



Research article

Role of hydrogen donor and non-donor binary solvents in product distribution and hydrogen consumption during direct coal liquefaction

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ABSTRACT

Direct liquefaction of Chinese Hami sub-bituminous coal was conducted with binary mixtures of hydrogen donor solvent tetralin (THN) and non-donor 1-methylnaphthalene (1-MN) or naphthalene (Nap.). Effects of solvent composition, temperature, atmosphere, and catalyst FeS₂ on product distribution and hydrogen consumption were investigated at solvent/coal mass ratio of 2. The results show that oil yield increases from 47.70% to 59.95% with 1-MN/THN ratio changing from 2:1 to 1:2. Hydrogen donating ability of binary solvents increases with the rising ratio of THN. H₂ contributes noticeably positive effect on coal conversion in the case of liquefaction with insufficient hydrogen donor solvent. Oil yield obtained during direct coal liquefaction (DCL) with Nap./THN is 58.32%, which is 10.62% higher than that with 1-MN/THN at same solvent ratio of 2:1. This is owing to demethylation effect of 1-MN under liquefaction condition. 1-MN demethylation is induced by active hydrogen and coal radicals, and could consume noticeable hydrogen during DCL. This indicates that the amount of alkylarenes included in liquefaction mixed solvents should be limited, or sufficient hydrogen donor solvent is required to achieve high coal conversion.

1. Introduction

Solvent plays important roles during direct coal liquefaction (DCL) process [1], including swelling the feed coal and extracting small molecules [2–5]; supplying or transferring hydrogen for coal cracking radicals [6–9]; and ensuring the homogeneous thermal transfer in reactor. Extraction yield and liquefaction conversion differ with the variations of solvent composition. For example, different extraction yields of sub-bituminous coal are obtained in 1-methylnaphthalene (1-MN), tetralin (THN), quinolone, and crude methyl naphthalene oil at the same temperature. The difference is mainly caused by the variation of polar property of solvent and its solubility for coal [2, 10]. Moreover, properties of the extracted fraction of coal depend on hydrogen donating ability of solvent. Fraction extracted in THN has higher H/C ratio than that extracted in other hydrogen non-donor solvents [11]. In addition, hydrogen donor solvent is hydroaromatic compounds, which are more beneficial to liquefaction conversion than their corresponding aromatics [12]. Therefore, extracting capacity and hydrogen donating ability of solvent are important in DCL.

In practical industry, recycle oil, which is derived from DCL process and contains multi-component chemicals, is used as liquefaction solvent by considering a balance of cost and benefit on coal conversion [13–15]. Because of the multiple effects among mixed solvents used in liquefaction, behaviors of coal are different from those in pure solvent [16–17]. It is not possible to analyze the total components in recycle oil because of their diversity and complexity. Mixed binary model solvents, as the simplest multiple interacting system, are generally used to investigate the effects of multi-component solvents on DCL. Artok et al. [18] found that cleavage of C_{ar}-O in dinaphthyl ether and diphenyl ether varies with donor ability of liquefaction solvent. Smith et al. [19] studied a series of polycyclic aromatics and found that hydrogenolyses of 1-undecylnaphthalene and 1-alkylpyrene are both affected by addition of different alkylaromatics. McMillen et al. [20] and Mochida et al. [21] demonstrated that partial replacement of hydroaromatics by the corresponding non-donor aromatics could increase hydrogen efficiency by promoting the cleavage of coal.

Role of mixed solvents during DCL is affected by property of solvent and interaction between different components. Mochida et al. [22–23]

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found that THFL (tetrahydrofluoranthene) and OHA (octahydroanthracene) have different hydrogen donating ability, and the two solvents compete for hydrogenation of coal radicals in their binary solvents. Ali et al. [24] and Lee et al. [17] disclosed that mixed ratios of solvents impact on liquefaction conversion, and the optimal composition is varying with the solvent type, indicating that mechanism of solvents' effect is different during DCL. Niu et al. [16, 25] have investigated effects of mixture of hydrogen donor and non-donor solvents on product distribution during DCL. The results showed that addition of some non-donor solvents like phenanthrene and fluoranthene in THN can increase coal conversion, which are attributed to the mixed solvents' good dissolving ability for coal particles. In addition, they observed alkylarenes like 1-MN could be hydrogenated into naphthalene, resulting in low coal conversion. However, hydrogenolysis of 1-MN is not quantified and the subsequent effect on DCL needs to be further studied because of its wide utilization during DCL [8, 19, 26–29]. In addition, the interactions among hydrogen donor, non-donor and coal are little studied so far, despite numbers of studies have been devoted to compare the effect of binary solvents on product distribution and coal conversion during liquefaction.

