The effect of different treatment conditions on biomass binder preparation for lignite briquette

Xianglan Zhang a,*, Deping Xu b, Zhihua Xu c, Qingru Cheng c

a China University of Mining and Technology, Beijing Campus, Beijing 100083, People’s Republic of China
b China Institute of Coal Chemistry (CCMRI), Beijing 100013, People’s Republic of China
c China University of Mining and Technology, Xuzhou, Jiangsu 221008, People’s Republic of China

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Abstract

The tests of treating rice straw with sodium hydroxide, lime and sulfuric acid were individually done and the possibility of using a binding agent based on rice straw as lignite briquette binder was studied. In this study, the lignite from Pingzhuang coal basin was selected as the coal for briquetting. It was found that the type of chemical agents and their concentration were the main factors influencing preparation of a binding agent based on rice straw. The binding mechanisms of a rice straw-based binder containing sodium hydroxide were quite different from that made with lime. The experiment showed that the rice straw treated with sulfuric acid could not be used as a briquette binding agent. Additionally, it made clear that comprehensive binders, which were prepared by adding bentonite, coal tar and/or polypropylene amide into rice straw-based binder, would have waterproof property and would benefit the quality of briquettes. © 2001 Published by Elsevier Science B.V.

Keywords: Binder preparation; Coal briquette; Biomass

1. Introduction

Coal is the primary energy source in China and in 1996, the proportion of coal consumption was 75% of the total energy consumption [1]. However, considering that
environmental protection is being paid attention in recent years and the fact that coal flue is one of the main sources of air pollution, coal should be used cleanly and the usage of coal should be improved much. The coal briquette is a clean fuel for boiler; in the making of which, the briquette binders play an important role.

It is known that many materials are used as coal briquette binders, such as coal tar, coal pitch, petroleum residues, starch, humic acid, synthetic organic polymers (e.g. PVC [2], atactic polypropylene (APP) [3], plastic waster [4], wood pulp waster liquor [5–8], molasses [9–12], biomass) and inorganic materials of lime, clay, ceramic, etc.

Some components in biomass, such as cellulose, semi-cellulose and lignin, have binding property when they are heated or hydrolyzed, which made the biomass being used as binders. In general, there are three types of biomass-based binding agents.

- Waste liquor binder—black liquor from preparation of wood pulp, which should be thickened during utilization;
- Hydrolyzed material from biomass [13–15];
- Biomass, which would be directly blended, as binding agent, with coal power to make briquettes [14,16–19].

Five hundred million tons of waste biomass come out every year in China, which is a trouble due to large quantity, low calorific value and poor utilization. However, after these waste biomass are processed properly, they can be use as a good binding agent for lignite briquetting. Compared with inorganic binder, this kind of binder possesses advantages, such as reduction of ignition point and increase in heating value of briquettes, which are favorable for burning of briquette as a boiler fuel. Additionally, the price of biomass-based binder is lower compared with organic binder. This experiment aimed to know the possibility of using chemical-treated biomass as a binding agent in briquette making.

2. Materials and methods

2.1. Raw materials

- Rice straw: taken from Xuzhou, Jiangsu Province, dried naturally and cut by forage cutter.

| Table 1 | Proximate analysis and ash analysis of Pingzhuang lignite

<table>
<thead>
<tr>
<th>$M_{ad}$ (%)</th>
<th>$A_{ad}$ (%)</th>
<th>$V_{ad}$ (%)</th>
<th>$O_{ad}$ (M.D. kg$^{-1}$)</th>
<th>$S_{ad}$ (%)</th>
<th>$T_{2}$ (°C)</th>
<th>SiO$_2$ (%)</th>
<th>Fe$_2$O$_3$ (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>Al$_2$O$_3$ (%)</th>
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<td>6.73</td>
<td>30.8</td>
<td>43.79</td>
<td>19.12</td>
<td>1.47</td>
<td>1340</td>
<td>63.14</td>
<td>9.86</td>
<td>8.18</td>
<td>2.20</td>
<td>14.39</td>
</tr>
</tbody>
</table>
Table 2
Sieve analysis of Pingzhuang lignite

