Application of Carbon Nanocatalysts in Upgrading Heavy Crude Oil Assisted with Microwave Heating

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ABSTRACT: Heavy crude oil can be upgraded to lighter oil using several techniques. However, current methods usually require high temperatures, long reaction duration, and cause serious environmental pollution. This study shows that by using carbon nanocatalysts, heavy crude oil can be efficiently upgraded to lighter oil at a relatively low temperature of about 150 °C. The temperature of crude oil was increased by microwave heating. The technique proposed in this study has the following advantages: (1) great viscosity reduction ratio over 96%, (2) short reaction time (less than 1 h), (3) low required temperature, and (4) long viscosity regression time. Because of these advantages, upgrading heavy crude oil to light oil can be cheaper and more environment-friendly.

KEYWORDS: Carbon nanocatalysts, Particle size, Heavy crude oil upgrading, Microwave heating

Crude oil is one of the most important energy sources and chemical feed stocks1,2 and will remain to be important for many years to come. Heavy crude oil, whose API (American Petroleum Institute) gravity is generally less than 20, has a high viscosity and high solidification point. Currently, thermal recovery techniques (e.g., steam stimulation and steam flooding) are widely used in heavy crude oil production. Problems associated with these techniques, including high requisite temperatures, long reaction periods, and rapid viscosity regression (viscosity increases with time), could not be resolved in a short timeframe.2

It is believed that the high viscosity of heavy crude oil is due to the existence of internal macromolecular compounds, such as asphaltene with resin. Therefore, breaking down larger molecules into smaller ones is necessary for reducing the viscosity of heavy crude oil.3 At present, microwave energy has been of interest in many fields of petroleum industry.3 The main advantage of utilizing microwave energy over conventional thermal processing is the fundamentally different way energy is transferred from the source to the sample. By directly delivering energy to microwave-absorbing materials, complications such as rapid heat-up periods and energy lost to the system environment can often be avoided. Furthermore, the penetrating capacity of microwaves allows volumetric heating of samples.3

In general, heavy crude oil is a poor receptor of microwave energy and therefore cannot be heated directly to the required high temperatures of the cleavage reaction. Thus, if heavy crude oil could be mixed with some kind of effective catalytic materials, such as carbon5,6 or other metal oxides,7,8 which have great microwave-absorbing properties, the upgrading of heavy crude oil may be realized efficiently.2 In the past, metal and metal oxide catalysts9,10 were widely used for enhanced heavy crude oil recovery with or without combining microwave radiation.11-16 Unfortunately, utilizing metallic catalysts can inevitably contaminate the oil samples. This can be avoided with the use of carbon catalysts. The dielectric constant of carbon is relatively high and its electron density can vary in a wide range, which means carbon is an effective receptor of microwave energy. Few studies have been conducted on the efficacy of carbon nanomaterials as catalysts for heavy crude oil cracking. Therefore, using the nano carbon particles as nanocatalysts becomes one of our options. Recent developments of all types of carbon nanomaterials offer exciting opportunities for this purpose.5,6,17,18

In the chemical composition of the heavy crude oil molecules, S, O, and N, are heteroatoms.19 Because the bond energy and thermal stability of C−C and C−H bonds are too high for them to be broken, the main mechanism for upgrading heavy crude oil is to break groups containing heteroatoms, such as C−S bonds, etc. (see Scheme 1). The bond energy of C−S bonds is the smallest among heavy crude oil molecules.20 As a result, the organic sulfur existing in the heavy components of heavy crude oil is the key substance during the reaction of catalytic cracking. Traditional catalyst particles are relatively large with limited surface area, so their interaction with many C−S bonds may be difficult. Nanocatalyst particles have a much...
larger surface-to-volume ratio, so it may be easier for them to interact with the C=S bonds and eventually break these C=S bonds to reduce the viscosity of heavy oil (as shown in Scheme 1).

In the reactions of catalytic cracking, some active fragments will be produced in heavy crude oil samples. Active groups, such as hydrogen, can be used to restrain the polymerization of active fragments in order to realize the irreversible cleavage of heavy oil. In this case, the addition of a small amount of hydrogen donor can undoubtedly promote the effect of viscosity reduction.21,22

Previous studies20-23 show that the simultaneous use of a hydrogen donor and catalyst has a synergistic effect on cracking heavy oil. When a hydrogen donor is nonexistent, the activated carbon chains may conduct a polymerized reaction as follows:

\[
C + C \rightarrow C - C
\]  

(1)

