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Minimizing Asphaltene Precipitation in Malaysian Reservoir

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Abstract

Unstable Asphaltene is major concern in oil reservoir under CO_2 Water alternating Gas injection due to its unrecoverable damage to reservoir and expensive treatments for production system. Therefore, the effective strategy to control Asphaltene precipitation should be the part of reservoir management. Dealing unstable Asphaltene in Malaysian reservoir was divided into three main parts that were evaluating Asphaltene colloidal stability, Asphaltene Prediction and Asphaltene prevention
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Solid Detection System was used to measure the stability and onset pressure of crude oil under reservoir conditions with different amount of gas injections. Various PVT experiments were performed in the laboratory using the PVT cell. PVT data obtained from PVT cell is then fitted with the reliable equation of state (EOS) to generate the Asphaltene phase envelopes.
An inhibitor design program was initiated and four inhibitors, Inhibitor A, Inhibitor B, Inhibitor C and Inhibitor D were selected to evaluate their performance in neutral, acidic and basic environment. Titration Test was performed to evaluate the inhibitor efficiency. Inhibitor B in acidic environment was then selected as efficient inhibitor to inject in situ to control Asphaltene precipitation with injection gas.

Using this strategy, Asphaltene precipitation is expected to be minimized which will keep the reservoir undamaged and will save large amount of remedial cost.
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Keywords: Asphaltene strategy, Asphaltene Prediction, Asphaltene Prevention, Asphaltene inhibitors.

Introduction

Asphaltene is a complex solid fraction of crude oil consisting of black or brown solid particles. It is defined as a solubility class which is precipitated by the addition of normal alkane i.e. heptanes, hexane. Asphaltene stability in crude oil at reservoir conditions depends upon the composition, pressure and temperature [1]. Asphaltene instability is independent of the amount of Asphaltene content present in the crude oil [2].

With the decreasing reserves, oil industry is now moving to enhanced oil recovery (EOR) operations to increase oil production. CO_2-Water Alternating Gas injection is the most popular EOR method. However injecting CO_2 flooding in the reservoir can cause Asphaltene precipitation due to sudden change in composition [3]. Asphaltene flocculation in reservoir can cause wettability alterations which can affect the water alternating gas performance. Its deposition in reservoir can cause formation damage by plugging the pore spaces (Figure 1). It can also plug the tubing and pipeline system requiring expensive treatments for flow assurance [4].

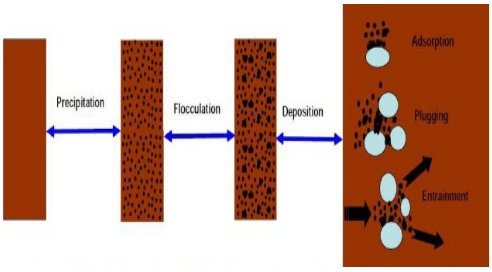

Figure 1- Asphaltene precipitation

Figure 2 - light transmittance technique

Solid Detection system is one of the popular methods which identify the Asphaltene stability under reservoir conditions. This system is the part of PVT equipment and is based on the light transmittance technique. A laser beam (light source) is generated and is guided through an optical fiber. This laser beam crosses the sample fluid inside the pvt cell. The transmitted light is measured by a power meter especially designed for precipitated near infra red measurements as shown in Figure 2 [5].

Prediction of Asphaltene precipitation depends upon the correct identification of injection gas behavior with crude oil under reservoir conditions. The composition of injection gas changes rapidly in the reservoir due to the enrichment of injection gas with lighter components of crude oil [6].

Many inhibitors have been applied previously to keep the Asphaltene particles dispersed in the crude oil. Lian used various surfactants to keep the Asphaltene dispersed. Particle precipitation was still observed[7] . Natural resins, Sulfonic acids, phenols, -dodecyl resorcinol (DR), Dodecyl Benzene Sulfonic Acid (DBSA) and Dodecyl Trimethyl Ammonium Bromide (DTAB), Titanium di oxide ($TiO_{2)}$ nano particles were also used to act as a Asphaltene dispersant [8] [9]. Vegetable oil, almond, andiroba, coconut essential oil also showed good performances in peptizing the Asphaltene particles [10].

