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An approach for utilization of direct coal liquefaction residue: Blending with low-rank coal to prepare slurries for gasification

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HIGHLIGHTS

- The liquefaction residue can improve the slurryability of low-rank coals.
- YM and SM coal have synergistic effect with the residue in slurryability.
- Blending slurries with the residue and low-rank coal have strong pseudoplasticity.
- Static stability of blending slurries is remarkable.

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ABSTRACT

Direct coal liquefaction residue (DCLR) is a main byproduct in direct coal liquefaction process and its clean and high-efficient utilization is important. If DCLR could be gasified for hydrogen production, it will compensate hydrogen consumption during liquefaction and lower the operation cost, which makes DCLR utilization more promising. We proposed to blend DCLR with low-rank coals to prepare DCLR–coal–water slurries (DCLRCWS) as feedstock for gasification. In this work, one DCLR and four low-rank coals were used to prepare the individual DCLR–water slurries (DCLRWS), coal water slurries (CWS) and the mixed DCLRCWS at the weight ratio of 1:1. The slurryability, static stability and rheology of various slurries were investigated. The results show that DCLR and the low-rank coals are complementary in terms of slurry properties and DCLRCWS could meet the requirement of gasification process. Adding 50 wt.% DCLR apparently improves the slurryability of low-rank coals, and the maximum solid loading (C_{max}) of DCLRCWS prepared with ZLNR coal and DCLR is about 10% higher than that of the corresponding CWS. The effects of coal properties, dispersant adsorption, zeta potential on preparation of highly loaded slurries were examined in terms of slurryability. Moreover, compared with DCLRWS, DCLRCWS display higher degree of pseudoplasticity and better static stability owing to the addition of low-rank coals.

1. Introduction

Recently, interest in the development of coal hydroliquefaction has increased considerably, as driven by the surging global oil demand and increasing concerns about energy security in China. However, the high cost of coal hydroliquefaction is a main obstacle for its further development, which has brought unprecedented opportunity and challenge to research areas at the same time [1]. As a main byproduct of direct coal liquefaction process, direct coal liquefaction residue (DCLR) should be disposed and utilized reasonably. The direct coal liquefaction plants tend to gasify DCLR to supply hydrogen needed in the liquefaction process, which can realize self-sufficiency in hydrogen consumption and significantly increase the economy of the process [2].

Generally, DCLR accounts for 20–30% of the coal consumed in the process [3], but it is still not enough for the operational capacity of a single gasifier and the stability and running period of the liquefaction process should be considered as well. Thus, it is urgent to find suitable raw materials to co-gasify with DCLR for the normal operation of the whole system.

Usually, DCLR is separated by reduced pressure distillation, which contains considerable heavy oil and asphaltenes. Accordingly, dry feeding gasification is not suitable for DCLR due to its low softening point (about 180 °C), leading to great difficulty in milling system, while wet feeding could be operated easily. The

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results of our previous work [4] indicate that the slurryability of DCLR is relatively high, its static stability determined by rod dropping method is 2 days, and the shear-thinning behavior of direct coal liquefaction residue-water slurry (DCLRWS) is not strong, which fairly accords with other reported results [5,6].

Low-rank coals account for nearly half of the coal reserve worldwide and have an advantage of low price, regarded as a promising raw material for preparation of coal water slurry (CWS) [7]. But it is assumed that low-rank coals, especially brown coal, are difficult to make highly loaded CWS. Over the years, various measures have been taken to improve the slurryability of low-rank coals by thermal treatment [8], hydrothermal dewatering process [9,10], microwave/ultrasonic irradiation [8,11], developing high-efficient dispersant [12,13] and blending with petroleum coke [14], etc.

Blending DCLR with low-rank coals to prepare DCLRCWS may be an energy-efficient and environmental approach, which could not only supply sufficient feedstock to the gasification process but also have the potential to enhance the slurryability of low-rank coals. However, the studies on the blending principles of DCLR and low-rank coal as well as the properties of DCLRCWS have not been reported yet. In this work, four low-rank coals were selected to prepare CWS, whose properties were compared with that of DCLRWS. DCLR was blended with the coal samples to prepare DCLRCWS at the weight ratio of 1:1 and the slurryability, rheology and static stability of DCLRCWS were systematically investigated. The surface physical and chemical properties of DCLR and coal samples, dispersant adsorption isotherms, zeta potential, and SEM pictures of slurries were analyzed to study the interactions between DCLR and coal samples in terms of slurry properties. The blending principles of DCLRCWS can provide experimental data and theoretical basis for the integration of coal liquefaction and gasification process.

