The molecular structure analysis of Foundry Formed Coke prepared by semi-coke

JingruZu; Jianjun wu; Jun qiao; Guoli zhou; Zhiyuan Gao

Abstract:
In order to furtherly study carbonization mechanism of foundry formed coke prepared by semi-coke, more essential study was carried on about molecular structure analysis of raw materials and the carbonized products. In this paper, the tests were carried on by FTIR, which included molecular structure analysis of raw materials and the carbonized products structure at the different heating rates. The conclusions showed that the essence of carbonization of briquette was the break of bridge bond, decomposition of side chain, drop of function and aromatization. The reason for different thermal decomposition property was molecular structure of different raw materials. With lower condensation extent of aromatic ring, richer functional groups, more and longer side-chains, more bridge bonds, the pyrolysis became easier, and could get more pyrogenation gas.

Key words: foundry formed coke molecular structure FTIR TG-FTIR

In the coal carbonization stage, the change of molecular structure is important component of carbonizes mechanism, in this paper Fourier transformation infrared spectrum (FTIR) is used to test the molecular structure of raw material, carbonization product under each heating rate condition. FTIR may determine the material the molecular characteristic, in order to analysis the substructure change of coal carbonization, know more about carbonization mechanism.

[1-4]

1 experiment
1.1 test pieces: raw coal, coke
1.2 testing instruments:
American NICOLET- Nenus470 FTIR is used in the tests, makes the quadrat type is the KBr sheeting, the proportion of sample and the KBr is 1:160, resolution 4 cm-1, scanning number of times 32. The automatic smooth and automatic base adjustment is used in the process.
2 test results and analysis:

2.1 the analysis raw material molecular structure

According to the coal spectrum analysis, after 3300 cm\(^{-1}\) was the absorption peak of OH and the NH, restrained by environmental effect greatly; the absorption peak at 3043 cm\(^{-1}\) place was aromatic CH; at 2850~2950 cm\(^{-1}\) was the fatty group CH absorption peak; at 2360 cm\(^{-1}\) place was caused by noise materials and CO\(_2\) and so on; at 1600 cm\(^{-1}\) had a very strong absorption peak, there were many explanation about it, Xie Kechang and Norman\(^{[1,2]}\) thought that this peak was caused by the key of fragrant hydrogen C=C, but increased it intensity by the including the oxygen functional group; at 1440 cm\(^{-1}\) was the absorption peak caused by CH\(_2\) scissoring vibration; at 1034 cm\(^{-1}\) was the inorganic mineral substance absorption peak; between 700~900 cm\(^{-1}\) was called the fragrant belt, which generally had three absorption peaks, belonged to the different substitution of aromatic hydrocarbon.

The different absorption peak's ownership sees the next table.

Usually KCNS is used as calibration object in the infrared functional group's quantitative analysis\(^{[7]}\), obtaining the spectrogram with the sample according to 1:1 proportion through the sheeting law, according to Lambert - the beer law calculated the formula:
FTIR peak assignment of raw materials

<table>
<thead>
<tr>
<th>Wave number, cm⁻¹</th>
<th>Ar1</th>
<th>2850-2950</th>
<th>1600</th>
<th>1440</th>
<th>875</th>
<th>811</th>
<th>750</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mark</td>
<td>R</td>
<td>Ar2</td>
<td>R1</td>
<td>Ar3</td>
<td>Ar4</td>
<td>Ar5</td>
<td></td>
</tr>
</tbody>
</table>

| Peak ownership    | Absorption peak of Aromatic C-H expansion and vibration | Absorption peak of Fatty group C=O scissoring vibration absorption peak | Aromatic C=O scissoring vibration absorption peak | CH₂ scissoring vibration absorption peak | CH₂ scissoring vibration absorption peak | Outside single hydrogen substituted benzene ring bending vibrations absorption peak | Outside neighboring double hydrogen substituted benzene anchor ring bending vibrations absorption peak | Outside neighboring four hydrogen substituted benzene anchor ring bending vibrations absorption peak |

\[ c = K \left( \frac{A}{A_c} \right) \]

In the formula, c: Relative Content of Some functional group, A: integral area of Some functional group, \( A_c \): integral area of In calibration object, K: constant related Sheeting thickness.

Two functional groups In the identical spectrogram

\[ \frac{c_1}{c_2} = \frac{A_1}{A_2} \]

Therefore we could consider using the ratio of functional group area to attributes how many the functional group relatively content.

