



Thermal dissolution of Shenfu coal in different solvents

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HIGHLIGHTS

- ▶ 1-MN has high thermal dissolution ability to sub-bituminous coal.
- ▶ The TDSY of Shenfu coal in 1-MN was 56% at 360 °C.
- ▶ Addition of methanol or NMP into 1-MN obviously increased TDSY.
- ▶ Addition of methanol into 1-MN may cause methylation of OH group in the coal.
- ▶ CMNO has higher thermal dissolution ability than 1-MN for Shenfu coal.

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ABSTRACT

The thermal dissolution (TD) behaviors of Shenfu (SF) coal, a kind of Chinese sub-bituminous coal at different temperatures in different solvents were investigated in this study. The results show that almost all of the ash in the raw coal was transferred into the TD residue. The TD soluble yield (TDSY) of SF coal increased with the raising of TD temperatures from 300 to 360 °C for 60 min with 1-methylnaphthalene (1-MN) as solvent, and the highest TDSY of 56% was obtained at 360 °C. Further raising temperature to 380 °C, the TDSY decreased rapidly. The highest TDSY obtained at 360 °C can be attributed to the partial pyrolysis of SF coal.

When *N*-methyl-2-pyrrolidinone (NMP) or methanol was added into 1-MN, the TDSY greatly increased. Especially, when 20% NMP was added, the TDSY reached up to 75%. Since NMP is a strongly polar solvent, it can dissociate the strong cross-links in the coal, resulting in the increase of the TDSY. However, when both of NMP and methanol were added into 1-MN, the TDSY dramatically decreased, indicating that there are some interactions between the two solvents.

Crude methyl naphthalene oil (CMNO) was a more effective solvent for the TD of SF coal than 1-MN, and its TDSY achieved 66% at 360 °C for 60 min. Addition of various polar solvents into CMNO, the TDSY decreased, especially for the addition of methanol, the TDSY decreased by about 15%. The result indicated that methanol may react with some active fractions in CMNO, resulting in the decrease of the TD effect. When both of NMP and methanol were added into CMNO, the TDSY dramatically decreased due to the interaction between them. The TD soluble fractions (TDSFs) obtained from various solvents were characterized by elemental and FTIR analyses.

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1. Introduction

Coal is one of important fossil energy resources with immense reserves in many countries. For example, in China coal took up more than 70% in the primary energy consumption in 2011. The cleaning coal utilization becomes the challenge for the sustainable economy developing because of the environmental effects including CO₂ emission in the large amount of coal utilizations. In recent

years, the thermal extraction of coal with organic solvents to produce ash-free coal called HyperCoal has attracted much attention because of the various usages of this HyperCoal in the efficient and cleaning utilizations of low rank coals [1–6]. HyperCoal can be fired in gas turbines directly to achieve a higher net power output and results in reduced CO₂ emissions [1–4]. The catalytic hydrogenation liquefaction of HyperCoal is the other potential utilization due to the reusability of catalyst in this case [5]. In addition, HyperCoal can also be used in low temperature gasification [6,7] and as an additive in cokemaking [8]. The target in the production of HyperCoal is a thermal extraction yield exceeding 60% and ash content in HyperCoal lower than 200 ppm.

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Several studies involving the thermal extractions of low rank coals with various organic solvents have been reported, and the TD mechanism is studied. Yoshida et al. [2,3] reported that the extraction yields higher than 60% were obtained for several bituminous coals using a flowing solvent extractor with nonpolar solvents 1-MN and light cycle oil (LCO), whereas the extraction yields of sub-bituminous coals were less than 60% with these solvents. Miura et al. [9] reported that extraction yields of ~80 wt.% for sub-bituminous coals and lignites were obtained using polar solvent carbol oil. In order to obtain higher extraction yields for sub-bituminous coals, Masaki et al. [10] and Yoshida et al. [3] reported that the polar solvent CMNO gave a higher extraction yield than the slightly polar solvent, LCO. The extraction yield of Pasir sub-bituminous coal (C%, 73.0%) using CMNO at 360 °C got to 54.3%. When 20% of strongly polar compounds, such as NMP were added into CMNO, the extraction yield further increased to 64.2%. This is explained by the thermally induced relaxation of the aggregate occurred in the extraction with the nonpolar solvent, whereas both thermally induced and solvent-induced relaxations occurred with the polar solvent. Thus solvent-induced relaxation can be effective for releasing the interactions among functional groups containing heteroatoms, especially for sub-bituminous coals and lignites [11]. Kashimura et al. [12] reported that addition of a polar component contained in CMNO, such as indole and quinoline derivatives, into 1-MN also greatly enhanced the thermal extraction yield, and indole had a greater ability to extract coal constituents than quinoline. In addition, they also found that the addition of a small amount of methanol to the nitrogen containing polar solvent greatly increased the thermal extraction yield for Wyodak Anderson sub-bituminous coal (C%, 73%) at 360 °C. When 5 wt.% of methanol was added into CMNO and 1-MN, the extraction yield with CMNO increased from 41% to 53%, while it did not change that with 1-MN.