<table>
<thead>
<tr>
<th>Size (mm)</th>
<th>&lt;0.1</th>
<th>0.1–0.2</th>
<th>0.2–0.5</th>
<th>0.5–1.0</th>
<th>&gt;1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)</td>
<td>18.8</td>
<td>14.8</td>
<td>37.4</td>
<td>25.8</td>
<td>3.2</td>
</tr>
</tbody>
</table>

- Sodium hydroxide: a series of solution with a concentration of 0.5–4% (wt.) was prepared.
- Sulfuric acid: 5% (wt.), 10% (wt.), 30% (wt.) of \( \text{H}_2\text{SO}_4 \) solution.
- Lime: \( \text{CaO} \) content of 52.48% (wt.), 120–200 mesh.
- Coal: Pingzhuang lignite, crushed down to size fraction < 3 mm. Proximate and ash analyses as well as sieve analysis for this coal are given in Tables 1 and 2, respectively.
- Bentonite: selected from Liufangzi mine in Jinlin Province.

2.2. Procedure

2.2.1. Preparation of rice straw binder

Considering the properties of rice straw and with reference to the processing technology of pulping industry, rice straw was treated under atmospheric pressure and low temperature. The effects of different types and different concentrations of chemical agent and different heating times on preparation of rice straw binder were studied. These effects were examined according to the properties of corresponding briquettes. For the examination, a satisfied preparation condition for the rice straw binder was chosen before mixing with bentonite, coal tar and/or polypropylene amide to prepare rice straw-based coal binder. Sodium hydroxide, lime and sulfuric acid were selected and used as different chemical agents; heating time was varied from 1 to 8 h.

2.2.2. Preparation of lignite briquettes

Briquettes were prepared in a laboratory. Lignite was mixed with prepared rice straw binder of 20% (wt.) (water content of about 85%) or rice straw-based binder, and then the mixture was briquetted under a pressure of 294 MPa in a NYL-2000 trial press; the products of briquettes had a cylindrical shape and \( \phi \ 18 \times 20\)-mm size. The process of briquette preparation is given in Fig. 1.

![Fig. 1. Schematic of coal briquettes preparation.](image-url)
2.2.3. Physical properties of briquette testing

Drop shatter test and compressive test of briquettes were done. The briquettes with satisfied drop shatter strength and compressive strength were selected [20]. The abrasive, thermal stability and water resistance tests of these briquettes with satisfied strength were done further.

The drop shatter test was done after dropping 20 pieces of prepared briquettes from a height of 2.0 m onto a steel plate with 12-mm thickness three times. The briquettes with fracture over 13 mm were weighted and weight percentage shared in total of the specimen was calculated. The test method and calculation of compressive strength are in accordance with Richards' [20]. The other tests were done according to the literature [21].

3. Result

3.1. The influence of sodium hydroxide and lime concentration on briquettes’ strength

Rice straw was treated with 0.5–4% (wt.) of sodium hydroxide to prepare N-binder, heated 4 h with heating temperature of 100°C. Fig. 2 shows the compressive strength and drop shatter strength of corresponding briquettes. The compressive strength and drop shatter strength of briquettes increased with the concentration up to 2.1%, and then decreased. The variation of drop shatter strength with concentration of sodium hydroxide is smaller than that of compressive strength.

Rice straw was treated with a series of lime with different concentrations to prepare L-binder with heating time of 4 h and heating temperature of 100°C. The compressive strength and drop shatter strength of corresponding briquettes prepared with L-binder are shown in Fig. 3. Briquettes’ compressive strength increased with lime concentration up to 6.7%, and then decreased; drop shatter strength increased with the increase in lime concentration. Compressive strength and drop shatter strength showed different variation trend in case of increase in lime concentration. Under the treatment conditions of this study, briquette compressive strength increased up to 2.44 MPa when lime concentration...
was 6.7%, which fully satisfied the briquette strength requirement for combustion fuel of industrial boiler [24].

