



Thermal dissolution of lignite and liquefaction behaviors of its thermal dissolution soluble fractions



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HIGHLIGHTS

- TDSY of SL in 1-MN dramatically increased to 81.0% at 380 °C.
- Addition of methanol or ethanol into 1-MN and CMNO greatly increased TDSY.
- TDSF from 1-MN with polar solvent contained more oxygen groups and heavy components.
- TDSF can be almost completely converted with high yield of oil in hydro-liquefaction.
- Addition of polar solvent makes the liquefaction activities of TDSF to be decreased.

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ABSTRACT

Thermal dissolutions (TDs) of a Chinese Shengli lignite (SL) in various solvents at different temperatures were carried out, and the characterization and hydro-liquefaction behavior of thermal dissolution soluble fractions (TDSFs) were probed in this study. The results suggest that thermal dissolution soluble yield (TDSY) in 1-methylnaphthalene (1-MN) dramatically increased at 380 °C due to the obvious depolymerization of SL. Addition of polar solvent methanol or ethanol into 1-MN and crud methylnaphthalene oil (CMNO) can greatly increase the TDSY because of the methanolysis or ethanolysis reactions. Characterization of TDSFs suggests that the TDSF obtained from 1-MN at higher TD temperature contained more amounts of aromatic components. Addition of polar solvent into 1-MN, the TDSF obtained contained more amounts of oxygen groups and heavy components compared to that obtained from 1-MN. Liquefaction of TDSF suggests that TDSF can be almost completely converted by Ni–Mo–S/Al₂O₃ catalytic hydro-liquefaction with much higher yield of oil compared to SL raw coal. The liquefaction of the TDSF obtained from 1-MN with addition of polar solvent gave lower yield of oil and higher yield of gas than that of the TDSF obtained from 1-MN.

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1. Introduction

Low rank coals (LRCs) such as lignite and subbituminous coal are important energy resources due to their enormous reserves. About 13% of coal reserves are lignite in China. On the other hand, the limited petroleum resources as well as fluctuating petroleum price promotes the utilization of LRCs to meet the need of economic development and the ever-increasing demand of energy. Production of transportation fuels from coal has been an important option to lessen the deficiency in petroleum supply [1]. Therefore, direct coal liquefaction (DCL) using LRCs has been attracted more

and more interest to convert them into transportation fuels. LRCs generally have the advantages of high reactivity, low mining cost and low content of heteroatoms such as sulfur, nitrogen [2], therefore they are widely used in DCL compared to other coals with higher ranks. DCL is a process whereby coal is converted into liquid products through hydrogenation. There are three main process variants, namely, pyrolysis, solvent extraction, and catalytic liquefaction [3]. The high efficient DCL for LRCs needs the high solvent extraction yield of coal and high hydrogenation activity of catalyst used in the liquefaction system. When LRCs are used in DCL, the catalyst used is often deposable with low catalytic hydro-liquefaction activity due to the difficult separation of catalyst from the liquefaction residue, which includes much amount of minerals, and also the low solvent extraction yield of the raw

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coal. Therefore, the liquefaction efficiency of raw coal is normally low. In order to increase the liquefaction efficiency, the coal may be deashed prior to conversion [4,5] and the catalyst used should be reusable with high hydro-liquefaction activity. HyperCoal (HPC) [6–10] obtained from thermal extraction of LRCs is most suitable for the high efficient liquefaction, because it is soluble in solvent and the reusable catalyst with high hydro-liquefaction activity can be used in this case. Koyano et al. [11] found that the hydrogenation catalyst could be recycled five times with no detection of deactivation in the hydro-liquefaction of HPC.

Recently, the liquefaction of TDSF, which is from the TD of a Chinese sub-bituminous coal with $\text{BF}_3/\text{SBA-15}$ catalyst was carried out in our laboratory [12]. The results suggested that the catalyst used in the catalytic liquefaction of TDSF had a good reusability and carbon deposition in the reused catalyst slowly took place. Due to the high liquefaction activity of TDSF, the liquefaction conversion is near to 100%. That is to say, the TDSF is almost completely converted and the catalyst used is very easy to be separated and reused. In this study, a lignite was thermally dissolved in various solvents, and the characterization and liquefaction behaviors of the TDSFs were investigated.

