



Properties of direct coal liquefaction residue water slurry: Effect of treatment by low temperature pyrolysis



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HIGHLIGHTS

- The slurryability is improved from 73.5% of DCLR to 74.6% of P-400.
- The adsorption layer of P-450 is the thinnest among the four samples.
- Pyrolysis deoiling could cause obvious deterioration in the stability of DCLRCHWS.
- DCLRCHWS (P-300 and P-400) exhibit weak pseudoplastic behavior just as DCLRWS.
- 400 °C is the optimum pyrolysis temperature to prepare the gasification feedstock.

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ABSTRACT

Low-temperature pyrolysis could effectively recover heavy oil from direct coal liquefaction residue (DCLR), and the derived DCLR char (DCLRCH) could be gasified to compensate hydrogen consumption during liquefaction. The staged processing of DCLR, pyrolysis and gasification, is thought to be a promising method for its high-efficient usage. In the work, DCLR was pyrolyzed under different pyrolysis temperatures (300, 400 and 450 °C) in a fixed-bed reactor to prepare DCLRCH, designated as P-300, P-400 and P-450, which were then used to prepare DCLRCH water slurries. The results of FTIR and successive sequential extraction show that the oxygen-containing functional groups and aliphatic chains of DCLR are removed during pyrolysis and the aromaticity of DCLRCH increases with pyrolysis temperature increasing. The dispersant adsorption behavior suggests that the adsorption layer of P-450 is the thinnest among the four samples. The slurryability, rheological behavior and static stability of DCLRCH water slurries (DCLRCHWS) were systematically investigated. Compared with direct coal liquefaction residue water slurry (DCLRWS), the slurryability of DCLRCHWS prepared with P-300 and P-400 is enhanced and their static stability deteriorates further. DCLRWS and DCLRCHWS are all weak shear-thinning fluids. However, the mixture of P-450 and water is not a homogeneous and stable suspension. Under the experimental condition, 400 °C is the optimum pyrolysis temperature of DCLR for maximizing production of high-value components and preparing high-quality feedstock for gasification.

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1. Introduction

Currently, the slump in oil price has brought unprecedented challenges to coal liquefaction, and the cost reductions might be one effective strategy to boost its competitiveness. The target product of direct coal liquefaction is oil, but it is inevitable to generate gas and residue. DCLR usually accounts for 20–30% of the raw coal and its effective utilization closely correlates with the economic

performance of liquefaction [1]. The vacuum distillation residue of Shenhua Group Corporation contains about 30–50% of heavy oil and asphaltene to maintain its flowing for tapping residue [2]. Generally, DCLR goes indiscriminately to the process of gasification [1,3] or combustion [4], causing a waste of resources. Recently, vigorous efforts have been taken to explore more effective utilization of DCLR. It is reported that DCLR could manufacture products with high added-value, such as paving asphalt modifier [5] and carbon material [6]. On the other hand, the staged utilization of DCLR has attracted great attentions. The relatively light fractions (heavy oil and asphaltene) are firstly separated from DCLR via solvent

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extraction [7] or thermal pyrolysis [8] to produce liquid fuel or chemicals. And the remaining fraction (extraction residue or pyrolysis char) is used for gasification or combustion. Because solvent extraction needs high-dose solvent and solvent-recovery will extend technical flow process, pyrolysis appears to be more suitable for DCLR deoiling due to its mature process and simple operation. And then direct coal liquefaction residue char (DCLRCH) could be gasified to supply hydrogen for the liquefaction process.

The properties of direct coal liquefaction residue water slurry (DCLRWS) were investigated by several groups [9–11]. Our previous work suggested that DCLR could prepare a desirable wet feed-stock of gasification with high slurryability, weak pseudoplastic behavior and acceptable static stability [11]. DCLR could also be blended with low-rank coal to prepare desirable slurries [12]. Similar with DCLR, wet feeding is also suitable for DCLRCH, because its high-boiling components might cause great difficulty in milling system of dry powder gasifier. However, the properties of direct coal liquefaction residue char water slurries (DCLRCHWS) has seldom been reported in the literatures.

The properties of low-rank coal char water slurry have been systematically studied [13,14]. Pyrolysis is an effective upgrading technology for low-rank coal, especially for lignite, by increasing specific surface area [15] and reducing oxygen content [16]. This eventually results in the decreasing amount of bounding water on char particles and improving the slurryability of low-rank coal char water slurry. However, the amount of bounding water of DCLR is relatively less, and pyrolysis is to partly deoil from DCLR for realizing its staged utilization. Previous studies showed that pyrolysis could also increase specific surface area [17] and meanwhile, the graphitization degree could be improved [2], indicating that DCLRCH is a promising material for preparing highly loaded slurries.

