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# Asphaltene Deposition during CO<sub>2</sub> Injection and Pressure Depletion: A Visual Study

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ABSTRACT: Carbon dioxide miscible flooding has become a popular method for Enhanced Oil Recovery (EOR) because it not only efficiently enhances oil recovery but also considerably reduces green house gas emissions. However, it can significantly cause asphaltene deposition, which leads to serious production problems such as wettability alteration, plugging of the reservoir formation, blocking the transportation pipelines, etc. It is crucial to investigate the effects of different factors on asphaltene deposition. A novel experimental setup was prepared to employ a high-pressure visual cell for investigation of asphaltene deposition on a model rock under typical reservoir conditions. The evolution of asphaltene deposition was monitored via a highresolution microscope. Image processing software was utilized to check the amount of deposited asphaltene and its size distribution under different conditions. Crudes from two Iranian oil fields were used in the experiments. The amount of asphaltene deposition was measured during pressure depletion under two operating conditions: with/without CO<sub>2</sub>-injection. It was observed that the amount of deposited asphaltene decreases with pressure depletion. For instance, asphaltene deposition at 140 bar and 90 °C is 5.7 times greater compared to 30 bar and 90 °C condition. The results of CO<sub>2</sub> gas injection confirm that the deposited asphaltene increases with the concentration of injected CO2. According to the results, a temperature increase from 35 to 90 °C contributes to growth and aggregation of asphaltene particles. A comparison of two different asphaltene sources in terms of aggregation and flocculation behavior revealed that the asphaltene molecular structure could have a noticeable influence on asphaltene deposition. A new parameter was defined as the potential of deposition to describe, quantify, and compare the tendency of different asphaltene samples for flocculation and deposition.

### 1. INTRODUCTION

Crude oil generally contains different hydrocarbon compounds such as aromatics, waxes, resins, and asphaltenes. Asphaltenes are heaviest components of crude oil. On the basis of solubility, asphaltene is defined as a part of petroleum that is not soluble in *n*-alkenes but completely miscible in aromatic hydrocarbons such as toluene or benzene.1 According to their chemical structure, they are aromatic multicyclic molecules surrounded and linked by aliphatic chains and heteroatoms. Molar mass values reported for petroleum asphaltenes range from 1000 g/mol to as high as 10<sup>5</sup> g/mol.<sup>2-5</sup> Asphaltene molecules tend to aggregate and create larger agglomerates. The tendency of asphaltene molecules toward association and precipitation is related to their molecular structure,<sup>6</sup> but it is not determined clearly because of the complex nature of asphaltene molecules.

Asphaltene precipitation and deposition during oil production and processing ranks as one of the costliest technical problems which the petroleum industry currently faces. Asphaltene deposition within reservoir rocks and production facilities has been blamed for pronounced disturbances in hydrocarbon productivity.<sup>7</sup> Treatments to remove or prevent the deposition of asphaltenes increase operating costs; hence, it is desirable to inhibit or mitigate asphaltene deposition. Understanding asphaltene precipitation mechanisms and finding solutions to the relevant problems have been the driving forces behind many investigations in the past half century. Although the properties of asphaltene molecules have been studied extensively in the last few decades, 8-12 there are still many limitations for modeling and predicting asphaltene precipitation and deposition accurately.

Because of the critical and damaging role of these molecules, it is very important to monitor and evaluate any side effects of asphaltene deposition on enhanced oil recovery (EOR) processes. After the primary and secondary recovery, typical residual oil saturation in many reservoirs is in the 50-60% range of the original oil-in-place (OOIP). 13,14 Results of the extensive literature studies show that the EOR processes contribute significantly to much more oil production. 15 It is worthwhile mentioning that CO2 injection as an EOR technique has been commended for both its effective oil sweep efficiency and the considerable reduction of greenhouse gas emissions. 16,17 In general, it has been reported that this tertiary oil recovery process leads to an 8-16% increase in oil recovery efficiency.

