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# Enhanced slurryability and rheological behaviors of two low-rank coals by thermal and hydrothermal pretreatments

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ABSTRACT

The aim of this work is to study the slurryability of two low-rank coals (a Chinese YX lignite and a Chinese ZD subbituminous coal) and various upgraded coals or chars obtained by thermal and hydrothermal treatments. Thermal treatment was conducted in an air-isolated atmosphere at temperatures from 145 °C to 700 °C. Hydrothermal treatment of coal was carried out in an autoclave at temperatures from 150 °C to 300 °C with autogenous pressure from 0.8 MPa to 9.2 MPa. The two raw coals exhibited the poor slurryability, and a significant enhancement in the slurryability was achieved by both the thermal and hydrothermal treatments depending on the conditions. A coal or char slurry (CWS) with the solid loading of 59 wt.% was prepared from the YX lignite by the thermal treatment at 400 °C, which had the apparent viscosity of 1208 mPa s and the good stability. The apparent viscosity of CWS was found to be related to but not limited to the elimination of hydrophilic groups by pretreatment. The hydrothermal treatment was more effective to decompose the hydrophilic groups than the thermal treatment for YX lignite, while this was not the case for ZD coal. The enrichment of carboxyl-bound calcium in ZD coal enabled the hydrophilic groups to be more thermally refractory, and this calcium-combining structure appeared to have a negative effect on the slurryability and the dispersion stability. The CWSs prepared from the thermally treated YX coals or chars were less pseudoplastic and less easily subjected to a pseudoplastic change with increasing solid loading than those from the parent coal.



## 1. Introduction

Coal–water slurry (CWS) is an attractive fuel in engineering because of the nature of being easily pumpable and transportable in pipeline. It is customarily applied to boiler combustion and entrain flow gasification [1], and potentially to turbine or engine fueling as a substitute of oil [2] and even to electrolysis for hydrogen production [3]. It is always desired that CWS holds more coal under the guaranteed fluid properties. In practice, CWS is typically required to have a coal mass fraction as high as 55–70% with an apparent viscosity of lower than 1000–1200 mPa s at a shear rate of 100 $s^{-1}$, and also to be compliable with the storage stability.

A high-concentration CWS is generally viscous and thixotropic depending on the physicochemical and electrostatic interactions between coal particles, and between coal particles and water molecules. These interactions can be complex, which are influenced by a number of factors. Of the most fundamental factors are the concentration of coal, dispersants added, properties of coal, and granularity of coal. Many researchers have devoted to the investigation of such influencing factors [4,5] and to the finding of appropriate dispersants for reducing the viscosity of CWS and improving the static dispersion stability of CWS [6–9]. The pretreatment of coal by microwave irradiation has also been found to be effective for enhancement of the rheological characteristics of CWS [10,11].

Lignite is a low-rank, inferior and high-pollution but important fossil fuel resource, which shares around 40% of global coal reserves and around 13% of gross coal reserves in China. The preparation of lignite to CWS has drawn a whole lot of interest to efficient and clean transportation and utilization of lignite. However, lignite is more difficult to make CWS than higher-rank coals. Atesok et al. reported that the CWSs prepared from two Turkey lignites could only be up to 50–55% solid loading at the viscosity of 1000 mPa s, whereas the CWS from a Siberia bituminous coal reached a solid loading of 60% [12]. Wei et al. observed by examining 20 different rank coals that the slurryability of coal correlated well with the amounts of acidic groups in coal, and the more acidic groups in coal, the worse the slurryability of coal [13]. It is known that the enrichment of porosity and hydrophilic groups in low-rank coal enables more water molecule assemblages to immobilize inside the micropores, resulting in a worse slurryability of coal. To overcome this problem, researchers have investigated some CWS preparation methods by pretreatment of lignite [14–16]. A promising approach is to upgrade lignite by hydrothermal dewatering. Since lignite contains a large amount of moisture, sometimes as much as 60%, hydrothermal treatment has the advantage of recovering the latent

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heat of moisture evaporation. It is thus evaluated as an energetically efficient method to upgrade lignite [17]. Favas et al. found that the hydrothermal treatment of a Latrobe Valley brown coal led to an improvement in the slurryability of CWS, which correlated well with a decrease in the intra-particle porosity [15]. On the other hand, low-rank coal is suitable for production of gas and oil by thermal conversion processes such as pyrolysis, for it has a high content of volatile matter. The resultant char can be expected to be a better feedstock for the preparation of char–water slurry because the char is inclined to be hydrophobic. Fan et al. prepared the lignite char–water slurry (LCWS) at solid loading as high as 60% with a good viscosity by using sodium lignosulfonate and naphthalenesulfonate formaldehyde as dispersants [18].

In this work, we focus on the preparation of coal–water slurry or char–water slurry (either designated CWS) from two low-rank coals (a lignite coal and a sub-bituminous coal) by thermal and hydrothermal treatments at varying temperatures. Experiments are intended to bring insight into the influences of coal properties and pretreatments on the slurryability and rheological properties of CWS.

## 2. Experimental

### 2.1. Lignite samples and pretreatments

Two Chinese coals, a YX lignite from Yuxi city, Yunnan province, and a ZD sub-bituminous coal from Zhandong city, Xinjiang Uygur Autonomous Region were used in this study. The ultimate and proximate analyses of two coals are shown in Table 1. The ash compositions are shown in Table 2, where the elemental concentrations are represented on a basis of dry coal. It should be emphasized that ZD coal was enriched with alkali and alkaline earth metals, especially with calcium, whereas YX lignite contained a small amount of calcium and magnesium but enriched with silicon and aluminum. The coals were ground in a rod mill and then sieved to two fractions of sample with the particle sizes smaller than 74 μm and with the particle sizes between 74 μm and 177 μm.

