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Experimental Investigation on the Effect of CO_2 and WAG Injection on Permeability Reduction Induced by Asphaltene Precipitation in Light Oil

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***Abstract*—**Permeability reduction induced by asphaltene precipitation during gas injection is one of the serious problems in the oil industry. This problem can lead to formation damage and decrease the oil production rate. In this work, Malaysian light oil sample has been used to investigate the effect CO_2 injection and Water Alternating Gas (WAG) injection on permeability reduction. In this work, dynamic core flooding experiments were conducted to study the effect of CO_2 and WAG injection on the amount of asphaltene precipitated. Core properties after displacement were inspected for any permeability reduction to study the effect of asphaltene precipitation on rock properties.

The results showed that WAG injection gave less asphaltene precipitation and formation damage compared to CO_2 injection. The study suggested that WAG injection can be one of the important factors of managing asphaltene precipitation.

***Keywords*—**Asphaltene Precipitation, Permeability Reduction, CO_2 Injection, WAG Injection.

I. Introduction

ASPHALTENE is high molecular weight component of crude oil that exists in the oil as colloidal suspension, and is peptized or stabilized by resins that absorb on its surface. Asphaltene might lose its stability during different phases of production and especially during CO_2 gas injection. During CO_2 gas injection, the miscibility of the CO_2 gas with the reservoir oil will contribute to oil composition change which alters the asphaltene-to-resin ratio and favour the precipitation of asphaltene [1]-[3]. Water-alternating-gas (WAG) injection is the enhancement of CO_2 injection in providing mobility control over fingering problem.

Thus, it is inquisitive to determine if the WAG injection could give less asphaltene precipitation, less formation damage and higher oil recovery compare to CO_2 injection.

A reduction of mobility leads to improvement of sweep efficiency yielding higher oil recovery [4]. Okwen (2006), Sarma (2003), Walcot *et al*. (1989) and Srivastava *et al*., (1997) are researchers who reported that the presence of water can reduce the asphaltene precipitation [7], [8], [24], [26].

The objectives of this project are to investigate and compare the asphaltene precipitation induced by CO_2 injection and Water-Alternating-CO_2 (WAG) injection. It also aims to investigate the effects of asphaltene precipitation during CO_2 and WAG injection on permeability reduction. A dynamic core flooding study conducted for CO_2 and WAG injection are used on the same oil sample and under same operating conditions. The effect of asphaltene precipitation on formation properties was only focused on absolute permeability. From the results, the changes of formation permeability after the precipitation of asphaltene were related to the type of injection scheme and the amount of asphaltene precipitation.

Asphaltene

Asphaltene 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^{o}C (77F) such as methane, ethane and propane, and have no defined melting point [10]. 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 [9,11].

It is believed to exist as a colloidal suspension in the oil phase and is stabilized by a protective layer formed by the peptized of highly polar resins on its surface. A combination of these resins and asphaltene is called micelles. Micelles would not flocculate due to the presence of repulsive force in between the resin molecules absorbed on asphaltene surface [12]. The concept of asphaltene stabilization by resin is well recognized; however, the exact mechanism in behind is still remain not well known for light oil reservoir [8], [10]. Fig. 1 shows the illustrations of resins and asphaltene in crude oil. Resins and asphaltene have similar molecular structure but resins are less polar, less aromatic, and lower molecular mass compared to asphaltene.

Less asphaltene fraction in crude oil did not indicate less possibility of having less asphaltene precipitate problem [11], [10]. Field observations indicate that lower asphaltene content in crude oil contributes to higher possibility of asphaltene destabilization. For example, the Boscan field in Venezula with 17wt% asphaltene was observed to have no asphaltene

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problem, but the Hassi-Masoud in Algeria with only 0.15wt% asphaltene has asphaltene precipitation problem [9], [10], [11].

Many field and laboratory data have justified that the lighter oil which consists largely of paraffinic materials has lower asphaltene solubility [11]. On the other hand, the heavier oil contains a plenty of intermediate components which are good asphaltene solvents giving higher asphaltene solubility [9]. 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 a higher asphaltene precipitation possibility [12], [14].