Extensive laboratory studies, numerical simulations, and field applications of different CO2 EOR processes have been implemented in the past five decades. 19,20 Oil-viscosity reduction, oil-swelling effect, and variations in interfacial properties of the crude oil-CO2 system are the main effects of CO<sub>2</sub> flooding process, which result in an increase of ultimate oil recovery efficiency. 21,22 All the above-mentioned phenomena are directly caused by CO2 dissolution into the crude oil

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and are thus closely related to the mutual interactions between the crude oil molecules and  $\rm CO_2$ . However, the effects of mutual interactions between crude oil and  $\rm CO_2$  on EOR mechanisms are not well understood. <sup>23</sup>

One of the major technical challenges in CO<sub>2</sub> flooding for field applications is to determine the possibility of asphaltene precipitation during gas injection and its effects on the process performance. It is well-known that the injection of CO2 could lead to asphaltene precipitation yielding a sticky, asphalt-like substance that clogs the reservoir and the production equipment.<sup>24</sup> Asphaltene precipitation may cause produced crude oil to be deasphalted, becoming lighter and less viscous in comparison with the original crude oil.<sup>25</sup> In addition, asphaltene deposition on the rock surface may cause reservoir plugging and wettability alteration, which eventually leads to a reduction of enhanced oil recovery performance. 26-28 Asphaltene precipitation can also severely damage the wellbore region, plugging the production pipelines and reducing the capacity of surface facilities.<sup>29</sup> Hence, it is important to investigate the effects of different parameters such as pressure, temperature, fluid composition, and asphaltene molecular structure on asphaltene precipitation and deposition process. In previous studies done by several research groups, the effects of pressure, temperature, and/or CO<sub>2</sub> on the amount of asphaltene precipitation were investigated, considering various crude oils. 30,31

Nielsen et al.  $^{31}$  investigated the effects of temperature and pressure on asphaltene particle size distributions, in crude oils diluted with n-heptane. High-pressure laser cell apparatus was used to analyze the asphaltene particle size. According to their results, varying the temperature from 0 to 100 °C resulted in significant changes in mean particle size for the Border condensate. In the tests with the two higher molar mass crude oils, super agglomerates were observed at temperatures higher than 75 °C, which is attributed to the softening and adhesion of asphaltene particles. Their results also show a slight increase in mean particle size as the pressure increases for all crude oils except Lindbergh oil. Srivastava et al.  $^8$  indicated that  $\rm CO_2$  concentration linearly increases the asphaltene precipitation in the single-phase region. They used experimental analysis to conclude this result.

The effects of operating pressure and injected  $CO_2$  concentration on the amount of asphaltene precipitation under reservoir temperature were studied by Hu et al. According to their experiments, no asphaltene precipitation was detected during the pressure depletion process without  $CO_2$  injection. For the  $CO_2$ -injected systems, the amount of asphaltene precipitation increased with the concentration of injected  $CO_2$ .

Takahashi et al. studied Middle East carbonate reservoir crude oil in a PVT cell using a light-scattering technique. They gradually decreased the pressure of the mixture at each predetermined CO<sub>2</sub> concentration and compared the results to find the effect of concentration on asphaltene precipitation. Their results show that the amount of precipitated asphaltene became noticeable when the CO<sub>2</sub> mol exceeded more than 50 mol %. Verdier et al. concluded that in the presence of a gas component, decreasing temperature and increasing pressure resulted in reduced asphaltene precipitation.

The aim of this study is to investigate the asphaltene deposition mechanism during natural depletion and  $\mathrm{CO}_2$  injection at different pressures, temperatures, and compositions. The effect of asphaltene molecular structure as one of the most

important factors that have a considerable influence on the size, flocculation, and deposition of asphaltene particles was considered in the present study. A novel high-pressure PVT cell was designed and constructed to investigate the desired and effective parameters. The great advantage of this device is its capability to visually record the entire process using a highresolution microscope. This apparatus enabled us to analyze the formation and deposition of asphaltene particles at different stages of the experiments. Several different tests were performed to assess the effects of different parameters such as pressure, temperature, asphaltene molecular structure, and CO<sub>2</sub>-fluid composition on this process. To quantify and analyze the results, image-processing software was used. To investigate the effect of asphaltene molecular structure on deposition mechanism, two types of crude oil samples from Iranian fields were used. Asphaltene from these two samples was extracted and used to prepare the synthetic model oil, such as a heptanetoluene (Heptol) mixture.

