DESULFURIZATION OF COAL THROUGH PYROLYSIS IN A FLUIDIZED-BED REACTOR

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Introduction

Sulfur in coal has greatly limited its utilization and much attention has been paid to the air pollution caused by combustion of coal in recent years. Sulfur removal is one of the most important problems in coal utilization. So far, many methods have been developed to either remove sulfur from the coal, or from the flue gas. Among these methods, pyrolysis, an intermediate stage in various conversion processes such as liquefaction, gasification and combustion, is an important method of sulfur removal from coal prior to combustion because its cost is relatively low and can remove both inorganic and organic sulfur. The sulfur removal from coal through pyrolysis depends on many factors, such as coal rank, the quantity of sulfur and the sulfur forms distribution in the coal, the quantity and kind of mineral matter, the conditions in which the process is conducted. In this aspect, many important conclusions have been obtained, which are mainly based on studies in a fixed-bed reactor. In the present study, Yima (YM) and Datong(DT) coal were pyrolyzed in a fluidized-bed reactor in inert atmosphere to examine the sulfur removal efficiency.

Experimental

Coal samples

Raw coal with 0.15-0.25mm was washed by HCl / HF to remove minerals. Demineralized coals were further washed by CrCl3 in order to remove pyrite. Table 1 and Table 2 show proximate, ultimate and sulfur form analysis of the samples.

Table 1 Proximate and ultimate analysis of samples w/%

<table>
<thead>
<tr>
<th>Samples</th>
<th>M_daf</th>
<th>A_daf</th>
<th>V_daf</th>
<th>C_daf</th>
<th>H_daf</th>
<th>N_daf</th>
<th>S_daf</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM</td>
<td>8.82</td>
<td>17.3</td>
<td>40.1</td>
<td>78.1</td>
<td>3.90</td>
<td>0.86</td>
<td>0.60</td>
</tr>
<tr>
<td>YM-ash</td>
<td>3.31</td>
<td>2.86</td>
<td>37.7</td>
<td>74.7</td>
<td>5.29</td>
<td>0.85</td>
<td>0.51</td>
</tr>
<tr>
<td>YM-p</td>
<td>2.38</td>
<td>1.45</td>
<td>37.6</td>
<td>73.6</td>
<td>5.18</td>
<td>0.81</td>
<td>0.61</td>
</tr>
<tr>
<td>DT</td>
<td>3.56</td>
<td>7.93</td>
<td>36.5</td>
<td>82.8</td>
<td>4.88</td>
<td>1.02</td>
<td>0.40</td>
</tr>
<tr>
<td>DT-ash</td>
<td>2.16</td>
<td>0.91</td>
<td>28.6</td>
<td>83.3</td>
<td>4.55</td>
<td>0.58</td>
<td>0.37</td>
</tr>
<tr>
<td>DT-p</td>
<td>2.51</td>
<td>0.65</td>
<td>28.4</td>
<td>83.4</td>
<td>4.59</td>
<td>0.69</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 2 Analysis results of sulfur forms in samples w/%

<table>
<thead>
<tr>
<th>Samples</th>
<th>S_o,ad</th>
<th>S_t,ad</th>
<th>S_a,ad</th>
<th>S_d,ad</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM-ash</td>
<td>1.95</td>
<td>1.42</td>
<td>0.08</td>
<td>0.45</td>
</tr>
<tr>
<td>YM-p</td>
<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>DT-ash</td>
<td>1.04</td>
<td>0.06</td>
<td>0.62</td>
<td>0.36</td>
</tr>
<tr>
<td>DT-p</td>
<td>1.08</td>
<td>0.01</td>
<td>0.71</td>
<td>0.36</td>
</tr>
<tr>
<td>DT-ash</td>
<td>0.37</td>
<td>0.00</td>
<td>0.00</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Pyrolysis

Pyrolysis was conducted in a quartz tube reactor (i.d 50mm) in nitrogen. There is a sintered quartz disk in the middle of tube to support coal, which can also be used as gas distributor. Pyrolytic temperature ranged from 500°C to 900°C and residence time was 30 minutes. The flow of fluidized-gas was from 0.15 to 0.21 m³/h. 20g of coal was fed into the reactor at 5g/min after the desired temperature was reached. The char was collected and weighed after temperature naturally dropped to ambient temperature. Sulfur removal (SR) was calculated according to the following equation:

\[ \text{SR}\% = \frac{St_{\text{coal}} - St_{\text{char}} \times \text{Yield}}{St_{\text{coal}}} \times 100 \]

