

## Investigation of Inhibitors Performance on Asphaltene Precipitation due to CO<sub>2</sub> Injection

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### ABSTRACT

In a CO<sub>2</sub> gas displacement process, the injected CO<sub>2</sub> can disturb the reservoir fluid stability; induce flocculation and deposition of asphaltenes. Several procedures are used to remove or prevent asphaltene precipitation, but the uses of asphaltene inhibitors provide most practical and economical solution for deposits treatment. In this work, the results obtained on the inhibition effect of one commercial inhibitor namely IR95 and five non-commercial inhibitors namely Benzoic Acid, Nonylphenol, Phenanthrene, Phthalic Acid and Salicylic Acid is presented. Static tests indicate that CO<sub>2</sub> concentration and temperature are the most important factors on which the asphaltene precipitation depended. Results of inhibitor tests reveal that IR95 with more than 50% precipitation reduction, have best efficiency among other inhibitors.

### INTRODUCTION

When CO<sub>2</sub> injected to reservoir, it contact to the reservoir oil and can cause change in the fluid behavior and equilibrium condition which favor precipitation of organic solids, mainly asphaltenes [1]. Asphaltene precipitation can change the wet ability of the reservoir matrix and consequently affect the flood performance [2]. It can also cause formation damage and well bore plugging, requiring expensive treatment and cleanup procedure [3; 4; 5; 6; 7].

Several authors defined asphaltene over the years, since 1924 by Nellensteyn [8] to 2006 by Wang et al.[9]. Asphaltenes are the polar, polyaromatic and high molecular weight hydrocarbon fraction of crude oil that are generally characterized as insoluble in n-heptanes or in n-pentanes. They are believed to exist either dissolved in oil or as a finely dispersed colloidal suspension in oil stabilized by resins adsorbed on their surface. The asphaltene/resin ratio

and high/low molecular weight component ratio determines which crude oil can precipitate asphaltenes. Application of chemical or mechanical forces can alter these ratio and destabilized resins and asphaltenes.

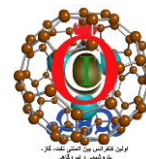
The Colloidal Instability Index (CII) is one accurate test for measurement of stability of asphaltenes in crude oils. It considers the crude oil as a colloidal solution made up of the pseudo components: saturates aromatics, resins and asphaltenes and expresses the stability of asphaltenes in terms of these components. CII is defined as the sum of the asphaltenes and its flocculants (saturates) to the sum of asphaltene peptizers (resins and aromatics) in crude oils.

$$CII = \frac{\text{Asphaltene} + \text{Sarurate}}{\text{Aromatic} + \text{Resins}}$$

Empirical evidence has shown that values of 0.9 and more indicate oil with unstable asphaltene, while values below 0.7 indicate stable asphaltenes. Between 0.7 and 0.9, the stability of the asphaltenes is uncertain [10].

Prevention of asphaltene deposition by the application of chemical inhibitors has been studied extensively. Different chemistries for asphaltene inhibition have been developed and evaluated at recent years [11]. Asphaltene inhibitors act in a way similar to resins, peptizing the asphaltenes and keeping them in solution.

The main objective of this paper is to investigate the asphaltene precipitation problem due to CO<sub>2</sub> injection and the performance of one commercial and five non-commercial inhibitors for one of the Iranian oil reservoir located in producing areas in south of Iran.



## MATERIAL AND EXPERIMENTAL PROCEDURE

### Crude oil and Inhibitors

Oil sample was used in this work came from one of important Iranian petroleum field. The properties of crude oil are given in Table 1.

Table 1: properties of crude oil

Initial Pressure (Pisa)	5750
Saturation Pressure (Pisa)	3904
Temperature (°F)	241.7
API	29.5
Oil Molecular weight (gr/mole)	90.55

There are different methods to find out the asphaltene content of crude oil, such as D2007 [12] and IP/143 [13]. In this work IP/143 method was used. D4124 [14] is a method to separate crude oil into four fractions based on their solubility properties. This four fractions are saturates, aromatic, resin and asphaltene. Table2 display result of D4124 test.