#### 2. MATERIALS

Asphaltene used in this study was extracted from two Iranian oil field samples located in southern Iran, namely, Gachsaran and Kuh-e-Mond, according to ASTM-D86 procedure. To prepare the synthetic oil, toluene and normal heptane (Merck, high performance liquid chromatography grade) were used. Glass substrates were utilized as the solid surface to simulate sandstone. The SARA (saturate, aromatic, resin, and asphaltene) analysis, compositions, and other properties of the crude oils are presented in Tables 138,39 and 2.40

Table 1. SARA Tests (wt %) and API $^{\circ}$  of Oils Used in This Work

test name	Kuh-e-Mond <sup>37</sup>	Gachsaran <sup>38</sup>
saturates (wt %)	12.8	53.4802
aromatics (wt %)	21.83	34.45
resins (wt %)	53.39	8.5
asphaltene (wt %)	14.7	5.3
$API^{\circ}$	12.8	31

#### 3. EXPERIMENTAL SECTION

**3.1. Experimental Apparatus.** The high-pressure cell was designed in the EOR Research Center, Shiraz University, to study the asphaltene precipitation and deposition. The schematic diagram of this apparatus is illustrated in Figure 1.

The main part of the apparatus consists of a high-pressure cell, which is filled with synthetic oil. A rotating metal disk, as shown in Figure 1, is placed horizontally inside the cell. Substrate plates of different types were mounted on the disk in order to study evolution of asphaltene deposition. The rotator could handle eight transparent substrates in a single run. The precipitated asphaltene was deposited on the substrates during experimental tests. A microscope (KRÜSS, MBL2000) with an optical resolution up to 480×, was installed on the top of the cell to capture high-resolution images of asphaltene depositions on the substrates. Clear images of particles in the space between the substrate and side-glass were captured precisely by focusing the microscope. Glass substrates were  $0.5 \text{ mm} \times 0.5 \text{ mm}$ . The movement of the rotating disk was controlled by a magnetic device located outside the cell, in order to keep each substrate in front of the microscope for a specific time. A more detailed description of experimental apparatus is reported elsewhere.  $^{37,39}$ 

Table 2. Compositions (mol %) of the Crude Oils

	compositions (mole fraction)			
components	Gachsaran	Kuh-e-Mond		
$H_2S$	0.24	0		
$N_2$	0.01	0.66		
$CO_2$	0.77	0.23		
$C_1$	35.46	10.35		
$C_2$	6.03	2.35		
$C_3$	4.93	1.95		
$iC_4$	1.14	1.62		
$nC_4$	2.92	4		
iC <sub>5</sub>	1.26	3.6		
$nC_5$	1.27	2.28		
$C_6$	4.67	2.74		
$C_7$	5.12	2.15		
$C_8$	3.42	2.42		
C <sub>9</sub>	3.60	2.15		
$C_{10}$	3.02	3.13		
$C_{11}$	2.37	2.52		
$C_{12}^{+}$	23.69	57.86		
Other Properties				
$C_{12}^{+}$ mol wt (g/mol)	333	485		
C <sub>12</sub> <sup>+</sup> sp gr at 293 K	0.9640	1.0473		

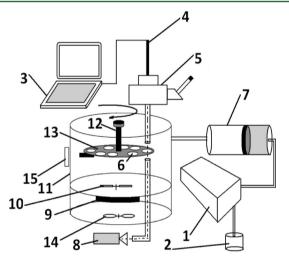


Figure 1. Schematic diagram of the experimental apparatus including (1) peristaltic pump, (2) distilled water reservoir, (3) computer, (4) CCD camera, (5) microscope, (6) sight glass, (7) piston—cylinder, (8) cold light source, (9) heater, (10) magnetic mixer, (11) high-pressure cell, (12) rotator, (13) metal disk, (14) fan, and (15) magnetic device.