In this work, an effective strategy is considered during the CO_2 WAG injection to stabilize the Asphaltene particles for field-x, Malaysia which consists of Asphaltene stability evaluation, Asphaltene onset pressure measurements and Asphaltene prevention using inhibitors in-situ.

Field-x is the light crude oil offshore field located in Malaysia. The average production ramped up to 50,000 barrels / day of crude oil and 45 mft3/ day. It is among of 11 oil fields of PETRONAS Carigaly which is under the enhanced oil recovery. The main reservoir comprises Miocene age sands. Stratigraphically, 20reservoir units have been identified. The drive mechanism is edge water. The Asphaltene content was measured 0.3 weight percent in given crude oil of said field.

Solid Detection system was used to measure the stability and onset pressure of crude oil under reservoir conditions with different amount of gas injections. Various PVT experiments were performed in the laboratory using the PVT cell. PVT data obtained from PVT cell is then fitted with the reliable equation of state (EOS) to generate the Asphaltene phase envelopes. An inhibitor design program was initiated and four inhibitors, Inhibitor A, Inhibitor B, Inhibitor C and Inhibitor D were selected to evaluate their performance. Titration Test was performed to evaluate the inhibitor efficiency. In the end, based on the Asphaltene onset pressure measurements, the selected inhibitor is proposed to inject in the reservoir in-situ to stabilize the Asphaltene particles during CO_2 injection.

Experimental Section

Material and Preparation

The compositions and basic properties of the crude oil studied in this work are given in Table 1 and Table 3. 60 % CO_2 and 40 % C_1 mixed composition gas was purchased from the supplier. Buffer solutions of acid and base, ethanol, n-heptane, toluene, Inhibitor-A, Inhibitor- B, Inhibitor C, Inhibitor D were purchased from the supplier and were used as provided.

Table 1- Crude oil Composition

Component	Wt Percent	MW
CO2	17.15	44.01
C1	11.5	16.04
Nc5	0.00285	72.15
C6	1.331	86.17
C7	5.509	100.2
C8	4.284	114.2
C9	2.625	128.3
C10	3.3421	142.3
C11+	54.334	213.35

Table 2 inhibitor Preparation

	Inhibitor A	
Acid Solution	**Neutral Solution**	**Base Solution**
1 gm Inhibitor A + 5ml Acid Buffer Solution	1gm Inhibitor A + 5ml of Ethanol	1gm Inhibitor A + 5ml of Base Buffer Solution
	Inhibitor B	
1 gm Inhibitor B + 5ml Acid Buffer Solution	1gm Inhibitor B + 5ml of Ethanol	1gm Inhibitor B + 5ml of Base Buffer Solution
	Inhibitor C	
1 gm Inhibitor C + 5ml Acid Buffer Solution	1gm Inhibitor C + 5ml of Ethanol	1gm Inhibitor C + 5ml of Base Buffer Solution
	Inhibitor D	
1 gm Inhibitor D + 5ml Acid Buffer Solution	1gm Inhibitor D + 5ml of Ethanol	1gm Inhibitor D + 5ml of Base Buffer Solution

PVT Test: Recombination cell was used to create live oil used for Asphaltene precipitation study. Mixed composition gas was mixed with the dead crude oil to make it live to represent reservoir conditions. The reservoir temperature is 100 C and current reservoir pressure is around 2000 Psi. According to swelling test results, the given oil is in liquid phase till 80 % as described in figure 4, A calculated volume of injection gas is added to the reservoir fluid at reservoir pressure and temperature at three concentrations (20, 40, 60 weight percent of crude oil). For each concentration, mix composition injection gas and reservoir fluid mixture was stabilized and homogenized at reservoir conditions.

