



Degradative solvent extraction of low-rank coals by the mixture of low molecular weight extract and solvent as recycled solvent

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ABSTRACT

The authors have proposed a degradative solvent extraction method to dewater, upgrade and separate low-rank coals to upgraded coal, high molecular weight extract (Deposit), low molecular weight extract (Soluble), and a little amount of liquid and gas products. For the practical application of this extraction method, the solvent must be recycled. Furthermore, the separation of the Soluble and solvent, which was implemented by distillation, consumed much energy and added the cost of the whole system significantly. In order to solve these issues, the utilization of the Soluble and solvent as the recycled mixture solvent was proposed and investigated in this work. The results showed that the yields of the Deposit increased by more than two times with the mixture solvent recycle, and got almost stable after 5–7 extraction cycles. This made up for the loss of the part of the extraction product (Soluble) to a large extent. Furthermore, the ratios of O/C, N/C, and S/C of the Deposit decreased with the mixture solvent recycle, indicating that the Deposit was further upgraded. The aromaticity and reactivity of the Deposit decreased and increased with the mixture solvent recycle, respectively. The C_{al}/C_{ar} of the Deposits ranged from 0.35 to 0.84. The ash content of the Deposit increased slightly from 0.25% to 0.29%, and then got almost constant after 4 times of the mixture solvent recycle. Only 0.2–0.4% of the main inorganic elements were transformed from raw coal to the Deposit. The main inorganic elements in the Deposit were Si, Al and Fe. The relatively high contents of some inorganic elements in the Deposit were caused by their high contents and existing form in the raw coal. Thus, it was showed that using the Soluble and solvent as recycled mixture solvent is a feasible way for the practical application of the degradative solvent extraction of low-rank coals.

1. Introduction

The utilization of low-rank coals, such as lignites and subbituminous coals, have got more and more attention [1]. But the high moisture content, high oxygen content, low heating value and obvious self-ignition tendency suppress their thermal conversion and utilization [2]. Furthermore, the low-rank coals contain much small molecular weight fractions and have relatively high chemical activity, compared to the high rank coals [2, 3]. So, the multipurpose utilization of the low-rank coals by poly-generation technology is considered to be more promising compared to the direct combustion and gasification [3]. The authors have proposed a degradative solvent extraction method which treats low-rank coals in a nonpolar solvent at around 350 °C using an autoclave to dewater, upgrade and separate them to three solid fractions

and a small amount of liquid and gas products [4–6]. The three solid fractions were the extraction residue which is the so-called upgraded coal, high molecular weight extract (named as Deposit) which extracted at the extraction temperature and precipitated as solid from the solvent at room temperature, and low molecular weight extract (Soluble) which was soluble in the solvent at room temperature. The solid Soluble can be obtained after removing the solvent by distillation. The Soluble and Deposit have the carbon content of higher than 80%, oxygen content of lower than 10%, rather low moisture content, and are almost ash free. It was found in our previous work that the two extracts can be used as a good binder for coke making [7–9], to produce high-quality liquid fuel and chemical by further liquefaction [10, 11], and as a precursor for high value-added carbon material preparation, such as carbon fiber [12, 13] and porous carbon materials [14]. The upgraded coal has much

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better combustion and gasification characteristics [15, 16], and can be used as a good precursor for activated carbon preparation [17], compared to the raw coals. So, the degradative solvent extraction of low-rank coal is believed to be one of the promising multi-purpose utilization approaches of the low-rank coals.

For the practical application of this degradative solvent extraction method, the solvent must be recycled to minimize the solvent needed [18]. Furthermore, the best approach for the separation of the Soluble and solvent is distillation technology, such as flash separator. But it consumes much energy and adds the complexity and cost of the whole system significantly, because the solvent commonly used have rather high boiling point [19]. In order to solve these issues, the authors proposed to use the mixture of the Soluble and solvent as the recycled solvent for the degradative solvent extraction. By this way, it not only realized the solvent recycling, but also avoided the separation of the Soluble and solvent. When using the mixture of the Soluble and solvent as the recycled solvent for the degradative solvent extraction, the Soluble will no longer be the target product during each extraction experiment. So, the Soluble, which is one of the main products of the degradative solvent extraction, was lost by this way. Also, the effect of the Soluble in the recycled solvent on the subsequent extraction was not clear. In our previous work, we preliminarily studied the degradative solvent extraction of bituminous coal by the recycled mixture of the Soluble and solvent using a flow-type reactor [18]. It was found the recycled solvent can enhance the extraction yield. But the reason is not clear. The physicochemical property of the main product, such as Deposit, was not characterized in detail. Furthermore, the authors are currently focusing on the degradative solvent extraction of low-rank coals, rather than bituminous coal. It was found that the two type coals have different reaction behavior and product property for the degradative solvent extraction. Thus, in this work the degradative solvent extraction of low-rank coals by the mixture of the Soluble and solvent as recycled solvent was studied in an autoclave. The effects of solvent recycling and the Soluble concentration in the recycled solvent on the yields and properties of the extraction products were investigated in detail. The mechanism of this process was also discussed preliminarily.

