7-3-2 攪拌反応器を用いたオイルスラッジとオイルスラッジ焼却

灰の混合熱分解

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Pyrolysis of Oil Sludge with Oil Sludge Ash Additive Employing a Stirred Tank Reactor

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SUMMARY
In this study, pyrolysis of oilfield sludge from Shandong Province, China with oil sludge ash additive was conducted using a stirred tank reactor. The effect of the pyrolysis conditions, such as the temperature, the stirring rate and the use of additive on the recovery ratio and the quality of the oil product were investigated. The results reveal that the recovery ratio of the oil product was improved by increasing the stirring rate and the addition of oil sludge ash. The carbon residue of the oil product from the pyrolysis with the oil sludge ash additive is much lower than the oil product of the pyrolysis with the quartz sand as the additive. The increasing of the oil recovery ratio was considered to be mainly contributed by the physical effects of the oil sludge ash additive. The decreasing of carbon residue value was due to the chemical effects of the metal oxides in the oil sludge ash. To determine the effects of the main metal oxide compounds of the oil sludge ash, a series of pyrolysis experiments of oilfield sludge with SiO2, Al2O3, Fe2O3, and CaO were carried out. Then, the chemical characterization of a part of the pyrolytic oil was measured by FT-IR, GC-MS, and NMR analysis to investigate which chemical routes or additives in the pyrolysis process lead to the change of the oil quality.

[1] INTRODUCTION
Oil sludge include a wide variety of reddish brown to black petroleum hydrocarbons of liquid to semisolid, viscous to brittle character that can occur wherever exploitation, transportation and refining processes of petroleum industry. It is a complex mixture of petroleum and water with mineral matter contents that exceed 30% by weight, and is comprised with abundant toxic substances from the most carcinogenic polycyclic aromatic to heavy metals, and even to radioactive material. It is estimated that more than 60 million tons of oil sludge can be produced every year and more than 1 billion tons of oil sludge has been accumulated worldwide [1]. On the other hand, oil sludge is also a potential recycling resource for its high heating value. So the conversion of the stored energy of oil sludge to various fuel sources for power plant or engine has been recognized as an attractive approach.

Oilfield sludge, which is also called as hydrocarbon contaminated soil, is one of the main oily wastes generated from the upstream of petroleum industry. The oilfield sludge used in this study was sampled from Shandong Province, China.

In our previous study, we have used a bench-scale fixed bed reactor to carry out the pyrolysis experiment of oil sludge with oil sludge ash. Although, the chemical effects or the catalytic effects of the oil sludge ash were confirmed, the increase of the oil recovery ratio was limited, and the action mechanism of the oil sludge ash was not determined on a chemical level.

In the present study, a stirred tank reactor was employed to improve the mixing of the oil sludge with the additive. The action mechanism of the oil sludge ash was mapped out with the assistance of FT-IR, NMR, and GC-MS analysis tools.
[2] EXPERIMENT AND METHOD

Table 1 shows the results of the proximate analysis and the ultimate analysis of the oil sludge. The pyrolysis experiment was conducted using the self-designed stainless steel stirred tank reactor coupled with the condenser made of the same material. 200 g of oilfield sludge was mixed with 0-400 g of the additive, and then the mixture was placed in the reactor. N₂ carrier gas with the flow rate of 100 ml/min was passed through the pyrolysis and reforming reactors before the experiments for 1 hour, to remove the air in the reactors. After the air in the reactors was replaced with N₂, the motor of the mixer blade was started. When the stirring rate of the motor was stable, the reactor was heated from 30°C to the desired experimental temperature (450-600°C) at the heating rate of 30°C/min, and held at this temperature for 1 hour.

Table 1 Proximate and ultimate analysis of the oilfield sludge

<table>
<thead>
<tr>
<th>Proximate analysis (Wt% wet basis)</th>
<th>Moisture</th>
<th>Volatile matter</th>
<th>Ash</th>
<th>Fixed carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate analysis (Wt% dry basis)</td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>S</td>
</tr>
<tr>
<td></td>
<td>3.95</td>
<td>20.02</td>
<td>75.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20.77</td>
<td>3.44</td>
<td>0.27</td>
<td>0.58</td>
</tr>
</tbody>
</table>

a: By difference

[3] Results and Discussion

The recovery ratio of the oil product in this study is expressed as:

\[
\text{Oil product yield (wt%)} = \frac{\text{Recovery ratio} \times \text{Oil content of oil sludge} \times \text{oil sludge yield (wt%)}}{100}
\]

The effect of the stirring rate on the recovery ratio of the oil product at the final temperature of 450°C is presented in Fig.1. The oil recovery ratio increased from 46.5% to 55.7% at the stirring speed of 0 to 5rpm. This might be due to the heat transfer improvement and the even heating of the material. However, a decrease of the oil recovery ratio appeared when the stirring speed exceeded 5rpm. It is indicated that an excessive mixing might go against the oil recovery during the pyrolysis process.

In Fig.2, the carbon residues of the oil product under different experiment conditions are shown by the line graphs whose Y-axis is on the right side. The bars whose Y-axis on the left side shows the boiling point range distributions of the oil product. Although the distillation characteristics of the oil products from the pyrolysis with the oil sludge ash and the quartz sand additive are similar, the carbon residue of the case with the oil sludge ash (0.9%) is much lower than the quartz sand case (3.62%). Therefore, the addition of the oil sludge ash is considered to affect the oil product quality on the chemical level.

![Figure 1 Effect of the stirring rate on the recovery ratio of the oil product at 30°C/min heating rate in 30-450°C](image1)

![Figure 2 Distillation characteristics and carbon residues of oil product with the stirring speed of 5rpm and at the final temperature of 450°C (Raw oil: Extracted from the oil field sludge by the soxhlet extraction)](image2)

[4] CONCLUSIONS

The results of this study indicate that the optimum stirring rate for oil recovery is 5rpm. The addition of the oil sludge ash can reduce the carbon residue of the oil product.