

## Research Article

# Hybrid Method Carbon Dioxide Flooding with Solvent and Temperature for Asphaltene Precipitation

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## Abstract

Asphaltene precipitation and deposition are well-known problems in the transportation and processing of oil recovery. The cause of asphaltene is triggered by various factors such as changes in pressure, temperature (T), and gas (carbon dioxide) flooding (CO<sub>2</sub>). The study aimed to investigate the best economical method that can best enhance oil recovery (EOR). Two hybrid methods carbon dioxide flooding/ solvent (C<sub>5</sub>) and carbon dioxide flooding/ solvent (C<sub>5</sub>) /temperature were considered for the study. Firstly, the study was explored by singly utilizing pentane, hexane and heptane alkane solvents at different volumes to each of the three dead crude oils A, B and C. The study proves that the lower molecular weight and boiling point (C<sub>5</sub>) managed to deasphaltene 24.0 g/mL from solvent/oil ratio 20:1/2; 100 mL into 2.5 g. This was due to the higher repulsive force between the solvent and the asphaltene. The study was further extended using the hybrid method and proven carbon dioxide/solvent (C<sub>5</sub>)/temperature (90°) in precipitating higher asphaltene. The selection of pentane was based on its ability to meet the saturation point of the oil reservoir and EOR. The weaker London dispersion and the intermolecular forces between asphaltene and crude oil were the mechanisms responsible for the asphaltene precipitation.

## Keywords

Asphaltene, Solvents, Temperature, Carbon Dioxide, Precipitation

## 1. Introduction

Crude oil is considered the most used resource in the energy supply. It is a complex organic compound that consists of various other components however, asphaltene is the heaviest polyaromatic component that causes severe damage in the pipelines during the production of crude oil [1]. Asphaltene is a polar fraction of crude oil that is soluble in aromatic solvents such as toluene, benzene and xylene but insoluble in a normal straight chain of alkane solvents such as pentane,

hexane and heptane [2].

Asphaltene is known as the “cholesterol of petroleum” due to its ability to precipitate as solids and subsequently deposit to the surface from various conditions such as the change in pressure, temperature and oil composition [3, 4]. Asphaltene precipitation is a process in which asphaltene becomes a separate phase from crude oil. The remaining suspended are in the liquid phase (crude oil) where the quantity and the size of

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the asphaltene are relatively small. The precipitate asphaltene is clumped together (aggregation) to form larger particles called flocs. The asphaltene aggregates are initially suspended in crude oil. Their deposition occurs as soon they accumulate as flocs and then attached to the surface where the process is called asphaltene deposition [3].

A study by Hu and Guo [5] investigated the influence of temperature on asphaltene precipitation and proved that higher temperature increases the solubility of asphaltene by resulting in a smaller mass of asphaltenes. The mechanism of asphaltene precipitation is described as a process of destabilization of asphaltene nanoaggregates from crude oil due to the addition of a precipitant. The destabilization of asphaltene is followed by its aggregation and particle growth [6].

Higher temperature could lead to a few particle collisions in a slower rate of aggregation which can take the particle a long time to reach its micrometer size to be detected under optical microscopy [7]. The precipitant used to help asphaltene to precipitate is importantly similar to the role of temperature on the solubility of asphaltene [7]. Alkane solvents were identified to enhance asphaltene to precipitate and be less soluble as temperature increases [7]. Asphaltene solubility and its destabilization are influenced by temperature [8].