Results and discussion

1. Effect of coal type on sulfur removal

Figure 1(a) shows the change of sulfur removal with temperature. YM is a lower rank coal compared with DT, hence YM is more active during pyrolysis than DT coal due to its low aromaticity. YM coal has a higher desulfurization than DT coal which reaches maximum desulfurization yield at relatively higher temperature. From demineralized and de-pyrite coal (Figure 1(b)), we can get the same conclusion. This proves that coal rank has effect on sulfur removal. At the earlier stage of pyrolysis, desulfurization has remarkable increase because decomposition of pyrite and thermally labile organic sulfur play an important role. The desulfurization decreases starting from 700°C for YM coal and 750°C for DT coal. According to a previous study, sulfur fixation by alkaline-earth mineral begins at 700°C, which leads to increase of sulfur in char. On the other hand, high temperature leads to collapse of the pore structure, which inhibits further release of sulfur. Moreover, the desulfurization tends to be constant between 800°C and 900°C because stable organic sulfur is difficult to be removed and sulfide sulfur can not further decompose. Hence there is an optimal temperature for maximum desulfurization and varies with coal rank.

2. Effect of mineral on sulfur removal

Figure 2 indicates that sulfur content in char of demineralized coal first decreases to lowest value at 700°C, and then increases slightly for DT and evidently for YM. There is 10.42% and 1.69% CaO in the ash of YM and DT. The sulfur retention by CaO is contributed to the sulfur increase for raw coal. The transformation of inorganic sulfur to organic sulfur is responsible for the sulfur increase in the demineralized coal, mainly the transformation of pyrite to stable organic sulfur due to the influence of indigenous hydrogen and oxygen. The Sulfation product by CaO will turn into sulphate during combustion and will not cause pollution.
3. Organic sulfur removal through pyrolysis

![Figure 3](image)

**Figure 3** Organic sulfur removal vs temperature

Organic sulfur content in char has no apparent variation according to Figure 3(a). However, yield of char decreases with increasing temperature, hence in fact part of organic sulfur is removed through pyrolysis as shown in Figure 3(b). According to our AP-TPR study, there is more aliphatic sulfur in YM and more thiophenes in DT, which results in the high organic sulfur removal for YM. Figure 3(c) shows organic sulfur content in char through pyrolysis of YM raw and demineralized coal. It shows that organic sulfur tends to accumulate in char with increasing temperature. Attar\(^8\) believes that pyrolysis of sulfur compounds is the decomposition of C-S bond to free radicals R' and RS'. In pyrolysis, other hydrocarbon molecules supply the hydrogen to stabilize the radicals, but at high temperature there is no enough hydrogen and the radicals may transform into stable organic sulfur. In addition, lack of indigenous hydrogen may also leads to the transformation of pyritic sulfur into organic sulfur\(^7\). Cernic-Simic believes that sulfide contributes to increase of organic sulfur\(^9\). Therefore, alkaline-earth mineral leads to organic sulfur increase to some extent in raw YM. Organic sulfur in the char of YM-ash still accumulates with increasing temperature, clearly sulfide is not the main reason here. Contrasting Figure 3(c) with (a), we deduce that the interaction of pyrite with the organic matrix of coal plays an important role in organic sulfur accumulation in char.

4. Effect of residence time on sulfur removal

![Figure 4](image)

**Figure 4** Effect of residence time on total sulfur content of char

The effect of residence time on desulfurization is examined at the temperature for maximum desulfurization. For YM coal the sulfur content in char varies little with time and yield of char is almost not changed at the same temperature. Hence longer residence time has no enhancement effect on sulfur removal for YM coal. However, sulfur content in char of DT coal decreases with increasing time during the first 30 minutes, which leads to increase of sulfur removal. This indicates that DT coal is less active than YM coal to some extent. Therefore, sulfur is difficult to release rapidly in DT coal. However, when most of labile sulfur has released after a period of time, stable sulfur can not decompose and sulfur content in char has little change. Hence for different coal, there is also optimal residence time for maximum desulfurization.

**Conclusions**

1. There is optimal temperature and residence time for maximum desulfurization, varying with type of coal.
2. The alkaline-earth mineral in the raw coal plays an important role for the fixation of sulfur and makes desulfurization decrease.
3. The interaction of pyrite with the organic matrix of coal is the main reason that leads to organic sulfur accumulation in char.

**Acknowledgment**

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**References**