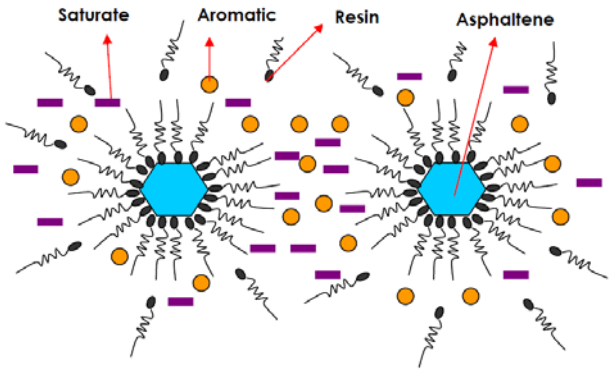


Fig. 1 Resins and asphaltene in crude oil [13]

Mechanism of Asphaltene Precipitation

Asphaltene itself is not problematic but the asphaltene precipitation is the major operational concern [11]. The terminologies for both precipitation and deposition are different [13], [16]. The asphaltene precipitation involved three steps, which are precipitation, flocculation, and deposition. Precipitation is defined as the solid phase (solid particle) coming out 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 [9], [10].

Asphaltene precipitation problems are usually firstly observed in production facilities, and then tubing moved towards formation [1], [8], [11], [15]. 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 [9].

Asphaltene Destabilizes Factors

The asphaltene stabilized by resin, remain in thermodynamics equilibrium under colloidal state at normal reservoir conditions. Asphaltene will lose its stability when the initial equilibrium state is 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 [1], [2], [3].

A. Temperature Drop

The studies conducted by Verdier *et al.* (2005) on pressure and temperature effects on the asphaltene stability indicated that asphaltene is less stable when temperature decreases; however, in the presence of CO_2, asphaltene becomes more stable when temperature decreases [17]. 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 asphaltenes and resins [17], [18].

B. Pressure Drop

Pressure effect is likely to be the major reason in destabilizing asphaltene. The lower the reservoir pressure, the lower is the asphaltene solubility [11], [17], [19]. 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 the bubble point [9], [10]. When pressure is depleting from above the bubble point, the crude oil density reduces while the molar mass increases. The minimum asphaltene solubility occurs at bubble point when there is a maximum difference in molar mass between asphaltene and bulk oil [2], [3]. With the lighter hydrocarbon increasing with pressure drop, the solubility parameter between resin and lighter ends decreases, which induces resin solved constantly causing asphaltene to precipitate [1], [10], [18].

With further pressure drop below the bubble point, some lighter hydrocarbons vaporize from reservoir fluid, leaving the heavier reservoir fluid with higher resin fraction, the resins 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 the bottom hole pressure dropped below the bubble point.

C. Compositional Change

The addition of compound may alter the existing resin-asphaltene solubility parameter and phase equilibrium in crude oil [1], [11], [15], [19]. For example mixing of hydrocarbon fluids, miscible flooding, CO_2 injection, gas lift operation using gases and/or acidizing jobs [16]. 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 [18]. When the resin ratio drops to a point which the absorbed amount is not enough to cover the asphaltene, the asphaltene particles will deposit. It is also reported that the increase of alkane carbon number decreases the amount of asphaltene precipitate [20]. Most miscible solvents have the potential to cause asphaltene instability. Gholoum *et al.* (2003) reported that the CO_2 is the most effective asphaltene precipitant followed by alkanes (C_1 to C_7) [5], [21].

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D. Effect of CO_2 Injection on Asphaltene Precipitation

During gas flooding of CO_2, the miscibility between the CO_2 gas with the reservoir oil contributes to the change of phase behaviour and composition, which cause asphaltene to precipitate [1], [11], [15], [19], [20]. CO_2 gas and the crude can be miscible through first contact or multiple contacts [8], [10]. 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 [8].

Based on the experimental investigation conducted by Sima *et al.* (2011) on the effect of CO_2 injection on asphaltene precipitation, more pore volume of CO_2 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 increases from 0.11 wt% to 0.31 wt% until the end of the flooding process. However, as the injected pressure increases, 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 this causes 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% [11]. Srivastava *et al.* (1999) studied the effects of oil properties and CO_2 gas concentration on asphaltene precipitation by means of static and dynamic tests. Their studies on asphaltene onset pressure have indicated that the amount of asphaltene precipitation at the bubble point was the maximum. They also concluded that the asphaltene precipitation is dependent on the concentration and pore volume of CO_2 gas injected. CO_2 gas concentration is the most important parameter which affects the asphaltene precipitation [8]. This is agreed by Chukwudeme and Hamouda (2009) who reported that the asphaltene deposition is proportional to the injected CO_2 concentration, and will rise rapidly when the injected CO_2 gas exceed it critical value. They suggested that higher recovery may be obtained if the injected CO_2 gas is remained below the critical content point [6], [8], [10], [20].

Khosravi *et al.* (2009) reported in his studies that the presence of CO_2 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 recovery [19]. The mass transfer which takes place during miscibility development would enhance the asphaltene precipition[22].