Two pretreatment methods were used to upgrade lignite. One method was by thermal treatment or pyrolysis, and another by hydrothermal treatment. Thermal treatment was conducted using a muffle furnace, which was pre-heated to a predetermined temperature from 145 °C to 700 °C. Around 50 g of YX lignite or ZD coal was held in a capped alumina crucible and swiftly placed into the heated furnace for a holding time of 45 min. The heated coal sample or char was collected after cooling down. Hydrothermal treatment was carried out in a stirring autoclave. In each run, around 50 g of lignite sample was mixed with 150 g distilled water, and the mixture was heated from room temperature to a predetermined temperature from 150 °C to 300 °C with a final autogenous pressure from 0.8 MPa to 9.2 MPa. The heating rate was about 10 °C/min, and the holding time at the final temperature was 30 min. The autoclaved coal suspension was filtrated, and then dried in vacuo at 50 °C.

For brevity, the treated sample or char obtained, for example, from the thermal treatment or pyrolysis of YX lignite at a temperature of 700 °C is named as YX-PC700, and the treated sample obtained, for example, from the hydrothermal treatment of ZD coal at a temperature of 300 °C is named as ZD-HTC300, and the like.

**Table 1**
Proximate analysis, ultimate analysis and heating value of YX lignite and ZD coal.

| Coal | Proximate analysis (%)[a] | | | | Ultimate analysis (%, daf. coal basis) | | | | | HHV[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | M | A | V | FC | C | H | N | S | O[c] | |
| YX | 8.1 | 23.16 | 50.12 | 26.72 | 63.60 | 5.81 | 1.39 | 0.51 | 28.70 | 17.7 |
| ZD | 13.5 | 8.94 | 31.35 | 59.70 | 73.39 | 3.55 | 0.70 | 0.62 | 21.74 | 21.7 |

[a] M, moisture, air-dry basis; A, ash, dry basis; V, volatile matter, dry basis; FC, fixed carbon, dry basis.
[b] High heating value ($MJ \cdot kg^{-1}$, dry coal basis).
[c] By difference.

### 2.2. Preparation and analysis of CWS

The coal sample with the particle size of smaller than 74 μm was mixed with the coal sample with the particle size of 74–177 μm at a mass ratio of 3:1 for preparation of CWS. The particle size distributions of the mixtures of two raw coals are shown in Fig. 1. In each slurry preparation, about 30 g of the mixture was slurried with a predetermined quantity of distilled water in a glass beaker, with addition of 1% sulfonated alkyl naphtalene as a dispersant. The slurry was then agitated at a gradually increasing speed and kept agitating at 1000 rpm for 20 min to ensure the sufficient homogenization of CWS. In the case of preparing CWS from the treated coal or char, the raw coal samples with two different fractions of particle size were individually pretreated. CWS was prepared from the mixture of individually treated coals in the same manner.

Viscosity measurement was performed employing a rotating-type viscosimeter (model NXS-4C, Chengdu Instrument Factory, China). The data of shear rate, shear stress and apparent viscosity were automatically recorded in a computer. The apparent viscosity was an average determined by repetitive measurements at the shear rate of 100 $s^{-1}$.

The fluidity of CWS was measured by eyeballing [19]. In this method, a quantity of CWS was filled into a glass cylinder, and then was poured out by gradually tilting the cylinder. According to the visualized flow states, the fluidity of CWS is graded to A for a continuous flow, B for an intermittent flow, and C for no formation of flow.

The static dispersion stability of CWS was assessed by a glass-rod-penetration method [20]. After CWS was ready, part of it was transferred to a 50 mL cylinder till the layer height of CWS was up to 40 cm, and then statically stored at room temperature for a week. The top surface of CWS was covered with an about 5 mm thick layer of whiteruss to prevent moisture from evaporation to air. The stability was expressed by two parameters, separation ratio and glass rod sinking status. Separation phenomenon occurred that CWS was visually divided into the upper water layer and the lower suspension layer or the upper soft suspension layer and the lower hard settling layer. The separation ratio was defined as the ratio of the height of the upper layer to the total height, represented in percentage. The glass rod sinking test classified 3 grades, the best grade A in that the glass rod could sink spontaneously through the slurry, followed by a good grade B in that the glass rod could sink through the slurry with hand pushing, then by the bad grade C in that the slurry was hard settling, and the glass rod could not be hand-pushed through it.

### 2.3. Other analyses

Determination of oxygen-containing functional groups in lignite and char was performed by using a chemical titration method [21]. Briefly, the total amount of acidic groups (COOH + OH) was determined via the following steps: (1) addition of excess $Ba(OH)_2$ to neutralize the acidic groups in coal at a boiling point; (2) addition of a proper amount of HCl to neutralize the $Ba(OH)_2$ remainder; (3) use of NaOH to titrate the overplus HCl. Carboxyl group was determined by an ion exchange method with calcium acetate via the following steps: (1) use of HCl to acidify coal or char sample; (2) addition of calcium acetate to ion-exchange proton in the carboxyl group with $Ca^{2+}$ at a boiling point; (3) use of NaOH to neutralize the released $H^+$. The amount of phenolic hydroxyl group was indirectly calculated in terms of the difference between the total acidity and the amount of carboxyl group.

Elemental analysis (C, H, N, and S) of coal and char was conducted on an Elementar instrument (vario MACRO cube). FT-IR spectroscopy was implemented on a FTIR spectrometer (Nicolet 6700) in a scanning range of 4000–400 $cm^{-1}$, in which the coal or char sample was mixed with KBr to mold a pellet for analysis. The caloric value of coal or char