The acceleration of asphaltene solubility results in an increase in asphaltene precipitation which is related to the kinetics of asphaltene in suspension in crude oil [9]. The term asphaltene is typically used in its most general sense which refers to the high molecular weight of cyclic polyaromatic of a condensed ring in crude oil. It exists in a delicate balance with other components in crude oil described as saturates, aromatics and resins [10]. The most effective asphaltene-precipitation-preventive action is maintaining the reservoir pressure above the asphaltene precipitation onset. In many cases, this condition is difficult or impossible to accomplish due to the reservoir depletion and/or inconvenience in a gas injection, allowing asphaltene dispersants and inhibitors as alternatives [11]. A vapour extraction (VAPEX) is technique that has been employed for decades. A study by Li, et al. [12] used VAPEX technique which was one of the economic techniques used and proven to be effective in enhancing oil re-

covery (EOR). The selection of solvent based on the saturation condition at the oil reservoir is important. Therefore, the effect of a lower molecular weight solvent (pentane) with a higher temperature than the boiling point was preferred and tested on asphaltene precipitation.

A study by Mohammadi, et al. [13] investigated the effect of temperature on three live crude oil, and it was found that, an increase in temperature resulted in decelerating asphaltene content. A similar observation was obtained in crude oil with higher density. Another study by Yang, et al. [14] used the ratios of heptane with toluene with an increase in temperature; resulting in accelerating asphaltene content. According to Torkaman, et al. [15], it can best be explained, using the surface charge and greater repulsive force between the ratios to obtain a higher asphaltene content from a zeta potential.

A study by Huang, et al. [16] demonstrated that the injection of CO<sub>2</sub> flooding can reduce the crude oil's viscosity by anticipating asphaltene to precipitate. The injection of CO<sub>2</sub> flooding not only improves oil recovery but also causes major complications that result in pipeline blockage.

Several researches and articles were conducted and published on asphaltene precipitation using alkane solvents or gas injection alone. In the present study, a constant flowrate of 0.5 min/mL of the CO<sub>2</sub> gas injection in a self-made rancimat reactor using different solvents at different temperatures is carried out. The purpose of the study is to evaluate the relationship between temperature and solvent on the asphaltene precipitation; interestingly, the influence of the gas injection in the presence of the solvent and temperature for monitoring asphaltene precipitation.

## 2. Material and Methods

Solvents such as pentane, hexane and heptane were purchased at Merck and crude oils were supplied by Chevron, Cape Town, South Africa. The self-made rancimat model (EN 14112 and IS15607) was used for the study. Table 1 represents the characteristics of the alkane solvents used in the study.

**Table 1.** Characteristics of the various solvents in their physical state.

Name	Formula	Molar Weight	Boiling Point (°C)	Boiling Point (°C)	Density (20°C)	Physical state (20°C)
Pentane	C <sub>5</sub> H <sub>12</sub>	72.15	-130	36	0.626 g/mL	Liquid
Hexane	C <sub>6</sub> H <sub>14</sub>	86.18	-95	69	0.659 g/mL	Liquid
Heptane	C <sub>7</sub> H <sub>16</sub>	100.20	-91	98	0.684 g/mL	Liquid

### 2.1. Asphaltene Extraction from N-alkanes

The mixture of oil and solvent was prepared as follows; A

solvent of 200 mL, 150 mL, 100 mL or 50 mL was solely poured in 5g of each dead crude oil A, B or C at different ratios 40:1; 30:1; 20:1; and 20:1/2 (mixture of 2.5g of dead crude oil into 50 mL) of solvent for asphaltene precipitation

as described elsewhere (Luo et al., 2010). A magnetic stirrer at 170 RPM was used for 7 min; thereafter a 0.22 $\mu$ m filter Whatman paper was used to obtain asphaltene solid and dried at ambient temperature for 48 hours; then weighed.

