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Study of Asphaltene Precipitation induced formation Damage during CO_2 Injection for a Malaysian light oil

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Abstract**—**In this work, the precipitation of asphaltene from a Malaysian light oil reservoir was studies. A series of experiments were designed and carried out to examine the effect of CO_2 injection on asphaltene precipitation. Different pressures of injections were used in Dynamic flooding experiment in order to investigate the effect of pressure versus injection pore volume of CO_2. These dynamic displacement tests simulate reservoir condition. Results show that by increasing the pore volume of injected gas asphaltene precipitation will increases, also rise in injection pressure causes less precipitation. Sandstone core plug was used to represent reservoir formation during displacement test; therefore it made it possible to study the effect of present of asphaltene on formation. It is found out that the precipitated asphaltene can reduce permeability and porosity which is not favorable during oil production.

Keywords**—** Asphaltene, Asphaltene Precipitation, Enhanced Oil Recovery

I. INTRODUCTION

ASPHALTENES are defined as the non-volatile and polar fraction of petroleum that is insoluble in *n*-alkanes (i.e. pentane or heptane). [1]. But the definition of asphaltene itself is a place of so many confusions, because to study asphaltene it should be extracted first. Different solvents and methods of extraction produce different asphaltene. However, some scientists argue that extraction of asphaltene may change its properties so it should be studied in place. It can be concluded that the definition of asphaltene itself is quite controversial [2]. For that reason Asphaltene is defined based on its solubility class rather than its molecular structure [3],[4]. According to IP 143 standard: the asphaltenes content of a petroleum product is the percentage by weight of wax-free material insoluble in n-heptane but soluble in hot benzene [5].

Asphaltene itself is not problematic, but asphaltene precipitation is a big concern. Precipitation may happens during different phases of production specially CO_2 flooding. It is well known that light and medium oil reservoirs are good candidate for CO_2 injection as a tertiary recovery after water flooding.

Asphaltene content of light oils is not high but the interesting point is that the amount of the asphaltene in crude oil is not the cause of precipitation. Normally in light oil reservoirs, asphaltene solubility is low. Low solubility makes asphaltene very unstable and increases the possibility of precipitation. That is why in some fields with 17 wt% asphaltene (Boscan field in Venezuela) no asphaltene precipitation was observed while other fields with 0.15wt% asphaltene (Hassi-Masoud in Algeria) has many production problems due to asphaltene precipitation and deposition. [6]

Usually asphaltene precipitation problems firstly observed in production facilities, then tubing, afterward the asphaltene deposit area can move toward bottomhole and well neighboring formation as reservoir depletion proceeds. However recently in few fields it is observed that well impairment has begun in early stages which cause to draw concern toward reservoir itself [7]. Asphaltene precipitation and deposition may affect large region in the reservoir, it would be started from wellbore and extend over large distances from its origin. In contrast, the reservoir damage due to wax deposition is rather limited to a short distance, maximum 1 feet away from the wellbore. Although wax may deposit just like asphaltene but wax deposition is a reversible process which can be eliminated by thermal treatment methods [3],[8]. Asphaltene treatment would not be as easy as wax removal, especially if precipitation and deposition happens within the oil reservoir; it can reduce formation permeability and porosity and alter wettability of the rock. Asphaltene stability inside the crude depends on a number of factors including pressure, temperature, and composition of the fluid. So any changes in these three factors may alter the stability and lead to asphaltene precipitation [9], [10]. The effect of composition and pressure on asphaltene precipitation is generally believed to be stronger than the effect of temperature [11]. When CO_2 injected to the oil reservoir it will contribute to the asphaltene precipitation by composition change. Changes in composition normally happen during gas injection processes employed in enhanced oil recovery (EOR). Gas injection includes processes such as miscible flooding with CO_2, N_2 or Natural Gas [9]. Burke (1988) observed that dissolved gas affect the solubility of asphaltene in live oil [12]. During production life of a well composition of reservoir fluid will change as the result of pressure depletion. Therefore lighter components will leave the oil phase and GOR(gas-oil ratio) will be reduced and density will increase. In this case lesser asphaltene would precipitate since it goes into solution with oil [4]. Asphaltene precipitation is different from flocculation and deposition but all three of them may cause serious damage to the formation. The process of asphaltene precipitation consists of few important steps: (1). first step

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which is precipitation happens when the solid particles form a distinct phase as they come out of solution. The quantity and size of solid particles at this stage could be quite small (2). At The second step which is called flocculation stage, the small solid particles clump together and grow larger. (3). Deposition is the third stage, a point at which the particles are so large that they can no longer be supported by the liquid and therefore settle out on solid surfaces [13,14].