To capture the microscopic images, a charge couple device (CCD) camera (IDS, UI-1485LE-C5 HQ $_1$  5.7 megapixels) was installed on the microscope. The resolution of the images was controlled by the operator, and they were stored to be analyzed by image processing software. This device was also able to capture video films during the deposition process, enabling further investigations of precipitation/deposition mechanisms. The geometric properties of asphaltene aggregation were determined by analyzing the captured images using Sigma Scan Pro 5 software. The pressure of the cell was maintained by a high-pressure liquid chromatography (HPLC) pump (Agilent Technologies 1200 series). The tests were carried out at four different pressures:  $P_1$  = 140 bar,  $P_2$  = 100 bar,  $P_3$  = 60 bar, and  $P_4$  = 30 bar. The temperature of the cell was adjusted using a highly accurate controlled heater, installed outside the cell.

**3.2. Experimental Procedure.** The experimental procedure used in this study is summarized as follows:

- 1. A specific amount of extracted asphaltene was dissolved in 1 L of toluene—heptane solution (Heptol) of 30 and 45 vol % heptane to mimic the crude. The solutions were mixed for 1 h, using a magnetic stirrer.
- The synthetic oil solution was poured into the cell, and the temperature was raised to the desired value through a number of steps, to avoid heater over load.
- The system pressure was increased gradually to 140 bar using the HPLC pump.
- 4. In the course of fixing the temperature and pressure of the cell, asphaltene particles are liable to deposit on the substrates. Therefore, the solution was stirred by an external magnet to remove any particles deposited during steps 1–3.
- 5. The solution was allowed to deposit asphaltene on the substrates for about 2 h for the system to reach to the equilibrium state. Still images were taken sequentially from the glass surfaces through the microscope, carefully monitoring the substrates from the side glass. The equilibrium state for these tests is considered to be achieved when no more asphaltene is deposited on the substrates, which is monitored through the cell.
- 6. The pressure was then reduced to 100 bar at constant temperature. Once more, the solution was stirred to remove all the asphaltene particles deposited on the glass surfaces from the previous steps. Consequently, deposited asphaltene on the substrate was carefully viewed and imaged for the new pressure at equilibrium conditions.
- 7. Step 6 was repeated for all desired pressures (60 and 30 bar).
- 8. The asphaltene deposited area and particle size distribution were measured by image analysis software.

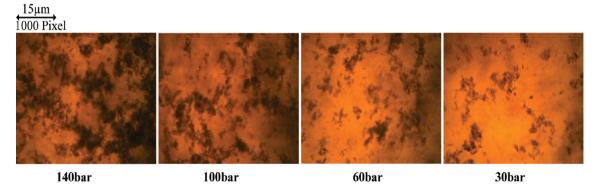


Figure 2. Kuh-e-Mond synthetic oil at 90 °C and different pressures, without CO<sub>2</sub> injection.

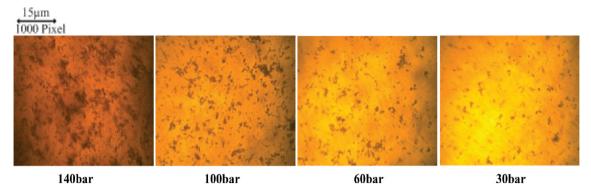


Figure 3. Gachsaran synthetic oil at 90 °C and different pressures, without CO<sub>2</sub> injection.

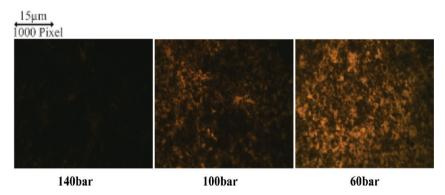


Figure 4. Kuh-e-Mond synthetic oil at 90 °C and different pressures, 10 mol % CO<sub>2</sub>.

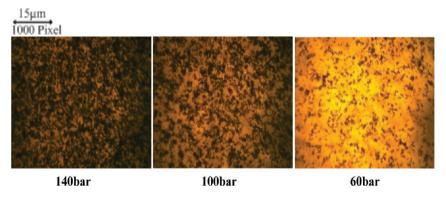


Figure 5. Gachsaran synthetic oil at 90  $^{\circ}$ C and different pressures, 10 mol % CO<sub>2</sub>.