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 [23]. This is also supported by Shedid and Zekri (2004). They claimed that the increase of flow rate will increase the formation damage due to more asphaltene deposited [5].

E. Effect of Water 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.[8] 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 [24].

According to Okwen (2006), the formation water would act as a CO_2 buffer during CO_2 injection. When the injected CO_2 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 weak water wet surface than the strong 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 [25], [26]. This paper also recommended further researches to be carried out on the optimum concentrations of CO_2 and formation water which can minimize the asphaltene deposition [26].

Wang and Civan (2005) conducted an 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 [27]. The issue of the role of brine on the precipitation and its effect on asphaltene precipitation has been raised up by Sarma (2003) too [7].

II. Methodology

In this project, operation conditions were fixed at 3000 Psi and 100^{o}C, with an injection rate of 0.2 cc/min and 2000 Psi injection pressure. Berea sandstone cores were used as formation representative. The simple schematic of the core flood equipment is illustrated in Fig. 2.

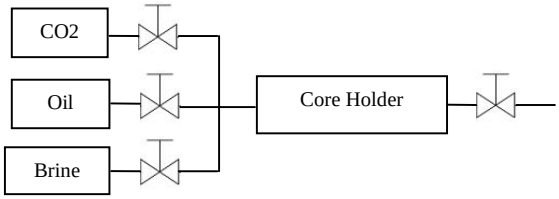


Fig. 2 Simple schematic of core flooding equipment

To restore the irreducible water saturation, two cores were saturated with brine follow by oil. Water flooding is then conducted as secondary recovery before the application of CO_2 and WAG injection. The CO_2 injection was injected continuously while the WAG injection was conducted with 10 minute injection length for gas followed by water

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continuously until no oil production was obtained. To measure the change in asphaltene content, the effluent oil were collected every 25 minutes for both CO_2 and WAG injection.

The core properties such as porosity and permeability are determined before running the core flooding test. The core properties are presents in Table I. The porosity and permeability are determined through nitrogen gas using gas permeameter and porosimeter (Poro-perm System), while wettability was determined through sessile drop method using Interfacial Tension System (IFT 700 Equipment). For asphaltene content measurement, ASTM D3279-07 Standard Test Method for n-Heptane Insoluble was used. Knowing the initial asphaltene content enables us to study the amount of asphaltene content variation during CO_2 and WAG injection. Table II shows the properties of the oil sample used which includes also the oil density.

The effects of CO_2 and WAG injection on asphaltene precipitation are determined by measuring the change of asphaltene content in the effluent oil. The reduction of the asphaltene content in the effluent oil indicates the amount of asphaltene precipitated inside the core.

TABLE I
ORIGINAL CORE SAMPLES PROPERTIES

Parameters	Core 1 CO_2 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 II
CRUDE OIL PROPERTIES

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

The formation damage induced by asphaltene precipitation is indicated by the rock porosity and permeability reduction after core flooding test. In order to indicate the change of rock properties due to the presence of asphaltene, each core was treated with n-heptane after core flooding. The n-heptane will removes the residual oil while only leaves asphaltene fraction inside the core. In addition, the change in core wettability was also evaluated to study the effect of asphaltene precipitation on rock properties.

III. RESULTS AND DISCUSSION

During CO_2 and WAG injection, the injected gas will dissolve into the oil during the displacement. 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 its absorbed amount is insufficient in cover the entire surface of asphaltene particles. The flocculation of asphaltene particle may follow by precipitation and deposition.

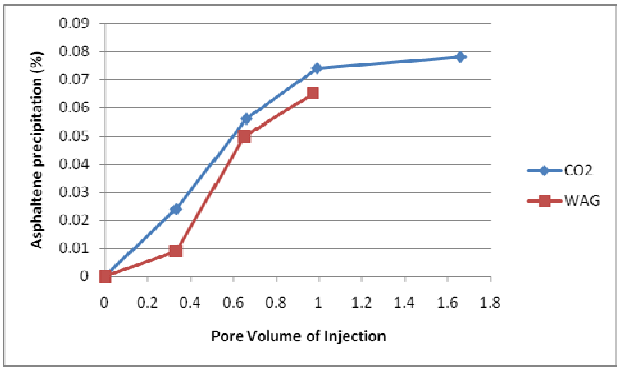


Fig. 3 Asphaltene precipitation inside the core versus pore volume of injection

Fig. 3 shows the percentage of asphaltene deposited inside the core during CO_2 and WAG injection. In run 1 of core flooding using CO_2 injection, the amount of asphaltene precipitate inside the core at 0.33 pore volumes was 0.024 wt%. When the CO_2 injection reaches 0.66 pore volume, the precipitated asphaltene 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 CO_2 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.

