



# The Effect of P-1-D Thickener on CO<sub>2</sub> Mobility Control During Enhanced Oil Recovery

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## Introduction

The very low gas viscosity is a controversial challenge during gas based enhanced oil recovery (EOR), because it provides an undesirable mobility ratio which leads to early gas breakthrough (BT) and then high residual oil saturation. Therefore, during the recent decades, the investigation of polymer thickeners for gas based enhanced oil recovery has been performed instead of foam injection and WAG process. The polymer thickeners must be both gas-soluble and capable of significantly increasing the gas viscosity at reservoir conditions. The gas viscosity is approximately between 0.02 to 0.06 cP during the typical EOR processes, and it must be increased about 20 or 30 fold to achieve a viscosity similar to water and typical light oil respectively [1]. Previously, most of the researchers focused on CO<sub>2</sub> thickeners because it is widely used in gas based enhanced oil recovery projects around the world such as Canada, United States, Middle East and elsewhere [2]. There are few investigations for identifying polymers which can thicken pure gases. Therefore, the improvement of the gas mobility control may be occurred by the dissolution of ultra-high molecular weight polymers and also small molecules as direct thickeners into gases which all lead to viscosity enhancement. Moreover, in case of high and ultra-molecular weights thickeners, the remarkable amount of co-solvent is controversial for gases [3]. However, the high molecular weights of fluorinated based thickeners are still the only agents which

have been illustrated which can thicken gas during gas based enhanced oil recovery projects without any co-solvent requirement. Despite that, the fluoroacrylate monomer is very expensive and it causes impractical as gas thickeners during EOR projects unless the polymer is effective at extremely low concentrations. Also, the unfavorable environmental impacts are another significant challenge related to fluorinated compounds [4]. However, in the case of the high molecular weight, the significant amount of co-solvent (e.g. toluene) is problematic and causes the field application of this mixture impractical. Accordingly, it is more sufficient to use low molecular weight thickeners and non-fluorinated, as these are more economically agents to thicken CO<sub>2</sub> [5]. This study focused on the phase behaviour of P-1-D-CO<sub>2</sub> thickener at different concentrations up to 100000 ppm. Also, it eliminates the requirement of co-solvents along with the high molecular weight gas thickeners. The cloud point pressure, relative viscosity, and IFT measurements were performed at different temperature and pressure conditions.

## Experimental Procedure

In this study, small molecular weight of Poly 1-decene (P-1-D, MW=910 g/mol) was considered to improve the CO<sub>2</sub> viscosity without any co-solvent. The P-1-D is an affordable, gas-philic agent, and environmentally safe polymer. Also, the effect of P-1-D thickener on IFT and CO<sub>2</sub> viscosity was investigated. The physical properties and chemical composition of crude oil were reported in Table 1.

**Table 1.** Physical properties and chemical composition of crude oil.

| Physical properties              |       | Hydrocarbon Type                       | Mole % |
|----------------------------------|-------|--|--------|
| SG (60°F), ASTM D40452           | 0.9   | N.Paraffins                            | 28.6   |
| Molecular weight, g/mol, IP-86   | 130.2 | Iso.Paraffins                          | 26.1   |
| Acid Number, mg/g (KOH)          | 1.4   | Naphthenes                             | 20.2   |
| Base Number, mg/g (KOH)          | 0.45  | Aromatics                              | 21.7   |
| Asphaltene Content, wt.%, IP 143 | 4.7   | Saturates C <sub>15</sub> <sup>+</sup> | 1.6    |
| BS and W (volume %)              | 0     | Aromatics C <sub>15</sub> <sup>+</sup> | 1.8    |