2. Experimental

2.1. Degradative solvent extraction procedure

Three typical low-rank coals, which are Huolinhe lignite (HLH), Hefeng subbituminous coal (HF) and Naomaohu subbituminous coal (NMH), were used for the degradative solvent extraction. The proximate and ultimate analyses were shown in Table 1. Non-polar solvent 1-methylnaphthalene (1-MN) was used as the solvent for the extraction.

The detailed procedure of the degradative solvent extraction was already described in our previous papers [5,20]. It was carried out by using a specially designed autoclave. There was a filter (0.5 μm diameter opening) equipped at the bottom of the autoclave. About 20 g of dried raw coal and 300 mL of 1-MN were placed in the autoclave. After purged adequately by N_2 , the autoclave was heated up to 350 $^{\circ}\text{C}$ at the heating rate of 5 $^{\circ}\text{C}/\text{min}$, and maintained for 60 min. A valve below the

filter was then quickly opened at the extraction temperature after the residence time, in order to allow the mixture of the extract and solvent to be transferred to a reservoir. The reservoir was maintained at ambient temperature by circulating cooling water. A part of the extract, which precipitated as solid from the solvent in the reservoir at ambient temperature, was the Deposit. Another part of the extract, which was still solubilized in the solvent, was the Soluble. All of the substance in the reservoir was collected and separated by filtration. The filter cake was obtained as the Deposit. The residue remained in the autoclave above the filter. The detailed process flow diagram can be found in previous work [20, 21]. The filtrate, which was the mixture of the solvent and Soluble, was used as the recycled solvent for next extraction of fresh coal. Around 10 mL of the filtrate was sampled and separated by rotary evaporator, in order to obtain solid Soluble and solvent for yield calculation and characterization. 10 mL of fresh solvent was then added to the recycled solvent to ensure the same amount of solvent used for each run. This change of the solvent was rather small and the effect for the extraction was ignored in this work. So, the Soluble concentration in the recycled solvent and the total Soluble yield were calculated. The un-extracted fraction, remained in the autoclave after the extraction, was the Residue (upgraded coal). The gaseous products were collected in a gas bag for analysis. The degradative solvent extractions with different ratio of coal to fresh solvent were also performed at the same condition.

The Soluble, Deposit and Residue, obtained from the extraction with recycled solvent and with different ratio of coal to solvent, were further dried in a drying oven under vacuum at 150 $^{\circ}\text{C}$ for 6 h to remove the residual solvent completely. The gaseous product was analyzed quantitatively by a gas chromatograph (Agilent MicroGC3000). The yields of Soluble, Deposit, Residue and Gas were calculated by their weights. The yield of Liquid was calculated by mass balance.

2.2. Product characterization

The proximate analyses of the raw coals were carried out by a muffle furnace according to GB/T212-2008 standard procedure. The elemental analysis was performed by an elemental analyzer (CHN EL-2, Vario). Thermal decomposition behaviors of solid products were characterized by a thermogravimetric (TG) analyzer (Diamond TG/DTA, PerkinElmer). About 10 mg sample was heated up to 900 $^{\circ}\text{C}$ at the heating rate of 10 K/min in flowing pure nitrogen of 80 mL/min. The chemical structure analyses of the solid products were performed using a Bruker VERTEX-70 FTIR spectrometer ranging from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} . The chemical compositions of the minerals in raw coals and products were estimated by X-ray fluorescence (XRF, PANalytical B.V., Zetium) with a Rh target X-ray tube (60 kV, 160 mA).

3. Results and discussion

3.1. Product yields of the extraction with solvent cycle

The product yield distributions of the extraction using initial solvent were firstly investigated and shown in Fig. 1. It shows that the NMH coal gave highest Soluble and Deposit yields. On the contrary, the lowest Soluble and Deposit yields were obtained from HLH coal. The highest gaseous product yield was obtained from HLH coal. The difference of the yield distributions for the three coals was attributed to the property of the raw coals. Besides, the figure also shows that the Soluble yield was always higher than the Deposit yield for the three coals, consisting with our previous work [5].

The lower figure in Fig. 2 shows the yield changes of Solubles and Deposits against the extraction cycle. The gaseous product, Liquid and Residue yields were not shown in Fig. 2. It was because they were rather close to the yields of the extraction using initial solvent which was shown in Fig. 1. The total yields of Soluble and Deposit were also almost

Table 1
Proximate and ultimate analysis of the raw coals.

	Proximate analysis				Ultimate analysis			
	(wt%)				(wt%, daf)			
	M_{ad}	A_{db}	V_{daf}	FC_{daf}	C	H	N	O ^a
HLH	27.1	20.1	45.6	54.4	63.7	4.7	1.3	30.2
HF	6.4	14.7	46.9	53.1	75.4	6.4	1.4	16.8
NMH	15.8	6.4	41.8	58.2	75.7	5.0	1.0	18.3

^a Calculated by difference.

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