



# Effects of solvent thermal treatment on the functional groups transformation and pyrolysis kinetics of Indonesian lignite



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## ARTICLE INFO

### Article history:

Received 12 April 2015

Accepted 16 June 2015

Available online 26 June 2015

### Keywords:

Functional groups transformation

Pyrolysis reactivity

Solvent

Lignite

Thermal treatment

## ABSTRACT

Organic solvent upgrading Indonesian lignite was performed in a 1 L autoclave under moderate temperature. The chemical structure and functional groups transformation of lignite upgraded by two organic solvents (ethanol and n-hexane) were analyzed to explore the upgrading mechanism of solvent thermal treatment by using Fourier transform infrared (FTIR) and  $^{13}\text{C}$  nuclear magnetic resonance (NMR). In addition, the characteristics of pyrolysis of treated samples were investigated using thermo gravimetric (TG) to clarify the variance of pyrolysis reactivity. Results showed that the carbon content and calorific value of upgraded lignite were significantly improved, and H/C and O/C ratios of treated samples were significantly reduced with the temperature increasing. The relative percentage of carbonyl and carboxyl carbon, oxygenated aliphatic carbon and methoxyl carbon of lignite upgraded at 300 °C decreased by 20–30%. However, the carbon-substituted and protonated aromatic carbon at 120–135 ppm and protonated aromatic carbon at 90–120 ppm were significantly increased after lignite was upgraded by the two solvents at above 200 °C. These transformations indicated that oxygen-containing functional group was substituted by hydrogen or carbon-substituent as temperature increased, and were intensified at above 200 °C. In addition, oxygen-loss in the treated samples was attributed to the loss of carbonyl group at 175 ppm, dihydric phenol at 147 ppm, and methoxyl group at 55 ppm. The activation energy of upgraded lignite at 300 °C were higher than those of raw lignite and upgraded lignite at 100 and 200 °C, indicating the low reactivity of pyrolysis of the treated lignite with the temperature increasing.

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## 1. Introduction

Lignite exhibits the characterization of low degree of coalification, has highly volatile matter (VM) content and reactivity, and has low sulfur, nitrogen, and heavy metal contents [1–4]. Thus, lignite is suitable for liquefaction [5]. Previous studies [6,7] proved that lignite could be hydrocracked into liquid hydrocarbons through the action of a catalyst under certain temperature and pressure; the oxygen, nitrogen, and sulfur were removed during liquefaction process. However, high moisture content of lignite reduced the efficiency and economy of liquefaction plant [7,8]. Therefore, dewatering lignite is a crucial process before the lignite being utilized. After dewatering, the internal moisture is removed, and the rank and calorific value are improved. In addition, some of the inorganic components of lignite are decomposed, thus the deposition of ash in the combustion, gasification, and liquefaction process is reduced [9–12].

Currently, dewatering of lignite is divided into evaporative and non-evaporative dewatering. For the non-evaporative dewatering,

moisture in lignite is removed in the liquid form; hence the use of high energy of latent heat of evaporation is avoided. Three non-evaporative dewatering technologies have been developed, including hydrothermal, mechanical thermal pressing, and organic solvent upgrading [11–15]. Favas and Jackson [11] investigated the dewatering of Australian brown coal using hydrothermal treatment. They found that internal moisture was reduced from 55.2% to 15.4% after the treatment, and temperature was the main factor affecting the slurryability and the pore structure of lignite, whereas the total organic carbon (TOC) in the wastewater after hydrothermal treatment increased with the temperature increasing. Morimoto et al. [13] studied the dewatering of low rank coal mixed with biomass at 300 °C and 12 MPa. Results indicated that low-rank coal and biomass underwent coalification during the hydrothermal treatment process, and the solid product showed strong hydrophobic and low water reabsorption. Yu et al. [14] conducted basic research on lignite hydrothermal treatment, and found the content of carboxyl, carbonyl, and phenolic hydroxyl in solid product was significantly reduced. In addition, contact angle increased and zeta potential decreased.

Organic solvent upgrading is a non-evaporative dewatering method that moisture in lignite can be removed and separated by

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using organic solvents at mild condition [15]. Kanda and Makino [16] found that sub-bituminous upgraded by liquid dimethyl ether at 0.8 MPa could be removed 98.3% of moisture, and calculated that removal of 1 kg moisture required 2069 kJ. Fujitsuka et al. [17] demonstrated that lignite upgraded at around 350 °C using methyl-naphthalene solvent nearly had no moisture, and the calorific value was close to bituminous. Sato et al. [18] reported that the calorific value of lignite upgraded at 350–440 °C and 2 MPa using decalin (non-polar) attained 35.4 MJ/kg(daf). CH<sub>4</sub> and CO<sub>2</sub> were produced during the process due to the decomposition of carboxyl group. The results of NMR and FTIR analyses showed that the carboxyl group in YN lignite was easily decomposed and removed at 150 °C, although C–O only decomposed at above 200 °C [19].

According to the above mentioned data [16–19], the chemical structure and functional groups of lignite would inevitably change during solvent upgrading, and these changes would have a significantly effect on the subsequent utilizations, including pyrolysis, liquefaction, and gasification. Although many studies on the changes in the physicochemical properties of lignite after upgrading have been published [14–19], functional groups transformation during the lignite upgrading process are yet to be identified. Moreover, the mechanism of demethylation, dehydroxylation, and aromatization of chain during the lignite upgrading process is not yet fully understood. In this work, chemical structure changes and functional groups transformation of lignite upgraded by ethanol and n-hexane at 100–300 °C and 0–17 MPa were studied by using FTIR and <sup>13</sup>C NMR, and reactivity of pyrolysis of treated samples was investigated by using TG.

