



## Full Length Article

## Effect of hydrogenation of liquefied heavy oil on direct coal liquefaction



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## HIGHLIGHTS

- DCL result of liquefied oil is dependent on its boiling range and composition.
- Hydrogenation of liquefied heavy oil help to improve its hydrogen donating ability.
- A new method to prepare recycle solvent by hydrogenation of heavy oil is proposed.

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## ABSTRACT

The effect of hydrotreatment of liquefied heavy oil on direct coal liquefaction (DCL) was studied by hydrogenating the liquefied heavy oil (initial boiling point greater than 320 °C) in a 30 ml continuous hydrogenation apparatus at operating conditions of pressure ( $P$ ) 13–19 MPa, temperature ( $T$ ) 360–400 °C, liquid space velocity ( $LHSV$ ) 0.6–1.4 h<sup>-1</sup>. After hydrogenation, the properties and hydrocarbon composition of liquefied heavy oil were regulated, leading to the enhancement of hydrogen donating ability and 5.6% increase in oil yield of DCL as compared with non-hydrogenated raw oil. Based on the results, a new method of preparing recycle solvent for direct coal liquefaction by mixing hydrogenated heavy oil and un-hydrogenated middle oil in a suitable proportion was proposed, which has been verified to be effective and efficient to increase oil yield.

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## 1. Introduction

Direct coal liquefaction (DCL) is an advanced approach for the clean and effective utilization of coal with high energy utilization efficiency and super low sulfur and nitrogen content in the liquid product. From chemical point of view, liquefaction reactions are complex combinations of physical and chemical processes, which primarily include the thermal cleavage of short alkyl chains cross-linking large aromatic units in the coal and hydrogenation and stabilization of the free radicals by providing active hydrogen from solvent [1]. In order to get maximum yield of the desired product, a suitable solvent should contain reasonable hydrocarbons composition and release active hydrogen to make free radicals stable and prevent formation of light gas and asphalt, which requires that the preparation of solvent should be hydrogenated in an appropriate manner [2–7].

Crude liquefied oil has a wide distillation range and a relatively complex composition. In typical DCL process, the recycle solvent

was hydrogenated as a whole to improve hydrogen-donating performance by ameliorating hydrocarbon composition [1,8–10]. In Shenhua DCL process, all liquid products from liquefied product separation unit are hydrogenated, part of which are recycled as solvents to prepare coal slurry [1]. NEDOL process has a solvent hydrogenation section that enhances the hydrogen-donating ability of the recycle solvent, and the liquefied product separated in the distillation section is hydrogenated before being recycled to the coal liquefaction reactors [8–11]. However, it has been reported that the hydrogenation rate of aromatics was reduced when average molecular weight of narrow-cut fraction increased [12–14]. If the narrow-cut fraction of liquefied oil is hydrogenated without difference, a competitive hydrogenation will happen that the light oil may be over hydrogenated, while the heavy oil insufficient. As a result, the narrow-cut fraction should be treated separately in order to improve its hydrogen donating ability [12–15].

In the present study, the hydrogenation characteristics of liquefied heavy oil are reported and the changes of hydrogen donating ability before and after hydrogenation was investigated to provide a new method of preparing recycle solvents for DCL.

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## 2. Experimental

### 2.1. Materials

Shenhua Shangwan bituminous coal was used with the properties listed in Table 1.

The liquefied heavy oil (initial boiling point greater than 320 °C) was produced from Shenhua 0.18 t/d process development facility, and its properties shown in Table 2.

### 2.2. Experiment procedures

The hydrotreatment were conducted in a 30 ml hydrogenation apparatus, which have two fixed bed reactors in series with diameter of 15 mm. A bimodal Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst (HTS-358 by Axens) was pre-sulfied by dimethyl disulfide and used as catalyst for hydrotreatment. Before the experiment, the length of the catalyst was adjusted to 2–3 mm to meet the packing need of fixed bed. The run conditions of hydrogenation are shown in Table 3.

A 0.5 L stirred autoclave was used for direct coal liquefaction evaluation experiments. The mass ratio of coal to solvent was 1:1.5, and gamma hydroxy ferric oxide synthesized from ferrous sulfate, ammonia and oxygen was loaded on the coal and used as catalyst with the addition of Fe (1.0 wt% of coal (daf)) and co-catalyst sulfur. The H<sub>2</sub> initial pressure was set 10.0 MPa and the coal slurry was heated to the reaction temperature of 455 °C and kept for 60 min.

