The Effect of Minerals on Transformation of Sulfur During Pyrolysis and Partial Gasification

LI Bin, DU Xiaoru, LI Qingfeng, ZHANG Jiemin, WANG Yang
(Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China, E-mail: libin@sxic.ac.cn)

Abstract: In this study, the effect of acid treatment of Yima coal on predesulfurization during pyrolysis and partial gasification was investigated. The coal was treated with HCl, HCl+HF, and HCl+HNO₃ solution, in which different minerals were eliminated. The whole process could be divided into pyrolysis and partial gasification. In pyrolysis process, the evolution of H₂S and COS show two peaks, which were 450 ºC and 600 ºC respectively. At high temperature, the amount of H₂S evolution from acid treated coal was markedly increased compared to the raw coal through the elimination of minerals. In the case of HCl+HNO₃ treated sample, the H₂S evolution in the low temperature region, below 500 ºC, was reduced and the COS evolution in higher temperature region, above 500 ºC, was increased by the chemical oxidation. In the partial gasification process, the sulfide sulfur removal of acid treated coal char was increased, reached about 100% at 800 ºC. The maximum of total and sulfide sulfur removal of parent coal char were 46.39% and 52.97% at 700 ºC. Compared to acid treated coal char, the effect of alkaline minerals for fixing sulfur was strengthened with increasing the temperature. The organic sulfur of acid treated coal char was released with carbon gasification, and the value could be constant.

Keywords: sulfur; pyrolysis; partial gasification; acid treatment; minerals; predesulfurization

1.0 Methods

1.1 Reaction conditions

230μm

1.2 Reactor

1.3 Effects of acid treatment on sulfur content

1.4 Effects of acid treatment on pyrolysis and gasification
Table 1  The proximate and ultimate analysis of Yima coal and acid-treated coals

<table>
<thead>
<tr>
<th></th>
<th>M_d</th>
<th>N_d</th>
<th>V_d</th>
<th>S_d</th>
<th>C_d</th>
<th>H_d</th>
<th>O_d (diff.)</th>
<th>N_d</th>
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</thead>
<tbody>
<tr>
<td>HCl</td>
<td>7.03</td>
<td>13.25</td>
<td>32.88</td>
<td>3.91</td>
<td>57.75</td>
<td>4.20</td>
<td>13.07</td>
<td>0.79</td>
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<tr>
<td>HCl-HF</td>
<td>0.00</td>
<td>9.24</td>
<td>32.75</td>
<td>3.56</td>
<td>64.8</td>
<td>4.91</td>
<td>16.7</td>
<td>0.79</td>
</tr>
<tr>
<td>HCl-HNO_3</td>
<td>0.00</td>
<td>5.23</td>
<td>35.40</td>
<td>4.28</td>
<td>66.2</td>
<td>5.20</td>
<td>18.21</td>
<td>0.88</td>
</tr>
<tr>
<td>HCl-HNO_3</td>
<td>0.00</td>
<td>6.73</td>
<td>36.69</td>
<td>2.85</td>
<td>61.4</td>
<td>5.10</td>
<td>23.48</td>
<td>0.84</td>
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Table 2  The sulfur forms of Yima coal and acid-treated coals

<table>
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<tr>
<th></th>
<th>S_{cal}</th>
<th>S_{act}</th>
<th>S_{act-cal}</th>
<th>S_{act-cal}'</th>
<th>N_d</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>3.91</td>
<td>0.00</td>
<td>2.88</td>
<td>0.00</td>
<td>1.03</td>
</tr>
<tr>
<td>HCl-HF</td>
<td>3.56</td>
<td>0.00</td>
<td>2.40</td>
<td>0.00</td>
<td>1.16</td>
</tr>
<tr>
<td>HCl-HNO_3</td>
<td>4.01</td>
<td>0.00</td>
<td>2.91</td>
<td>0.00</td>
<td>1.10</td>
</tr>
<tr>
<td>HCl-HNO_3</td>
<td>2.85</td>
<td>0.00</td>
<td>1.31</td>
<td>0.00</td>
<td>1.54</td>
</tr>
</tbody>
</table>

Table 3  The composition of ash in Yima coal

<table>
<thead>
<tr>
<th></th>
<th>SiO_2</th>
<th>Al_2O_3</th>
<th>Fe_2O_3</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO_2</th>
<th>S_0</th>
<th>K_2O</th>
<th>Na_2O</th>
<th>P_2O_5</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>15.71</td>
<td>9.53</td>
<td>39.50</td>
<td>17.61</td>
<td>1.72</td>
<td>1.04</td>
<td>11.30</td>
<td>0.84</td>
<td>1.98</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Fig. 1  The schematic diagram of fixed-bed apparatus

2. H2S + COS → HCl + HCl-HF + HCl-HNO_3

2.1  H2S + COS → HCl + HCl-HF + HCl-HNO_3

2.1.1  H2S + COS → HCl + HCl-HF + HCl-HNO_3

2.1.2  H2S + COS → HCl + HCl-HF + HCl-HNO_3
HCl·HNO₃
HNO₃
H₂S
Calkins等
0.500℃~700℃
0.700℃~900℃
HCl·HCl-HF
H₂S
COS
HCl·HNO₃
HNO₃
COS

Fig. 2 H₂S evolution vs. temperature in pyrolysis

Fig. 3 COS evolution vs. temperature in pyrolysis

2.1.2

Fig. 4 Sulfur removal and carbon conversion of different samples in pyrolysis
Fig. 5 Sulfur removal and carbon conversion of samples vs. temperature in partial gasification

Fig. 6 Sulfur forms of different treated samples vs. temperature in partial gasification
3

(1) \( \text{H}_2\text{S} \rightarrow \text{COS} \)
\( \rightarrow \text{HNO}_3 \)
\( \rightarrow \text{NO}_2 \)
\( > 700 \ ^\circ\text{C} \)

(2) \( \text{600} \ ^\circ\text{C} - \text{900} \ ^\circ\text{C} \)
50\% - 80\%
800 \ ^\circ\text{C} \)
52.97\%
700 \ ^\circ\text{C} \)
46.39\%
5.22 \%
900 \ ^\circ\text{C} \)
19.81\%
28.99\%

\[ \begin{align*}
\end{align*} \]