#### *Asphaltene Solid from dead crude oil/carbon dioxide flooding (Room Temperature)*

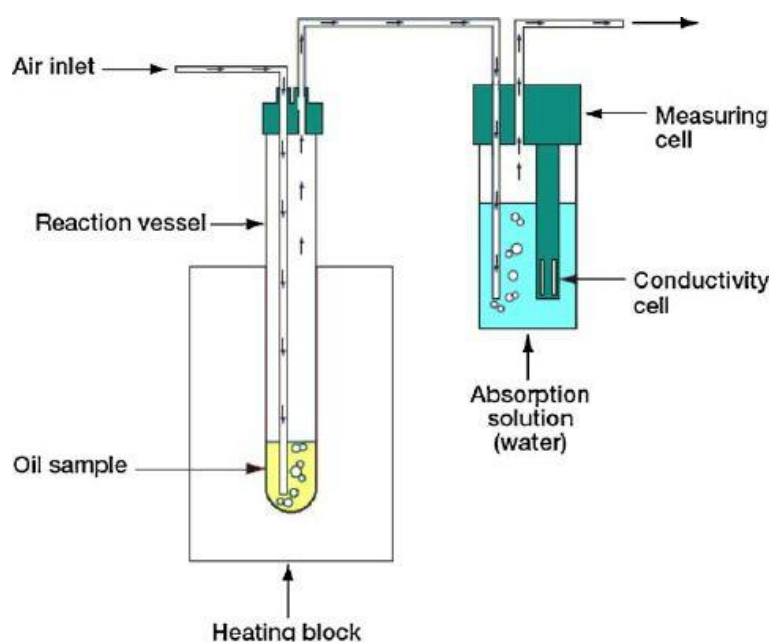
Firstly, the density of each dead crude oil A, B and C was measured to be  $9.65 \times 10^5$  mg/L,  $9.72 \times 10^5$  mg/L and  $9.85 \times 10^5$  mg/L respectively.

Different volumes of 500 mL, 10 mL, 6.6 mL and 5.5 mL of three dead crude oils were weighted and used to calculate the molar ratio using equation 1:

$$\text{Molar ratio} = (\text{carbon dioxide} \div \text{dead crude oil}) \times 100 \quad (1)$$

## 2.2. Asphaltene Extraction from N-alkanes and Carbon Dioxide Flooding

A constant carbon dioxide flooding flow-rate with increments by 10 from 0.5 mL/min to 5 mL/min for 48 hours in a rancimat system (Figure 1) containing 100 mL of pentane, hexane or heptane into a 2.5g of each of the dead crude oils in a reaction vessel for 48 hours. A similar procedure but this time considering the temperature ranging from 25°C to 90°C was also investigated.



**Figure 1.** The rancimat reactor test for CO<sub>2</sub> flooding (EN 14112 and ISO 15607).

## 3. Results and Discussion

### 3.1. Deasphaltene of Three Crude Oil Types Using Pentane, Hexane and Heptane

The asphaltene solid was precipitated from different dead crude oils A, B and C using C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub> at various ratios of solvent to oil (40:1), (30:1), (20:1) and (20:1)/2 represented in Table 2.

**Table 2.** Asphaltene solid from the dead crude oil A, B and C.

Solvents	Solvent/Oil Ratio (40:1) 200 mL into 5 g	Solvent/Oil Ratio (30:1) 150 mL into 5 g	Solvent/Oil Ratio (20:1) 100 mL into 5 g	Solvent/Oil Ratio (20:1)/2 100 mL into 2.5 g
Crude oil A	Pentane (C <sub>5</sub> ) 7.0	11.0	9.0	13.0
	Hexane (C <sub>6</sub> ) 4.0	11.0	7.0	6.0
	Heptane (C <sub>7</sub> ) 4.0	3.0	4.0	5.0
Crude oil B	Pentane (C <sub>5</sub> ) 7.0	9.0	10.0	9.0
	Hexane (C <sub>6</sub> ) 6.0	5.0	6.0	6.0

	Solvents	Solvent/Oil Ratio (40:1) 200 mL into 5 g	Solvent/Oil Ratio (30:1) 150 mL into 5 g	Solvent/Oil Ratio (20:1) 100 mL into 5 g	Solvent/Oil Ratio (20:1)/2 100 mL into 2.5 g
Crude oil C	Heptane (C <sub>7</sub> )	3.0	3.0	4.0	4.0
	Pentane (C <sub>5</sub> )	23.0	23.0	24.0	24.0
	Hexane (C <sub>6</sub> )	22.0	22.0	23.0	23.0
	Heptane (C <sub>7</sub> )	22.0	22.0	22.0	22.0

The deasphaltene of dead crude oils using n-alkanes revealed that pentane was considerably the better solvent for the deasphaltene of the three dead crude oils [17].

