Study onto Bioliquefaction Conditions of Zhaotong Lignite

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Abstract. In the experiment, 6mol/L, 8mol/L, 10mol/L three different concentrations of nitric acid were used to oxidize 0.15~0.25mm, 0.25~0.50mm, +0.50mm three different sizes of particle sizes for 24, 48 and 60h, respectively. Nine different kinds of coal pretreated samples were used. Then the dominant coal samples were screened in DOX medium. Finally, bioliquefaction test for 3 kinds of dominant coal samples were selected in DOX liquid medium with different concentrations of Na+, Mg2+, and Cu2+, to investigate the effects of the type and amount of trace elements, coal sample on the dissolution test. Results show that the liquefaction effect of 8# coal sample is optimum, with best solution of adding Cu2+ 0.05g/L. Its absorbance at 450nm is 18.9, and the peroxidase activity is 233U in 12th days.

Introduction

Coal is an important energy in China. While the normal utilization causing series of pollution. Coal bio-liquefaction is a degradation process of coal macromolecule to low molecules or solution process of small molecules in coal by microorganisms excretion products such as enzymes [1]. Because of benefits such as mild reaction, no secondary pollution, etc., it is one of the most important part of coal clean efficient utilization, which has received extensive attention in worldwide since the first reported in early 1980s[2,3]. However, over the past 30 years, coal bio-liquefaction is still at the stage of laboratory research, and fails to get the application in industry[4,5]. One of the most important facts is the complex composition in liquefaction products, thus it is unable to gain high purity products.

One of the most important aspect in coal bio-liquefaction is to improve its liquefaction product ratio. This paper takes Zhaotong lignite as coal sample, and a white rot fungus named coriolus versicolor was used to liquefy the coal. Some liquefaction conditions were considered in this paper.

Experimental Materials Analyzer

Sample Pretreatment

The gas coal obtained from Zhaotong Coal Mine and natural air drying, after the crush by crusher, into different size. In order to enhancing coal bio-liquefaction ratio, nitric acid was used to pretreated coal before microorganism liquefaction.[8].

Microorganism Liquefaction

Culture media in liquefaction is DOX medium, with component as 40g maltose, 10g peptone, 20g agar and 1000mL water. White-rot fungi coriolus versicolor was inoculated onto DOX medium in 9 cm petri dish. After mycelium covered the medium, Fushun nitric acid oxidized long flame coal was sprinkled evenly over the surface of mycelium, and then cultivated at 28℃ incubator. After black drop formation on coal, it was extracted by pipette in clean bench for next step analysis.

 Peroxidase Analysis

Activity of peroxidase was detected by phosphate way. 2.9mL 0.05mol/L phosphate buffer, 1.0mL 2% H2O2, 1.0mL 0.05mol/L methyl catechol solution and 0.1 mL crude enzyme were added into a test
tube, absorption at 470nm was detected immediately after the tube was keeping in water bath with temperature at 37 °C for 5 to 10 minutes. A unit of enzyme activity was defined as variation of 0.01 at 470nm per minute [6], as shown in Equation (1).

\[
(U) = \frac{\Delta A}{0.01 \times t \times D}
\]

(1)

Where, \( \Delta A \) absorption of variation of 0.01 at 470nm in certain minutes, \( t \) is the reaction time (min), and \( D \) is the dilution factor of crude enzyme.

**Results and Discussion**

**Influence of Coal Pretreatment on to Coal Bioliquefaction**

Nitric acid oxidation time, concentration of nitric acid, and coal size were investigated onto coal bioliquefation. As shown in Figure 1. According to Figure, concentration of nitric acid is the most sensitive factor, the higher concentration, the higher liquefaction. Followed by coal size, that is, the smaller the coal size is, the better effect. While oxidation time is not so obvious.

![Figure 1. Bioliquefation of Zhaotong lignite with fungus coriolus versicolor.](image)

**Influence of Trace Element onto Coal Bioliquefaction**

The different elements with different concentration were analyzed, that is \( \text{Na}^+ \), \( \text{Mg}^{2+} \) and \( \text{Cu}^{2+} \). Orthogonal test design method was used to design the test with three factors and three levels, as shown in Table 1. Different trace element with different concentration was added to the liquid medium as well as fungus and corresponding coal sample, number them from 1 to 9. And number 10 to 12 are contrast samples, without adding any trace elements. These flasks were cultivated in 27 °C shaking table for certain days. Liquid in different flasks were sampled out and detected in UV-Vis spectrophotometer with wavelength at 450nm[7].

