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Preparation of commercially applicable slurry fuels from rapid hydrogasification char by blending with coal

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ABSTRACT

The purpose of this work is first to investigate the slurryability of two chars produced from the rapid hydrogasification of two bituminous coals (YY coal and FG coal) in a pilot-scale entrained flow gasifier (abbreviated as RH char). Results showed that both RH chars had very poor slurryability mainly owing to the microporous and capillary structures of particles and the high water holding capacity, in sharp contrast to the properties of the parent coals and the char obtained from a common slow pyrolysis. The work thereafter aims at making a commercially usable water slurry by using the blends of RH char and YY coal. The slurry containing an adjusted solid blend of 60% total solid weight loading with 0.5% naphthalene sulfonate formaldehyde dispersant showed all satisfactory performances in the apparent viscosity, fluidity and static dispersion stability. Furthermore, it was found that the slurryability could be improved by an interactive effect between RH char and raw coal, which depended on the blending pairs and blending proportions.

1. Introduction

In recent years, the natural gas (NG) consumption in China has risen explosively with the booming economy. This situation exerts an urgent need to diversify the NG supply sources. China is quite short in gas reserve but has vast coal resources. Coal gasification is applied commercially on a large scale to fill the shortage of gas [1]. Coal hydrogasification, as a state-of-the-art technology which is based on the thermal reactions of coal with pressurized hydrogen to produce synthetic natural gas (SNG) and value-added liquid products [2,3], has been attracting a great interest. A pilot-scale coal hydrogasification process, which uses an entrained refraction flow reactor, has been developed in ENN Group, Co. Ltd. The coal hydrogasification was operated successfully with the handling capacity of 10 t/d coal at the reaction temperature of 850 °C and hydrogen pressure of 7 MPa. RH char was the by-product produced from the coal hydrogasification. The whole process is devised to use RH char for production of hydrogen by slurry entrained flow gasification. Hydrogen is supplied to coal hydrogasification in the system itself. In this context, it is imperative to study the slurryability of RH char.

For industrial coal gasification, coal water slurry (CWS) is required to meet a coal mass fraction of 55–70% with the apparent viscosity lower than 1200 mPa s at a shear rate of 100 s^{-1} as well as a good storage stability. A high-concentration CWS is always pursued because of its benefit to the enhancement of gasification efficiency. It is well known that the coal slurryability depends on many properties of coal such as coal rank [4–6], granularity [7–11], porosity [12,13], functionality [14–16], and mineralogy [14,17,18]. Nishino et al. [5] investigated the relation between the viscosity characteristics of CWS and coal rank. They found that all of the high rank coals with carbon content of greater than 85% exhibited the outstanding viscosity features. Atesok et al. [6] reported that the apparent viscosity of a Siberian bituminous coal water slurry remained below 1000 mPa s even with a solid loading up to 60%, whereas the slurries of two Turkey lignite coals could at best reach a 55% solid loading at the apparent viscosity of 1000 mPa s. Wei et al. [15] observed an overall declining trend of the coal slurryability with the increase of hydrophilic groups (carboxyl and hydroxyl groups) in coal. Favas et al. [12] revealed a unified relationship from their own study and the literature, that the maximum solid concentration was linearly reduced with the increase of intraparticle porosity of coal. In general, the high hydrophilicity and porosity of coal enables a mass of water molecules to assemble and immobilize inside the micropore, so that such a coal, typically lignite, is difficult to make a high-concentration slurry. Kaji et al. [13] obtained a near linear relation between the water holding capacity and a mathematical product of the micropore surface area and the weight fraction of oxygen in coal. They pointed out that the water holding capacity could be a primary parameter affecting the viscosity and rheology of CWS.

The preparation of CWS from coal char [14,19,20], biochar [21] and petroleum coke [11,22] has been the subject of recent studies. Fan et al. [19] prepared the lignite char water slurry of 60% solid loading with a good viscosity by using some appropriate dispersants. Zhu et al. [20] carried out a thermal pretreatment of a Ximeng lignite coal in the

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temperature range of 100–350 °C. They observed that the micropore surface area remarkably decreased with the temperature increasing from 100 °C to 350 °C, and the water re-adsorption ability was impaired when the temperature was elevated above 250 °C. These alterations improved the slurryability of the pretreated lignite. Fu and Wang [14] reported that all the chars obtained by the thermal pretreatment up to 700 °C showed an improvement in the slurry apparent viscosity, which was related to the elimination of the hydrophilic groups but not limited to it. On the whole, since lignite char becomes less hydrophilic, lower porosity and weaker water adsorption ability than raw lignite, the former is inclined to be better slurrying. Petroleum coke was found to be hydrophobic [11] and have a much higher grindability than bituminous coal [22]. It was made into a suspension of a high concentration as 70 wt.% using black liquor as a dispersant and stabilizer [22]. In contrast, an Australian mallee biochar was observed to have a poor slurryability, although the biochar also contained little oxygen like the coal char [21].

Lignite is an inferior feedstock of CWS because it has not only a poor slurryability but also a low heat value. Blending lignite with some well-slurryable and high-calorie carbonaceous solid feedstock is a rational way to improve the slurry characteristics. Several recent studies [23–26] have been directed to this way. Liu et al. [23] made use of a low rank Shenmu coal for preparing a high-concentration CWS by mixing with some individual high rank coals. They found that the maximum concentrations of the blends of two coals varied nonlinearly with the blending ratios. Lv et al. [24] prepared the slurry by blending a direct coal liquefaction residue with lignite. These two kinds of feedstock appeared to be mutually complementary with each other. Wu et al. [25] investigated the viscosity, rheology and dispersion stability of the slurry made from the blend of lignite with petroleum coke. They observed that the blend could be optimized to a solid concentration as high as 71.3%, by far higher than that of 46.7% for lignite alone. However, the addition of more petroleum coke to the blend had a negative influence on the stability of slurry. Xu et al. [26] attempted to prepare the slurry by blending an Indonesian low-rank coal with a petroleum coke using a specific nano-stablizer. They found that the use of a small amount of the stabilizer was beneficial to the static stability.