Infrared functional group analysis of Various raw material is as follow:
Figure 2-2 Semi-quantitative analysis of groups content of raw materials

The figure shows, there were great difference in molecular structure between the pitch, the bituminous coal and the semi-coke. On the pitch there were a lot of substituting group on the benzene ring, but the aromatic CH content were more than fatty group CH, explained that on the benzene ring there were many other functional group contain the oxygen substitution, less the alkylation substitution. The aromatic C=C absorption strength was low indicated that there were less the pitch aromatic ring, this had also confirmed the pitch molecular weight less than 500 which the preamble measured. The molecular structure of Da Lou Gou coal and the Liulin coal was similar, because the aromatic nucleus condensation degree of bituminous coal was high, therefore its aromatic C=C comparative content were more. The fatty group CH content was higher than aromatic CH, so we may extrapolated, although the bituminous coal had less the benzene ring substituting group, but on the benzene ring side chain had more the alkyl substituting group. There were more and long said-chain in flame coal, also had many the functional group, which after 600~700 °C dry distillation systems getting semi-coke, there were many fatty group CH content also. We can got, as a result of the decomposition and the condensation, on the semi-coke four hydrogen substitutions of aromatic nucleus already vanished, but one hydrogen substitutions and the double hydrogen substitution still existed, and most of which was the alkylation.

2.2 molecular structure analysis of stage carbonization product
Carbonization product under each heating rate had been analysed by FTIR.

FTIR analysis of SCE products
Figure 2-3 infrared spectrogram each absorption peak's ownership sees Table 2-1, we may got, along with the enhancement of the carbonization temperature, it reduced gradually that 2850~2950 cm\(^{-1}\) on behalf of the fatty group CH expansion vibration absorption peaks, simultaneously represents \(-\text{CH}_2-\) scissoring vibration 1434 cm\(^{-1}\) also reduced gradually, explained in the carbonization process to experience the aromatic nucleus side chain's break and bridge bond's break, this also confirmed the front experimental result. 3043 cm\(^{-1}\) absorbed oscillation peak on behalf of the aromatic CH was weaken along with temperature increment until vanishing, regarding 1 \(^{\circ}\)C/min evanishment temperature is 700 \(^{\circ}\)C, regarding 2 \(^{\circ}\)C/min is 800 \(^{\circ}\)C, regarding 5 \(^{\circ}\)C/min is 900 \(^{\circ}\)C, which explained the trend of coal carbonizes was on the aromatic nucleus the side chain are getting fewer and fewer, the molecular structure tended a fused ring more. Usually along with the temperature increased, the condensation extent of aromatic nucleus of reaction deepens, the aromatic nucleus polymerization degree also enhanced, but also reduced on behalf of aromatic C\(=\text{C}\) 1600 cm\(^{-1}\) along with temperature increment, this was quite unusual, some scholar \(^{[8]}\) discovered that on the fragrant nucleus the neighboring hydrogen bond formed the conjugate Pi key to reduce aromatic C\(=\text{C}\) to the infrared absorption strength, increased along with the grade of metamorphism, from the lignite, reduced in turn the bituminous coal to the anthracite C\(=\text{C}\) absorption strength. But the coal grade of metamorphism and the coal carbonization process by the homophyly, was the side chain and the functional group reduction or the break, the aromatic nucleus extent of polymerization increasesed gradually.

3 conclusions

(1) molecular structure analysis of raw material indicated that On the pitch there were a lot of substituting group on the benzene ring, but the aromatic CH content were more than fatty group CH, explained that on the benzene ring there were many other functional group contain the oxygen substitution, less the alkylation substitution. molecular structure of Da Lou Gou coal and the Liulin coal had more similar , in the bituminous coal although substituting group on the benzene ring reduced, but on the benzene ring side chain the alkyl had more substituting group. on the semi-coke four hydrogen substitutions of aromatic nucleus already vanished, but one hydrogen substitutions and the double hydrogen substitution still existed, and most of which were the alkylation..

(2) molecular structure analysis of stage carbonization product: The carbonization product along with the temperature increasing the absorption strength of C\(=\text{C}\) reduced gradually ,even vanishes in the end, also explained that the carbonization process essence was the aromatization process, infrared absorption peak at 875 cm\(^{-1}\), 811 cm\(^{-1}\) and 750 cm\(^{-1}\) are on behalf of benzene ring each kind of substituting group, also reduced along with temperature
increment, and the heating rate quicker benzene ring various substituting groups absorption strength vanishing temperature was higher. In brief, looking from the molecular viewpoint that the essence of casting burnt carbonization process was the process which the bridge bond and the side chain break and the functional group fell off, the essence of the carbonization process was the aromatization process.

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