In addition, the dissolution of polymer thickener in gases for EOR processes investigates by calculation of cloud point pressures. The P-1-D solubility in CO<sub>2</sub> was measured by HPHT visual cell with different concentrations. At first, a determined amount of thickener is weighed out and insert into the window cell. After that a specified amount of gas was added to the sample to provide the desired composition. The mixture with constant total composition was pressurized and then used a magnetic stirrer. It was continued to clear and single phase solutions were achieved from the window cell at favorable temperatures and pressures. Finally, the reduction in pressure of all samples was considered at the intervals of 40 psi. The equilibrium condition was about two hours to detect any visual changes, and also more time may be needed for the low solubility thickeners. In general, the cloud point pressures of gas/thickeners were indicated in the fog form by visual monitoring in the bulk sample. The measurements were repeated at least three times with a reproducibility of ±5 psi. After that, the high pressure-high temperature falling ball viscometer was considered to measure the relative viscosity of polymer thickener. All viscosity measurements were conducted at 500 psi above; in addition, it's cloud point pressure to make sure that the single phase solutions have occurred. Relative viscosity is considered as the ratio of the gas thickener viscosity to the viscosity of the CO<sub>2</sub> at different temperatures and pressures. Suppose that if the gas density is not seriously affected by the dilute thickeners

concentrations, the fall time ratio between two points also shows the relative viscosity. Furthermore, the measurements were repeated several times, and the error margins in viscosity measurements were lower than ± 0.01. Also, the IFT measurements between the crude oil and gas thickeners were performed using the high-pressure high-temperature IFT 700 apparatus by DSA method. An oil droplet is produced from the end of the capillary needle, which surrounded by gas or thickened gas at desirable conditions. However, the IFT was measured with advanced drop shape analysis software. In addition, the IFT error calculated via the standard deviation of 4 repeat measurements of each mixture was about ± 0.1 [4,5].

**Results And Discussion**

**The dissolution of P-1-D in CO<sub>2</sub>**

The results of cloud point measurements were presented in Table 2. From these results, increasing in both temperature and P-1-D concentration leads to the cloud point pressures generally increase. Also, the P-1-D solubility in carbon dioxide increases at lower temperatures and leads to achieve lower cloud point pressures. It can be referred to the entropy of mixing, which can control this condition. The polymer density does not change extremely with temperature, while the gas density increases by decreasing temperature. Therefore, the difference in density increases and the entropy of mixing becomes more negative and so the temperature behaves inversely during thickened gas process.

**Table 2.** Cloud point pressures of P-1-D and CO<sub>2</sub>.

| Gas thickener | P-1-D concentration(ppm) | Cloud point pressure (psi) |       |       |       |       |        |
|---------------|--------------------------|----------------------------|-------|-------|-------|-------|--------|
|               |                          | 25 °C                      | 40 °C | 50 °C | 60 °C | 80 °C | 100 °C |
| P-1-D         | 5000                     | 1100                       | 1350  | 1500  | 1700  | 1900  | 2200   |
|               | 10000                    | 1300                       | 1450  | 1600  | 1750  | 1950  | 2250   |
|               | 30000                    | 1400                       | 1600  | 1700  | 1900  | 2300  | 2600   |
|               | 50000                    | 1500                       | 1700  | 1800  | 2000  | 2500  | 2700   |
|               | 80000                    | 2000                       | 2150  | 2300  | 2400  | 2650  | 2900   |
|               | 100000                   | 2700                       | 2850  | 3000  | 3100  | 3300  | 3500   |

### The Effect of P-1-D Thickener on CO<sub>2</sub> Viscosity

The relative viscosities were determined at the conditions of at least 500 psi over the cloud point pressure to certify a single-phase mixture occurred. Based on Figure 1, CO<sub>2</sub>/thickener viscosities increase at 5000, 10000, 30000, 50000, 80000, and 100000 ppm P-1-D concentration. The CO<sub>2</sub> viscosity increases up to 10.1 fold for temperature 25 oC and 100000 ppm polymer concentration. The relative viscosity of P-1-D/CO<sub>2</sub> thickener increases by increasing gas thickener. It refers to the repeating unit of P-1-D monomers which can provide more thicken CO<sub>2</sub>. Therefore, P-1-D may be a more sufficient CO<sub>2</sub> thickener to attain a good solubility in pure carbon dioxide at a condition above the cloud point pressures.

