-5 times the first contact precipitation values (Parra-Ramirez *et al*, 2001).

Beliveau and Payne (1991) have conducted an analyses of laboratory and field data which affirmed that gradual diffusion of CO_2 into the oil, which was being produced at a low rate of about 100BPD had led to the precipitation of asphaltenes from the parent oil (Beliveau and Payne, 1991). However, Srivastava *et al.* (1999) have investigated that based on dynamic and static tests on Weyburn crude oil for CO_2 injection, the concentration of CO_2 during injection is vary directly with the precipitation of asphaltene. The graph showed linear relationship which mean that by increasing the concentration of CO_2, the asphaltene precepitation will also increase. Based on CO_2 oil system in Permian Basin, West Texas, Huang (1992) observed that when asphaltene content in the oil exceeded 4.6-wt% which resulting to a lower oil recovery and for higher asphaltene content (>5%), the minimum mescibility pressure (MMP) determined by slim tube test is less reliable. For high pressure, high temperature corefloods using 34°API crude oil from Rangely Field, Colorado which is having mature CO_2 flood, the studies resulted that asphaltene precipitation has started even within the reservoir because of changes in oil composition caused by multiple contacts of CO_2 and the oil. However, the operator of the field only concerned about the asphaltene precipitation around the well perforations and surface facilities (Parra-Ramirez *et al.*, 2001).

Expected asphaltene precipitation may occurred in light crudes reservoirs where having a condition of undersaturated with respect to gas. Plus, if the hydrocarbon column is of large vertical extent, strong undersaturation may also occur in fields with a natural gas cap which explains that wells at lower horizons are expected to show more asphaltene problems than wells higher in structure. Ventura oil field having a reservoir pressure above bubble point experienced heavy asphaltene precipitation in the tubing. However when the well reached bubble point, there are no more asphaltene problems occurred. (Tuttle, 1983) Pressure decreasing above bubble point will reduce asphaltene solubility which increasing the precipitation problems. But the change in composition at below bubble point which cause by gas liberation will result in enhanced solubility upon pressure decrease (Hirschberg, *et al.,* 1984).

Many areas in Venezuela have experienced severe asphaltene precipitation and deposition problems. Lichaa (1977) described the problems at Mata-Acema which contained about 0.4% to 9.8% by weight of asphaltene and has causes partial or complete plugging of the well. While Boscan field having API gravities 9 to 12 degrees is produces heavy oils and contained 17.2 percent of asphaltenes. However, no asphaltene problem was determined here. From here, it can be concluded that serious asphaltenes problems might only occur when the CO_2 injection is conducted in light oil reservoir (Lichaa, 1977).

Injected CO_2 when it is in contact with the crude oil, it can cause several changes in fluid behavior and equilibrium conditions which favor precipitation of asphaltene (Kokal and Sayegh, 1995; Sarma, 2003;Srivastava and Huang, 1997). Either in the process of CO_2 miscible or immiscible flooding, the solubility of CO_2 asphaltene precipitation is an adverse for it leads to formation damage and wettability alteration (Binshan *et al.*, 2010). Srivastava and Huang (1997) studied the behavior of asphaltene deposition during CO_2 flooding by experimental approach. At the operating conditions of 16MPa and 59-61°C, there are a relationship between the CO_2 concentration and asphaltene flocculated for Weyburn oil samples where only high enough CO_2 concentration can caused the asphaltene dissolved in oil begins to flocculate. Flocculated asphaltene from oil may be suspended in oil and may be adsorbed on pore surfaces or captured by pore throats. Asphaltene in soluble state will flow with oil flow in porous media (Srivastava and Huang, 1997).

During CO_2 injection, phase behavior characteristic is very intricate. The contact of injected CO_2 and formation oil may induce multiple phase coexistence. And because of precipitated asphaltene is black or dark brown and opaque, it can't be clearly identified with the interphase between asphaltene and oil. This has cause the difficulty for the equipment to accurately determine asphaltene precipitation onset point and asphaltene precipitation quantity. Thus, multiphase equilibrium thermodynamic model for asphaltic oil and CO_2 system is used to overcome the problem and handle the research on the asphaltene precipitation. Since CO_2 injection caused the phase behavior characteristic to be very complex, under some temperature and pressure, not only CO_2

can dissolve into oil, but also some hydrocarbon molecule can be extracted into CO2 gas phase. This is the basis of CO_2 dynamic miscibility (Jia Ying *et al.*, 2006).