An isothermal depressurization run was then conducted on each mixture to obtain the onset pressure of asphaltene precipitation at reservoir conditions. Figure 3 shows the composition of crude oil after three different additions of mixed composition gas.

Asphaltene Flocculation point test: 1 gm of crude oil was mixed with 3 ml of toluene to dissolve and stabilize the Asphaltene particles for 24 hours. Asphaltene was precipitated and measured using the ASTM D3279 method [11]. The Asphaltene content of given crude oil is 0.3 weight percent. Neutral, base and acid solutions of each inhibitor were prepared as described in table 2.

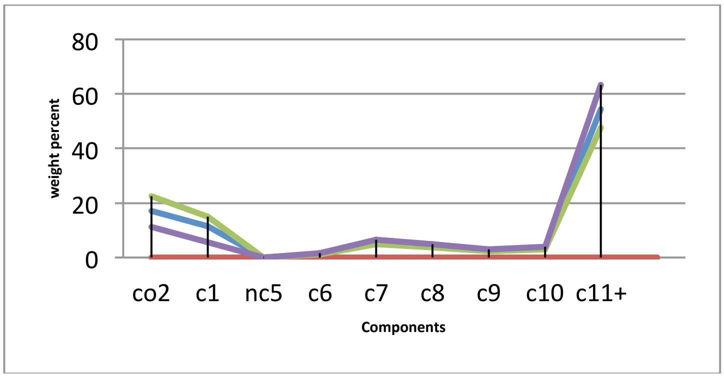

Figure 1- Composition of crude oil with additional gas concentration

Table 3- Properties

Properties	**Method**	**Result**	**Unit**
API gravity	ASTM D1298	37.5	degree
Density	ASTM D4052	0.85	Kg/l
Asphaltene Content	ASTM D3279	0.3 %	Wt %

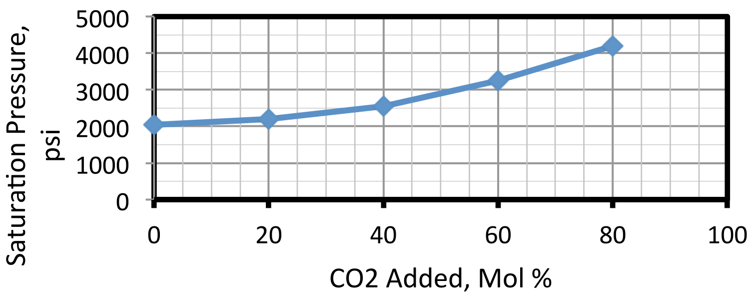

Figure 2– Swelling Test Result

Experiments:

Asphaltene stability evaluation and onset pressure measurements were done using the solid detection system. This equipment is based on light scattering technique using near infra red light. It consist of a mercury free , fully visual, PVT cell equipped with a floating piston, a magnetically coupled impeller mixer and fiber optics laser light transmission probes (source and detector) [6].

During the experiment to check colloidal stability and AOP measurement, a live oil crude oil sample was charged in the system at 2000 Psi and 100 ^{o}C and then cell pressure was raised to 3500 Psi. Stable baseline for near infra red light transmittance through the charged reservoir fluid sample is achieved.

The reservoir fluid sample is then depressurized to bubble point pressure in discreet steps. Each depressurization step was 200 psi and at each step, the fluid was stabilized for 10 minutes. During the depressurization the near infra light transmittance through the reservoir fluid was recorded as a function of pressure. The onset pressure is then measured by observing the NIR light transmittance signal. The process is repeated for all crude oil samples [12].

The results of stability of crude oil with different concentration of gas are shown in figure 5, figure 6 and figure 7.

Constant Composition Test (CCE) experiment was conduted to measure the bubble point pressure of reservoir fluid followed by the differential liberation experiment. Asphaltene Phase Envelopes were developed with the commercial software using the SRK Equation of state and on the basis of experiment results [6]. Asphaltene phase envelopes developed are shown in figure 8 and figure 9.