2. Experimental

2.1. Materials

DCLR used in this work was obtained from 6 t/d direct coal liquefaction pilot plant of Shenhua Group Corporation in China. Its raw coal is Shangwan coal from Inner Mongolia. Four low-rank coal samples from Shenmu, Yima, Yuxian and Zhalainuoer were employed and denoted as SM, YM, YX and ZLNR coal, respectively. The proximate and ultimate analyses of DCLR and four coal samples are listed in Table 1.

2.2. Preparation of slurries

The samples were separately crushed and sieved to several groups with different particle sizes: 280–154 μm, 157–74 μm and less than 74 μm. DCLR and four coal samples were separately graded on Alfred particle size distribution [15]. An anionic dispersant, naphtalenesulfonate-formaldehyde condensate (NSF), was used and the dosage of dispersant is 1 wt.% on dry basis of coal and/or DCLR. For DCLRCWS, certain amount of DCLR and coal sample at the weight ratio of 1:1 was successively transferred into the bottle containing a predetermined quantity of dispersant and deionized water. And then, the mixture was agitated at 3000 r/min for 10 min (CWS), while for 20 min (DCLRWS and DCLRCWS) for homogenization. All experiments were conducted at room temperature.

2.3. Determination of slurry properties

The rheology of slurries was determined by NXS-11 rotational viscometer (Chengdu Analytical Instrument Factory, China) at the shear rate range of 10–100 s^{-1} and the average of 6 values at shear rate of 100 s^{-1} was defined as the apparent viscosity. The maximum solid loading of slurry was designated as the solid loading when the apparent viscosity of slurries was 1000 mPa s at 20 °C [10]. The maximum solid loading of DCLRWS, CWS and DCLRCWS is denoted as $C_{max,1}$, $C_{max,2}$, $C_{max,3}$, respectively. The rod dropping method was used to evaluate the static stability of slurries with the apparent viscosity close to 1000 mPa s once a day till the appearance of hard sediment up to 14 days.

2.4. Characterization

2.4.1. Physical adsorption test

The texture properties analyses of the samples were carried out with isothermal N_2 adsorption at 77 K using ASAP 2020 – Physisorption Analyzer (Micromeritics, USA). All the samples were dried at 60 °C under vacuum for 24 h before physical adsorption test.

2.4.2. Chemical structure analysis

The samples with Alfred particle size distribution were ground to an appropriate size and dried at 60 °C under vacuum for 24 h before FTIR measurement. FTIR spectra of the samples were obtained on an IR spectrometer (VERTEX 70, Bruker, Germany), and the cell was the 0030–102 accessory (Pike Co. Ltd., USA) with ZnSe windows. The same Al_2O_3 crucible was used in measuring the five samples, so the thickness of the samples is also the same with the height of the crucible. The diffuse reflection mode was selected to record the spectra within 4000–600 cm^{-1} with the co-addition of 200 scans at 4 cm^{-1} resolution. Chemical titration was conducted to determine the content of hydrophilic function groups and the procedure was presented by Fan et al. [16].

2.4.3. Dispersant adsorption measurement

During dispersant adsorption tests, the mixture of graded samples and dispersant solution at weight ratio of 1:10 was charged into a 100 ml conical flask and shaken for 5 h at 200 rpm to make

Table 1
Proximate and ultimate analyses of five samples.

	Proximate analysis (wt.%, ad)			Ultimate analysis (wt.%, daf)					H/C	MHC
	M	A	V	C	H	N	S	O*		
DCLR	0.17	12.46	45.12	90.26	5.99	1.25	1.77	0.73	0.80	1.0
YM	4.37	38.69	23.34	73.46	5.78	1.05	1.07	18.64	0.94	7.5
SM	2.68	10.47	29.73	81.05	5.24	1.08	0.30	12.33	0.78	8.5
YX	13.00	14.23	23.83	80.76	5.58	0.99	1.02	11.65	0.83	16.6
ZLNR	12.07	12.39	30.19	75.32	6.50	1.05	0.30	16.83	1.04	24.7

ad: air dried basis; daf: dry and ash-free basis; * By difference.
M: moisture; A: ash; V: volatile; C: carbon; H: hydrogen; N: nitrogen; S: sulfur; O: oxygen.
H/C: the ratio of hydrogen atom to carbon atom.
MHC: the maximum moisture holding capacity.