However, CO_2 injections will perform better as a tertiary injectant where it can helps to yield higher recoveries compared when it was applied as a secondary recovery where water injection is the best choice. Because water is better in displacing fluid for secondary crude oil recovery compare to CO_2 injection. While for tertiary recovery, CO_2 injection can perform better because CO_2 is soluble in both water and crude oil. The appearances of water helps to dislove and reduce the free CO_2 concentration in the system. This leads to the reduction on asphaltene precipitation in the system (Okwen, 2006).

2.3 Summary

Enhanced Oil Recovery (EOR) is the most important technical development in the oil and gas industry. It consists of two (2) types which are thermal and non-thermal. However, the application of gas injection especially on the use of CO_2 as the solvent of injection is the most important topic to be discussed in the completion of this project. Besides the great impact of CO_2 injection in improving the production in a third stage of recovery, there are also problems or matters that need to be concerned about which is asphaltene. Asphaltene is a complex nature which is difficult to be analyzed. Thus, it has several definitions defined by researchers and scientists which are different from one another. Because of its complex nature, the problem created by asphaltene usually has been ignored and is not a matter of concerned. Unfortunately, the precipitation and deposition of asphaltene is a major problem during the production. And, the problem is greater and larger especially during the CO_2 injection in the light oil reservoirs because of the involvement of many factors especially the composition changes whenever the CO_2 is contact with the crude oil.

CHAPTER 3

3. METHODOLOGY

3.1. Research methodology

This section consists of project analysis where it involves data and information gathering and experimental analysis. Firstly research is conducted in order to gain a good knowledge and understanding related to the asphaltene precipitation. Then, another research process is conducted to understand all the information regarding Enhanced Oil Recovery (EOR) where for the purpose of this project it can be focus to the Carbon Dioxide (CO_2) injection. And finally, any related and available patents, journals and books are studied in order to find and carefully understand about the influences of CO_2 injection towards the asphaltene precipitation and the reasons why it is usually occurred in the light oil reservoir. Finally, all the important information, knowledge and understanding are compiled in the project's final report.

3.2. Experimental Methodology

3.2.1. Crude Oil Sample

- Dulang oil sample which is dead oil has been used for this project. It is a light oil sample.

- Dulang field has experienced with asphaltene problems which proven there are asphaltene content in the oil sample.
- Crude oil has been characterized by measuring the properties of the sample which are viscosity and asphaltene content.

3.2.2. Asphaltene Precipitation Experiment

For the purpose of this project, experiment of dynamic asphaltene precipitation test has been conducted. This test is the best method that can resemble exact reservoir conditions for the reliability of the project with three different injection pressure, constant temperature at 98°C and pure CO_2 (99.9 mole%). The objectives of this experiment are to investigate the possibility of asphaltene precipitation and deposition when Dulang oil make a contact with CO_2 under the dynamic conditions and to study the changes on asphaltene content in the recovered oil at different injection pressures.

Dynamic asphaltene precipitation test was carried out with several runs at different injection pressure where the temperature and CO_2 concentration were kept constant. The injection pressures used for this test are 2600, 2300 and 2000 psig.

Firstly, the core was fully saturated with brine. And then crude oil was injected to the core and now, the core was fully saturated with crude oil because of displacement process. After that, water was injected as a secondary recovery method until the porous media left with only residual oil saturation. Then, CO_2 were continuously injected as tertiary recovery and the output which is recovered oil was collected.

For each run, recovered oil has been collected for every 10 minutes until there was no more oil recovered during the test. The recovered oil sample was taken for the measurement of asphaltene content using ASTM D3270-07 method.