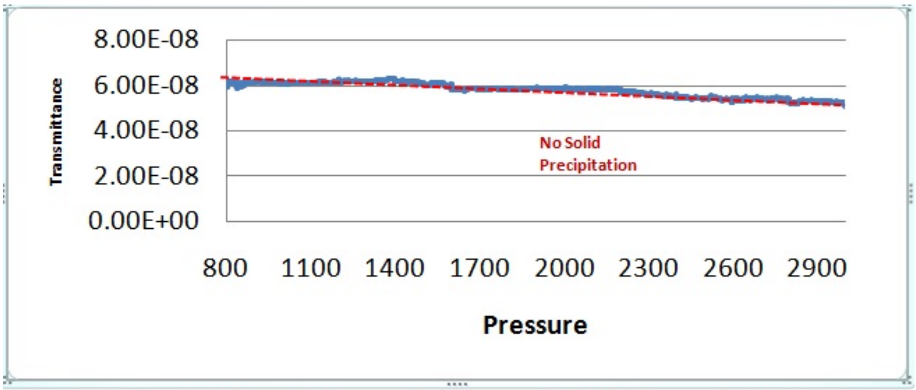

Figure 3- Isothermal depressurization with original reservoir fluid

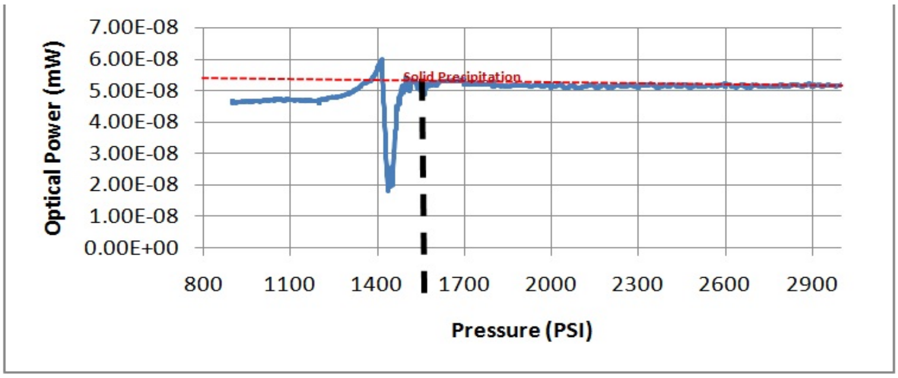

Figure 4- Isothermal depressurization with 40 % additional Gas

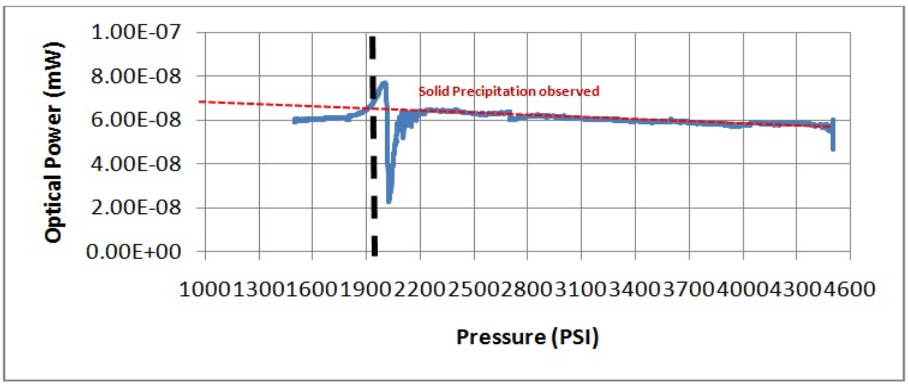

Figure 5- Isothermal depressurization with 60 % additional Gas

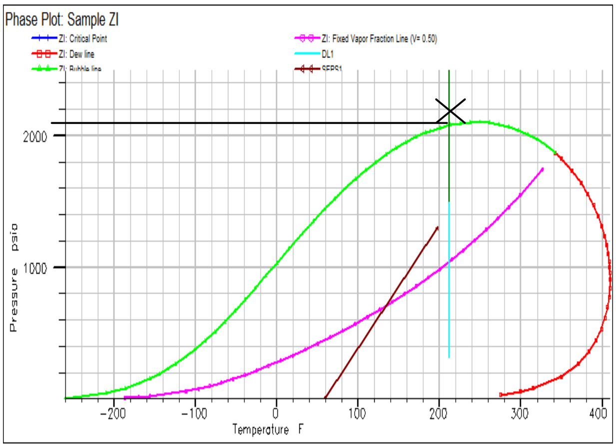

Figure 7- Phase envelope with crude oil of additional 60 % Gas

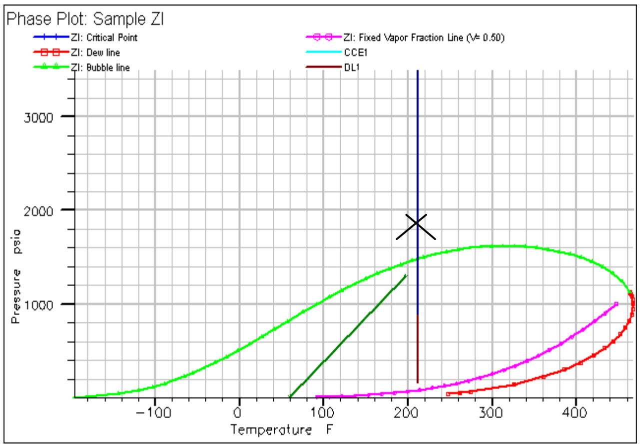

Figure 6- Phase envelope with crude oil of additional 40 % Gas

Flock Point Analysis- Titration Test

The prepared crude oil sample was used in all flock point analysis test. Oil was titrated with gradual addition of n-heptane which can destabilize the asphaltene aggregates leading to flocculation. 1 cc of n-heptane was added to the sample while stirring for 10 minutes using mangnetic stirrer. This procedure was repeated until all the asphaltene aggregates were precipitated. Precipitation of Asphaltene was studied using the digital polarized-light microscope. The amount of n-heptane was noted as a base case line at which the Asphaltene particles starts to precipitate. This base line was then used as a reference to evaluate the inhibitor efficiency [12] [13]. Figure 10 shows the microscopic pictures of blank crude oil which is titrated with n-heptane.

Once the base case has been established, 1 gm of blank crude oil was mixed with the 2 ml of prepared inhibitor solution. Inhibitor mixed oil is then titrated gradually using n-heptane as the procedure described above. The amount of n-heptanes is noted which is required to precipitate the Asphaltene particles. Inhibitor A, Inhibitor B, Inhibitor C and Inhibitor D in acid, base and neutral environment were evaluated using the described method. Higher amount of n-heptane requirement than base case shows more stability of Asphaltene particles in crude oil indicating the efficiency of inhibitor. The Figure 11, figure 12, figure 13 shows the result of Asphaltene inhibitors. After the evaluation, efficient Inhibitor was recommended for the Malaysian field to control the Asphaltene precipitation.