In this work, we are intended to report the slurryability of two RH chars, which were produced in a pilot-scale entrained flow hydrogasification process. To our knowledge, there is no open information on using RH chars to prepare water slurry. Also very little is known about the unique physicochemical properties of RH chars. For contrast, a comparative study is performed using a common char obtained by slow pyrolysis. Furthermore, we have tried to make a slurry by blending RH char with coal to comply with the requirements of slurry for practical application.

2. Experimental

2.1. Coal and char samples

Two Chinese bituminous coals (YY coal and FG coal), respectively, from Yuyang district and Fugu district, Shanxi Province, were used in this work. Two RH chars (YY–RH char, FG–RH char) obtained, respectively, from the hydrogasification of YY and FG coals in a pilot-scale entrained flow gasifier at the temperature of 850 °C, the pressure of 7 MPa and the residence time of about 10 s. A common pyrolysis char (designated as YY–CP char) was obtained by thermal treatment of YY coal in a muffle furnace at 850 °C. In each pyrolysis experiment, a capped alumina crucible filled almost fully with about 40 g coal sample was quickly pushed into the preheated furnace and held for 30 min. It should be noted that YY coal had a thermoplastic property, and the coal became a caked mass after pyrolysis. YY–CP char was subjected to pulverizing before use, but no delicate screening was conducted unless stated otherwise. The ultimate and proximate analyses of two raw coals and three chars are shown in Table 1. The particle size distributions of the coal and char samples used for preparing slurry are shown in Fig. 1.

Table 1
Proximate, ultimate analyses of two raw coals and three chars.

Sample	Proximate analysis (wt.%)				Ultimate analysis (wt.%, daf)				
	M_{ad}	A_d	V_d	FC_d	C	H	O[a]	N	S
YY coal	3.56	8.31	31.06	60.63	77.85	4.38	15.51	0.95	1.32
FG coal	3.96	8.70	28.41	62.89	82.17	4.50	11.88	1.16	0.29
YY–CP char	5.45	13.20	2.95	83.64	96.22	1.16	0.02	1.24	1.36
YY–RH char	3.73	12.07	4.89	83.04	96.19	2.00	0.22	1.13	0.46
FG–RH char	1.59	14.69	7.40	77.91	94.82	2.45	1.79	0.79	0.15

daf, dry ash free basis; M_{ad}, moisture, air dry basis; A_d, ash, dry basis; V_d, volatile, dry basis; FC_d, fixed carbon, dry basis.
[a] By difference.

2.2. Preparation and analysis of slurry

Approximately a 40 g sample of coal, char, or coal/char blend was mixed with a predetermined proportion of distilled water in a glass container to prepare the slurry (all abbreviated as CWS) with a desired solid loading. Naphthalene sulfonate formaldehyde (NSF) was used as a dispersant. The slurry was agitated as the rotating speed was increased gradually from 0 rpm to 1200 rpm, and then the agitation was held at 1200 rpm for 20 min to sufficiently homogenize the slurry. For brevity, the CWSs are named as follows. 60%CWS_20%FG–RH char/YY coal denotes a CWS with the total solid loading of 60%, which was prepared from the blend of FG–RH char and YY coal with 20 wt.% of FG–RH char in the blend. Similarly, 37%CWS_YY–RH char refers to a CWS prepared from YY–RH char alone with the solid loading of 37%. All weights of coal and char samples are represented on a dry basis.

Viscosity was measured with a rotating-type viscosimeter (model NXS-4C, Chengdu Instrument Factory, China). The readings of shear rate, shear stress and apparent viscosity were recorded automatically by an accessary computer. Each apparent viscosity was an average of the viscosity values measured six times at the shear rate of 100 s^{-1}. Prior to the measurement, the slurry was agitated for 2 min to stabilize the rheological state. Some repeated experiments of the slurry preparation and viscosity measurement showed that the relative error of apparent viscosity was 5.8%.

The fluidity of slurry was measured by an ocular estimation method [22]. At the moment when the slurry was prepared, a quantity of slurry was filled into a glass cylinder, and then poured out by slowly tilting the cylinder. As per the flow states, the fluidity was graded to A for a continuous flow, B for an intermittent flow, and C for no flow.

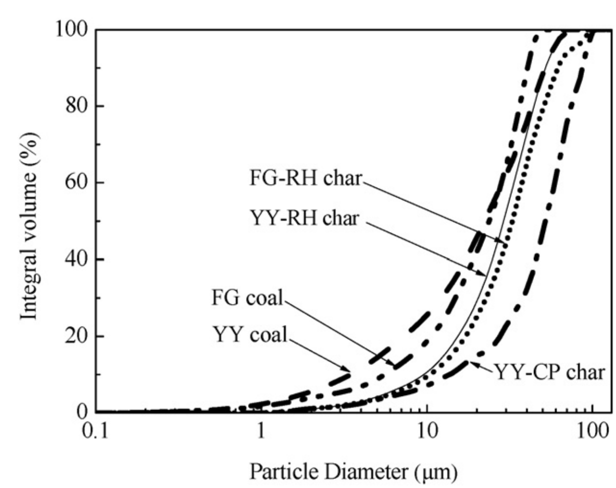

Fig. 1. Particle size distributions of two raw coals and three chars used for preparation of CWS. Dash line, YY coal; dash dot dot line, FG coal; solid line, YY–RH char; dot line, FG–RH char; dash dot line, YY–CP char.