Flocculated and deposited asphaltene may lead to formation damage by impairing the permeability by plugging the pore throat and altering wettability through adsorbing on the negatively charged mineral sites [15]. to this point there has been intensive research focus on the formation damage due to unstabilized and flocculated colloidal asphaltene deposition. Asphaltene flocculates contribute to the formation of organic deposits causing formation damage problem [16].

During the last 3 decades asphaltene problems have been studied intensively, however the majority of these researches deal with static asphaltene precipitation in closed systems. Although these works can help to investigate onset of precipitation with regards to different parameters such as pressure, CO_2 concentration and etc, but absence of a porous medium is a concern. Complex interaction between the fluid and porous medium is playing a very important role in asphaltene precipitation and deposition which should not be ignored. [17]. Nowadays lots of researchers have focused on asphaltene precipitation in dynamic manner with resembles, although not fully, but near reservoir condition. It would provide the circumstance for studying the effect of asphaltene on formation properties.

II. OUTLINE OF THE PRESENT WORK

In this research relative permeability core flood equipment was used to recreate reservoir condition. Simple schematic of core flood equipment is shown in fig.1.

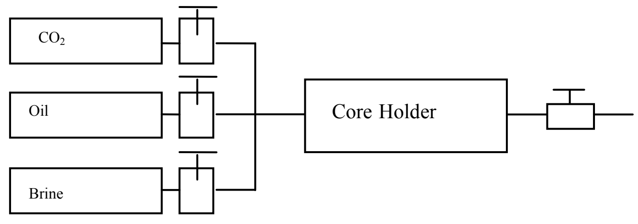

Fig.1 Simple Schematic of Core Flood Equipment

Operation conditions of the equipment were fixed at 3000 psig and 98℃.. Berea Sandstone cores were used as formation representative. Before running any test porous media properties such as permeability and porosity were measured. . Before conducting core flood experiment, in order to restore the core plugs to their original sub-surface reservoir condition, they have been saturated with brine which has been prepared in laboratory. The saturation procedure is used to restore the water-wet nature of the rocks.

Since light oils are the common candidates for asphaltene problem, a Malaysian light crude oil was chosen in this research. Initial asphaltene content of the crude oil was measured. Knowing the initial value will provide the chance to study asphaltene content variations during carbon dioxide recovery process. For asphaltene measurement ASTM D3279 - 07 Standard Test Method for n-Heptane Insoluble has been used [17]. Core evaluation was performed by Helium Porosimeter (Poroperm) as it is illustrated in fig. 2.

Fig.2 Helium Porosimeter (Poroperm)

III. EXPERIMENTAL SYSTEM

A. Materials

As it was mentioned oil sample was selected from one of Malaysian oil reservoirs. ASTM D3279 - 07 Standard Test Method for n-Heptane Insoluble was applied to measure initial asphaltene content. The configuration can be seen in **fig.3**.

Fig.3 ASTM D3279 - 07 Standard Test Method for n-Heptane Insoluble

Table 1 presents initial asphaltene content of the chosen oil. In addition, the viscosities of the samples were measured at 98˚C, by using U-tube Viscometer and High Temperature, High Pressure Viscometer.

Rock property tests were conducted for each core sample by Helium gas in Poroperm equipment, the results for porosity and permeability measurement are shown in Table2.

TABLE I
CRUDE PROPERTIES

Sample Name	Malaysian light oil
API	41
Asphaltene content (wt%)	0.42
Viscosity (Cst) @ 98℃	1.51
Viscosity (Cp)@ 98℃	0.80
Density (gr/cm^3)@ 98 ℃	0.52

TABLE II
CORE PROPERTIES BEFORE DISPLACEMENT TEST USING POROPERM

	Core 1	Core 2	Core 3
Weight(gr)	179.608	177.920	187.588
Diameter(mm)	37.90	37.90	37.90
Length (mm)	73.66	73.30	76.78
Kair (mD)	164.700	164.500	162.299
K∞(mD)	156.944	154.681	151.163
φ (%)	22.612	22.500	18.129

Other than the crude oil and sandstone cores, CO_2 gas with 99.9 % purity was applied for flooding test.

IV. EXPERIMENTAL PROCEDURE

To determine the effect of CO_2 induced asphaltene precipitation and deposition, asphaltene content of the produced was measured. Since initial asphaltene content of the crude sample is already known, the amount of asphaltene inside the core can be calculated. To do so Dynamic asphaltene precipitation test was carried out with several runs at different CO_2 injection pressure where the core holder's temperature and pressure were kept constant. Temperature of core holder was fixed at 98˚C, and the formation pressure was set at 3000 psig. Selected Pressures of injection were 2000, 2300 and 2600 psig. Variation in injection pressure makes it possible to assess the effect of carbon dioxide pressure on asphaltene precipitation phenomena. CO_2 were continuously injected as tertiary recovery after water flooding and the recovered oil was collected at every 10 minutes until there was no more produced oil was observed. Collected samples were analyzed for asphaltene content changes and the results were reported versus injected pore volume of injection (since flow rate was fixed at 0.4 cc/min, pore volume of injection at each 10 minutes was calculated).Fig.4 shows the results of asphaltene content analysis for the recovered oil versus pore volume of injected CO_2 at different pressure.

