Waste to Energy-Effects of Complex Components of Organic Wastewater on Coal Water Slurry Stabilizers

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Abstract: Coal water slurry is an advanced and efficient coal utilization technology, prepare coal water slurry by gasification wastewater can realize the recycling of wastewater and improve the combustion or gasification efficiency of the slurry. Stabilizer is an important component to ensure fluidity and stability in industrial applications of coal water slurry, and the complex substances in wastewater for coal water slurry preparation have a great influence on the stabilizer. Therefore, in this paper, the influence of the major substances in gasification wastewater on the stabilizer is studied. Results show that (a) Ammonia nitrogen substances have adverse effects on stabilizers, because the ionized NH₄⁺ in the solution will bond with the polar groups on the stabilizer, which will affect the stabilizer to lose its effectiveness and reduce the stability of the slurry. (b) Small organic molecules have little effect on stabilizers, this is because the binding strength and quantity of stabilizer to water molecules is much larger than that of organic matters such as phenolic substances. (c) High-valent metal ions have a greater impact on stabilizers, the metal ions easily form gels or precipitates with the stabilizer, causing it to lose its effectiveness, and also have an electrostatic effect with the carboxyl group on the side chain of the stabilizer, which makes the stabilizer easy to aggregate together and lose the steric hindrance effect, finally cause the stability of the slurry reduced. The conclusion of the influence of substances in wastewater on stabilizer can provide a technical reference for the selection of suitable wastewater and stabilizer to prepare coal water slurry, then promoting the efficient use of energy.

1. Introduction

The composition of organic wastewater is complex, and it comes from many sources and routes such as chemical industry[1], paper mill industry[2], pharmaceutical industry[3], textile industry[4], aquaculture[5] and other industries. In addition to containing a large amount of organic matter, it also contains metal cations, suspend solids, ammonia nitrogen, etc. If it is discharged without treatment, it will cause water pollution and do harm to environment. The conventional treatment of organic wastewater is mostly costly, the process is complicated, and the wastewater cannot be uniformly treated. Therefore, it is necessary to develop a new technology for resource utilization of organic wastewater with low cost and uniform treatment.

Coal water slurry(CWS) is a new type of coal-based fuel. It has been widely used in the field of power boilers in China. It has the characteristics of high combustion efficiency and low pollutant emission[6]. Therefore, for China, where coal is the main energy source, the CWS technology is an environmentally friendly and energy-saving technology suitable for utilization of coal. Developing CWS technology, using coal to produce clean fuel, and replacing oil with coal is a strategic and realistic choice for China's long-term and stable development of energy. Studies have shown that CWS can be prepared from wastewater for combustion and gasification, the application of CWS technology to treat organic wastewater can transform and utilize organic matter from wastewater, and achieve the purpose of organic wastewater’s resource utilization[7].

CWS is a coarse dispersion system of solid-liquid two-phase. Under the action of gravity or other external forces, the particles are easily aggregated together to cause precipitation. In order to prevent the slurry from hard precipitation, a certain amount of stabilizer needs to be added to the slurry. The stabilizer can effectively prevent the coal particles from agglomerating when the slurry is at rest, and the viscosity of the slurry can decrease rapidly when it is sheared[8].

In this paper, the influence of the main components of organic wastewater on CWS stabilizers was explored, and data support was provided for selecting suitable stabilizers according to the characteristics of wastewater, so as to prepare CWS energy with better performance.

2. Experimental

The coal sample used in this paper is Shenhua coal. After the raw coal is exposed to sunlight and dried for 3-4 hours, it is put into a steel ball coal mill for 6 hours. A 100-mesh sieve was used for screening to obtain an experimental...
sample, whose proximate analyses and ultimate analyses data are shown in Table 1. A laser particle size analyzer (BT-9300ST, Baite, China) was used for particle size determination. The particle size distribution of the coal sample was unimodal as shown in Figure 2, and the average particle size of the coal sample was about 31.19 μm.

### Table 1. Proximate and ultimate analyses of Shenhua coal

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analyses (%)</th>
<th>Ultimate analyses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_{ad} ) (MJ/kg)</td>
<td>( C_{ad} )</td>
</tr>
<tr>
<td></td>
<td>( M_{ad} )</td>
<td>( A_{ad} )</td>
</tr>
<tr>
<td>Shenhua coal</td>
<td>11.04</td>
<td>5.09</td>
</tr>
</tbody>
</table>

The gasification wastewater used in this paper, include gaswashing wastewater, sulfur wastewater, carbonation wastewater and industrial wastewater, comes from CWS gasification co-production ammonia process in ZJFD Co., Ltd. The main water quality indicators of the four types of wastewater are shown in Table 2, it can be seen that organic matter, ammonia nitrogen and metal ions are the main components contained in the wastewater.