Where C is the activated carbon chain formed in the cracking reaction. When adding hydrogen donor together with carbon nanocatalyst, the modified reaction equation is expressed as follows:

\[
\begin{align*}
C + H - E - H & \quad \text{carbon nanocatalyst} \rightarrow CH + E - H \\
C + E & \quad \text{carbon nanocatalyst} \rightarrow CH + \text{aromatic HC} \\
C + E - H & \quad \text{carbon nanocatalyst} \rightarrow C - EH
\end{align*}
\]

(2) (3) (4)

where E is the hydrogen donor. In this equation, one can see that the added hydrogen donor and carbon nanocatalyst may effectively decrease the polymerized reaction, form small molecules of chain and aromatic hydrocarbons, and reduce the viscosity of heavy oil more permanently.

In this study, two types of representative carbon nanocatalysts together with other two ordinary catalysts (graphitic, micrometer-sized) were chosen to conduct comparative experiments. In order to find the difference in microscopic or nanoscopic structures of the catalyst particles, the TEM images of the four catalysts have been obtained and are shown in Figure 1. Catalysts A (Figure 1a) and B (Figure 1b) are sub-100 nm carbon black nanoparticles with many graphitized carbon layers packed together but not in high enough order to form crystalline graphite. Such particles have high enough conductivity to be commonly used as conductive additives to enhance the conductivity in battery electrodes. These nanoparticles still have significant fraction of sp² carbon bonding, which is more active in catalysis. Catalysts C (Figure 1c) and D (Figure 1d) are multiple micrometer-sized graphite particles and their layered morphology can be seen. Graphite has high electrical conductivity but the basal plane is usually not catalytically active. The edge plane might provide catalysis sites but have a much smaller surface area.

With the structural information, it is clear that nanocatalysts A and B might provide better microwave-absorbing capability and better catalytic activity compared to the larger size catalysts C and D. Eventually nanocatalysts A and B might result in a greater reduction of the viscosity of heavy crude oil by upgrading.

Heavy crude oil samples used in this study were taken from an oilfield in Xinjiang, China. Table 1 lists the preparation information on heavy crude oil samples for the cracking experiments. On the basis of the results of previous studies, the concentrations of catalysts and hydrogen donor were set at 0.5 and 1 wt %, respectively.9,20,22

A Galanz G8023YSL-V1 800W microwave oven that operates at 2450 MHz was used during the process of microwave heating (see the Supporting Information for more details, including the entire experimental apparatus and procedures). After the cracking experiments, the rheological properties of oil samples were measured and observed continuously. Furthermore, the group compositions of oil samples were measured before and after the cracking experiments.24 Viscosity measurements were conducted using a viscometer (Anton Paar MCR-301).

Experiments for upgrading heavy crude oil samples were conducted using carbon catalysts with four different particle sizes (see Table 1). The results are presented and analyzed as follows. Figure 2 shows the heavy crude oil samples (no. 1) before and after upgrading by Catalyst A (21.0 nm diameter carbon black). One can see that the heavy crude oil sample with extremely high viscosity was almost in solid state before cracking and became a liquid with much lower viscosity after cracking at room temperature. The air-oil surface tilted, while the tube was tilted. This implies that the solidlike heavy crude oil could flow easily after upgrading by the nanocatalyst, as shown in Figure 2 (panels b-f).

One of the great challenges in upgrading heavy crude oil is viscosity regression, and the viscosity might increase close to the original value in a few days after the cracking tests.19-21,24,26 Considering the above problem, the oil mobility was observed at different time periods after the upgrading of heavy oil, and the results are shown in Figure 2. One can see that the oil mobility could be maintained over 20 days, which is a significant improvement compared with the previous results reported by Yu and Li.21

The efficacy of the nano upgrading technique for heavy oil developed in this study can be qualitatively confirmed by the significant change in oil mobility and viscosity before and after the cracking experiments. Furthermore, the fact that oil samples could maintain continuous mobility for over 20 days has also demonstrated one of the advantages of this method for upgrading heavy crude oil. The quantitative data in viscosity reduction after cracking tests will be presented and analyzed in the following section.