Given that the influence of deposited asphaltene in core sample are indicated by changes in porosity and permeability of the samples [18], changes in porosity and permeability of the core samples due to the presence of asphaltene were examined.

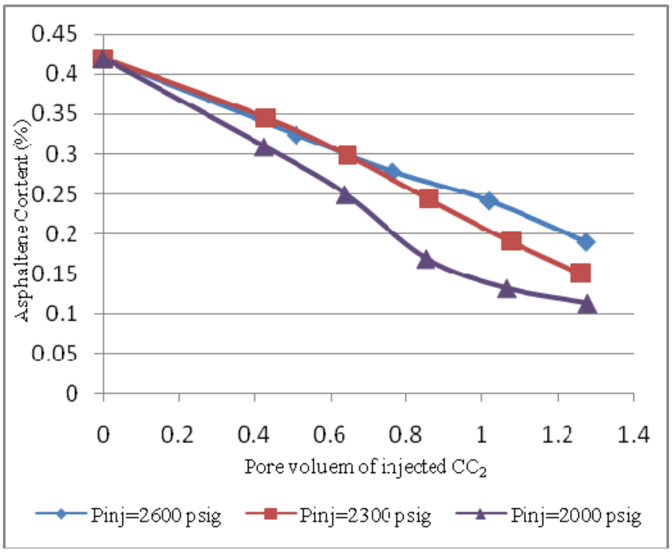

Fig.4: Asphaltene content of the recovered oil versus Pore Volume of Injection

V. RESULTS AND DISCUSSION

A. Influence of CO_2 on Asphaltene Precipitation

Based on fig. 4, in run 1 where pressure was 2000 psig, asphaltene started to precipitate as the injected CO_2 reached 0.43 pore volumes and the amount of asphaltene that already precipitated in the core was 0.11 wt %.At 0.64 pore volume, the amount of asphaltene precipitation in the porous media was 0.17 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.

In Run 2 Asphaltene started to precipitate as the CO_2 injection reached 0.43 pore volume 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. After that, the asphaltene content in the recovered oil is continued to decrease as the injected pore volume increases. it reaches from 0.07% at 0.43 injected pore volume to final value of 0.23 at 1.26 pore volume at the end of the flooding process. However, the percentage of deposition is still lower than deposition occurred during the injection pressure of 2000 psig.

In run 3 asphaltene started to deposit at 0.51 pore volume, the amount of asphaltene content left in the core was 0.330 wt %. It had more precipitation when compared to the injected pressure of 2300 psig. This can be due to streaming potential caused by sudden change in pressure however, as the injected pore volume went deeper to 0.76 pore volumes, the asphaltene content collected was just 0.27 wt %. Asphaltene precipitation increased as the pore volume of injected CO_2 got higher and at 1.27 pore volume of injected gas only 0.19 wt % of asphaltene was collected.

As it can be seen from all 3 cases asphaltene precipitation occurred. When CO_2 contacted the oil, it changed the

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composition of oil and caused asphaltene instability [4].
Fig.4 clearly shows that CO_2 induces asphaltene precipitation since CO_2 can cause changes in fluid behavior and equilibrium and alter the asphaltene resin ratio of crude oil which favors precipitation of asphaltene [4]. Moreover it is clear that pore volume of injected CO_2 has major influence on the amount of asphaltene precipitation. As pore volume of injection increases, asphaltene precipitation increases too. This increment explains that when more CO_2 gas is in contact with oil for longer time, asphaltene precipitates more. Addition of CO_2 affects the interaction between resin and asphaltene . Other than that during recovery by CO_2, some hydrocarbon molecules can be extracted into gas phase [19]. During CO_2 flooding, some of intermediate Hydro carbon molecules would be extracted by in-situ vaporization from reservoir oil into the injected gas [20]. It suggests that vaporizing drive would extract some of resin molecules, which disturbs the stability of asphaltene and leads to precipitation.

Fig.4 proves that as the pressure increases asphaltene precipitation decreases. This could be due to the difference in solubility of asphaltene in low and high pressure . It seems that when injection pressure increases asphaltene remains dissolved in the reservoir fluid however at low pressure this solubility decreases. furthermore large distance between asphaltene particles and the particles of the surronding fluid caused more precipitation of asphaltene at lower pressures. [21]. Other than that high energy injected gas can desorb the adsorbed asphaltene onto the core ; in the meantime some of precipitated and deposited asphaltene onto core may be carried away by high pressure gas and leave the core with flow of recovered oil [19].