3.2.3. Asphaltene Content Measurement using ASTM (D3279-07)

Asphaltene content was measured using ASTM D3279-07 method. The details of the standard test have been described in the Appendix A. This method is useful for measuring the asphaltene content of petroleum asphalts, gas oils, heavy fuel oils, and crude petroleum. And the most important fact is asphaltene is not soluble in n-heptane.

The measurement was carried out by mixing 1 g of Dulang crude oil sample with 100-mL n-heptane. And then, the mixture is heated and secured under reflux condenser with the magnetic stirrer in operation shown in Figure 3.1. The mixture was heated with a gentle refluxing for a period of 30 minutes and left at a room temperature for another 1 hour. Gooch crucible with glass filter pad (GFD) (shown in Figure 3.2 and Figure 3.3) were heated in the oven for 15 minutes and kept in the dessicator for another 15 minutes to remove the availability of humid. Then, crucible and filter pad were weighted to obtain the original weight before filtration was conducted.

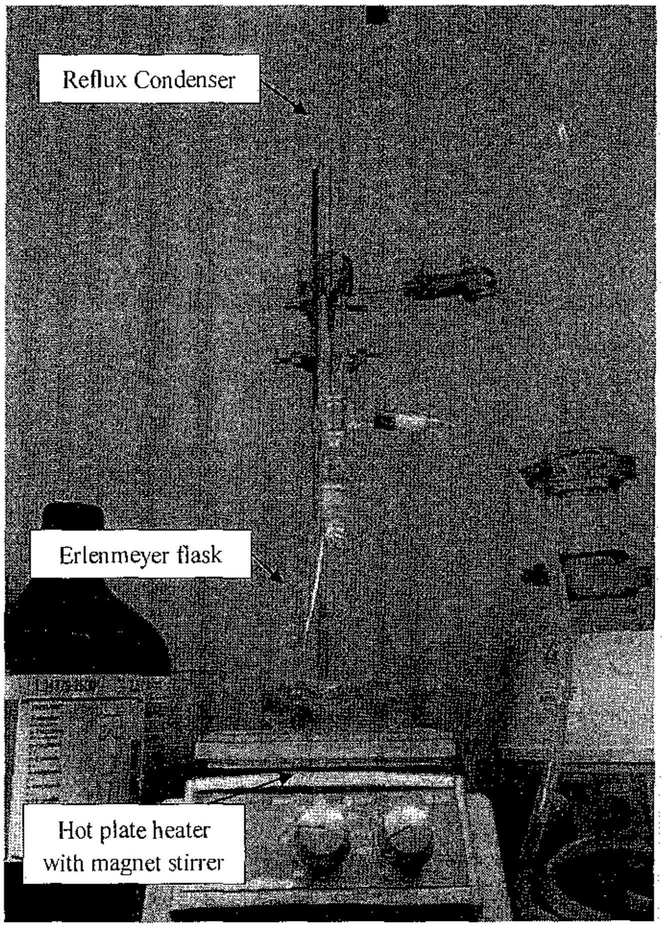

Figure 3.1: Mixture of 1 g sample with 100 mL of n-heptane was heated up and secured under reflux condenser

