Full Length Article

Study on the stability of hydro-liquefaction residue of Shenfu sub-bituminous coal

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HIGHLIGHTS

- DCLR and its components have different pyrolysis behaviors.
- THFI formed by the condensation of oxygen containing functional groups.
- THF soluble is more prone to form the THFI at lower temperature.

ARTICLE INFO

ABSTRACT

The stability of direct coal liquefaction residue (DCLR) has significant effects on the DCL technology and the utilization of DCLR. In this paper, the pyrolysis behaviors of the DCLR from 6 t/d Shenhua BDU technology and its components including tetrahydrofuran soluble (THFS) and insoluble (THFI) were investigated by thermogravimetric analysis (TGA). Then, its thermal stability and THFS hydrogenation activity were studied by thermal treatment and hydrogenation treatment, respectively. Results show that DCLR and its components have different pyrolysis behaviors. Inorganic components existed in DCLR and THFI show a catalytic effect on the pyrolysis of organic matrix, but THFS inhibits the decomposition of carbonates in DCLR. The weight loss of THFI mainly results from the decomposition of carbonates and the dehydrogenation rather than the cracking of organic matrix. The thermal stability of DCLR mainly depends on the hydrogen donating ability and the solvency of solvent, and THFI formed in the thermal treatment mainly originates from the condensation between oxygen containing functional groups. The spent catalyst in DCLR can inhibit the condensation of THFS, which is more prone to form THFI at lower temperature.

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1. Introduction

DCL is a promising approach for producing clean liquid fuels and valuable chemicals from coal [1,2]. The only industrial DCL plant in the word since WWII had been built in China. At present, the efficient utilization of a large amount of DCLR is becoming a challenge for current DCL [3]. Generally, DCLR separated by vacuum distillation accounts for 20–30% of coal consumed [4]. It not only contains of THFI consisted of minerals, spent catalyst, semi-coke and unreacted coal, but also has a large amount of the heavy materials (THFS) as heavy oil, asphaltene (AS, n-hexane insoluble/toluene soluble) and preasphaltene (PA, toluene insoluble/THF soluble) [5–7]. Since these heavy materials, especially PA, are prone to

aggregate and coke by retrograde reaction [8–10], DCLR is unstable at high temperature, for example in the processes of separation and vacuum distillation. So investigating DCLR stability is essential for the improvement of DCL technology and its efficient utilizations.

In the process of DCL, the benzene insolubles (similar to toluene insolubles) of coal liquid had deemed as precursor of carbon deposited on the catalyst [10,11]. Masuyama et al. [10] suggested that PA contained in the coal liquid bottoms is responsible for the deactivation of hydrogenation catalyst. Burke et al. [8] found that the principal retrograde reactant to form THFIs at SRC-I liquefaction conditions (450 °C, 10 MPa) is PA fraction, which was expected to significantly impede separator operation by forming anisotropic carbon. Tao and Brown [9] found that an improvement in solvency of solvent is only effective in decreasing the coking tendency of AS, and the hydrogen donor solvent is effective in reducing the coking

tendency of AS and PA. The donor hydrogen content of the solvent is the important solvent property controlling coking severity in the DCL process. In our previous works [12,13], some regressive transformations of AS and PA to form coke were also observed in the DCL process at high temperature. However, little formation has been available for the thermal stability of DCLR to the best of our knowledge, though it has significant effects on the process of DCL, especially the separation of slurry product.

Recently, the researches on the utilization of DCLR mainly focus on gasification [14–17], pyrolysis [18–20], hydro-liquefaction [21–24] and preparation of advanced carbon materials [25–27]. Cui et al. [14] found that DCLR has good reactivity of gasification because of the catalysis of spent catalyst and enriched minerals. Chu et al. [15] thought that the enriched mineral has catalysis on the steam gasification of the DCLR char, but the spent catalyst has no remarkably positive effect. Although the minerals, especially the alkaline earth metal minerals such as CaO, CaS and CaCO$_3$, can promote gasification of DCLR as catalyst [16,17], the gasification of DCLR is unfavorable for the high valuable utilization of heavy materials. In order to obtain more liquid fuels, the pyrolysis of DCLR has attracted much intention in China [7,18–20]. Li et al. [18] found a synergetic effect between different fractions of DCLR, which can inhibit the devolatilization of DCLR in the pyrolysis process. Xu et al. [7] investigated the pyrolysis of DCLR from China Shenhua industrial coal liquefaction plant, suggesting that the interaction among its fractions is unfavorable for the evolution of volatile matter, and the inorganic compounds in DCLR have catalysis on the DCLR pyrolysis. Due to hydrogen donor of DCLR, it can improve the tar yield of the co-pyrolysis of DCLR and lignite, but the minerals and the spent catalyst have no catalytic effect on the co-pyrolysis [19]. As another important utilization approach, the hydro-liquefaction of DCLR had also been studied [21–24]. Li et al. [21] observed that there are some synergetic effects in the hydro-treatment of DCLR as whole, and the PA as individual fraction is the most active during the hydro-treatment. However, the PA fraction is a main problem to yield non-soluble materials in the hydrogenation of the heavy liquids of DCLR catalyzed by NiMo/Al$_2$O$_3$ [22]. Wang et al. [23] found that the catalytic hydrotreatment of demineralized DCLR under microwave irradiation at relatively low temperature can increase the solubility of DCLR in methanol and ethanol solvents, especially using Ni as catalyst. In our previous work, it was found that SO$_4^{2-}$/ZrO$_2$ solid acid is in favor of the catalytic hydrocracking of PA, and inhibits the regressive reactions of PA [12]. Therefore, understanding stability of DCLR, especially pyrolysis and hydrogenation activity, is very important in its efficient utilization and the improvement of DCL process.