The results show that asphaltene precipitation is a function of pore volume of injection. As pore volume of gas injected increases, the asphaltene precipitated inside the core increases. Based on the results, it is also observed that the asphaltene precipitation from CO_2 injection is slightly more than that of WAG injection. This is due to the fact that CO_2 is soluble in both water and crude oil. During WAG injection, CO_2 gas will dissolve in brine and reduce its concentration. The reduction in CO_2 available to precipitate the asphaltene minimizes the asphaltene precipitation.

A. Effect of Asphaltene Precipitation on Permeability

Once asphaltene 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. The change of permeability from the original indicates the extent of asphaltene precipitation induced

formation damage. Table III shows the core properties before and after core flooding test.

TABLE III
CORE PROPERTIES BEFORE AND AFTER DISPLACEMENT TEST

	Displacement	Permeability, md	Difference
Run 1 CO_2	Before	78.028	75.85
	After	17.753	
Run 2 WAG	Before	80.359	71.92
	After	22.560	

Fig. 4 shows the percentage of permeability reduction during CO_2 and WAG injection. Results show an obvious reduction in permeability for both runs. It is justified that the precipitation of asphaltene would cause reduction in permeability. The permeability reduction is consider to due to the larger size asphaltene particles blocked the smaller pore throat or the smaller size asphaltene accumulated or absorbed in large pore throat causing reduction in pore throat radii.

A larger reduction in permeability is observed for the core undergoing CO_2 flooding. In CO_2 injection, permeability decline of 75.85% was detected. In WAG injection, the permeability decline was 71.91%. It is observed that the degree of permeability reduction is a function of the degree of asphaltene precipitation. This can explained why the permeability reduction of core undergo CO_2 injection is more than WAG injection.

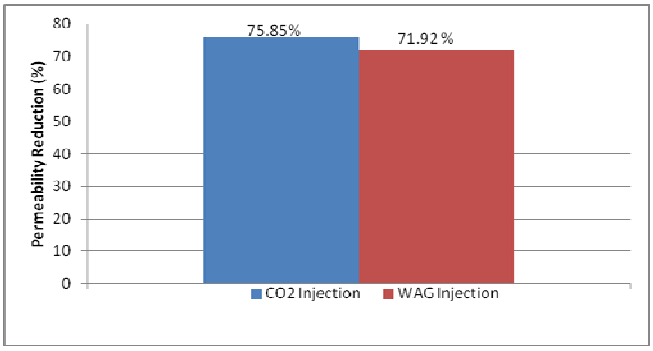


Fig. 4 Permeability reduction (%) during CO_2 and WAG injection

As discussed in the precious section, asphaltene precipitation is increase with the time the CO_2 gas contacted the oil. Thus, with time, it is anticipated that the 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 permeability reduction is depending on few factors. For instant, the pore size distribution, the degree of asphaltene deposition and the initial permeability of the formation.

B. CO_2 and WAG injection Oil Recovery Factor

Table IV presents the oil recovery factor for CO_2 and WAG injection. During CO_2 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 CO_2 and WAG injection can improve the oil recovery after waterflooding. It can be seen that WAG injection shows a better performance in oil recovery. The residual oil saturation after CO_2 injection is 0.63, which is less than that of 0.39 after WAG injection.

TABLE IV
RECOVERY CALCULATION FROM DISPLACEMENT TEST

	Water Flooding (%OOIP)	EOR (%OOIP)
Run 1 CO_2	17.18	18.92
Run 2 WAG	24.72	47.05
	78.028	80.359
	18.170	18.566

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 CO_2 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.

The results also illustrated that WAG injection gave a recovery of about 47.05 % of original oil in place (OOIP), while CO_2 injection only gave a recovery of about 18.92% OOIP.

IV. CONCLUSION

From the experimental work conducted, the following conclusion can be drawn:

1. Both CO_2 and WAG injection could cause asphaltene instability. The precipitation of asphaltene may lead to reduction in permeability.

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2. The asphaltene precipitation increases as the injected pore volume increases. A small decrease in asphaltene precipitation is observed with WAG injection.
3. During WAG injection, the CO_2 gas would be dissolved in brine, which reduces its concentration and minimizes the asphaltene precipitation.
4. The permeability reduction is higher during CO_2 injection than WAG injection due to more asphaltene precipitated.

Overall, CO_2 injection causes more asphaltene problems than WAG injection in terms of the amount of asphaltene precipitated, and permeability reduction.

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