### Table 2. The main water quality indicators of the four types of wastewater

<table>
<thead>
<tr>
<th>Sample</th>
<th>COD (mg·L⁻¹)</th>
<th>BOD₅ (mg·L⁻¹)</th>
<th>Potassium (mg·L⁻¹)</th>
<th>Sodium (mg·L⁻¹)</th>
<th>Phenol (mg·L⁻¹)</th>
<th>Ammonia nitrogen (mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas washing wastewater</td>
<td>2.12×10³</td>
<td>777</td>
<td>1.02×10³</td>
<td>7.66×10³</td>
<td>17.1</td>
<td>285</td>
</tr>
<tr>
<td>Carbonization wastewater</td>
<td>496</td>
<td>174</td>
<td>2.80×10³</td>
<td>35.9</td>
<td>0.01</td>
<td>2.91×10⁴</td>
</tr>
<tr>
<td>Sulfur wastewater</td>
<td>5.36×10⁴</td>
<td>1.8×10⁴</td>
<td>0.50</td>
<td>1.83×10⁵</td>
<td>0.46</td>
<td>187</td>
</tr>
<tr>
<td>Industrial wastewater</td>
<td>2.87×10⁵</td>
<td>3.1×10⁴</td>
<td>3.25</td>
<td>4.87×10³</td>
<td>0.17</td>
<td>8.88×10³</td>
</tr>
</tbody>
</table>

### 3. Results and discussion

#### 3.1. Influence of ammonia nitrogen in wastewater on stabilizer

In order to study the influence of ammonia nitrogen on stabilizers, amines were used to simulate wastewater to prepare CWS in this paper. Ammonium chloride (NH₄Cl), Ammonium sulfate ((NH₄)₂SO₄), Hexamethylenetetramine (C₆H₁₂N₄), ammonium acetate (CH₃COONH₄), and ammonia (NH₃·H₂O) were selected as experimental materials. The stabilizer adopts xanthan gum which commonly used in CWS preparation, and the addition ratio is 0.1%. According to the calculation, add the corresponding mass of amines to ensure that the content of NH₄⁺ is about 10⁴ppm. Figure 1 is the rheological characteristic curve and WSR of different CWS prepared with ammonia-nitrogen.

![Rheological characteristic curve and WSR of different CWS prepared with ammonia-nitrogen](image)

From Figure 1, compared with the apparent viscosity of ordinary CWS, the apparent viscosity of CWS with ammonia nitrogen substances is reduced to some extent. And WSR of CWS with ammonia nitrogen substances is higher than that of ordinary CWS. This indicates that ammonia nitrogen substances can cause the apparent viscosity of CWS to decrease and the WSR to increase. Among several different ammonia nitrogen substances, ammonia water has the greatest influence on the properties of CWS, indicating that the addition of ammonia nitrogen has an adverse effect on the stabilizer, as a result, the stability of the slurry is reduced, and the pseudoplasticity is also weakened.

The reasons for the analysis are as follows: There are many polar groups in the structure of xanthan gum. It is through the action of these groups that xanthan gum can form a stable network structure through bonding to enhance stability of slurry. Through the hydrogen bonds formed between hydroxyl and carboxyl groups and water molecules, the stabilizer can coat the water molecules in the
structure and form a hydration film on the surface of the particles[9], when the slurry is sheared, water molecules are released and the fluidity of the slurry is enhanced. However, with the addition of ammonia nitrogen, NH4+ enters the solution after ionization, and the hydrogen atoms in NH4+ can form hydrogen bonds with the oxygen on the hydroxyl and carboxyl groups, which affects the interaction between xanthan gum and water molecules. The number of water molecules that can be bound or coated by the stabilizer is reduced, so the apparent viscosity of the slurry will be reduced and the stability will be deteriorated. Influence of organic matter in wastewater on stabilizers

In order to study the effect of organic matter on stabilizer, this paper adopts some typical organic matter in wastewater to simulate wastewater to prepare CWS. Phenol, o-cresol, m-cresol, pyridine and ethanol were selected as experimental materials. The stabilizer adopts xanthan gum, the addition ratio is 0.1%, and the organic matter of the corresponding quality is added according to the calculation. Figure 2 is the rheological characteristic curve and WSR of the CWS prepared with different organic matters.