Figure 3 shows the relationships between viscosity and shear rate of the four oil samples after the cracking tests as well as the original heavy crude oil sample without upgrading at 30 °C. Because all of the heavy crude oil samples were obtained from the same container, the relationships between viscosity and shear rate of the four oil samples (nos. 1-4) before upgrading were the same as those of the sample labeled “Before upgrading” in Figure 3. As seen from the figure, the crude oil
sample 1 added with catalyst A, followed by sample 2 added with catalyst B, had the biggest reduction in viscosity after upgrading. The effects of catalysts C and D on viscosity reduction of the heavy crude oil are relatively poor.
The heavy crude oil samples used in this study, as in most of the cases, are non-Newtonian, and viscosities change with shear rates (see Figure 3). So, it is necessary to choose a fixed shear rate in order to compare the viscosity reduction ratio (the viscosity of oil after upgrading divided by the viscosity of original crude oil) by upgrading. The shear rate was set at 10 s$^{-1}$ because this value closely mimics the shear rate near the wellbore where crude oil is being produced. The viscosity data of the five heavy crude oil samples (including the original oil sample) at a shear rate of 10 s$^{-1}$ are shown in Figure 4a. The viscosity reduction ratios of the four oil samples after upgrading are shown in Figure 4b. One can see that the viscosity reduction ratio of the oil sample added with catalyst A could reach over 96%, which was the most significant in all cases studied. The viscosity reduction ratio by catalyst B was about 83%, while the viscosity reduction ratios by catalysts C and D were 20% and 5%, respectively.

It is widely believed that the breaking of long carbon chains in heavy crude oil contributes to viscosity reduction by upgrading. In order to provide evidence, the group compositions of the heavy crude oil samples before and after upgrading were measured using a column chromatography technique. The results are listed in Table 2.

For the heavy oil sample 1 added with catalyst A, the light components (contents of saturated and aromatic hydrocarbon) increased by approximately 11% after upgrading while the heavy components (the contents of resin and asphaltene) decreased by about 5%. The fact that the percentage of the light components has been increased significantly after upgrading implies that the long carbon chains in heavy crude oil were broken by catalyst A. The viscosity reduction ratio by catalyst B was about 83%, while the viscosity reduction ratios by catalysts C and D were 20% and 5%, respectively.

<table>
<thead>
<tr>
<th>oil samples</th>
<th>catalysts</th>
<th>particle size of catalysts (μm)</th>
<th>concentration of catalysts (wt %)</th>
<th>concentration of hydrogen donor (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>21.0 nm</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>B</td>
<td>70.0–80.0 nm</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>5.8–7.1 μm</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>D</td>
<td>40.0–51.5 μm</td>
<td>0.5</td>
<td>1</td>
</tr>
</tbody>
</table>

Note that all of the heavy crude oil samples were obtained from the same container and had the same rheological properties before upgrading experiments. Numbering them differently was to reflect the different catalysts added in these crude oil samples.

Figure 2. Heavy crude oil samples (no. 1) (catalyst A, 21.0 nm diameter carbon black) before and after cracking. (a) Before cracking: the viscosity of the heavy crude oil sample was extremely high and was in the solid state (the air–oil surface did not move when the tube was tilted) at room temperature. (b–f) After cracking: the air–oil surface tilted while the tube was tilted. The solidlike heavy oil became a liquid with a much lower viscosity and could flow easily under room temperature at different times (4, 8, 12, 16, and 20 days, respectively) after upgrading.

Figure 3. Viscosity at a temperature of 30 °C vs shear rate of the five heavy crude oil samples with and without upgrading. Red □ represent all of the heavy crude oil samples (nos. 1–4) before upgrading; blue ■ represent crude oil sample 1 added with catalyst A (particle size: 21.0 nm) after upgrading; red △ represent crude oil sample 2 added with catalyst B (particle size: 70.0–80.0 nm) after upgrading; brown ◆ represent crude oil sample 3 added with catalyst C (particle size: 5.8–7.1 μm) after upgrading; green ○ represent crude oil sample 4 added with catalyst D (particle size: 40.0–51.5 μm) after upgrading. Catalyst A with the smallest particle size had the greatest reduction of viscosity from upgrading, followed by catalysts B, C, and D.
broken into short chains with smaller molecular weight. In accordance with the results shown in Figures 3 and 4, catalyst A was the best among the four catalysts in terms of increasing light components and decreasing heavy components (i.e., breaking the long carbon chains).

What is the mechanism behind the different effects of upgrading heavy crude oil using the four different catalysts? The physical differences among the four different catalysts are the size and the microscopic (or nanoscopic) structures of the particles (see Table 1). Catalysts A and B had nanosized particles, while catalysts C and D had the particle size in the range of micrometers. In accordance with the results shown in Figure 5, the catalysts with nanosized particles are much better at reducing the viscosity than those whose particle size is on the order of micrometers. The catalyst with the smallest size (21.0 nm) of particles, catalyst A, had the greatest viscosity reduction ratio. On the basis of the above experimental results, particle size and specific area do matter for upgrading heavy crude oil (see Figure 5).