<table>
<thead>
<tr>
<th>factor</th>
<th>1</th>
<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td>sorts of Trace element</td>
<td>Na(^+)</td>
<td>Mg(^{2+})</td>
<td>Cu(^{2+})</td>
</tr>
<tr>
<td>concentration of element</td>
<td>0.5g/L</td>
<td>0.2g/L</td>
<td>0.08g/L</td>
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<tr>
<td>coal sample</td>
<td>7#</td>
<td>8#</td>
<td>9#</td>
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</table>

According to Figure 2, with liquefaction processes, liquefaction effect increases. In 6\(^{th}\) day, absorption at 450nm of No 6 is the maximum among the nine tests, with absorption of 17.6. Where No 6 test refers to adding 0.2 g/L Na\(^+\) and 8\# sample coal. While after liquefaction processes, absorption at 450nm of No 6 increases very slowly, with absorption of 18.3. While absorption at 45nm of No 9 test reaches the maximum among the 9 tests, with absorption of 18.9, which refers to 0.08g/L Cu\(^{2+}\) and 8\# coal sample were added. Besides, No 10 to 12 tests always keep in low level, indicating that trace elements promote bioliquefaction. Absorption at 450nm of No 7 test is lower than without adding trace elements, this is because adding too much trace element (with Cu\(^{2+}\) of 0.5g/L), inhibits the growth of fungus.
Variation of Activities of Peroxidase by Trace Element

After liquefaction for a period of time, a certain amount of medium in flasks were taken out and the peroxidase was detected according to section 1.3, as shown in Table 2. According to Table 2, adding coal sample promoting peroxidase production. Before adding coal sample into medium, peroxidase activity of each flask are all in very low level, ranging from 32U to 51U. When different coal samples were added, peroxidases increase immediately. Those without adding trace element (10#, 11# and 12#) increase to about 90U in the first day and reach 123 to 176. Peroxidases of test No 2, 6 and 9 are higher, with activity over 200U in the 12th day, 222U, 250U and 233U respectively.

Peroxidases of test No 4 and 7 increase lowly. In the first day, they are 81U and 68U respectively, and in the 12th day, are 149U and 121U respectively.

Table 2. Variation of activities of peroxidase by trace element coal (U).

<table>
<thead>
<tr>
<th>days before adding coal</th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
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<tr>
<td>1</td>
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<td>115</td>
<td>81</td>
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<tr>
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<td>233</td>
<td>123</td>
<td>164</td>
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</tbody>
</table>

In No 1 to 3 Tests, Na⁺ with different concentration was added, as shown in Figure 3. In different tests, activities of peroxidase are almost the same. They reach to a level in the second day and keep in line level. When concentration of Na⁺ is 0.2g/L, the peroxidase activity is maximal.

In No 4 to 6 Tests, Mg²⁺ with different concentration was added, as shown in Figure 4. In different tests, activities of peroxidase vary with the concentration, that is, the higher concentration, the lower peroxidase activity. Activity in each test increased with time. When concentration of Mg²⁺ is 0.08g/L, the peroxidase activity is 250U in the 12th day.
In No 7 to 9 Tests, \( \text{Cu}^{2+} \) with different concentration was added, as shown in Figure 5. In different tests, activities of peroxidase vary with the concentration. It is the same as that of adding \( \text{Mg}^{2+} \), that is, the higher concentration, the lower peroxidase activity. Activity in each test increase with time. When concentration of \( \text{Cu}^{2+} \) is 0.08g/L, the peroxidase activity is 233U in the 12\(^{th}\) day.

Conclusion

According to results above, several conclusion can be obtained. Pretreatment of coal, addition of trace element in culture medium effect coal bio-liquefaction. Concentration of nitric acid is the most sensitive factor, followed by coal size and oxidation time. Adding trace element \( \text{Na}^+ \), \( \text{Cu}^{2+} \) and \( \text{Mg}^{2+} \) promote coal bio-liquefaction, but the adding amount has a boundary. Excess amount of trace element may inhabit the activity of peroxidase.

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