For more efficient and more economical utilization of DCLR, effects of pyrolysis temperature on the properties of DCLRCH and the slurryability, rheological and static stability of DCLRCHWS were investigated in this work. The surface physical and chemical properties of DCLRCH were analyzed to shed light on the interaction among the particles, combined with dispersant adsorption isotherms, zeta potential and contact angle.

2. Experimental

2.1. Materials and DCLRCH preparation

DCLR, obtained from 6 t/d Shenhua direct coal liquefaction pilot plant, was milled to 1–3 mm. A fixed bed reactor (SYD-224, S. Y. D. Science and Technology, China) was used to prepare DCLRCH. In each run, about 250 g of pulverized DCLR was heated to the predetermined temperature (300, 400 and 450 °C) at 2 K/min holding for 1 h with 0.8 L/min N₂ flow. The char yield at 300, 400 and 450 °C is

Table 1
Proximate and ultimate analyses (wt%) and H/C of samples.

Sample	Proximate analysis (d)		Ultimate analysis (daf)				S _{t,d}	H/C
	A	V	C	H	N	O ^a		
DCLR	12.48	45.20	90.26	5.99	1.25	0.73	1.55	0.80
P-300	12.54	43.89	91.35	5.56	1.29	0	1.58	0.73
P-400	12.72	27.83	91.82	4.87	1.34	0	1.72	0.64
P-450	13.36	10.29	92.79	3.56	1.41	0	1.94	0.46

d: dried basis; daf: dry and ash-free basis.

A: ash; V: volatile; C: carbon; H: hydrogen; N: nitrogen; O: oxygen.

S_t: total sulfur.

H/C: the atomic ratio of H and C.

^a By difference.

84%, 70% and 64%, respectively. The proximate and ultimate analyses of the raw DCLR and DCLRCHs are listed in Table 1.

2.2. Fractionation of DCLR and DCLRCHs

DCLR and DCLRCHs were separated respectively into four fractions, including hexane soluble (HS), asphaltene (A), pre-asphaltene (PA), tetrahydrofuran insoluble (THFIS), by the sequential solvent extraction method with hexane, toluene, and tetrahydrofuran (THF) (Tianjin TIANLI Chemical Reagents Ltd. analytical grade), and the procedure was presented by Li et al. [8]. 1 g sample and 200 mL reagent were charged into Soxhlet apparatus and the extraction for each solvent lasted for 48 h. Then the insoluble fraction was dried under vacuum at 60 °C for 48 h for thoroughly removing the solvent. Before the next step, the dried insoluble fraction was weighed to calculate the extraction yield and the results are listed in Table 2.

2.3. Preparation of slurries

The milled and sieved particles of DCLR/DCLRCH were adequately mixed on the basis of Alfred particle size distribution [18]. Naphtalenesulfonate–formaldehyde condensate (NSF), an anionic dispersant, was selected and its dosage was 1 wt% on dry basis of DCLR/DCLRCH. The pre-weighed DCLRCH was charged into the desired dispersant solution, and then the mixture was stirred at 3000 r/min for 20 min for homogenization. All operations were conducted at ambient temperature.

2.4. Determination of slurry properties

The slurryability and rheological behavior of DCLRCHWS were determined by NXS-11 rotational viscometer (Chengdu Analytical Instrument Factory, China). The average of six measuring records at 100 s⁻¹ was defined as apparent viscosity of slurries. The maximum solid loading of slurries was designated as the solid loading when the apparent viscosity of slurries was 1000 mPa s at 20 °C [19]. Higher maximum solid loading indicates higher slurryability. The static stability of slurries with the apparent viscosity around 1000 mPa s was measured using the rod dropping method till the appearance of hard sediment [20].

2.5. Characterization

2.5.1. FTIR spectroscopic analysis

The DCLR and DCLRCHs (<154 μm) were dried under vacuum at 60 °C for 24 h and then were grounded for 15 min under nitrogen protection before test. FTIR analysis of samples was performed using a VERTEX70 FT-IR spectrometer (Bruker, Germany) with the same Al₂O₃ 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. The FTIR spectra of the samples for the 3117–2750 cm⁻¹ region owing to aromatic H and aliphatic H were studied by curve-fitting analysis [14].

Table 2
Solvent extraction yield (wt%) of samples.

Sample	HS	A	PA	THFIS
DCLR	21	16	20	43
P-300	16	9	23	52
P-400	0	3	25	72
P-450	0	0	0	100

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