### 2.3. Product separation and analysis

The liquid and solid products of direct coal liquefaction were separated into oil (*n*-hexanesoluble), PAA (THF-soluble but *n*-hexane soluble-insoluble), and residues (THF insoluble) by Soxhlet extraction with *n*-hexane, toluene, and THF, respectively. The conversion was defined as the percentage of coal into PAA, oil, gas, and H<sub>2</sub>O during the liquefaction. The conversion, yield of product and H<sub>2</sub> consumption were calculated on the basis of as the percentage of dried and ash free coal [6,7].

The C and H elemental compositions of the produced oils were analyzed by ThermoFlash 2000 (Thermo Fisher). The hydrocarbon compositions of the liquefied and hydrogenation oil were quantified by GC-MS analysis (Gas Chromatograph-Mass Spectrometer, Agilent 5975C). Aromaticity (*f*<sub>a</sub>) was calculated based on the <sup>1</sup>H NMR spectra and elemental composition.

## 3. Results and discussion

### 3.1. Effect of distillation range of liquefied oil on direct coal liquefaction

The narrow cut fraction of liquefied oil with low concentration of saturated hydrocarbons and relative high content of aromatics was usually chosen to produce recycle solvent to enhance its hydrogen donating ability [5]. Considering the hydrocarbon compositions were different for each narrow cut fraction [16], it is crucial to select suitable range of liquefied oil and hydrogenation thereof. Therefore, the crude liquefied oil (>220 °C) was used for

**Table 2**  
Properties of liquefied heavy oil.

Parameter	Value
Density, at 20 °C	1.047
<i>f</i> <sub>a</sub>	0.5827
<i>Elemental composition</i>	
C	88.89 wt%
H	8.54 wt%
S	147.3 ppm
N	2450 ppm
<i>Hydrocarbons composition</i>	
Paraffin	4.5 wt%
Naphthene	5.8 wt%
Monocyclic aromatics	19.2 wt%
Bicyclic aromatics	23.1 wt%
Polycyclic aromatics	35.8 wt%
Resin	11.6 wt%

**Table 3**  
Run conditions of hydrogenation of liquefied heavy oil.

Parameter	Value
<i>P</i>	13–19 MPa
<i>T</i>	360–400 °C
LHSV	0.6–1.4 h <sup>-1</sup>
H <sub>2</sub> oil ratio	800 Nm <sup>3</sup> /Nm <sup>3</sup>

physical distillation according to ASTM D 2892 method with the boiling range for each fraction is 20 °C, then the DCL evaluation experiments were conducted in autoclave, through which the liquefied product yield would be calculated. Fig. 1 implies that the coal conversion maintained substantially the same for different narrow cut fraction, while the corresponding oil yield kept constant in the range of 220–320 °C and then turned to be smaller gradually with the increase of boiling point, especially when the temperature greater than 380 °C. Thus, the crude liquefied oil from DCL was separated into light oil (<220 °C), middle oil (220–320 °C) and heavy oil (>320 °C), and the heavy oil was hydrogenated separately to study its reaction characteristic in DCL including coal conversion and product yield and obtain the optimized preparation method to prepare recycle solvent.

### 3.2. Effect of hydrogenation conditions on liquefied heavy oil

The hydrogen donating ability was enhanced by partial saturation of polyaromatics through hydrogenation. Typical hydrogen donors are usually six-membered mono- and bicyclic hydroaromatic compounds, such as 1,2,3,4-tetrahydronaphthalene and octahydro-anthracene, although other chemical functionalities have been recognized to hydrogen donors, but with a lower efficiency [17]. To illustrate the conversion of aromatic and the content of hydrogen donors, the saturation ratio of polycyclic aromatics was shown in Eq. (1):

$$SR = (C_r - C_a) / C_r * 100\% \quad (1)$$

SR: saturation ratio; C<sub>r</sub> and C<sub>a</sub> are concentration of resin, polycyclic aromatics before and after hydrogenation.

**Table 1**  
Properties of Shenhua Shangwan coal.

Proximate analysis (wt%)			Petrographic analysis (wt%)			Ultimate analysis (wt%) <sup>a</sup>				
M <sub>ad</sub>	A <sub>d</sub>	V <sub>daf</sub>	Vitrinite	Inertinite	Exinite	C	H	N	O	S
8.96	13.10	38.55	63.18	37.04	0.44	80.32	4.5	1.01	13.74	0.43

<sup>a</sup> In dry ash-free basis.

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