Structural evolution of a bituminous coal char relating to its gasification behavior with H$_2$O and/or CO$_2$

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Overview

1. Background
2. Experimental
3. Results and discussion
4. Conclusions
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Background

- Coal gasification can be divided into two processes: *pyrolysis of coal* and *gasification of residual char*

- Char gasification is regarded as the rate-limiting step during gasification.

- Char reactivity is an important aspect of understanding coal gasification.

- Char structure is a key property affecting its reactivity behavior.

- It is necessary to understand the char structure and *how they affect char reactivity*.
Pyrolysis is the formational process of char; Many factors affect its structure. Such as temperature, heating rate, pressure, etc.

The evolution of char structure with the gasification reaction is affected by the gasifying agent, etc.

A deep understanding of the reactivity of the char with gasifying agents such as $\text{H}_2\text{O}$ or/and $\text{CO}_2$ is vital for improving the gasification efficiency in the gasifier.

The purpose of this work:

To explore the reactivity and the structural development of the prepared char during gasification under the atmospheres of $\text{CO}_2$ or/and $\text{H}_2\text{O}$.

To explain the relationship between the changing physicochemical structure and char gasification reactivity in various gasifying agents.
Experimental

Tab. 1 Proximate and ultimate analyses of coal and char samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate Analysis (wt %)</th>
<th>Ultimate Analysis (wt % daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_{ad}$</td>
<td>$A_d$</td>
</tr>
<tr>
<td>BC</td>
<td>0.65</td>
<td>33.39</td>
</tr>
<tr>
<td>BC-C</td>
<td>0.24</td>
<td>45.93</td>
</tr>
</tbody>
</table>

Note: BC, bituminous coal; BC-C, bituminous coal char

Tab. 2 Analyses of ash composition in coal sample used in experiment

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>TiO$_2$</th>
<th>SO$_3$</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>P$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>46.48</td>
<td>42.51</td>
<td>2.09</td>
<td>1.2</td>
<td>0.25</td>
<td>2.27</td>
<td>0.3</td>
<td>0.58</td>
<td>1.92</td>
<td>0.06</td>
</tr>
</tbody>
</table>

- To prepare the chars, coal sample was loaded into a fixed-bed quartz reactor at atmospheric pressure in nitrogen atmosphere with a flow rate of 1L/min.
- The sample was heated from room temperature to 1000°C at a heating rate of 10°C/min and held for 1 h.
Low temperature reaction rates of char with $\text{H}_2\text{O}$ or/and $\text{CO}_2$

- Reactivity of char was measured using a laboratory-scale fixed bed reactor
- Temperature and other reaction conditions were chosen to maintain differential (Regime I)
- The different $X$ was performed by FBR, such as 10%, 20%, 30%, 40% and 50%

About 1.5 g of char was preset on the quartz frit of reactor, thermocouple is inserted to the sample bed for measuring its temperature.

<table>
<thead>
<tr>
<th>Carbon conversion:</th>
<th>Specific rate:</th>
<th>Intrinsic rate:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X = \frac{W_0 - W_t}{W_0}$</td>
<td>$R = -\frac{1}{W} \frac{dX}{dt}$</td>
<td>$R_{\text{Int.}} = \frac{R}{S}$</td>
</tr>
</tbody>
</table>
Char characterization

- Surface areas, chemical structures and morphology of chars were measured by specific instruments
  - Surface areas and pore structures of chars were measured by adsorption of N\textsubscript{2} at -196 °C, and the analyses of data using the BET method
  - Chemical structures of chars were reflected by Raman spectra, which recorded with a Renishew inVia Raman spectrometer
  - The morphology of chars partially-gasified were analyzed by a scanning electron microscope (SEM)
Results and discussion

Fig 1. Changes of specific surface areas with carbon conversion of char in various atmospheres

- The surface areas of chars increase with the increasing X in various atmospheres.
- A higher specific surface area of the char is observed under the H₂O-containing atmospheres.

Fig 2. SEM images of chars at 50% carbon conversion obtained in various atmospheres. 100.0kx
Results and discussion

- Total Raman peak area clearly increases with the increasing X, as the result of char reacting with H₂O or CO₂, this suggests an increase in the amount of electron-rich functional groups.

- Total peak areas for the Raman spectrum of the chars under CO₂ is higher than those of the chars reacted with H₂O or H₂O/CO₂ at the same carbon conversion.

- A major factor influencing the total Raman intensity is the amount of O-containing structure in the char, which could greatly enhance the observed Raman intensity due to the resonance effect.

Fig 3. Raman spectra of char at different carbon conversion during various atmospheres gasification
Results and discussion

Fig 4. Curve-fitting results of Raman spectra and changes of some structural parameters with increasing carbon conversions

- $I_{\text{Gr+Vl+Vr}}/I_D$ means the ratio of small (<6 rings) to large (>6 rings) aromatic rings
Results and discussion

- As expected, the order of the specific rates of char in various atmospheres is: $\text{H}_2\text{O}+\text{CO}_2 > \text{H}_2\text{O} > \text{CO}_2$
  - Specific rates of char in various atmospheres present various trend with the increase of $X$
  - The reaction rate of char-$\text{CO}_2$ is slightly decreased with increasing $X$
  - The reaction rates of char with $\text{H}_2\text{O}$-containing atmospheres is increased with increasing $X$

- There exist interactions between char-$\text{H}_2\text{O}$ and char-$\text{CO}_2$ make measured reaction rate higher than calculated value.

Fig 5. Changes of specific rates with carbon conversion of char in various atmospheres
Results and discussion

- The intrinsic reaction rate means the specific reactivity per unit of the pore surface area.
- The intrinsic reaction rate in CO\(_2\) shows a decreasing trend with the increasing \(X\); it tends to keep constant in other atmospheres.
- The intrinsic reaction rate in mixture atmosphere is higher than the sum in two single atmospheres.
- The structural evolution during gasification can provide new active site for the reaction of char-H\(_2\)O and char-CO\(_2\).

**Fig 6.** Changes of intrinsic reaction rate with carbon conversion of char in various atmospheres
Results and discussion

- The experimental amount of H$_2$ that is almost constant at different carbon conversion ranges and lower than the calculated value.
- While the experimental amount of CO is higher than expected.
- The reaction between C and CO$_2$ is mostly enhanced during the whole gasification process.
- The reduction of H$_2$ and the increase of CO demonstrate the reserve effect of CO$_2$ during gasification for water gas shift reaction.

**Fig. 7** Gas release quantity at various carbon conversion ranges of char in mixed atmosphere
Conclusions

- The tested char shows different physical and chemical changes under varying atmospheres.
- The presence of H₂O can cause a more porous structure than CO₂ that plays a decisive role in condensing the char structure, and two reactants have different reaction pathways.
- Active cooperation is observed in the mixture of H₂O and CO₂, and the synergistic effect increases with the increasing carbon conversion.
- The interactions between H₂O and CO₂ enhances the reaction between C and CO₂ due to the significant specific surface area caused by H₂O.
- The interactions finally lead to a lower amount of H₂ and higher amount of CO than calculated.
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Thank you for your attention!

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