In the present study, the pyrolyses of DCLR from 6 t/d Shenhua BDU and its components were carried out by TGA to investigate the effects of THFS and THFI components on the pyrolytic property of DCLR. Then, the stabilities of DCLR at lower than the temperature of DCL were investigated by thermal treatments of DCLR under different conditions and the hydrogenation treatments of THFS. The influences of thermal treatment and hydrogenation conditions on the thermal stability of DCLR were discussed.

2. Experimental section

2.1. Samples

DCLR comes from a 6 t/d Shenhua BDU. Its true density and softening point are 1.59 g/cm^3 and 148 °C, respectively. As a solid block at room temperature, it is ground to sizes smaller than 0.5 mm before use. Since the DCLR contains very little of the n-hexane soluble (ca. 6.5%), it was only separated into THFS and THFI

by tetrahydrofuran (THF) solvent extraction in this study. Ultimate and proximate analyses of DCLR, THFS and THFI are listed in Table 1.

2.2. Pyrolysis experiment

The pyrolysis behaviors of DCLR and its components, including THFS and THFI, were investigated using a STA 449 F3 Jupiter thermogravimetric apparatus. Firstly, approximately 10 mg of sample was heated from room temperature to 900 °C at 10 °C/min under 100 ml/min N$_2$ flow (99.999%). In order to obtain the semi-cokes of pyrolysis at different temperatures, the sample of DCLR was heated from room temperature to different setting temperatures under above conditions, subsequently cooled to room temperature under N$_2$ flow. All obtained semi-coke samples were used to determine FTIR spectra and element compositions.

2.3. Thermal treatment experiment

Thermal treatment of DCLR was carried out in a 30 mL tubing reactor shaken vertically. In a typical process, 2.0 g of DCLR and 4 mL solvent were charged into the reactor. The reactor was pressurized to 5.0 MPa with H$_2$ or N$_2$ after purged several times. Then it was submerged into a salt bath and maintained at desired temperature for 1 or 2 h. Finally, the reactor was quenched to ambient temperature in a water bath. Toluene, tetralin, decalin and methyl naphthalene (MN) are respectively used as thermal treatment solvent. The treated product was filtrated and washed with THF solvent. Then the filter residue was exhaustively extracted by THF solvent in Soxhelt extractor. The extraction residue was dried under vacuum at 80 °C for 24 h to obtain THFI. Finally, THF solvent was evaporated from the mixed solution of filtrate and extraction liquid to obtain THFS. THFI yield of thermal treatment sample was calculated by the mass of THFI.

2.4. THFS hydrogenation experiment

The procedure of THFS hydrogenation was similar to that of thermal treatment. In a typical process, 2.0 g of THFS and 4 mL tetralin solvent were used. The initial pressure of H$_2$ was set at 5.0 MPa, and the treatment time was 1 h. 0.1 g of catalyst was added in the catalytic hydrogenation experiment. Since the separation temperature of liquefaction products in the commercial plant is lower than the reaction temperature, the hydrogenation of THFS was carried out at 200, 250 and 300 °C, respectively. Six homemade Ni-base catalysts, including Ni/γ-Al$_2$O$_3$ (Cat-A), Ni–Cu/γ-Al$_2$O$_3$ (Cat-B), Ni–Cu$_2$P/γ-Al$_2$O$_3$ (Cat-C), Ni/OMMT (Organic Montmorillonite) (Cat-D), Ni–Cu/OMMT (Cat-E), Ni/MMT single crystal (Cat-F), were used. The hydrogenised product was separated into THFS and THFI by THF solvent extraction, and THFI yields was calculated.

Table 1
Proximate, ultimate analyses (wt%) of DCLR, THFS and THFI.

Sample	Proximate analysis/wt%			Ultimate analysis/wt%, daf				
	A_d	M_{ad}	VM_{daf}	C_{daf}	H_{daf}	N_{daf}	$S_{t,d}$	O_{daf}[a]
DCLR	20.6	0.4	33.8	85.1	4.7	0.8	1.8	7.6
THFS	–	–	–	91.2	5.8	1.2	0.4	1.4
THFI	41.7	–	17.22	78.6	3.5	0.8	3.6	13.5

Dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base, i.e., moisture-free base); VM_{daf}: volatile matter (dry and ash-free base); $S_{t,d}$: total sulphur (dry base).

[a] By difference.