3.2. Influence of heating time on briquette strength

The influence of heating time on briquette strength was studied with heating temperature of 100°C and sodium hydroxide concentration of 1.41%. Fig. 4 illustrates that under trial concentration, prolong heating time is a benefit for enhancing briquettes’ compressive strength and drop shatter strength; but when the heating time is about 4 h, briquettes’ strength is the highest.

The same test was done for treated agent of lime. It is found that by using the binder obtained under the treatment conditions of 4.11% lime concentration and heating temperature of 100°C, the change trend with the heating time for briquettes’ compressive strength and drop shatter strength is the same with the lime concentration, but the variation is small (Fig. 5). Therefore, lime concentration is the main factor influencing binder property.

In fact, both heating time and alkali concentration indicate decomposed degree of rice straw. The change of binding component with prolong time followed the same rule as that with the increase in alkali concentration.
3.3. Influence of sulfuric acid concentration on the treating of rice straw

Biomass hydrolysis with H$_2$SO$_4$ of 0.5% (wt.) concentration and under 180°C usually gives higher sugar yield [23]. Rice straw was decomposed a little under the atmospheric pressure and 100°C; despite this, the sulfuric acid concentration increased. The elasticity of rice straw could not be cleaned off under this treatment condition. The rice straw treated with H$_2$SO$_4$ cannot be used as briquette binder. The results are given in Table 3.

3.4. Influence of inorganic / organic additives on briquette strength

Coal briquette strength reached 2.44 MPa using only a binding agent based on rice straw. To make waterproof briquettes, the prescription and properties of compound binder were studied, which was made by adding bentonite, coal tar and/or polypropylene amide into binder based on rice straw. The properties of briquette processed with compound binder are shown in Table 4.

By using the comprehensive binding agent with bentonite, the briquette would have high compressive strength, and the compressive strength of briquette increased with the increasing additive quantity of bentonite. By using the comprehensive binding agent with coal tar of 3% or polypropylene amide of 0.1%, the briquettes would have waterproof property and the compressive strength and drop shatter strength would be enhanced. When the briquette prepared with comprehensive binding agent with polypropylene amide was put into water, the volume expansion was found, but the briquette was not destroyed under hand press and the strength recovered after drying.

Table 3

<table>
<thead>
<tr>
<th>H$_2$SO$_4$ concentration (%)</th>
<th>Compressive strength (MPa)</th>
<th>Drop shatter strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.91</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>10</td>
<td>0.67</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>30</td>
<td>0.31</td>
<td>&lt; 5</td>
</tr>
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</table>
Table 4
Properties of briquettes using compound binders