The tests were repeated under different conditions using new synthetic oil samples.

9. To investigate the effect of carbon dioxide on the asphaltene deposition, CO<sub>2</sub> was injected into the solution through a piston—cylinder apparatus at different mole percents. All the above-mentioned steps were also repeated for the case of CO<sub>2</sub> injection.

#### 4. RESULTS AND DISCUSSION

The experimental procedure was performed for two synthetic oils containing asphaltene from two different fields. The still images taken at different pressures showed that, by increasing pressure, the amount of deposition on the glass surfaces was increased. Figures 2 and 3 show the results indicating the effects of pressure changes on asphaltene deposition.

Dark particles on the images are aggregated asphaltenes deposited on the substrates because asphaltene was the only heavy component dissolved in the synthetic oil used in this study. A comparison of the results clearly indicates that different asphaltene sources would affect deposition process, which will be discussed later. To investigate the effect of  $CO_2$  injection on the asphaltene deposition, 10 mol % of  $CO_2$  was injected into the cell. Still images that are taken at different pressures are shown in Figures 4 and 5. The tests were repeated using different mole percents of  $CO_2$ .

A comparison of the results shows that  $CO_2$  injection leads to an increase in asphaltene precipitation and by increasing the mole percent of injected  $CO_2$  more deposition has occurred, as shown in Figure 6.

The image for 20 mol % CO<sub>2</sub> is shown to be fully covered by asphaltene particles. The amount of deposited asphaltene is the most desired parameter in asphaltene studies. This parameter must be measured *in situ*, because removing the substrates from the cell causes major errors, as a result of the overall change in

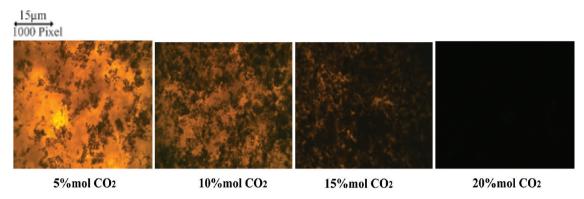


Figure 6. Effect of different CO2 mol % on deposition at 90 °C and 100 bar for the Kuh-e-Mond asphaltene sample.

experimental conditions. Therefore, to quantify the amount of deposited asphaltene under the right experimental conditions, the area of deposited asphaltene was calculated using image processing software. This is an indication of the amount of asphaltene deposited in this process.<sup>39</sup> The results are listed in Tables 3, 4, and 5.

Table 3. Area of Deposited Asphaltene Particles at 90 °C, without CO<sub>2</sub> Injection

	pressure (bar)			
	30	60	100	140
deposition area, Kuh-e-Mond asphaltene $(\mu m^2)$	2203.25	3147.5	7239.25	12590
deposition area, Gachsaran asphaltene $(\mu m^2)$	1573.75	2045.875	4721	10386

Table 4. Area of Kuh-e-Mond Asphaltene Deposition at 90 °C, with CO<sub>2</sub> Injection

	pressure(bar)			
	30	60	100	140
area of deposition, 5 mol % $CO_2$ $(\mu m^2)$	3777	5350.75	9442.5	20773
area of deposition, 10 mol % $CO_2 (\mu m^2)$	6295	7868.75	15737	27698
area of deposition, 15 mol % $CO_2(\mu m^2)$		20458	28957	30530
area of deposition, 20 mol % ${\rm CO}_2(\mu{\rm m}^2)$		31475	31475	31475

Table 5. Area of Gachsaran Asphaltene Deposition at 90 °C, with CO<sub>2</sub> Injection

	pressure (bar)			
	30	60	100	140
area of deposition, 5 mol % $CO_2 (\mu m^2)$	3147	4721.25	8498.25	15108
area of deposition, 10 mol % ${\rm CO_2}~(\mu{\rm m}^2)$	5665.5	6924	12590	22032
area of deposition, 15 mol % $CO_2 (\mu m^2)$		9442	19199	26124
area of deposition, 20 mol % $CO_2 (\mu m^2)$		25180	29901	31475

For the cases of 15 and 20 mol % CO<sub>2</sub> injection, the gas was released from the synthetic oil at a pressure of 30 bar. Subsequently, the miscibility condition was missed, and two separate phases were formed; therefore, they are not reported in Table 5.