We speculate that there may be two mechanisms associated with the above size effect on upgrading heavy crude oil to reduce viscosity significantly. One may be the heat enhancement, and the other may be the accessibility enhancement. The surface area, also the contacting area with heavy oil, of catalyst particles with smaller size is greater in the case of the same amount or concentration in the oil. The free electron is the main reason to contribute the microwave absorption. For the same weight percentage of carbon particles, smaller size particles allow more microwave penetration compared to the larger size particles. Therefore, the microwave absorption efficiency is expected to be more on the per weight basis, leading to the better heat production. Consequently, the temperature of the heavy oil after heated by the microwave might be higher. This has been proven by the experimental

Table 2. Group Compositions of the Five Heavy Crude Oil Samples

<table>
<thead>
<tr>
<th>oil samples</th>
<th>saturated HC (%)</th>
<th>aromatic HC (%)</th>
<th>resin (%)</th>
<th>asphaltene (%)</th>
<th>light component (%)</th>
<th>heavy component (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>original sample</td>
<td>24.05</td>
<td>31.62</td>
<td>13.78</td>
<td>24.05</td>
<td>55.67</td>
<td>37.83</td>
</tr>
<tr>
<td>sample 1, (catalyst A)</td>
<td>30.75</td>
<td>35.25</td>
<td>14.25</td>
<td>19.50</td>
<td>66.00</td>
<td>32.75</td>
</tr>
<tr>
<td>sample 2, (catalyst B)</td>
<td>30.15</td>
<td>33.68</td>
<td>15.44</td>
<td>18.53</td>
<td>63.83</td>
<td>33.97</td>
</tr>
<tr>
<td>sample 3, (catalyst C)</td>
<td>30.26</td>
<td>31.05</td>
<td>17.89</td>
<td>18.95</td>
<td>61.31</td>
<td>36.84</td>
</tr>
<tr>
<td>sample 4, (catalyst D)</td>
<td>30.08</td>
<td>30.48</td>
<td>17.53</td>
<td>19.32</td>
<td>60.56</td>
<td>36.85</td>
</tr>
</tbody>
</table>

*Note that because of the existence of nonhydrocarbons reserved in the column when using column chromatography to conduct group composition of heavy crude oil samples, the sum of the percentage of the light and heavy components is not 100%.

Figure 4. (a) Comparison of viscosity at a temperature of 30 °C and a shear rate of 10 s⁻¹ for the five heavy crude oil samples with and without upgrading. (b) Viscosity reduction ratios by the four catalysts (30 °C, 10 s⁻¹). Catalyst A with the smallest particle size had the biggest viscosity reduction ratio by upgrading, followed by catalysts B, C, and D with greater particle sizes.

Figure 5. (a) Viscosity reduction ratio vs particle size for the four catalysts. (b) Viscosity reduction ratio vs specific area for the four catalysts. The viscosity reduction ratio by upgrading, to some extent, is inversely proportional to the particle size and the specific area of the catalysts.
temperature data shown in Figure 6. The temperature of oil sample 1 with the smallest catalyst particles (21.0 nm, catalyst A) raised the fastest and reached the highest temperature of about 142 °C among the four samples; dashed red line, crude oil sample 2 with the second smallest catalyst particles (70.0–80.0 nm, catalyst B) reached the second highest temperature of 134 °C; solid red line, crude oil sample 3 with the catalyst particle size of micrometers (5.8–7.1 μm, catalyst C) reached a temperature of 125 °C; solid blue line, crude oil sample 4 with the particle size of micrometers (40.0–51.5 μm, catalyst D) reached a temperature of about 107 °C. The maximum temperature reached during upgrading played an important role in reducing the viscosity of the heavy crude oil (see Figure 4).

In accordance with the above analysis and discussion, the small size, the physical and chemical properties, and the special structures of the nanoparticles may be the mechanisms that catalyst A served as the best catalyst in upgrading the heavy crude oils to light oils with less heavy components and much lower viscosity.

In summary, our experimental results show that the catalyst particle size and nanostructures do matter for upgrading heavy crude oil. The carbon nanocatalyst with a particle size of 21.0 nm could reduce the viscosity of heavy crude oil to less than 4% of the original value at a temperature of less than 150 °C, assisted with microwave heating. With further optimization of the associated parameters, the method presented in this study could offer a realistic alternative to the current approaches to upgrading heavy crude oils.

ASSOCIATED CONTENT
S Supporting Information
Entire experimental apparatus and detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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