## 2. Experimental sections

### 2.1. Materials

Indonesian lignite was crushed, milled down to less than 0.35 mm, and sealed in a dry glass bottle. Proximate and ultimate analyses of samples are listed in Table 1. Two types of solvents with purity ≥99.6%, namely, ethanol (polar solvent) and n-hexane (non-polar solvent), were used in experiment. A schematic diagram of hydrothermal reactor is shown in Fig. 1. The autoclave reactor (1 L in volume) was made of stainless steel, and a magnet agitator was equipped in the reactor. Electric furnace was wrapped around the reactor to provide heat, and reaction temperature was controlled by temperature controller. In each run, 100 g of Indonesian lignite was mixed with 500 mL of solvent in the reactor, which was pressurized by N<sub>2</sub>. The speed of agitator was 700 rpm and residence time is 1 h at 100, 200, and 300 °C, respectively. The solid–liquid mixture was separated by filtration after reactor was cooled to room temperature by using water, and solid products and raw lignite were dried in a vacuum oven at 80 °C for 24 h. The residual solvent (n-hexane) in the solid products was removed and washed by using ethanol because ethanol has good solubility and low boiling point (78.3 °C). The yield of

solid products is the weight ratio of solid product and raw lignite based on dry basis at 100 °C for 2 h.

### 2.2. Analysis

The ultimate and proximate analysis of the treated samples were performed using elemental analyzer (Vario EL, Germany) and industrial analyzer (Hengke HKGF-8000, China), respectively. In addition, calorific value analysis of treated samples was performed by using calorimeter (IKA C200, Germany). The FTIR spectra were obtained using VECTOR 22 spectrometer (BRUKER, Germany), and the treated samples were scanned from 400 to 4000 cm<sup>-1</sup>. The solid-state <sup>13</sup>C DP/MAS NMR spectrometer (BRUKER, Avance III 400 MHz, Germany) with a carbon frequency of 100.62 MHz was used to get more insight into the chemical structure and functional groups transformation of treated samples. A spinning speed of 9 kHz and a pulse delay of 0.5 s and 5800 scan were used. Furthermore, the relative percentage of bands can be semi-quantitatively calculated from the solid-state <sup>13</sup>C DP/MAS NMR spectra [20]. Although limitations exist in the semi-quantitative analysis of NMR spectra, this technique can be used to analyze the changes in peak intensity among similar samples.

### 2.3. Pyrolysis properties and kinetic parameters

Thermo gravimetric analyzer (Setaram TGA92, France) was used to determine the pyrolysis behavior of fuels. The curves of TG and derivative thermogravimetry (DTG) of treated lignite were recorded at a heating rate of β 10 °C/min from 20 to 1000 °C. About 10 mg sample was placed in the TG pan.

The reaction kinetic of pyrolysis behavior of samples is expressed in the following equations:

$$\frac{d\alpha}{d\tau} = kf(\alpha) \quad (1)$$

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

$$\alpha = \frac{m_i - m}{m_i - m_f} \quad (3)$$

where  $f(\alpha)$  is a function of the reaction mechanism;  $m$ ,  $m_i$ , and  $m_f$  are the instantaneous, initial, and final mass of the samples, respectively;  $n$  is the reaction order;  $\alpha$  is the thermal conversion fraction of samples at time  $t$ ; rate constant  $k$  is given by Arrhenius equation, as follows:

$$k = A \exp(-E/RT) \quad (4)$$

where  $E$ ,  $A$  and  $R$  are the activation energy (kJ mol<sup>-1</sup>), pre-exponential factor (min<sup>-1</sup>), and gas constant 8.314 J K<sup>-1</sup> mol<sup>-1</sup>, respectively.

**Table 1**  
Proximate and ultimate analysis of samples.

Samples	Proximate analysis (wt%)				Ultimate analysis (wt%)					Q <sub>ad,d</sub> (kJ/kg)	Atomic ratio		Solid yield (%)
	M <sub>ad</sub>	A <sub>ad</sub>	V <sub>daf</sub>	FC <sub>daf</sub>	C <sub>daf</sub>	H <sub>daf</sub>	N <sub>daf</sub>	S <sub>daf</sub>	O <sub>daf</sub>		H/C	O/C	
Raw lignite	17.15	18.11	35.82	28.78	68.23	5.22	0.68	0.16	25.71	15,892	0.92	0.28	100
Ethanol 100 °C	8.18	19.83	33.33	38.53	69.84	5.11	0.59	0.18	24.28	20,178	0.88	0.26	98.1
Ethanol 200 °C	7.22	20.34	31.42	40.99	71.21	4.92	0.52	0.19	23.16	21,548	0.83	0.24	92.6
Ethanol 300 °C	6.68	21.12	29.45	42.65	74.85	4.51	0.48	0.2	19.96	22,812	0.72	0.20	65.1
n-Hexane 100 °C	7.98	19.54	33.01	39.43	70.18	5.03	0.56	0.17	24.06	20,979	0.86	0.26	98.1
n-Hexane 200 °C	6.92	20.68	30.78	41.61	72.09	4.57	0.47	0.15	22.72	22,158	0.76	0.24	97
n-Hexane 300 °C	6.27	21.83	28.45	43.38	76.15	4.36	0.44	0.17	18.88	23,258	0.69	0.19	74.4

M – Moisture, wt%; A – Ash, wt%; V – Volatile, wt%; FC – Fixed Carbon, wt%; Q-Value fever; ad – air dried; daf – dry ash free.

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