The study proves that as the volume of the solvent decreases considering a constant mass of 5g of each dead crude oil demonstrated a significant effect on asphaltene precipitation yield. It is believed that, at a lower volume, the intermolecular force between solvent and asphaltene is higher by weakening the London force responsible for maintaining the asphaltene particles together. A volume of 100 mL into a mass of 2.5 g of dead crude oil was found to obtain asphaltene at a peak.

According to Nguele, et al. [9], asphaltene solubility relies on the kinetics of the asphaltene in a solvent. Asphaltene precipitation occurs as soon as all the forces responsible for maintaining asphaltene monomers in suspension in crude oil are unbalanced; including the mechanism such as hydrogen bonding, metal rearrangement,  $\pi$ - $\pi$  bonding and hydrophobic binding. The asphaltene solubility reaches the threshold faster at a lower solvent which happens to be at 100 mL. The higher dissolution of the asphaltene under the utilization of a lower solvent volume resulted in a higher mass transfer of asphaltene where the asphaltene solubility was intended to decrease and increase its precipitation yield.

### 3.2. Deasphaltene of Three Dead Crude Oil Types Using CO<sub>2</sub> Flooding/C<sub>5</sub>

Pentane at the volume of 100 mL in section 3.1, was demonstrated to be effectively favourable for precipitating asphaltene and cooperating with CO<sub>2</sub> flooding in rancimat system. The deasphaltene of the three dead crude oils A, B and C are denoted in Table 3.

**Table 3.** Deasphaltene of dead crude oils using CO<sub>2</sub> flooding/ C<sub>5</sub>.

CO <sub>2</sub> to oil ratio, %	1	50	75	90
Deasphaltene, wt% (Crude oil A)	4.9	4.8	4.6	3.4
Deasphaltene, wt% (Crude oil B)	4.9	4.9	4.6	3.4
Deasphaltene, wt% (Crude oil C)	5.6	5.2	5.2	4.9

The deasphaltene of the three dead crude oils showed that, as

the molar ratio increases, the asphaltene precipitation decreases.

A study by Fakher, et al. [18] revealed that, heavy crude oil with a relatively high American Petroleum Institute (APIg) contains a higher asphaltene constant. The study proves that crude oil C was denser than other crudes resulting in a higher asphaltene content. Although CO<sub>2</sub> can decrease the solubility of dead crude oil, the study proves that as the CO<sub>2</sub> flooding increments by 10 from 0.5 mL/min to 5 mL/min for 48 the asphaltene precipitation decreases. The higher injection of CO<sub>2</sub> purpose was to alter the pH of the reservoir. The CO<sub>2</sub> to oil ratio of 90% demonstrated a lesser asphaltene content.

### 3.3. Deasphaltene of Three Crude Oil Types Using CO<sub>2</sub> Flooding/C<sub>5</sub>/Temperature

The desphaltene of three dead crude oil A, B and C was conducted using CO<sub>2</sub>/C<sub>5</sub>/Temperature ranging from 25°C to 90°C. Table 4 denotes the asphaltene content obtained from the dead crude oils.

**Table 4.** Asphaltene content from a temperature range of 25°C – 90°C during CO<sub>2</sub>/C<sub>5</sub>/T.

Temperature (°C)	Crude oil A	Crude oil B	Crude oil C
Asphaltene Content (g/mL)			
25	4.7	4.9	5.1
30	4.3	4.8	4.8
60	4.4	4.8	4.9
90	4.7	4.9	5.0

The deasphaltene of the crude oil shows that crude oil C contained higher asphaltene precipitation followed by crude oil B and C at temperatures ranging from 25°C to 90°C. The study proves that although deasphaltene of crude oil is inevitable, it was important to investigate the factors that influence asphaltene to precipitate. Temperature is among the factors that induce asphaltene to settle. According to Moud [19], deasphaltene of the crude oil at room temperature was

comparatively different than other experimental temperatures.