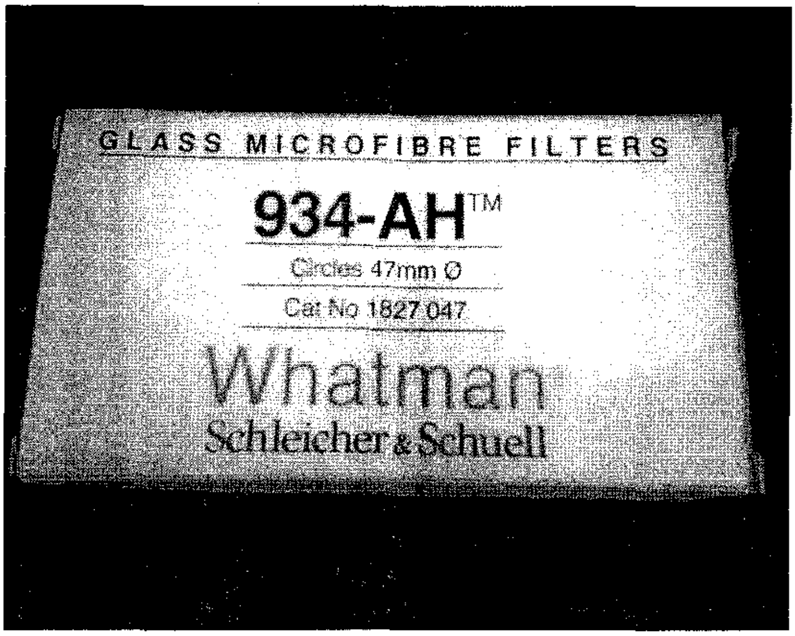

Figure 3.2 : Glass Fiber Filter Pad (GFD)

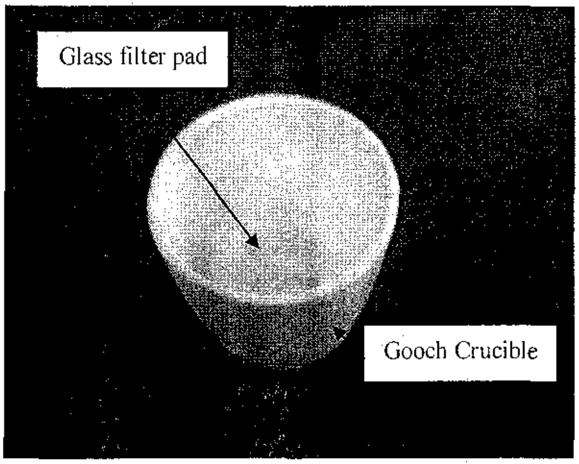

Figure 3.3: Gooch crucible with glass filter paper (GFD)

The mixture of sample was heated again at the temperature 39-40°C while a vacuum filter was prepared with a suction flask for filtration processes. Filtration apparatus is shown in Figure 3.4. Sample mixture was poured to the crucible at the top of suction flask using a gentle vacuum. After filtration finish, the crucible plus filter pad was heated in the oven at the temperature 107°C for 15 minutes and kept in the dessicator for another 15 minutes. Then they were weighted and final weight after filtration was measured.

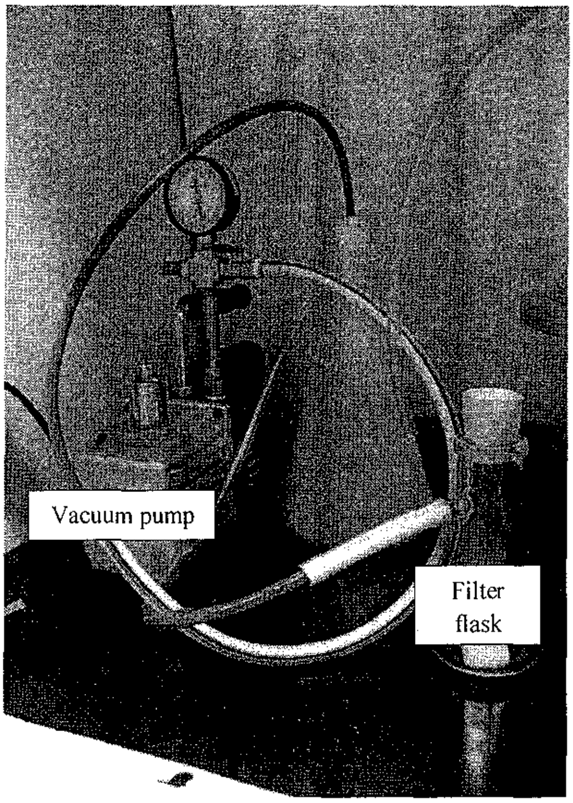

Figure 3.4: Filtration apparatus

The calculation of the mass percent of normal-heptane insolubles (NHI) as the percentage by weight of the original sample is as follows:

$$NHI\,\% = A/B * 100$$

where:

A = Total mass of insolubles, gram (Final weight after filtration – Initial weight after filtration)

B = Total mass of sample, gram

For each of the recovered oil during dynamic asphaltene precipitation test, they were using the same procedure as describe in the Appendix A to measure the weight percent of the asphaltene content.