B. Influnce of CO_2 Induced Asphaltene Precipitation on Formation Properties

As it was mentioned earlier, permeability and porosity of the core samples were measured before core flooding test. In order to see the asphaltene precipitation influence on core characteristics, each core was treated with suitable solvent in such a way that removes residual oil while only asphaltene remain inside the core sample [22]. By doing so, one can investigate the changes in permeability and porosity due to the presence of asphaltene. Obtained results, which are illustrated in fig. 6 and 7, show that there is an obvious reduction in permeability and porosity of the core due to asphaltene precipitation.In Run 1 (P= 2000 psig) with the most asphaltene precipitation, permeability decline of 21.75% and porosity reduction of 18.73% was detected. At Run 2 (P= 2300 psig) permeability was reduced by 17.12 % while porosity reduction was 12.63 %. Run 3 (P= 2600 psig) demonstrates the minimum reduction in permeability and porosity, which are 15.81% and 6.19 % respectively. It is obvious that the run with the most asphaltene precipitation which is associated to the lowest injection pressure (P= 2000 psig) has the most permeability and porosity reduction.

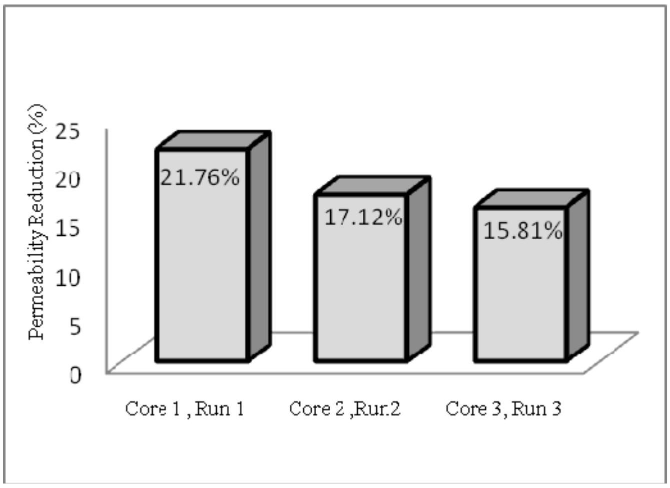

Fig.6 Permeability Reduction

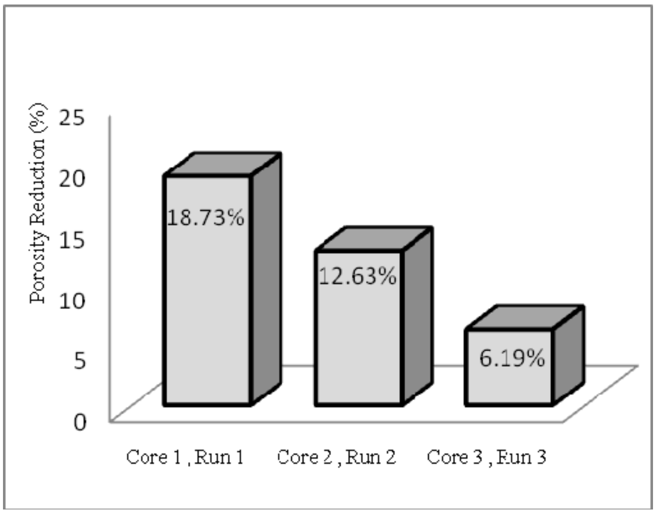

Fig.7 Porosity Reduction

VI. CONCLUSION

Injection of CO_2 into porous media would change the oil composition and causes asphaltene instability. Instable asphaltene has the tendency to precipitate. During continuous CO_2 flooding, increase in injected t pore would result in more asphaltene precipitation. Besides that, by increasing the injection pressure of CO_2, less asphaltene would deposit.. The dynamic flow experiments depict that due to the presence of asphaltene inside the core samples, porosity and permeability of the porous media would be reduced. The reduction values confirm the fact that at highest pressure, less asphaltene deposits , because less permeability and porosity reduction was reported at P= 2600 psig .At the same time as Run 1 with injection pressure of 2000 psig demonstrates the most decline in permeability and porosity. Since asphaltene content of the crude oil is not high, one may assume that its effect on pore spaces may not be considerable but the results show otherwise. By considering the random distribution of pore spaces, even few asphaltene components can plug small pore throats in such a way that porosity and permeability would be affected severely as it is shown in fig.8. For gaining better understanding it is recommended to study rock composition, heterogeneity and porosity and permeability distribution along with precipitation phenomenon. Although the reduction value might not be very significant but one have to consider the fact that it is associated with a small core sample, still in reservoir scale even small decline in permeability and porosity may have negative effect on oil production.

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