The study disagrees with the findings by Ghasemirad, et al. [20] that reveals higher temperatures to increase the viscosity of the crude oil by decreasing asphaltene content. According to Li, et al. [21], the high temperature was responsible for easing the diffusion of the resins into asphaltene which resulted in asphaltene to precipitate. The temperatures of 25°C and 90°C were considered for diffusing the resins into asphaltene to obtain higher asphaltene precipitation. According to Hosseini-Moghadam, et al. [22], the increase in temperature also increases the rate of asphaltene aggregation.

The thermal expansion of hydrocarbons and the ability to evaporate the solvent with the potential oxidation of asphaltene resulted in the temperature influencing the viscosity of the crude oil.

Therefore, high temperatures could facilitate the penetration of resins into asphaltene aggregates and ultimately improve the dispersion of asphaltenes. It is not certain why the asphaltene precipitation from 25°C and 90°C demonstrated to have a significant effect on precipitations.

Table 5 represents the comparative analysis of the hybrid methods used in the study for asphaltene precipitation from three dead crude oils.

**Table 5.** Asphaltene content from solvent, CO<sub>2</sub> flooding and temperature.

Type of crude oil	Solvent	CO <sub>2</sub> / Solvent (C <sub>5</sub> )	CO <sub>2</sub> /Solvent (C <sub>5</sub> )/T (90°)
Crude oil A	13.0	3.4	4.7
Crude oil B	9.0	3.4	4.9
Crude oil C	24.0	4.9	5.0

#### 4. Comparative Analysis on the Hybrid of Solvent, CO<sub>2</sub> Flooding and Temperature

Factors such as solvent, temperature and carbon dioxide gas are the parameters that influence asphaltene to precipitate. Since asphaltene contains both hydrophilic and hydrophobic sites, pentane as a non-polar solvent was favoured on the hydrophilic part of asphaltene to trigger asphaltene to precipitate. The arrangement of hydrogen bonds dominates over  $\pi$ -stacking by revealing the influence of CO<sub>2</sub> flooding to precipitate asphaltene since CO<sub>2</sub> easily reacts with hydrogen bonds to form methane and water. In this study, the stabilization energy was high in the dead crude oil with a higher density (Crude oil C). The solvent plays a vital role in asphaltene precipitation and has a greater conductivity that influences CO<sub>2</sub> flooding.

Higher temperature, higher molar ratio and lower molecular weight of alkane resulted in higher destabilization of asphaltene at a peak that reaches its micrometres point to precipitate by weakening the London and intermolecular forces within the asphaltene. These hybrid methods have been proven to have the potential to effectively replace other methods that have been employed in EOR economically.

#### 5. Conclusion

Asphaltene was highly found in dead crude with a higher

density. The hybrid methods indicated to have an exceptional performance for precipitating asphaltene. Pentane solvent was successfully found to have greater saturation ability on the conditions that influence the reservoir by improving enhanced oil recovery. The understanding of the recovery mechanisms to upscale asphaltene precipitation demonstrated in the study that hybrid methods CO<sub>2</sub>/ Solvent (C<sub>5</sub>) and CO<sub>2</sub>/Solvent (C<sub>5</sub>)/T (90°) were effective. The lower solvent had stronger intermolecular and London forces due to the larger collision between the asphaltene and the solvent. Temperatures of 25 °C and 90 °C exhibited asphaltene to be at its peak.

#### Abbreviations

CO <sub>2</sub>	Carbon Dioxide
C <sub>5</sub>	Pentane
C <sub>6</sub>	Hexane
C <sub>7</sub>	Heptane
T	Temperature

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#### Author Contributions

Jean Bedel Batchamen Mougnoil is the sole author. The author read and approved the final manuscript.



## Conflicts of Interest

The authors declare no conflicts of interest.

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