3.2.4. Injected Pore Volume Calculation

Each run of experiment was conducted using different porous media with different value of pore volume, Vp. The calculation of pore volume for the experiment is explained below:

1. Assume 1 PV = X cc Vp of each core.

2. Sample was taken every 10 minutes with injection rate 0.4cc/min.

   Vp for every 10 minutes = 0.4 cc/min * 10 minutes

   = 4 cc

3. PV for each 10 minutes was depends on the Vp of each core.

   PV = ΣVp every 10 minutes / X cc Vp of each core

Example:

Run 1: Pinj = 2000 psig, Vp = 18.771 cc

At 10 minutes, PV = 4 cc / 18.771 cc = 0.21 %

3.3. Gantt chart FYP I

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Topic selection/confirmation	■	■	■												
2	Preliminary Research Work			■	■											
3	Submission of Preliminary Report				■											
4	Literature Review on the project				■	■	■	■	■	■						
5	Submission of Progress Report									■						
6	FYP 1 Seminar							▨								
7	Project Work Continues									■	■	■	■	■		
8	Analysis of Result and Discussion												■	■		
9	Report Preparation													■	■	
10	Submission of Interim Report														■	
11	Oral Presentation (study week)															■

3.4. Gantt Chart FYP II

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Conducting experiments	▨	▨	▨	▨	▨	▨	▨							
2	Analysis of the results								▨						
3	Submission of Progress Report														
4	Analysis of Result and Discussion									▨	▨	▨			
5	FYP II Seminar														
6	Paper Writing										▨	▨	▨	▨	
7	Report Preparation												▨	▨	▨
8	Submission of Final Report														
9	Oral Presentation (Study week)														

CHAPTER 4

4. RESULTS AND DISCUSSIONS

For this section, all the results from experimental work are presented and discussed here. The results are in the scope of changes on the asphaltene content in the recovered oil during CO_2 injection for light oil which Dulang crude oil has been used. All the recovered oil was taken every 4 cc of CO_2 injected pore volume.

4.2.1. Run 1 with Injection Pressure = 2000 psig

The summarized results for the first run are available in Table 4.1. The recovered oil that has been collected at the injection pressure of 2000 psig was 3.3 cc.

Table 4.1: Results for Pinj= 2000 psig with initial asphaltene content = 0.42 wt %

Injected Pore Volume (PV)	Asphaltene Content in the recovered oil (wt %)	Asphaltene content precipitated in the core (wt %)
0.43	0.31	0.11
0.64	0.25	0.17
0.85	0.17	0.25
1.07	0.13	0.29
1.28	0.11	0.31

Based on the results stated in the Table 4.1, it shows that the asphaltene content in the recovered oil was decreasing as the injected pore volume increased. Asphaltene started to precipitate as the injected CO_2 reached 0.43 PV and the amount of asphaltene that already precipitated in the core was 0.11 wt %.

At 0.64 PV, the amount of asphaltene precipitation in the porous media was 0.17 wt %. The deposition occurred is even greater than the first deposition which is 0.11

wt %. Then the asphaltene precipitation rose to 0.25 wt %, 0.29 wt % and 0.31 wt % for the increment of every 4 cc pore volume that has been injected by CO_2.

The increment in asphaltene precipitation is due to the increasing in the CO_2 concentration contacted with the oil sample during the injection. At the early stage of injection, CO_2 concentration contacted with the oil sample is lesser compare to the contacted at the end of injection. Even though pure CO2 concentration has been used in the experiment, the mole % contacted with the oil sample is not constant for every 4 cc of injected pore volume thus directly affect the amount of asphaltene precipitation in the core sample.

Alta'ee *et al.* (2009) has done a study on the change of asphaltene precipitation using light oi (41.5° API) at constant temperature and pressure on the change in CO_2 concentration. They found that as the concentration of CO_2 increased, the precipitation of asphaltene also increased. From their study, the results showed that at 22 mole % of CO_2 concentration, the asphaltene started to precipitate, and then it was slowly increases until the concentration reached 40 mole %. After that, there was linear increase on asphaltene precipitation observed with the increase amount of injected CO2 (Alta'ee *et al*, 2009).