<table>
<thead>
<tr>
<th></th>
<th>Compressive strength (MPa×10^2)</th>
<th>Drop shatter strength (%)</th>
<th>Thermal stability (%)</th>
<th>Abrasive strength (%)</th>
<th>M&lt;sub&gt;ad&lt;/sub&gt;</th>
<th>A&lt;sub&gt;ad&lt;/sub&gt;</th>
<th>V&lt;sub&gt;ad&lt;/sub&gt;</th>
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<tbody>
<tr>
<td></td>
<td>A&lt;sub&gt;1&lt;/sub&gt;</td>
<td>A&lt;sub&gt;2&lt;/sub&gt;</td>
<td>A&lt;sub&gt;3&lt;/sub&gt;</td>
<td>A&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt;</td>
<td>287</td>
<td>0</td>
<td>/</td>
<td>/</td>
<td>93.2</td>
<td>45.1</td>
<td>74.2</td>
</tr>
<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt; + Tar&lt;sup&gt;6&lt;/sup&gt; 3%</td>
<td>366</td>
<td>20</td>
<td>272</td>
<td>74.3</td>
<td>89</td>
<td>89</td>
<td>89</td>
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<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt; + H&lt;sub&gt;2&lt;/sub&gt; 0.1%</td>
<td>217</td>
<td>12</td>
<td>201</td>
<td>92.6</td>
<td>75.2</td>
<td>80.7</td>
<td>80.7</td>
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<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt; + Tar 3% + B&lt;sup&gt;1&lt;/sup&gt; 1%</td>
<td>331</td>
<td></td>
<td></td>
<td></td>
<td>93.4</td>
<td>93.8</td>
<td>90</td>
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<td>C + T&lt;sub&gt;1&lt;/sub&gt; + Tar 3% + B 2%</td>
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<td></td>
<td></td>
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<td>96.2</td>
<td>98</td>
<td>84.4</td>
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<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt; + Tar 3% + B 3%</td>
<td>409</td>
<td>8</td>
<td>185</td>
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<td>C + Tar 3% + B 1%</td>
<td>185</td>
<td></td>
<td></td>
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<td>92.8</td>
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<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt;</td>
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<td>0</td>
<td>/</td>
<td>/</td>
<td>96.9</td>
<td>92.6</td>
<td>91.2</td>
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<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt; + Tar 3%</td>
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<td>20</td>
<td>295</td>
<td>100</td>
<td>85.6</td>
<td>82.7</td>
<td></td>
</tr>
<tr>
<td>C + Tar 3% + Tar 4%</td>
<td>335</td>
<td>51</td>
<td>413</td>
<td>82.2</td>
<td>78.2</td>
<td>76.3</td>
<td></td>
</tr>
<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt; + H 0.075%</td>
<td>339</td>
<td>24</td>
<td>291</td>
<td>85.8</td>
<td>12.51</td>
<td>30.84</td>
<td>44.19</td>
</tr>
<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt; + H 0.1%</td>
<td>339</td>
<td>35</td>
<td>339</td>
<td>100</td>
<td>92.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C + T&lt;sub&gt;1&lt;/sub&gt; + H 0.08% + B 3%</td>
<td>378</td>
<td>24</td>
<td>382</td>
<td>101</td>
<td>97.6</td>
<td>93.1</td>
<td>94.4</td>
</tr>
</tbody>
</table>

*Mean strength of original dried briquettes.
1Strength after immersion in water for 2 h.
2Wet briquettes dried strength after wetting and then dried again.
3<sub>A<sub>ad</sub> = (A<sub>1</sub> / A<sub>ad</sub>)×100%.</sub>
4Coal, size < 3 mm, 80% in total weight.
5Rice straw binder treated with lime, wet state, 20% in total weight.
6Coal tar, Q<sub>36.84 MJ kg</sub> - 1.<n>7Polypropylene amide.
8Bentonite.
9Rice straw binder treated with NaOH.
4. Discussion

4.1. Binding mechanism of rice straw treated with sodium hydroxide

In the paper-making industry, when temperature rises to 90°C, the decomposition rate of lignin in rice straw treated with sodium hydroxide can reach to 70% [22]; cellulose and semi-cellulose in the rice straw would be partially decomposed. This decomposition results in the removal of the elasticity of raw rice straw and the decomposition of lignin makes the cellulose separate from each other. This part of the cellulose acts as connection and strength material in the briquette with a function like a reinforcing steel bar in concrete. The carbohydrate material, pectin material and tannin material decomposed from rice straw have binding ability. Moreover, the liquor of rice straw is rich in silicon component and can reach as high as 50% [22]. It is supposed that an active silicon material reacts with alkali to create a new sodium silicate material in the treatment process of alkali, which has a binding ability. These two kinds of components attach to the surface of coal and act as binding agent functioning like cement in concrete.

Rice straw-based binder can be divided into two parts: solid part and liquor part. These two binders were obtained under the conditions of 2.53% NaOH concentration, temperature of 80°C, heating time of 4 h, and then the solid part (5.1%, dry basis) and the liquor part (18%) were used to prepare briquettes separately, with the briquettes’ compressive strength being 2.48 and 1.65 MPa. The additive amount of solid binder is less but the strength of its briquette is higher, which exposed that the binding ability of the solid part in the binder is higher than that of the liquors. From the SEM photo (Fig. 6; instrument type S250 MkIII, voltage 20 kV, mass sample adhered to the sample platform by conductor glue and gold sprayed on the sample surface), a lot of cellulose material can be seen. It also illustrated that the connection action of the remaining but separated cellulose in rice straw binder for briquette making is important. This is the obvious characteristic of rice straw binder different from other binders.