The deposited asphaltene area was divided by the total surface of the image in order to become independent from the image surface. The results presented in Figures 7 and 8 are reported as

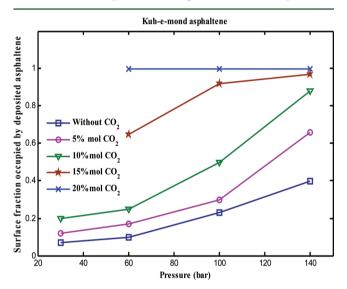


Figure 7. Surface fraction occupied by deposited as phaltene versus pressure, Kuh-e-Mond as phaltene at 90  $^{\circ}{\rm C}.$ 

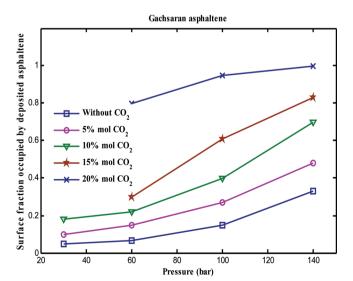


Figure 8. Surface fraction occupied by deposited asphaltene versus pressure, Gachsaran asphaltene at 90  $^{\circ}$ C.

"surface fraction occupied by deposited asphaltene", which it is defined as

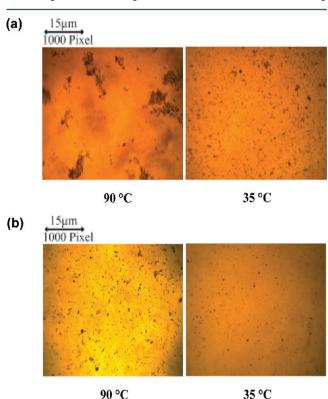
surface fraction occupied by deposited asphaltene

$$= \frac{\text{area of deposited asphaltene particles } (\mu \text{m}^2)}{\text{total surface of image } (\mu \text{m}^2)}$$

The total surface of each image is 31475  $\mu$ m<sup>2</sup>.

Therefore, the value of (1) on the *y*-axis refers to the state where all the surface of the glass substrates are covered by deposited asphaltene particles.

Moreover, asphaltene particle sizes at two different temperatures, (35 and 90  $^{\circ}$ C) at atmospheric pressure were analyzed. The images shown in Figures 9 (a, b) indicate that increasing



**Figure 9.** Effect of temperature on asphaltene at atmospheric pressure: (a) Kuh-e-Mond asphaltene and (b) Gachsaran asphaltene.

the temperature from 35 to 90  $^{\circ}$ C causes more aggregation of the small and separate particles of asphaltenes and results in asphaltene flocculation. The mean diameter and area of asphaltene particles are reported in Table 6 for both samples.

Table 6. Effect of Temperature on Asphaltene Particle Size

	35 (°C)		90 (°C)	
	Gachsaran	Kuh-e- Mond	Gachsaran	Kuh-e- Mond
mean diameter of deposited particles(µm)	0.18	0.209	0.402	2.973
mean area of deposited particles $(\mu m^2)$	1.023	1.193	2.765	8.997

An analysis of the results shows that the behavior of asphaltene precipitation from various oils is completely different. Kuh-e-Mond asphaltene particles have a high tendency to aggregate and create larger particles, while Gachsaran asphaltene particles

tend to deposit separately on the surface, and their tendency of aggregation is lower than that of the Kuh-e-Mond asphaltene particles. A detailed study of the effect of asphaltene structure on this process can be found in a paper by the authors.<sup>41</sup>

The ratio of *n*-heptane to toluene in synthetic oil is a very important parameter. Increasing this ratio causes high asphaltene flocculation in all pressure ranges, resulting in the glass surfaces being completely covered with asphaltene particles. As they are rendered totally dark, this problem prevents a clear view of the pressure effects on asphaltene precipitation.

