



Comparative study of low-temperature pyrolysis and solvent treatment on upgrading and hydro-liquefaction of brown coal



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ABSTRACT

Low-temperature pyrolysis (LTP) and solvent treatment (Sol-T) of Yunnan brown coal were conducted for purpose of comparing their effects on upgrading and hydro-liquefaction. Sol-T is effective in both dewatering and deoxygenation of the brown coal. LTP is also effective in dewatering but less effective in deoxygenation, and more extensive cross-linking occurred during LTP than in Sol-T. Sol-T at mild temperatures (less than 200 °C) enhances coal conversion and oil yield during hydro-liquefaction, while treatment at above 250 °C lowers coal conversion and oil yield. LTP of brown coal is definitely detrimental to its hydro-liquefaction, as both conversion and oil yield are significantly reduced. Thus, Sol-T at mild temperatures is more preferable for upgrading brown coals prior to their use in hydro-liquefaction.

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1. Introduction

Hydro-liquefaction or direct coal liquefaction is a process that convert solid coal into liquid fuels and chemicals under high temperature (425–450 °C) and H₂ pressures (≥ 14 MPa) with the aid of solvent and catalyst. Brown coals are promising feedstocks for hydro-liquefaction as they are abundant and more reactive than coals of higher rank [1]. Moreover, the price of brown coals is much lower than high rank coals so the operation cost can be reduced significantly. However, it is essential to upgrade brown coals prior to hydro-liquefaction because their plentiful moisture (25–65 wt%) increases the partial pressure of steam thus lowering efficiency of liquefaction reactor, while the abundant oxygen (often >25 wt%) increases the H₂ consumption and results in higher cost of operation [2].

In the past decades, considerable efforts have been made to dewater and upgrade brown coals. The research can be generally categorized as evaporative and non-evaporative dewatering methods [2–4]. Evaporative dewatering methods include combined grinding and drying, fluidized bed drying, pressurized steam drying, microwave drying and solar energy drying, etc. Non-evaporative drying methods include Leissner process, K-Fuel process, hydrothermal dewatering, upgrading brown coal technology, mechanical thermal extrusion, etc. Each method has its unique merits but also with some inevitable defects. For a technology to

be adopted to dewater brown coals, it is desirable that the upgrading treatment does not decrease the reactivity of brown coals because reactivity significantly affects the efficiency and conversion of hydro-liquefaction. It is extensively reported that pre-drying of low-rank coals impacts their reactivity towards liquefaction. For instance, thermal drying of low-rank coals in air could reduce the reactivity and lower coal the conversion and oil yield due to oxidation [5,6]. Microwave drying could lead to the collapse of pores by intensive localized heating, which enhanced the cross-linking of low-rank coals thus reducing coal conversion and oil yield. Chemical drying with 2, 2-dimethoxypropane improved conversion and oil yield of low-rank coals because of the retention of reaction products (methanol) and solvent in the treated samples [5]. Hydrothermal dewatering of low-rank coals at elevated temperatures was effective in removing moisture and metallic impurities, thus improving the space time yield of reactor by suppressing scale formation and increasing the concentration of coal-solvent slurry, respectively [7]. However, significant loss of organic matter into the hot water occurred, which makes wastewater treatment necessary and intractable.

Most of the above-mentioned dewatering technologies are not yet commercialized due to difficulties in scale-up, high cost or intensive energy demands, etc. In our previous work, we reported that solvent Sol-T of Yunnan brown coal in tetralin at relative mild conditions (less than 300 °C) was effective in dewatering and deoxygenation, but extraction and cross-linking reaction occurred simultaneously, which reduced its reactivity towards thermal conversion [8]. However, the effect of the Sol-T on hydro-liquefaction behavior was not investigated then. Thus this work aims to explore

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whether the Sol-T is beneficial or detrimental to the hydro-liquefaction of YN brown coal.

In this work, YN brown coal and the solvent treated coals (STCs) were subjected to hydro-liquefaction at mild conditions and products distribution was analyzed. For comparison, the brown coal was also upgraded through LTP and then subjected to hydro-liquefaction. This work supplements the previous study in elucidating the effects of Sol-T of YN on its conversion in hydro-liquefaction, thus shedding some light on the upgrading and utilization of brown coals.

2. Experimental section

2.1. Material, Sol-T and LTP

The coal used was a brown coal obtained in Xiaolongtan coal field, Yunnan province, China, thus it was designated as YN. The raw coal was crushed and ground to less than 154 μm . The air-dried sample was sealed in a plastic bag filled with N_2 and stored in a desiccator for use. The properties of YN are listed in Table 1.