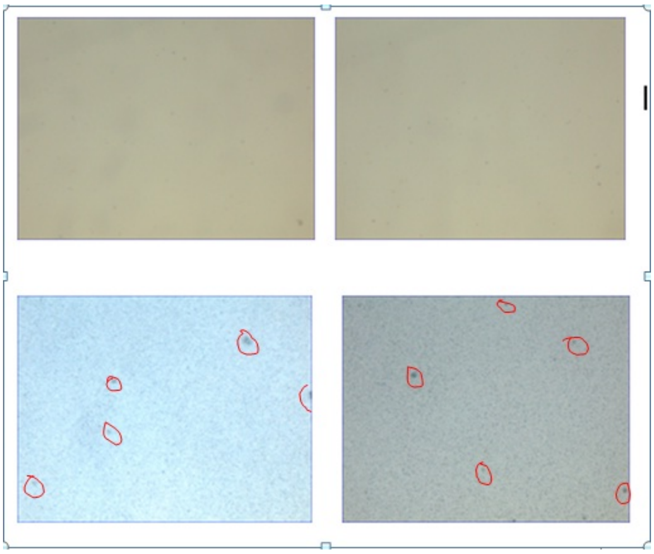

Figure 8- Microscopic pictures of blank crude oil precipitated with n-heptane

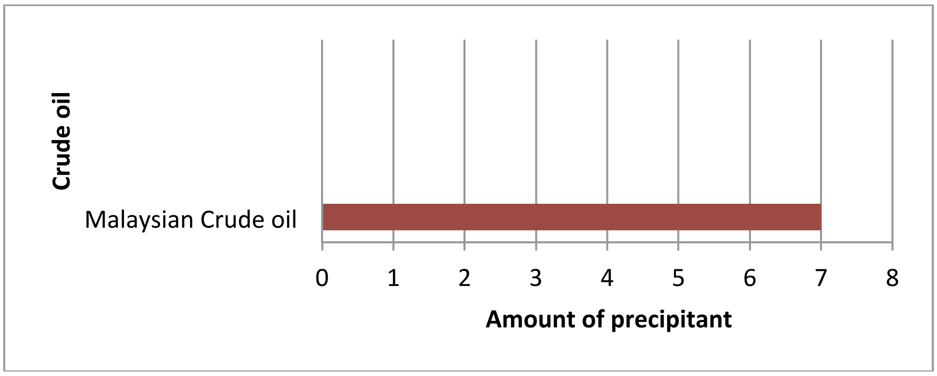

Figure 9- Base line amount of N-heptane required to precipitate Asphaltene particles