By increasing the concentration of CO_2 in contact with oil sample, this will change the composition of the oil sample which is a factor of precipitation of asphaltene to occur. The injected CO_2 cause the changes in fluid behavior and equilibrium conditions which lead to the precipitation of asphaltene (Kokal and Sayegh, 1995, Sarma, 2003 and Srivastava and Huang, 1997). The change in oil composition gives the instability in asphaltene-resins phases where it increases the potential of precipitation to occur (Dehghani *et al*, 2007).

Thus, at the early state of injection, since the concentration of CO_2 in contact with oil sample is low, there were less changes occurred in the oil composition. However, as the CO_2 concentration increases, the asphaltene-resins phases become more unstable resulted to the more asphaltene deposition as the injected pore volume reach a deeper level.

4.2.2. Run 2 with Injection Pressure 2300 psig

The recovered oil collected from second run also having the same procedure as the first run. The results of the asphaltene content in the recovered oil for second run have been summarized in Table 4.2. A total of 4.5 cc of oil has been recovered for 2300 psig injection pressure.

Table 4.2 : Results for Pinj= 2300 psig with initial asphaltene content = 0.42 wt %

Injected Pore Volume (PV)	Asphaltene Content in the recovered oil (wt %)	Asphaltene content precipitated in the core (wt %)
0.43	0.35	0.07
0.65	0.30	0.12
0.86	0.24	0.18
1.08	0.19	0.23

Asphaltene started to precipitate as the CO_2 injection reached 0.43 PV where the precipitation in the core sample is 0.07%. In compare with the precipitated asphaltene content in the core from the previous run with the injection pressure 2000 psig, the percentage of asphaltene precipitate for injection pressure 2300 psig is much lower. This is due to the difference in the injection pressure applied for the experiment. As the injection pressure increases, the solubility of the asphaltene in the oil sample is higher (Monger and Fu, 1987). However, the injection of CO_2 still will disturbed the stability of asphaltene-resins phases but the effect is lesser than before because now the consideration applied to the effects of injection pressure.

The increase in pressure cause the lighter component in the crude oil become lesser due to the compression that occurred between the molecules, thus increase the solubility between resins and lighter components. The asphaltene solubility will also increase which then resulted to the decreases in the asphaltene precipitation and deposition (Ying *et al.*, 2006).

After that, the asphaltene content in the recovered oil is continued to decrease as the injected pore volume increases. The decrease is caused by the deposition of some of the asphaltene in the porous media. The percentage of deposition is 0.12 wt % as the injected pore volume reached 0.65 PV, 0.18 wt % at 0.86 PV and finally, 0.23 wt % at the injected pore volume of 1.08 PV. However, the percentage of deposition is still lower than deposition occurred during the injection pressure of 2000 psig. The deposition occurred is due to the increase in the concentration of CO_2 having a contact with the oil sample. Reported from the studies conducted for the Bangestan field with undersaturated oil sample, the asphaltene began to precipitate at around 0.54 mole % of CO_2 concentration. After that, there was a linear increase in the asphaltene precipitation with CO_2 concentration as per illustrated in Figure 4.1 (Moghadasi *et al.*, 2006). The increases of the mole percent for the injected gas in contact with crude oil will causes more pressure drop along the core caused more asphaltene deposition within the porous media (Bagheri *et al.*, 2011).