Sol-T was conducted at 150–300 $^\circ\text{C}$ with air dried coal with the same procedures as reported in our previous work [8]. Briefly, mixture of YN and tetralin (mass ratio of coal to solvent was 1:3) and 2.0 MPa N_2 was charged into a 150 ml autoclave, which was then heated to prescribed temperature and held for 120 min before cooling down. The mixture was separated by filtration and the solid was then washed with benzene 3 times to remove remaining tetralin before drying under vacuum at 80 $^\circ\text{C}$ overnight. The coal sample treated at 150, 200, 250 and 300 $^\circ\text{C}$ was designated as 150S, 200S, 250S and 300S, respectively. The material balance for Sol-T is shown in Table 2.

LTP was conducted using a horizontal fixed bed reactor. In each run, 10.0 g of YN brown coal (ad.) was charged into the reactor and purged with N_2 (140 ml/min) for 20 min before heating. The heating rate, final temperature and retention time were exactly the same with those of the Sol-T. The char sample was denoted as 150C, 200C, etc., corresponding to the temperature at 150, 200 $^\circ\text{C}$, etc. The yield of char is 91.5%, 87.9%, 83.5% and 82.6% when

heating from 150 to 300 $^\circ\text{C}$. The errors of solid yield in duplicated runs were within $\pm 1.0\%$. The chars were stored similarly with the STCs for further analysis and hydro-liquefaction.

2.2. Hydro-liquefaction

Hydro-liquefaction was carried out using the same autoclave as that of the Sol-T. 7.0 g of coal sample was used in each run and mass ratio of coal (on daf. basis) to tetralin (purity $\geq 99.0\%$) was 1:2. After leak-checking and replacing air, the reactor was pressurized with H_2 to 3.0 MPa (cold pressure). The reactor was then heated to 400 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{min}$ with stirring at 500 rpm. The autoclave was soaked for 60 min at 400 $^\circ\text{C}$ before cooling down by air. It took less than 16 min to cool down the reactor from 400 to 200 $^\circ\text{C}$, below which little chemical reactions would occur. The gases in the reactor were collected and analyzed by a gas-chromatography (GC-950, Haixin Co. Ltd., China). The liquid-solid mixture was separated by Soxhlet extraction with tetrahydrofuran (THF, purity $\geq 99.0\%$) and *n*-hexane (purity $\geq 98.0\%$) consecutively. All reagents were purchased from Sinopharm Group Co. Ltd. and used without further purification. The material balance for hydro-liquefaction is shown in Table 3. The THF insoluble was defined as residue, from which the conversion was calculated. The THF soluble but *n*-hexane insoluble products were defined as preasphaltene and asphaltene, which were lumped together as one component (designated as PAA) due to their similar solubility. The oil yield was obtained by subtracting the gas and PAA yield from conversion. Details of the fractionation procedure and calculations can be found elsewhere [9]. The product yields were the average values of duplicate runs, and the errors were within $\pm 2.0\%$.

2.3. Structural characterization

The chemical structure and reactivity of YN, STCs and chars were characterized by infra-red spectroscopy (IR), ^{13}C nuclear magnetic resonance spectroscopy (^{13}C NMR) and thermogravimetric analyzer (TGA) coupled with mass spectroscopy (TG-MS) as reported [8]. The cross-linking densities of the samples were examined by

Table 1
Proximate and ultimate analyses of YN, STCs and chars.

Sample	Proximate analysis (wt%, ad.)			Ultimate analysis (wt%, daf.)					Atomic ratios	
	M	Ash	VM	C	H	O*	N	S	H/C	O/C
YN	13.52	8.84	42.26	66.10	5.36	26.41	1.47	0.66	0.97	0.30
150S	6.26	8.93	47.09	67.69	5.50	24.60	1.49	0.72	0.97	0.27
200S	6.89	8.98	46.32	71.13	5.40	21.19	1.59	0.69	0.91	0.22
250S	6.09	9.57	44.49	73.78	5.30	18.54	1.70	0.68	0.86	0.19
300S	4.65	10.99	39.34	76.83	5.35	15.37	1.79	0.66	0.84	0.15
150C	4.14	9.55	45.55	66.96	5.71	25.36	1.31	0.66	1.02	0.28
200C	3.22	9.85	45.82	67.70	5.63	24.69	1.33	0.66	1.00	0.27
250C	3.48	10.11	44.47	69.95	5.53	22.46	1.37	0.69	0.95	0.24
300C	3.73	10.79	38.68	72.34	5.33	20.20	1.45	0.67	0.88	0.21

ad: Air dried basis; daf: Dry ash-free basis; M, Moisture; VM, Volatile matter.

* By difference.

Table 2
Material balance for Sol-T.

Temperature ($^\circ\text{C}$)	Before Sol-T (g)			After Sol-T (g)	
	Coal	Tetralin	N_2	S-L mixture	Gas
150	9.80	29.50	2.41	38.12	2.57
200	10.20	30.40	2.38	39.47	2.66
250	10.20	30.50	2.38	38.78	3.09
300	9.80	29.70	2.41	37.62	3.17

S-L mixture: solid-liquid mixture in the reactor.

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