Therefore, this work aims to study the reason for different behaviors of binary solvents during DCL. THN, as a good hydrogen donor solvent [6], could increase oil yield and coal conversion by offering hydrogen to coal cracking radical fragments. In contrast, non-donor solvent naphthalene cannot offer hydrogen but is favorable for dispersion of coal radicals and can transfer gas phase hydrogen for coal radicals as 1-MN does [16, 30]. Thus, THN, 1-MN and naphthalene were adopted as donor and non-donor solvents, respectively. They were mixed to simulate practical solvents in industrial direct coal liquefaction, aiming to study the roles of binary solvents during DCL. In order to elucidate the interactions between solvents and coal at various conditions, effects of solvent composition, liquefaction temperature, and catalyst on product distribution and hydrogen consumption were studied in this work.

2. Experimental

2.1. Materials

A high volatile sub-bituminous coal from Hami, Xinjiang Province of China, was grounded and sieved to < 150 μm . Hami sub-bituminous coal (HM) was dried in a vacuum oven at 80 $^{\circ}\text{C}$ for 24 h before use. Table 1 shows the proximate and ultimate analyses of HM. The reagents used in the work including tetralin (Sinopharm, purity $\geq 99.0\%$), 1-methylnaphthalene (J&K, purity $\geq 99.0\%$), naphthalene (TCI, purity $\geq 99.5\%$), *n*-hexane (Tianjin Tianli, China, purity $\geq 98.0\%$), diphenyl (TCI, purity $\geq 99.5\%$), tetrahydrofuran (THF, Tianjin Tianli, China, purity $\geq 99.0\%$), and FeS_2 (Alfa Aesar, purity $\geq 99.9\%$) were analytical-grade and used without further purification.

2.2. Reaction procedure

In each run, 5.00 g coal (dry basis) and 10.00 g pure solvent or binary solvents were packed into a 100 mL autoclave (Parr 4598, USA). Binary solvents were premixed at desired mass ratio, and 1:1 of 1-MN/

THN binary solvents means that the solvents include 5.00 g 1-MN and 5.00 g THN. In case of catalytic liquefaction, the amount of FeS_2 used was 1% with respect to dried coal. And the coal sample and catalyst were mixed well before reaction. After leak-checking, the reactor was charged with N_2 or H_2 to 3 MPa (cold pressure) and heated to 350 or 400 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$ with 400 rpm stirring simultaneously. It was kept for 120 min at the desired temperature and then cooled to room temperature by cold air.

2.3. Products separation and analyses

The detailed method of product separation and analyses have been reported in our previous work [31]. The brief description is given as follows. The gaseous products collected after cooling were analyzed by a gas chromatograph. The solid-liquid mixture was recovered and extracted with *n*-hexane. *n*-Hexane soluble fraction derived from coal was named as oil. *n*-Hexane extraction after vacuum rotary evaporation was analyzed by GC–MS. The solid which is *n*-hexane insoluble was dried and weighed. The solid samples were further extracted with THF for 24 h to obtain preasphaltene and asphaltene (PAA), which are *n*-hexane insoluble but THF soluble. The THF insoluble fraction was named as residue. Calculations of oil, PAA, residue, and conversion are shown in Eqs. (1)–(4).

$$w_o = \frac{m_c - m_1}{m_c} \times 100 - w_g \quad (1)$$

$$w_p = \frac{m_1 - m_2}{m_c} \times 100 \quad (2)$$

$$w_r = \frac{m_2}{m_c} \times 100 \quad (3)$$

$$c = 100 - \frac{m_2}{m_c} \times 100 \quad (4)$$

where, w_o , w_g , w_p , and w_r are the yields of oil, gas, PAA, and residue, respectively, wt% (daf); m_1 , m_2 , and m_c are the weight of *n*-hexane insoluble solid fraction, THF insoluble fraction, and feed coal, respectively, g (daf); c is the conversion, wt% (daf).

The weight of naphthalene produced from dehydrogenation of THN in the recovered solvent constituent was calculated by Eq. (5). The amount of hydrogen consumed by coal from THN (H_T) and gas phase H_2 (H_G) during DCL process was calculated by using Eq. (6) and (7), respectively:

$$m_{\text{THN derived naphthalene}} = \left(m_{\text{THN feed}} - m_{\text{Residual THN}} - m_{\text{THN isomer}} - m_{\text{Butylbenzene}} \times \frac{132}{134} \right) \times \frac{128}{132} \quad (5)$$

$$H_T \text{ (wt, mg/g, daf)} = \frac{4 \times m_{\text{THN derived naphthalene}}}{128 \times m_c} \times 1000 \quad (6)$$

$$H_G \text{ (wt, mg/g, daf)} = \frac{m_0 - m_t}{m_c} \times 1000 \quad (7)$$

where, $m_{\text{THN derived naphthalene}}$ is the weight of naphthalene produced

Table 1
Proximate and ultimate analyses of HM coal.

Proximate analysis (wt%)			Ultimate analysis (wt%, daf)				$S_{t,d}$	Atomic ratio	
M_{ad}	A_d	V_{daf}	C	H	O^a	N		H/C	O/C
4.87	7.02	57.78	72.95	6.06	19.17	0.97	0.82	1.00	0.20

M: moisture; A: ash; V: volatiles.

ad: air dried basis; d: dry basis; daf: dry and ash-free basis.

S_t : total sulfur.

^a By difference.

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