In this work, TDs of a kind of Chinese sub-bituminous SF coal at different temperatures were carried out in different solvents and the TDSFs obtained were characterized by elemental and FTIR analyses. The addition of some polar solvents into 1-MN or CMNO resulted in some different results in this work from the reports before.

2. Experimental section

2.1. Materials

A Chinese sub-bituminous coal i.e. SF coal was used in this study. The coal sample was ground and sieved to particles of a size less than 200 μm, stored under a nitrogen atmosphere and dried for 12 h under vacuum at 80 °C before use. The ultimate and proximate analyses of SF coal are shown in Table 1. CMNO was derived from coal tar distillates obtained from Chemical Company of Bao Steel, China, and its composition is shown in Table 2. All solvents used are commercial pure chemical reagent (Purity higher than 99.5%) without further purification.

2.2. Thermal dissolution

TD of SF coal was conducted using a flow-type extractor, as shown in Fig. 1. Approximately 0.2 g of coal sample was charged

Table 1
Ultimate and proximate analyses (wt.%) of SF coal.

Ultimate analysis (daf)					Proximate analysis		
C	H	N	S	O _{diff}	A _d	VM _{daf}	M _{ad}
79.38	4.74	1.71	0.36	13.81	6.9	31.9	8.2

Table 2
Composition (wt.%) of CMNO.

1-MN	2-MN	DMN	QN	NA	AN	Indole	Others
22.0	48.5	10.9	3.5	11.0	1.5	0.4	2.2

DMN: dimethylnaphthalene; QN: quinoline; NA: naphthalene; AN: acenaphthylene.

into a stainless steel tuber cell sandwiched by a pair of sintered stainless steel filter plates (average pore size, 0.5 μm) on both sides and placed in an oven. After purging the cell with nitrogen gas, the pressure inside the cell was controlled to 6 MPa using a back-pressure regulator placed downstream in the cell. The cell was filled with the solvent, heated to required temperature at a rate of ~20 °C/min, and held at that temperature for 75 min. After the temperature inside the cell reached required temperature, the solvent was forced to flow through the cell at a rate of 1 mL/min. At the end of the holding-temperature period, the cell was cooled to ambient temperature by flowing cold solvent. The residual solid left in the cell was recovered, washed with toluene and acetone under ultrasonic irradiation, and dried at 80 °C for 12 h in vacuum referred as TD insoluble fraction (TDIF). The TDSY of coal on a dry-ash-free basis was calculated using the following equation:

$$\text{TDSY, \%} = \frac{m_r - m_c}{m_r \times (1 - A_d)} \times 100 \quad (1)$$

where m_r (g), m_c (g), and A_d (wt.%, db) are the initial mass of the coal, the mass of the TDIF, and the ash content of the initial coal, respectively. The TD solution obtained was evaporated at 150 °C in vacuum to remove the most of solvent and then added an excess of n-hexane to precipitate the TDSF after cooling to room temperature. The precipitate was washed with n-hexane and dried at 80 °C for 12 h in vacuum to obtain TDSF. When NMP was used as an additive, the precipitate was washed with a water/acetone mixed solvent (4:1 in volume) again to remove NMP after washing with n-hexane before drying.

2.3. Characterization of SF coal and its TD products

SF raw coal, and its TDSFs were characterized by FTIR spectra using a NICOLET6700 FT-IR spectrometer at a resolution of 4 cm⁻¹. Samples for the FTIR measurement were prepared by mixing 1 mg of coal sample with 100 mg of KBr and the mixture was pressed to form a pellet. The elemental analysis was carried out with an Elementar Vario EL III. All elemental analyses were duplicated, and the experimental error was within 5%.

3. Results and discussion

3.1. Effect of temperature on the TDSY

Fig. 2 shows the TDSY of SF coal in 1-MN at different temperatures. The TDSY of SF coal at 300 °C was 41%. With the raising of TD temperature, the TDSY increased. The highest TDSY of 56% was obtained at 360 °C. Further raising the TD temperature to 380 °C, the TDSY decreased to 40%. 1-MN is a nonpolar solvent, and the high TDSY of SF coal in 1-MN may be the result of heat-induced structural relaxation followed by dissolution of coal components in the solvent [2]. With the raising of TD temperature, some non-covalent bonds are released by thermal-induce, resulting in the increase of TDSY. The increased diffusion rate of 1-MN into coal macromolecular structural network at higher temperatures may also promote the TD process. 1-MN may swell the macromolecular structural network of coal by π–π interactions due to its naphthalene ring, and this will promote the soluble fractions included

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