![Figure 2. Rheological characteristic curve and WSR of the CWS prepared with different organic matters](image)

From Figure 2, the rheological curve of the CWS prepared with organic matters is almost coincident with that of the original CWS, indicating that the addition of organic matter has little effect on the apparent viscosity of the slurry. Studies have shown that the addition of small molecular organic compounds such as phenolic substances will increase the apparent viscosity of the slurry, mainly because the phenolic substances can be adsorbed to the surface of coal particles, making the hydration film thicker and free water reduced[10]. The reason for the phenomenon in the figure may be due to the formation of the network structure of xanthan gum between coal particles and water, which encapsulates a large number of water molecules through bonding energy, the binding of small molecular organics to water molecules on the surface of coal is far less strong than that of stabilizers. That is to say, the amount of the binding and coating of water molecules by xanthan gum is far greater than that of small molecular organic matter, so the addition of organic matter has little effect on the apparent viscosity. Figure 1 also shows the effect of different organics on the WSR. It is found that the WSR of the slurry added with the organic matter is not much different from that of the original slurry. From the above analysis, it can be concluded that the incorporation of small molecular organics such as phenol into the CWS will not have much influence on the stabilizer.

3.2. Influence of metal ions in wastewater on stabilizers

In order to study the effect of metal ions on stabilizers, this paper uses some typical metal ions in wastewater to simulate wastewater to prepare CWS. NaCl, KCl, MgCl2, CaCl2, CuCl2, FeCl3 was selected as experimental materials. The stabilizer adopts xanthan gum, and the addition ratio is 0.1%, and the corresponding mass of metal ion solution is added according to the calculation. Figure 3 is the rheological characteristic curve and WSR of the CWS prepared with different metal ions solution.

![Figure 3. Rheological characteristic curve and WSR of the CWS prepared with different metal ions solution](image)

From Figure 3, the apparent viscosity of CWS prepared from metal ion solution is lower than that of ordinary CWS, and the higher the valence state of metal ions, the greater the degree of apparent viscosity reduction. The WSR of the CWS prepared by metal ions solution has increased, and roughly shows the law that the higher the valence state of the metal ion, the higher the WSR. The reason for this phenomenon is that the incorporation of metal ions will cause the stabilizer to lose its effect, studies have shown that polyvalent metal salts can form gels or precipitates with xanthan gum, especially trivalent metal salts, which can form gels or precipitates at lower pH
values\[11\], this will render the stabilizer ineffective; In addition, xanthan gum molecules contain strong polar groups such as -COO- and –OH, in saline solution, metal cations can have electrostatic effects with carboxylic acid groups on the side chains of xanthan gum and neutralizes the charge, thereby reducing the repulsion of the side chain, making it easier for the side chain to entangle with the main chain and easier for xanthan molecules to aggregate\[12\]. Finally, the steric hindrance of xanthan gum molecules in the slurry is weakened.

4. Conclusion

As a clean and efficient coal-based fuel, CWS can be prepared from gasification wastewater to realize resource recycling and sustainable development. Stabilizer is an important component to ensure fluidity and stability in industrial applications of CWS. The influence of the main components of gasification wastewater on the stabilizer of CWS is studied. The conclusion can provide a technical reference for the selection of suitable wastewater and stabilizer to prepare high concentration coal water slurry, then promoting the efficient use of energy.

(1) Compared with ordinary CWS, the apparent viscosity of CWS prepared by ammonia nitrogen solution is slightly decreased, and the water separation rate is slightly increased. This is because the ionized NH\textsuperscript{4+} in the solution will bond with the polar groups in the xanthan gum, which will affect the effect of the xanthan gum on water molecules and reduce the stability of the CWS.

(2) Compared with ordinary CWS, the apparent viscosity and WSR of CWS prepared with organic matter solution do not change significantly. This is because the binding strength and quantity of xanthan gum to water molecules is much larger than that of phenolic substances to water molecules, so the addition of phenolic substances has little effect on the stabilizer, and the properties of the slurry do not change significantly.

(3) Compared with ordinary CWS, the apparent viscosity of CWS prepared with metal ion solution is obviously decreased, and the WSR is obviously increased, and the higher the ion valence state, the more obvious the difference is. This is because the metal ions easily form gels or precipitates with the stabilizer, causing it to lose its effect, and also have an electrostatic effect with the carboxyl group on the side chain of the stabilizer, which makes the xanthan gum molecules easy to aggregate together and lose the steric hindrance effect, so the stability of the slurry is reduced.

Acknowledgements

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References