Table 2: result of D4124 test

Asphaltene	2.5%
Resin	17.9%
Aromatic	20.3%
Saturate	59.3%

Result of D4124 test show that CII=1.61, it reveals that examined oil is very unstable.

The oil recombination was performed by charging a specified amount of dead oil into a recombination cell. The correspondent gasses were then injected into recombine cell and pressured to 5000 Psia and were

shaking for 14 days to ensure complete mixing of oil and gas into single phase liquid.

Examined inhibitors consist of five non-commercial inhibitors namely Benzoic Acid, Nonylphenol, Phenanthrene, Phthalic Acid and Salicylic Acid and one commercial inhibitor namely IR95 with patent number 70680 in Iran.

### Experimental procedure

A schematic sketch of high pressure-high temperature system which was used in this work is shown in fig.1. It includes the oven and shaker, 0.5 micron metal filter, PVT cell with total volume of 500cc, transfer vessel; recombine cell, hydraulic pump, lines and pressure gauges.

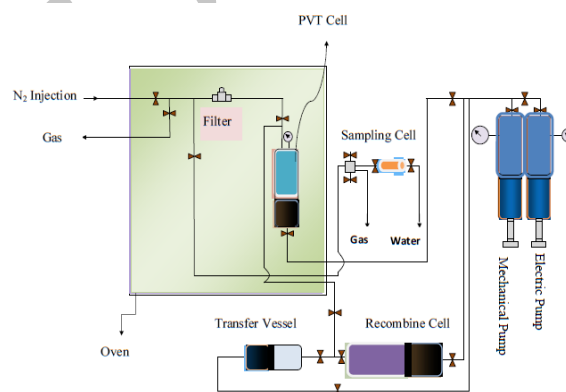
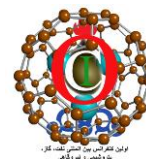


Fig.1: A schematic sketch of the high pressure-high temperature system

Five different percent of CO<sub>2</sub> was injected into the PVT cell to combine with synthetic oil. After the injection of gas into the synthetic oil, the pressure would be maintained on 4500 Psia. The temperature of PVT cell was maintained on (241.7°F, 228.9°F, 210.3°F and 190.4°F) by oven. PVT cell was shaken for 24hr, then do the sampling. During the sampling, oil was passed through the 0.5 micron filter and some asphaltene particles aggregated in that. Then a certain ppm of each inhibitor is injected into each of above tests and sampling will repeat. Standard condition tests shows that 250 ppm was optimum concentration for all inhibitors. Amount of asphaltene precipitated were determined by IP/143 test.



## RESULT AND DISCUSSION

A 99.5% pure CO<sub>2</sub> gas was used in these experiments. Fig.2 shows that the onset point concentrations of asphaltene precipitation at 190.4 to 241.7 °F are 22% to 26% CO<sub>2</sub> for mixture molar ratio consequently. After the onset, asphaltene precipitation follows almost linear trend. The experimental results indicate that by increasing the mole fraction of CO<sub>2</sub> gas in the mixture increases the amount of precipitation. It has been noted that the high CO<sub>2</sub> concentration result does not follow the linear trend as expected and this might represent the two phase region. The experimental results indicate increasing the temperature will reduced the amount of asphaltene precipitation. Hence, solubility is most effective on precipitation/flocculation procedure during this process.

