



## Full Length Article

# Effect of solvent and atmosphere on product distribution, hydrogen consumption and coal structural change during preheating stage in direct coal liquefaction



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## ABSTRACT

In order to study the necessity of hydrogen source at preheating stage of direct coal liquefaction, product distribution, hydrogen consumption, and coal structural change of Hami sub-bituminous coal (HM) with 1-methylnaphthalene (1-MN) and tetralin respectively were investigated under hydrogen and nitrogen atmosphere. The results show that oil could be generated from coal itself with 1-MN under N<sub>2</sub> and the yield increases with temperature rising at the range of 200–350 °C, whereas only 4.94% oil is obtained at 350 °C. Moreover, volatiles and H/C ratios of pretreated coal decrease dramatically above 250 °C. At 350 °C, preheating with gas phase H<sub>2</sub> in 1-MN promotes oil yield to 10.42%. In the presence of tetralin, oil yields of 28.55% and 26.15% are achieved under N<sub>2</sub> and H<sub>2</sub> at 350 °C, respectively. Approximately same total hydrogen consumption is observed under N<sub>2</sub> and H<sub>2</sub> with tetralin, and the hydrogen consumption from tetralin is higher than that from H<sub>2</sub>. With the addition of hydrogen sources, aromaticity of the residual solid decreases and reactivity increases. Decomposition of oxygen-containing functional groups like –COOH and C=O is not affected by the preheating solvent and atmosphere but relies on temperature. In addition, pretreated solid samples achieve increasing oil yield and conversion in the subsequent liquefaction with their rising thermal reactivity and H/C ratios.

## 1. Introduction

Converting low rank coal into oil, which has potential to substitute petroleum distillate fuels and improve the efficiency of coal utilization, has been dramatically developed in coal-rich countries, such as China [1,2]. By adding hydrogen donor, direct coal liquefaction (DCL) achieves high quality liquid fuels as well as other chemicals at high thermal efficiencies of 65–70% [3]. During the front-end of DCL process, coal-oil slurry is taken into the heating pipeline or preheater to be heated to the desired liquefaction temperature. Variation of coal-oil slurry occurs in this stage because of interaction between coal and liquefaction solvent. Haghghat et al. [4] found that physical coal dissolution could take place when coal and solvent contact at ambient temperature, resulting in pore volume increasing. And some weak non-covalent bonds, like hydrogen bond, would be broken in solvent thermal dissolution or extraction with temperature rising [5–7]. Meanwhile, a fraction of coal soluble small molecules transfer into the solvent, and the characteristics of coal-oil slurry would change with the

variation of coal-oil slurry components [8,9].

Solvent in DCL plays important roles [10] in swelling or dissolving coal small molecules [4,6,11,12], and transferring free hydrogen to coal thermal cracking fragments [13–15]. In the heating-up stage and liquefaction process, interaction between coal and solvent is noticeable [16]. It has been reported that swelling and dissolution effect of solvent on coal differs with the type of aromatic structure. Higher extraction yield of coal in 1-methylnaphthalene (1-MN) is observed than in tetralin (THN) at same temperature [6]. The coal particles dispersion at same temperature in decalin and paraffin oil is not as good as in tetralin and creosote oil, leading to the different dissolution of coal-oil slurry [17]. Wei et al. [18] have reported that effect of hydroaromatic solvent type on diphenylmethane (DPM) hydrocracking is different in the presence of same catalyst. Aromatic hydrocarbons such as naphthalene and 1-MN inhibit DPM hydrocracking more remarkably than the corresponding hydroaromatic hydrocarbons, due to the stronger adsorption abilities of aromatic hydrocarbons on catalyst surface and scavenging effects on free hydrogen during their hydrogenation.

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However, Niu et al. [19,20] investigated the liquefaction process with 1-MN or tetralin at 445 °C, showing that tetralin inhibits oil formation and 1-MN could achieve high conversion in the presence of nano-size iron catalyst. The difference may be caused by the utilization of catalyst. In addition, atmosphere also has different effect on product distribution and conversion [20,21]. H<sub>2</sub> obtains higher liquefaction conversion than N<sub>2</sub> does in the presence of same solvents at liquefaction stage. Moreover, H<sub>2</sub> consumption amount is also affected by liquefaction solvent [22,23]. These studies all indicate the influential action of solvent type in liquefaction.

The solvent employed for industrial application of DCL is typically derived from the coal liquefaction process, called recycling solvent. It is a mixture of aromatic ring compounds [24], including hydrogen donor and non-hydrogen donor solvents. Before being mixed with coal, the recycling solvent would be hydrogenated by gas phase hydrogen to donate hydrogen for liquefaction [2]. Therefore, hydrogen sources in liquefaction include donor solvent and H<sub>2</sub>. As described above, the effect of solvent type and atmosphere should be studied both in preheating stage and liquefaction. However, most reports focus on effect of hydrogen source on liquefaction stage [20,21] and few studies concern preheating stage below 400 °C. In addition, it is controversial that whether gas phase hydrogen transfers into coal fragment radicals directly [25–27] or by solvent shuttling effect [21,26].