With the reaction between rice straw and alkali going on, lignin was decomposed, and separated cellulose material and liquor binders become more and more, so the

![Fig. 6. The scanning electron micrograph (SEM) of briquette.](image)
briquette strength increases with an increase in alkali concentration. However, with the alkali concentration increasing further, cellulose and semi-cellulose were decomposed largely but the binding ability of the decomposed product—carbohydrate—was lower. Moreover, the quantity of insoluble pectin material, tannin material and silicate material, which have binding ability, is fixed and do not increase with the alkali concentration. It means that the solid connection materials were reduced with intensification of reaction, although liquor components were increased. Thus, as a general trend, the binding ability of decomposed material from rice straw was decreased, which caused the strength of briquette to decrease.

4.2. Binding mechanism of rice straw treated with lime

When rice straw was treated with lime, its texture was softened and elasticity was removed. Since the alkalescence of lime is low, the lignin could not be decomposed and remaining cellulose material still possessed very high strength. The binder was obtained with the conditions of 8.26% Ca(OH)₂ concentration, temperature of 90°C and heating time of 4 h. The briquettes with the solid part (5.1%, dry basis) and the liquor part (18%) were prepared separately, and their compressive strength was measured to be 2.28 and 1.34 MPa, accordingly. It was revealed that the binding ability of liquor in the binder is weak (the compressive strength of briquette without binder is 1.22 MPa). By adopting viscosity measurement method of black liquor of pulp, the viscosity of the liquor part was measured to be 2.0 mPa s. It was obvious that the remaining, but separated cellulose material, was the main binding component in the binder. Briquettes’ compressive strength and drop shatter strength increased with Ca(OH)₂ concentration, which made it clear that the binding ability of rice straw was very important in lignite briquette making. Fig. 3 shows that the variation trend of compressive strength with an increase in lime concentration was different from that of drop shatter strength. The compressive strength indicates the anti-static pressure ability of the briquette and that the drop shatter strength represents anti-impact pressure ability of the briquette. The elasticity of briquetting materials could destroy the structure of the briquette, which would place a larger effect on the drop shatter strength and a smaller one on the compressive strength.

Rice straw-based binder was tested in Nicolet710-type FTIR spectrophotometer and multiple inner reflection set. Fig. 7a shows the IR spectra of N-binder and L-binder. The characteristic peaks of cellulose are 2900, 1425 and 895 cm⁻¹ [23] (Fig. 7b). These peaks are obviously smaller in N-binder than those in L-binder. It reveals that cellulose decomposed more strongly in N-binder than that in L-binder. In L-binder, the carbohydrate material that was decomposed from cellulose was small in quantity; the strength of solid part of cellulose was lost slightly, which was a benefit in providing binding function in case of deformation with shear force in briquette making.

4.3. Hydrophobic mechanism of polypropylene

By using rice straw-based binder added with coal tar or polypropylene amide, briquettes would have waterproof property. Coal tar is a good waterproof agent;
polypropylene amide is an amphipathic material, its hydrophilic group acting with the hydrophilic group of the rice straw-based binder; its hydrophobic group acting with the hydrophobic group of the rice straw binder. Hence, briquette strength increased and this action made the briquette hydrophobic.

5. Conclusions

(1) Rice straw treated with different chemical agents gave different results and the binding mechanisms of corresponding binders are different. Rice straw treated with sodium hydroxide can be used as a lignite briquette binder, both the solid and liquor components have binding ability, with the solid component’s binding ability being stronger. For rice straw treated with lime only, the solid part has a binding ability. Rice straw treated with sulfuric acid at this experiment cannot be used as a binder.
(2) Concentration of different chemical agents, heating time and heating temperature have influence on lignite briquette binder.

(3) Briquette strength is improved by adding bentonite, coal tar and/or polypropylene amide into rice straw-based binder, which gave the briquette its hydrophobic property.

(4) Compared with industrial briquettes used presently, the briquettes prepared in this experiment meet the requirement of industrial boilers. (The compressive strength of briquettes prepared with clay binder is 1.23–1.47 MPa; for waste pulp liquor binder 2.50–2.94 MPa.)

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References