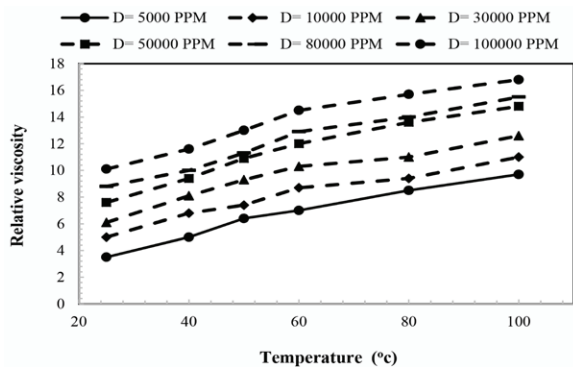


Fig 1. Relative viscosity of CO<sub>2</sub> in presence of gas thickener.

**IFT Measurements and Minimum Miscibility Pressure**  
The equilibrium interfacial tension between the intermediate crude oil ( $\alpha$ API= 25.72) and the pure/P-1-D thickened CO<sub>2</sub> are measured at 80 oC and pressures above the cloud point pressure (varied from 22000 to 3050 psi). Figure 2 indicates a significant IFT reduction by increasing P-1-D concentration. However, from Figure 3, the MMPs of crude oil and CO<sub>2</sub>/thickener were calculated by VIT method based on the interfacial tension data. The results showed that the P-1-D could significantly reduce the minimum miscibility pressure. The thickened CO<sub>2</sub> had higher density than pure CO<sub>2</sub>, while the difference in density in both cases (between crude oil and pure/thickened CO<sub>2</sub> systems) leads to a reduction in IFTs and MMPs. Also, about the P-1-D with concentrations above the 10000 ppm, the MMP reduced, and it is below the reservoir pressure. Therefore, the MMP for pure CO<sub>2</sub>, P-1-D/thickened CO<sub>2</sub> with concentration below the 10000 ppm were above the reservoir pressure (Pres=3050 psi); and so the immiscible injection will be occurred at reservoir conditions. In addition, the MMP values for P-1-D/thickened CO<sub>2</sub> with concentrations above the 10000 ppm indicated that these would provide the miscible flooding at reservoir conditions.

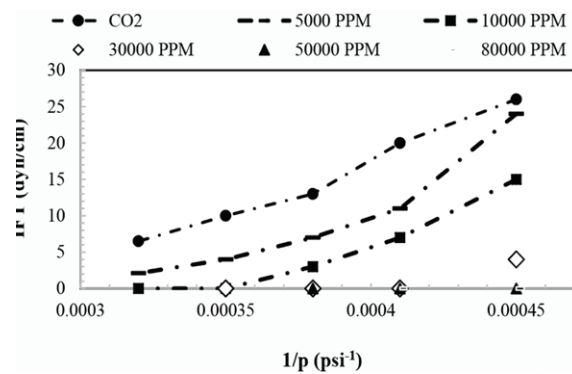


Fig. 2 IFTs between oil and gas in presence of gas thickener.

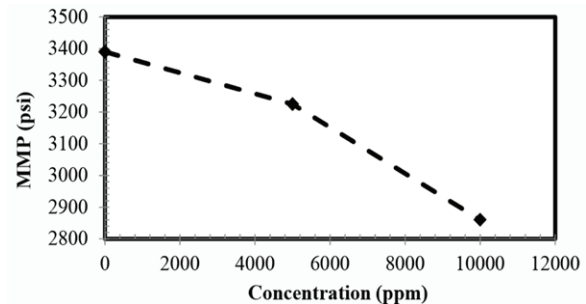


Fig. 3 MMPs of oil and gas in presence of gas thickener.

### Conclusions

According to this study, the following results which could be concluded are as follows:

- The cloud point pressure increases by increasing temperature and P-1-D concentration.
- The dissolution of gas thickener in CO<sub>2</sub> occurs at pressures below the reservoir pressure.
- The pure CO<sub>2</sub> viscosity is 0.0484 cP, and it increases to 0.76 cP using the P-1-D thickener.
- Gas thickener can provide the miscible conditions during the injection of the CO<sub>2</sub>/P-1-D at 10000 ppm.

### Nomenclatures

BT: Breakthrough  
IFT: Interfacial Tension

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