In our previous work [28], the product distribution, coal structural change, and hydrogen transfer amount between coal and donor solvent tetralin under N<sub>2</sub> were investigated at different temperatures. The results show that hydrogen transferred from tetralin affects oil yield and coal conversion significantly in the preheating stage. However, effect of hydrogen sources on product distribution and coal structural change at liquefaction preheating stage is unknown and the hydrogen transfer behavior of coal-oil slurry at different hydrogen sources has been little studied. Moreover, the hydrogen consumed from solvent and gas phase H<sub>2</sub> is required to be further clarified. The objective of this work is to explore the effects of hydrogen sources on product distribution and structural change of low rank coal in preheating stage of liquefaction. Chinese Hami sub-bituminous coal from Xinjiang Province was used in this work. Good hydrogen donor solvent tetralin and non-donor solvent 1-methylnaphthalene were adopted to reveal the necessity of hydrogen source. Reactions were conducted under N<sub>2</sub> and H<sub>2</sub> atmosphere respectively, for investigating the effect of hydrogen transfer or hydrogen shuttling from solvent and gas phase to coal.

## 2. Experimental

### 2.1. Materials

Hami sub-bituminous coal (HM) was grounded and sieved to less than 150 μm, dried in a vacuum oven at 80 °C for 24 h. Table 1 shows the proximate and ultimate analyses of HM. The solvents used in the

work including tetralin (purity ≥ 99.0%), 1-methylnaphthalene (purity ≥ 99.0%), *n*-hexane (purity ≥ 98.0%), diphenyl (purity ≥ 99.5%), and tetrahydrofuran (purity ≥ 99.0%) were analytical-grade chemical reagents and used without further purification.

### 2.2. Reaction procedure and products separation

Reactions were carried out in a 100 mL autoclave (Parr 4598, USA). The weight ratio of solvent to coal in each run was 2:1, that is, 5.00 g coal and 10.00 g solvent were used. When the feed was packed into the reactor, it was then charged with N<sub>2</sub> or H<sub>2</sub> to 3 MPa (cold pressure) after leak-checking and preheated to the desired temperature at 5 °C/min with 400 rpm simultaneously. It was maintained for 120 min at the desired temperature. After reactor cooling by air, the gaseous products were collected and analyzed by a gas chromatograph (GC-950, Haixin, China). The solid-liquid mixture was recovered and extracted with *n*-hexane according to the method from the previous work [28]. Solvent and its derivatives, and light products from coal conversion were included in the extraction. Oil was named for the light products derived from coal. Water is insoluble in *n*-hexane, therefore, oil did not include water in this work. Then the remaining solvent, its derivatives and oil were analyzed by GC-MS without further separation. The yield of solid which is *n*-hexane insoluble was calculated by using Eq. (1). The solid samples obtained in 1-MN at 200–350 °C were named as 1-MN/N<sub>2</sub>-200, 1-MN/N<sub>2</sub>-250, 1-MN/N<sub>2</sub>-300, 1-MN/N<sub>2</sub>-350; and solid samples obtained in different solvents and atmosphere at 350 °C were named as 1-MN/H<sub>2</sub>-350, THN/N<sub>2</sub>-350, and THN/H<sub>2</sub>-350, respectively. Water and oil yields were calculated by Eqs. (2) and (3), respectively. In order to ensure the duplicability, each run was repeated and the experimental deviations were less than 2%.

$$w_s = \frac{m_1}{m_c} \times 100 \quad (1)$$

$$w_w = 18 \times \frac{O_c - O_s - O_g - O_o}{16 \times m_c} \times 100 \quad (2)$$

$$w_o = 100 - w_s - w_w - w_g \quad (3)$$

where,  $w_s$ ,  $w_w$ ,  $w_o$ , and  $w_g$  are the yields of solid, water, oil, and gas, wt % (daf), respectively;  $m_1$  and  $m_c$  are the weight of *n*-hexane insoluble solid fraction and feed coal, g (daf), respectively;  $O_c$ ,  $O_s$ ,  $O_g$ , and  $O_o$  are the content of oxygen in feed coal, solid, gas, and oil, respectively.

### 2.3. Liquefaction of the pretreated solid samples

Solid samples obtained above at 350 °C were mixed with tetralin at coal-tetralin weight ratio of 1:2, and then packed into the autoclave under 3 MPa H<sub>2</sub> (cold pressure) after leak-checking. The reactor was heated from ambient temperature to 400 °C at 5 °C/min with stirring rate of 400 rpm simultaneously. It was kept at 400 °C for 60 min and

**Table 1**  
Proximate and ultimate analyses of HM and treated samples under different conditions.

Run	Sample	Proximate analysis (wt%)			Ultimate analysis (daf, wt%)				S <sub>t,d</sub>	Atomic ratio	
		M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	C	H	O <sup>a</sup>	N		H/C	O/C
1	HM	6.94	6.76	54.19	74.35	5.61	18.68	1.07	0.27	0.91	0.19
2	1-MN/N <sub>2</sub> -200	5.80	6.55	54.44	75.55	5.53	17.37	1.23	0.30	0.88	0.17
3	1-MN/N <sub>2</sub> -250	5.51	6.95	49.35	76.34	5.45	16.69	1.24	0.26	0.86	0.16
4	1-MN/N <sub>2</sub> -300	4.13	7.90	39.84	79.64	5.10	13.61	1.30	0.32	0.77	0.13
5	1-MN/N <sub>2</sub> -350	3.85	8.65	32.21	82.49	4.63	11.01	1.38	0.45	0.67	0.10
6	1-MN/H <sub>2</sub> -350	1.77	8.38	40.50	82.87	5.40	9.88	1.39	0.43	0.78	0.09
7	THN/N <sub>2</sub> -350 <sup>b</sup>	1.55	10.23	48.78	81.34	5.89	11.00	1.46	0.28	0.87	0.10
8	THN/H <sub>2</sub> -350	2.77	9.76	49.19	80.68	5.94	11.60	1.47	0.30	0.88	0.11

ad: air dry basis; d: dry basis; daf: dry ash free basis.

<sup>a</sup> By difference.

<sup>b</sup> Data from Ref. [28].

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