2. Experimental section

2.1. Materials

A Chinese Shengli lignite (SL) was used in this study. It was pulverized to pass through a 200-mesh sieve (particle size < 74 μm) followed by desiccation in a vacuum at 80 °C over night before use. Table 1 shows the data of ultimate and proximate analyses of SL. CMNO was derived from coal tar distillates obtained from Chemical Company of Bao Steel, China, and its composition was shown elsewhere [13]. All solvents used are commercially purchased analytical reagents without further purification.

2.2. Thermal dissolution

TD of SL was conducted in a flow-type extractor, as shown in Fig. 1. Approximately 0.2 g of SL was charged 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, and heated to required temperature at a rate of ~ 20 °C/min. After the temperature inside the cell reached required temperature, the solvent was forced to flow through the cell to thermally dissolve SL at a rate of 1 mL/min for 75 min. Then 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 is calculated using Eq. (1):

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

where m_c (g), m_r (g), and A_d (wt%, db) are the initial masses of the coal, the TDIF, and the ash content of the initial coal, respectively.

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

Sample	Proximate analysis			Ultimate analysis (daf)				
	M_{ad}	A_d	V_{daf}	C	H	N	S	O_{diff}
SL	14.7	15.1	33.3	68.2	5.2	1.1	1.1	24.4

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. Hydro-liquefaction

The liquefactions of coal and TDSFs were carried out in a 30 ml tubing reactor at 400 °C. 1.0 g of the dried coal or TDSF loaded with 0.1 g Ni–Mo–S/ Al_2O_3 catalyst was charged into the reactor together with 2 ml of tetralin. The initial pressure of liquefaction was 5.0 MPa with hydrogen. The reactor, agitated with shaking vertically at 120 times per minute, was submerged into a eutectic salt bath, which had been heated to the required temperature, and maintained at that temperature for 1 h. Then the reactor was quenched to ambient temperature in a water bath.

The liquefaction mixture was separated by Soxhlet solvent extraction with tetrahydrofuran (THF), n-hexane and toluene in turn. The n-hexane insoluble but toluene soluble fraction is defined as asphaltene (AS), and the toluene insoluble but THF soluble fraction is defined as preasphaltene (PA). The fractionation procedure of hydro-liquefied product is shown in Fig. 2.

The THF soluble fraction, which is calculated from the THF insoluble residue (THFI) is defined as liquefaction conversion of feedstock. Gas yield is calculated from the material weight difference before and after liquefaction with gas released. Oil yield is calculated as:

$$\text{Oil \%} = \text{Conversion} - \text{PA} - \text{AS} - \text{Gas}$$

The repeatability of the fractionation analysis is 1%.

2.4. TG measurement

Thermo gravimetric (TG) analysis was carried out on a STA-449-F3 Jupiter TG analyzer. About 10 mg of sample was placed in an alumina pan and heated from 25 °C to 800 °C at a rate of 10 °C/min under 50 ml/min argon gas flow. The first point of inflexion after de-watering in the TG curve is defined as thermal decomposition temperature.

2.5. Estimation of molecular size distribution of TDSF

Estimation of molecular size distribution was carried out on Shimadzu LC-20AT high performance liquid chromatography with an UV detector ($k = 254$ nm). A Shim-pack GPC-802.5 (30 cm length; 0.8 cm i.d.) separation column was operated isothermally at 25 °C. THF was used as the mobile phase with a flow rate of 1.0 ml/min. The GPC column was calibrated with polystyrene standards. The molecular weight in the figure is obtained from the calibration curve depending on the retention time.

3. Results and discussion

3.1. Thermal dissolution of SL

Fig. 3 shows the TDSYs of SL in 1-MN at different temperatures. It can be observed that with TD temperature rising, the TDSYs increase till to 380 °C. Further raising temperature to 400 °C, the TDSY hardly changed, suggesting condensation reactions partially taken place. It is interesting that when the TD temperature increased from 360 to 380 °C, the TDSF drastically increased from

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