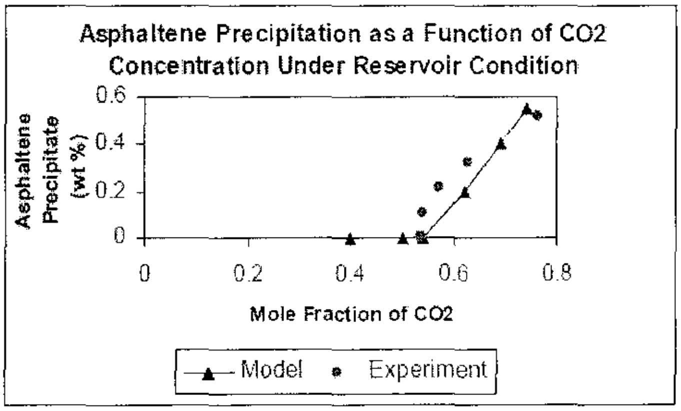

Figure 4.1: Amount of precipitated asphaltene for Bangestan oil with CO2 at 6000 psia and 160°F. (Moghadasi *et al.*, 2006)

Increase of CO_2 concentration in contact with the oil sample growth the changes of oil composition. The changes in composition of the oil create the instability in the micelles structures that happened to consist of asphaltene and resins fractions (Dehghani *et al*, 2007).

The asphaltene instability occurred during the flocculation processes where micelles started to separate with its protective layer which is resins and left asphaltene to precipitate and finally deposited. The factors that contribute to the flocculation process are temperature, pressure and composition changes. During flocculation, the asphaltene particles started to form large entities (Leontaritis *et al.,* 1994). For this project, the flocculation happened due to the changes of injection pressure and it contributes to the composition changes of the crude oil sample. The larger entities formed during flocculation process has explained the permeability impairment caused by the deposited asphaltene. However, the instability of asphaltene in the crude oil also resulted from the pH change during the injection of CO_2 (Sarma, 2003).

As pressure increases, the density and solubility differences between oil and asphaltene content will be decreases, which reduce the possibility of precipitation to occur. The molecular weight distribution also will increase, when the pressure increases, which lead to be more precipitation occurred at injection pressure 2000 psig (Moqadam *et al.,*2009).

4.2.3. Run 3 with Injection Pressure 2600 psig

For the third run, the injected pressure was 2600 psig. Before the CO_2 injection was conducted, oil was injected to replace brine in the core until no more recovered water produced and after that water was injected to apply the secondary recovery method. The injection of water ended after the recovered fluid contained no oil. CO_2 injection can be started to represent tertiary recovery method. A total of 4.9 cc oil has been recovered. The results of the third run have been summarized in Table 4.3.

Table 4.3 : Results for Pinj= 2600 psig with initial asphaltene content = 0.42 wt %

Injected Pore Volume (PV)	Asphaltene Content in the recovered oil (wt %)	Asphaltene content precipitated in the core (wt %)
0.51	0.270	0.150
0.76	0.265	0.155
1.02	0.240	0.180
1.27	0.190	0.230

CHAPTER 5

5. CONCLUSION

- CO_2 injection in light crude oil induced asphaltene precipitation and deposition in the core sample.

  1. Asphaltene content in the recovered oil is decreasing as the increasing of CO_2 injected in the pore volume of the core sample. This is due to the precipitation and deposition of apshaltene in the core sample induced by CO2 injection.
  2. As the injection pressure increases, the asphaltene precipitation and deposition is decreases because the asphaltene is more soluble in the crude oil at high pressure.

- Basically, CO_2 injection will decrease the important properties of reservoir which are permeability and porosity which lead to the reduction in the oil recovery.

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CHAPTER 7

7. APPENDICES

Appendix A: Standard Method Procedure

1.0. Standard Test Method for n-Heptane Insoluble (ASTM D3279)

1. Scope

   1.1. This test method covers determination of the mass percent of asphaltenes as defined by insolubility in normalheptane solvent. It is applicable to all solid and semi solid petroleum asphalts containing little or no mineral matter, to gas oils, to heavy fuel oils, and to crude oil petroleum that has been topped to a cut-point of 343°C or higher.

   1.2. The values stated in SI units are to be regarded as the standard.

   1.3. This standard does not support to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. See Section 7 for a specific hazard statement .

2. References Documents

   2.1. ASTM Standards: C 670 for Preparing Precision and Bias Statement for Tests Methods for Construction Materials.

3. Summary of Test Method

3.1. The sample is dispersed in n-heptane and filtered through a glass-fiber pad. The insoluble material is washed, dried, and weighed.