Furthermore, reducing this ratio caused the asphaltene particles to appear as small and separated particles, which did not flocculate in all pressure ranges; therefore, the pressure effect could not be seen visually.

The proper ratio is the minimum ratio of heptane to toluene in which we are able to visualize the asphaltene flocculation (onset of flocculation).<sup>42</sup> By performing several tests at different ratios, the proper ratio for two synthetic oils was achieved. Appropriate volume ratios of *n*-heptane to toluene for the Kuh-e-Mond and Gachsaran asphaltene types are 30:70 and 45:55, respectively.

As seen in Figure 10, a ratio of 30:70 is not proper for Gachsaran asphaltene, which clearly shows the different

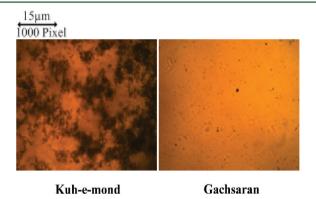


Figure 10. Ratio of *n*-heptane to toluene, 30:70. 140 bar, 90 °C.

behavior of asphaltenes. In order to determine this difference better, a new parameter, potential of deposition was defined:

potential of deposition

= surface fraction occupied by deposited asphaltene at 60 bar,90°C/proper volume ratio of *n*-heptane to toluene

The ratio of *n*-heptane used as the antisolvent agent to prepare the synthetic oil for Gachsaran asphaltene is more than that used for the Kuh-e-Mond example; however, the potential of deposition in Kuh-e-Mond is about three times greater than that in Gachsaran, as shown in Table 7.

Table 7. Potential of Deposition for Two Asphaltene Types

	asphaltene type		
	Kuh-e-Mond	Gachsaran	
potential of deposition	0.23	0.079	

A higher value of this quantity initiates a greater tendency of the asphaltene to flocculate, making larger particle sizes, which

are more appropriate for deposition. This specific behavior in Kuh-e-Mond asphaltene is related to its structure.

The different molecular structure of asphaltenes could be one of the reasons to explain the difference in deposition behavior. Our previous study on Kuh-e-Mond and Gachsaran asphaltenes<sup>41</sup> showed that Kuh-e-Mond asphaltene molecules have more aromatic rings with more hydrocarbon chains, compared to Gachsarn asphaltene molecules. It seems that larger asphaltene molecules with more chains and aromatic rings enhance attraction and interaction. The greater the number of chains in the structure, the greater the possibility of increased contacts with the other molecules and the creation of larger asphaltene aggregations, compared to the smaller molecules.

#### 5. CONCLUSIONS

A high-pressure cell and image processing technique was used to visualize the asphaltene deposition process. Experimental results of asphaltene deposition at different pressures, temperatures, and  $\rm CO_2$  mol % for two different crude oils resulted in several conclusions, as follows.

- 1. As the pressure increases, the area of deposition (which is seen at higher pressures), the asphaltene precipitation, and deposition all increase.
- 2. The effect of CO<sub>2</sub> on asphaltene deposition was investigated, showing that CO<sub>2</sub> injection increases asphaltene deposition in all pressure ranges, as compared to tests without CO<sub>2</sub> injection.
- According to the results, by increasing the mole percent of CO<sub>2</sub> from 5 to 20%, the area of deposited asphaltene was increased at all pressure ranges investigated in this study, from 30 to 140 bar.
- 4. The effect of temperature (from 35 to 90 °C) on asphaltene particle size is that, by increasing the temperature, asphaltene particles tend to flocculate and make larger particles. This effect could be critical, especially during thermal EOR methods if the crude is subjected to asphaltene precipitation.
- 5. A new parameter to describe and quantify the potential of deposition was defined. Higher values of this parameter show that specific types of oil may have greater tendency to deposit asphaltene, compared to the other crudes. This is attributed to the specific structure of asphaltene in the crude oil. According to this parameter, we were able to predict if a specific oil reservoir would encounter the problem of asphaltene precipitation and therefore increase the chance of formation damage.
- 6. The differences in asphaltene molecular structures could be one of the main factors affecting asphaltene aggregation, deposition, and size distribution.

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