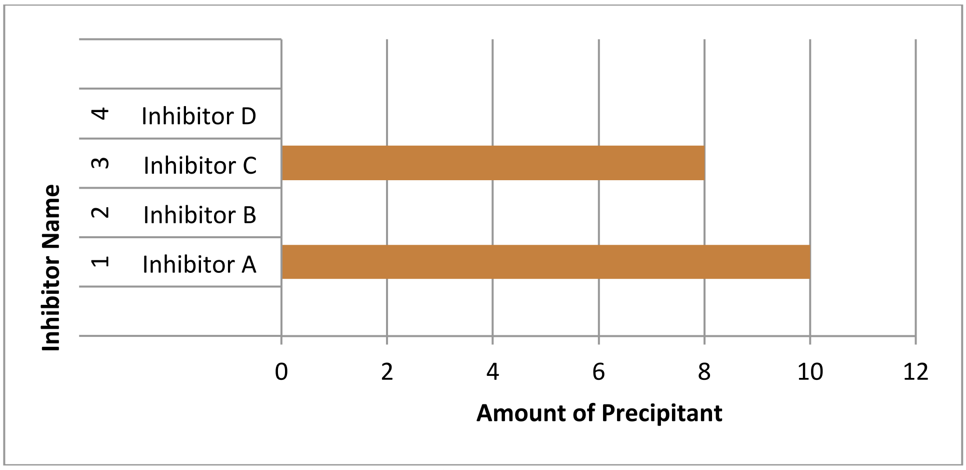

Figure 10- Inhibitor effecincy in Neutral Enviroment

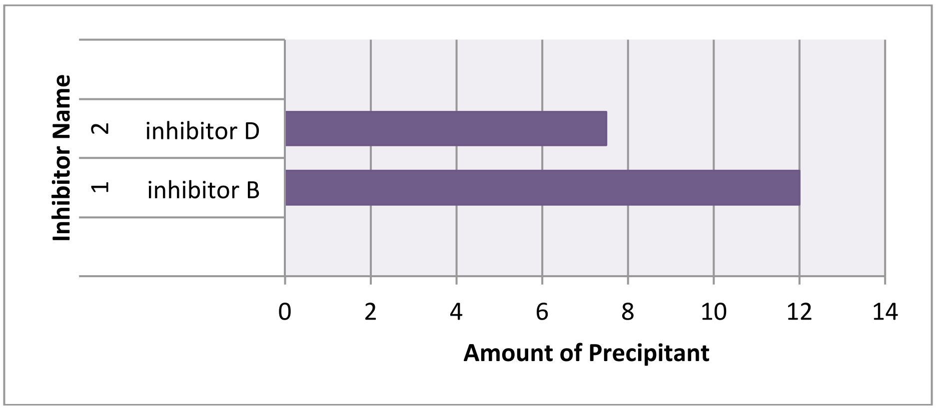

Figure 11- Inhibitor effecincy in Acidic Enviroment

Results and Discussion:

Figure-5 shows the light transmittance curve versus pressure for the blank crude oil with original reservoir fluid. The result showed that light transmittance has increased with decrease in pressure. No drop of light transmittance observed during the whole isothermal pressure depletion experiment. This result indicates that asphaltene particles were quite stable before the injection of additional gas and no Asphaltene was precipitated.

Figure 6 and figure 7 represents the isothermal depressurization test using solid detection system with the 40 % and 60 % addition of gas. The results show that increase in gas concentration in the reservoir has made the Asphaltene unstable. Asphaltene precipitation was observed 1600 Psi and 100°C for 40 % increment of gas and at 2250 Psi and 100°C for the 60 % increment of gas in composition Asphaltene particles are quite unstable during wag injection program even though the Asphaltene content is only 0.3 weight percent.

Since the Asphaltene particles are unstable during the CO2-Water alternating gas injection, there is a need to determine the Asphaltene onset pressure and to inject the efficient inhibitor in the reservoir. Asphaltene phase envelopes were developed using the SRK equation of state, the bubble point pressure and Asphaltene onset pressure were identified using the light transmittance curve versus pressure. Figure 8 and figure 9 represents the Asphaltene phase envelope of reservoir fluid with 40 % and 60 % additional gas. The Asphaltene onset pressure is 1600 for 40 % and is 2250 for 60 % injection gas at the reservoir temperature of 100° C. Both the results have showed that Asphaltene starts to precipitate just near the bubble point pressure for this reservoir. Hence, since the reservoir is already depleted to bubble point pressure, it means that Asphaltene has already precipitated due to addition of CO_2 in the reservoir.

Inhibitor program was designed to identify the potential inhibitor for this reservoir. Inhibitor A, inhibitor B, inhibitor C and inhibitor D were chosen to be tested. The results of base case in figure 11 showed that blank crude oil precipitated with the addition of 7 cc of n-heptane and is considered as base line.

Figure 12 represents the results of the inhibitors tested in the neutral environment. It was observed that inhibitor B and inhibitor D are not completely miscible with the crude oil and their particles are stick to the bottom of beaker. 8 cc of n-heptane was needed to precipitate the Asphaltene for inhibitor B which is near to the base line. Inhibitor D showed good performance and Asphaltene was stable even at 10cc addition of n-heptane.

All the inhibitors were also tested in the acidic environment. In this case, inhibitor A and inhibitor C were not miscible with the crude oil while inhibitor D kept the asphaltene stable at 7.5 cc and inhibitor B showed the good performance and Asphaltene is stable at 12cc addition of n-heptane.

None of the inhibitor was completely miscible with the crude oil when the inhibitors were tested in the base environment and their particles had separate distinct phase in the crude oil hence it is not recommend to use the inhibitor in base enviroment acting as Asphaltene dispersant.