4. Significance and Use

4.1. This test method is useful in quantifying the asphaltene content of petroleum asphalts, gas oils, heavy fuel oils, and crude petroleum. Asphaltene content is defined as those components not soluble in n-heptane.

5. Apparatus and Materials

5.1. The assembly of the dispersing apparatus is illustrated in XXX

The details of the component parts as follows:

5.1.1. Erlenmeyer Flask, of 250-mL capacity adapted to an Allihn-type reflux condenser, each with a 32/25 ball joint.

5.1.2. Magnetic Stirrer and Magnetic-Stirrer Hot Plate, equipped with a voltage regulator.

5.1.3. Gooch Crocible, glazed inside and outside with the exception of the outside bottom surface. The approximate dimensions shall be a diameter of 44mm at the top tapering to 36mm at the bottom and a depth of 20-30 mm.

5.1.4. Filter Pad, glass-fiber 32 mm in diameter.

5.1.5.. Filter Flask, heavy wall with side tube, 500-mL capacity.

5.1.6. Filter Tube, 40 to 42 mm in inside diameter.

5.1.7. Rubber Tubing, or adapter for holding Gooch crucible on the filter tube.

6. Solvent

6.1. n-Heptane, 99.0 minimum mol % (Pure Grade).

7. Hazards

7.1. n-Heptane has a boiling point of 98°C and a flash point of -1°C, which means that it should be handled with care. It is recommended that both the reflux dispersion and filtration steps be conducted in a ventilated hood and away from flames or other sources of heat.

8. Procedure

8.1. Into the 250-mL Erlenmeyer flsk, weigh to the nearest 0.1 mg a quantity of the sample to be tested, using 0.5 to 0.6 g for airblown asphalts, 0.7 to 0.8 g for asphalt paving binders and crude residues, and 1.0 to 1.3 g for gas oils and heavy fuel oils. Add n-heptane in the ratio 100mL of solvent per 1 g of sample, using proportionally less or more solvent as dependent upon the sample size. Unless the asphalt is in a granular form, heat the flask gently and turn it to cause the sample to the distributed somewhat over the bottom or lower sides of the flask. Erlenmeyer flask is recommended. After all possible precipitate has been washed from the flask to the filtering crucible in 8.3, include the flask with crucible for the drying, weighing, and calculation procedures in 8.3 and 9.1.

8.2. Place the Erlenmeyer falsk, containing the sample plus solvent with magnetic stirrer added, on the magnetic-stirrer hot plate and secure under the reflux condenser. With the magnetic stirrer in operation adjust for gentle refluxing for a period of 15 to 20 min when testing paving binders, fuel oils, gas oils, or crude residues. For airblown asphalts, a reflux period of 25 to 30 min is recommended. In all cases, allow the dispersed mixture to cool to room temperature for a period of 1hour.

8.3. Place the Gooch crucible plus one thickness of the glass-fiber filter pad in an oven at about 107°C for 15 min, allow to cool in a dessicator, and then weigh to the nearest 0.1 mg. Set up the filtering crucible plus filter pad in the suction flask and pre-wet with 5 mL of n-heptane. Warm the flask containing the sample plus solvent to 38 to 49°C on the hot plate and pour its contents (except for the magnetic stirrer) through the filter using a gentle vacuum. Filtration will proceed most rapidly if the supernatant liquid is filtered first with the insolubles transferred to the filter last. Police the beaker of flask while transferring the final precipitate, using either a rubber policeman or stainless steel spatula with a squared end. Wash the precipitate with three portions of n-heptane of about 10 mL each, first rinsing out the flask therewith. Place the crucible in the 107°C oven for a period of 15 min, cool in the dessicator, and weigh.

9. Calculation and Report

9.1. Calculate the mass percent of normalheptane insolubles (NHI) as the percentage by weigh of the original sample as follows:

NHI, % = A/B * 100

where:

A = total mass of insolubles, and

B = total mass of sample.

For percentage of insolubles less than 1.0, report to the nearest 0.01%; for percentages of insolubles of 1.0 or more, report to the nearest 0.1%.