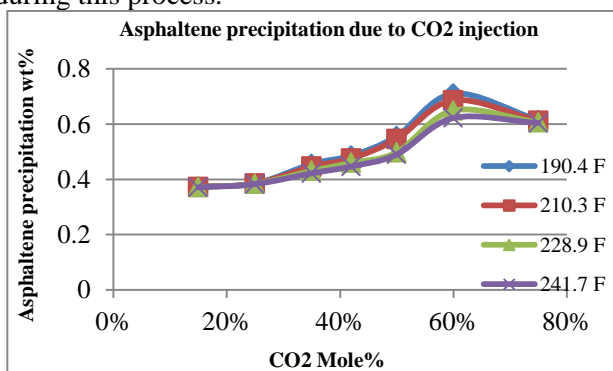


Fig.2: Asphaltene precipitation due to CO<sub>2</sub> injection After CO<sub>2</sub> injection tests, 250 ppm of each inhibitor was injected to PVT cell and the previous tests were repeated. The result of these test are shown in fig.3. As can be seen the percentage of asphaltene precipitation was reduced after inhibitor addition. Results of these tests reveal that IR95 with 51% asphaltene precipitation reduction has best efficiency among all inhibitors. IR95 have high polarity and aromatic compositions and act similar way to the natural state of resins, causing digesting asphaltene particles and keeping them in solution. Among non-commercial inhibitors, salicylic acid with 35% precipitation reduction has best efficiency. The reason of the most effective Salicylic Acid is the existence of extra hydroxyl functional group (-OH) connected to Benzoic ring. It causes to react and contact polar group in inhibitor structure to asphaltene particles and

stabilize them. The polar head group has different potential to connect to asphaltene micelles, exactly polarity of these groups determine the power of bond.

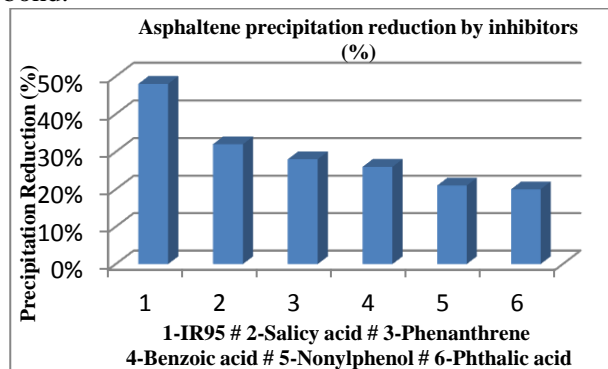


Fig.3: Asphaltene precipitation reduction by inhibitors (%)

Effects of self-association cause the low efficiency in the inhibitors. When the concentration of inhibitors is increased, the potential of self-association in the inhibitors under hydrogenous bonding mechanism in mixture and on solid surface of asphaltene particles increase [15]. It can say at higher concentrations of inhibitors tendency of self-association between inhibitor-inhibitor is more than interaction between inhibitor-asphaltene.

By considering technical and economic parameters it might be concluded that the use of salicylic acid in field scale is non-commercial. It should be mentioned that salicylic acid is expensive and its application in field scale needs great volume of aromatic solvent. Further, after contact non-commercial inhibitors with reservoir water, H<sup>+</sup> ions are released. This phenomenon causes the accumulation of asphaltene particles around the H<sup>+</sup> ions. It should be noted that the cores of asphaltene particles are negatively charged. Accumulation of asphaltene particles around the H<sup>+</sup> ions can increased asphaltene deposition. Fig.4 shows the asphaltene precipitation due to CO<sub>2</sub> injection after IR95 injection.

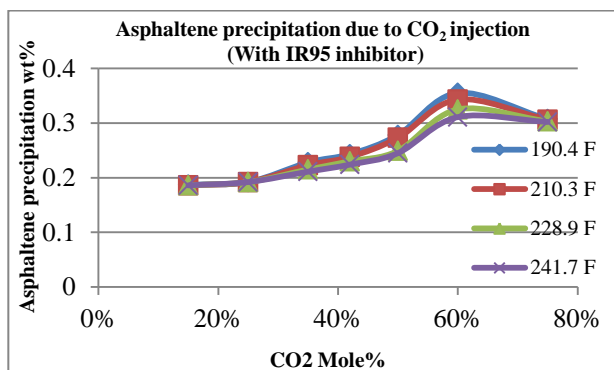
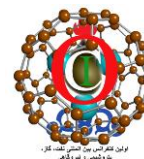


Fig.4: Asphaltene precipitation due to CO<sub>2</sub> injection (With IR95 inhibitor)

## CONCLUSION

Based on the results of this study the following conclusions are obtained:

1. Temperature has an efficient role on deposition of asphaltene result for CO<sub>2</sub> injection. Recovery of gas injection will be decreases in lower temperatures.
2. A 99.5% pure CO<sub>2</sub> gas was used in these experiments. The obtained data show that the onset point concentrations of asphaltene precipitation at 190.4 to 241.7 °F are 22% to 26% CO<sub>2</sub> for mixture molar ratio consequently. After the onset, asphaltene precipitation follows almost linear trend.
3. Solubility has most effect on precipitation/flocculation procedure during Asphaltene deposition.
4. Results of this work reveal that commercial inhibitor (IR95) with 51% asphaltene precipitation reduction have best efficiency among all inhibitors.
5. Inhibitors with high polarity and aromatic compositions, act similar way to the natural state of resins and cause digesting asphaltene particles and keeping them in solution. Thus inhibitors that compounds with high polarity and aromatic compositions can be better inhibitors.
7. Existence of extra hydroxyl functional group (-OH) connected to Benzoic ring causes to react and contact polar group in inhibitor structure to asphaltene particles and stabilize them.
8. Release the H<sup>+</sup> ions causes the accumulation of asphaltene particles around that; accumulation of asphaltene particles around the H<sup>+</sup> ions can increase asphaltene deposition.

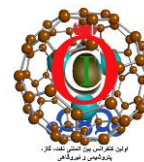
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## REFERENCES

1. Kokal, S.L. and Sayegh, S.G., (1995). "Asphaltene: The cholesterol of petroleum". SPE paper 29787 presented at the Middle East Oil Show, Bahrain.
2. Buckley, J.S.; (2001). "Asphaltene Precipitation and Crude Oil Wetting". SPE paper 26675 presented at the 68<sup>th</sup> Annual Technical Conference and Exhibition, Huston, Texas.
3. Leontaritis, K.J. and Mansoori, G.A., (1988). "Asphaltene Deposition: A Survey of Field Experiences and Research Approach". Journal of Petroleum Science and Engineering, 1, pp. 229-239.
4. Novosad, Z. and Costain, T.G., (1990). "Experimental and Modeling Studies of Asphaltene Equilibria for a Reservoir under CO<sub>2</sub> Injection". SPE paper 20530 presented at the 65<sup>th</sup> Annual Technical Conference and Exhibition, New Orleans, Louisiana.
5. Baker, H.L., Thomas, D.C., Doddridge, W.R. and McDougall, D.B., (1992). "Asphaltene Deposition Control Using Chemical Control Agents". Paper CIM92-7, presented at the CIM Annual Technical Conference, Calgary, Alberta.
6. Leontaritis, K.J., Amaefile, J.O. and Charles, R.E., (1992). "A Systematic Approach for the Prevention and Treatment of Formation Damage Caused by Asphaltene Deposition". SPE paper 23810 presented at the SPE International Symposium on Formation Damage Control, Lafayette, Louisiana.
7. Kamath, V.A., Yang, J. and Sharma, G.D., (1993). "Effect of Asphaltene Deposition on Dynamic Displacement of Oil by water". SPE paper 26946 presented at the Western Regional Meeting, Anchorage, Alaska.
8. Nellensteyn, F.J., (1924). "The constitution of asphalt." J. Inst. Pet. Technol. 10, 311-323.
9. Wang, X., Creek, J.L., and Buckley, J.S.; (2006) "Screening for potential asphaltene problems". SPE 103137.
10. Gaestel, C., Smadja, R., Lamminan, K., (1971). Rev. Gen. Routes Aerodr. 466, 85.
11. Squicciarini, M. and Yen, A.; (2007) "Characterization of the chemical properties of crude oils to explain observed asphaltene inhibitor specificity". SPE 106209.



12. ASTM D2007-93, (1993) "Standard test method for characteristic group in rubber extender and processing oils by the clay-gel adsorption chromatographic method,"
13. IP 143/84, (1989). "Standard Methods for Analysis and Testing of Petroleum and Related Products".
14. ASTM D4124 – 97, (1997) "Standard Test Methods for Separation of Asphalt into Four Fractions", Approved Aug. 10. Published April 1998.
15. León, O., Contreras, E., Rogel, E., Dambakli, G., Espidel, J., And Acevedo, S.;(2001) "The influence of the adsorption of amphiphiles and resins in controlling asphaltene flocculation". Energy and Fuels, Vol. 15 , pp. 1028-1032.

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