In all of the inhibitors tested, it is observed that inhibitor B in acidic environment showed the best performance and can be used as inhibitor to keep the Asphaltene particles dispersed in the crude oil.

Conclusion:

Asphaltene particles are unstable during CO_2-water alternating gas injection for the tested Malaysian oil reservoir even though the Asphaltene content is 0.3% which is considered as low.

It is important to keep the Asphaltene particles dispersed in the reservoir to prevent the formation damage and to assure a smooth flow in tubing string and pipelines.

Inhibitor B in acidic environment is considered as efficient to keep the Asphaltene particles dispersed.
Core flooding program should be designed to evaluate the inhibitor-rock interaction before injecting it in the reservoir.

It is recommended that proposed inhibitor should be injected in the reservoir according to phase behavior and Asphaltene onset pressure predictions.

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References

1. Juan C. Pereira, Isbet Lopez. (2007) “Resins: The Molecules Responsible for the stability/ instability Phenomena of Asphaltene”, J Energy & Fuels, Vol 21, 1317-1321.

2. S. Negahban, N. Joshio, “A Systematic Approach for Experimental Study of Asphaltene Deposition for an Abu Dhabi Reservoir Under WAG Development Plan”, Paper SPE 80261, Presented at SPE Oilfield Chemistry Symposium, Texas, 2003.

3. M. Sadeqi Moqadam, H. Firoozinia, R. Kharrat,” Effect of Pressure and CO2 Composition Changes on Distribution of Asphaltene Molecular Weight in Heavy Crude Oil”, SPE- 2009-037, presented at Canadian International Petroleum Conference, Jun 16 - 18, 2009 2009, Calgary, Alberta.

4. Bahram S. Soulgani, Bahman Tohidi. (2011) “Modeling Formation Damage due to Asphaltene Deposition in the Porous Media”, J Energy Fuels, Vol 25, 753-761.

5. Solid Detection System, User Manual v1.10, VINCI Technologies FRANCE

6. Hideharu Yonebayashi. Tsutomu Masuzawa, “Ready for Gas Injection: Asphaltene Risk Evaluation by Mathematical Modeling of Asphaltene-Preciptation Envelope(APE) With Integration of All laboratory Deliverables” Paper SPE 125643, presented at the SPE-EAGE Reservoir Charachterization and Simulation Conference, Abu Dhabi, UAE, 2010.

7. Lian, H, J Lin, “Peptization studies of asphaltene and solubility parameter spectra” J Fuel vol. 73 issue 3 March, 1994. p. 423-428

8. Mohsen Mohammadi, Mahdi Akbari (2011). “Inhibition of Asphaltene Precipitation by TiO_2, SiO_2, and ZrO_2 Nanofluids”. J Energy & Fuels, Vol 25, 3150-3156.

9. Olga Leon, Estrella Rogel, (1999) “Study of the Adsorption of Alkyl Benzene- Derived Amphiphiles on Asphaltene Particles”. J Langmuir, Vol 15, 7653-7657.

10. Luiz Carlos Rocha Junior, Maira Silva Ferreira, M, “ Inhibition of Asphaltene Precipitation in Brazilian crude oils using new oil soluble Amphiphiles”, Journal of Petroleum Scinece and Engineering, 2006, 51 26-36

11. ASTM D3279 – 12, “Standard Test Method for n-Heptane Insolubles”.

12. G.P. Oskui, M Salman, E.F Gholoum, A Rashed, “Laboratory Technique for Screening Asphaltene Inhibitors for Kuwaiti Reservoirs”, Paper SPE-106361, Presentated at SPE Technical Symposium of Saudi Arabia, Dahran, 2006.

13. Ebtisam F. Ghloum, Misfera Al Qahatani, (2010.) "Effect of Inhibitors on precipitation for Marrat Kuwaiti Reservoir" J. Petroleum. Science &. Technolgy, 70, 99-106.