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Research article

Study on the thermal liquefaction of Xilinguole lignite in solvent at high temperature

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ABSTRACT

In this paper, thermal liquefaction (TL) of Xilinguole lignite (XL) in the range of 400–540 °C have been carried out in toluene, tetralin (THN) and their mixed solvent, respectively. Results indicated that the conversion of XL primarily depends on the hydrogen donor ability of solvent. The highest conversions of XL in toluene and THN were obtained at 480 °C, which are 25.8% and 98.6%, respectively. The condensation of pyrolytic free radicals dominates the TL in toluene solvent but there is hardly obvious coking occurred in THN at below 510 °C. In toluene and THN mixed solvent, the conversion of XL increases with the THN content. The products of TL in toluene mainly consist of oil and gas (O + G) fraction, but the asphaltene (AS) and preasphaltene (PA) factions prevail in the products of TL in THN. Hydrogen donor solvent has obvious improvement on the deoxygenation in the TL process. Therefore, TL in hydrogen donor solvent is a potential conversion technology of XL due to low reaction pressure and without H_2 and catalyst used.

1. Introduction

Lignite is a very important coal resource due to its abundant reserve (approximately 45% and 55% of total coal reserves in the world and in China, respectively) and low mining cost [1]. Unfortunately, compared to high-rank coal, lignite is not utilized extensively because of its low energy density and high moisture content [2]. Recently, the clean and high-efficient utilization of lignite is attracting increasing attentions all over the world [3,4]. Thermal conversions such as liquefaction [5,6], gasification [7,8], and pyrolysis [9–11] are the main approaches for the utilization of lignite due to its high reactivity and volatiles. In addition, thermal dissolution [12,13] and oxidizing depolymerisation [14] were also used to convert lignite into high value-added chemicals under mild conditions. Since low rank coals liquefy more readily than bituminous coals and produce higher yield of liquid products [15–17], the direct liquefaction of lignite is a high-efficient utilization technology.

As well known, coal is mainly composed of a macromolecular network structure containing polycyclic aromatic clusters connected by bridged bonds [18]. In primary stage of liquefaction, the macromolecular structure is thermally decomposed and subsequently hydrogenated by the active hydrogen from hydrogen donor solvent to form primary products, and then the primary products are further hydrocracked on the catalyst by H_2 [19]. Patrakov et al. [20] found that there are two substantially different stages in the liquefaction process with a boundary at a value of coal conversion 10–15%, which respond to the extraction of molecular phase of coal and the decomposition of the macromolecular network of the coal, respectively. Thus the liquefaction of coal mainly depends on the pyrolysis of coal structure and the hydrogen donatability including hydrogen donor solvent and/or H_2 pressure along with catalyst, so it has to be carried out under high temperature and high pressure. Since harshly liquefaction conditions and high hydrogen consumption evidently improve the cost of direct coal liquefaction (DCL), so to develop mild DCL technology is very significant.

Although substantial efforts for the mild liquefaction of coal were done by pre-treatment upgrading of raw coal [21–23], the liquefaction in hydrogen donor solvent without H_2 may be another efficient liquefaction technology of lignite. With hydrogenated petroleum pitch-based solvent as hydrogen donor solvent, Mochida et al. [24] carried out the liquefaction of Australian brown coal under atmospheric pressure. The highest yields of quinoline soluble and benzene soluble of LY coal respectively reached to 90 and 60% at 420 °C, and the gas and oil yields increased with temperature up to 460 °C. Philip et al. [25] investigated the liquefaction of Texas lignite in a hydrogen-donor solvent system at 380–390 °C, and found that the tetralin (THN) solvent mainly provided active hydrogen atom to stabilize depolymerised products. Karaca et al. [26] studied the catalytic dissolution of two Turkish lignites in THN

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under nitrogen atmosphere in range of 325–425 °C. Their results showed that the conversion of lignite mainly occurred at 375 °C and above, and the catalyst enhanced mainly the oil formation. Further, the dissolution of bituminous coal in THN and naphthalene at 300–450 °C under N_2 atmosphere disclosed that the hydrogen transfer from THN to coal radicals only occurred above 350 °C, and to abstract hydrogen for coal radicals from itself and its extraction residue might be easier than that from hydrogen donor solvent [27]. In addition, Cronauer et al. [28] thought that much of the hydrogen necessary to stabilize free radicals comes from the donor solvent or intramolecular rearrangement and not from dissolved gas. Meanwhile, it was also found that the C-C cracking of analogues of dibenzyl is purely a thermal reaction. So it is the abstraction reaction of pyrolytic free radical to cause the hydrogen transfer. According to the proposal of Shi et al. [29], the breakage of C_{al}-C_{al} and C_{ar}-C_{al} bonds in coal occur around 450 and 550 °C, respectively. From that more than conventional liquefaction temperature may be essential for the TL of lignite.

As a low rank coal, XL consists of a great deal of premature coal structures, such as methylene bridges and hydrogenated aromatic rings, which endow it high reactivity and active hydrogen content. In present work, XL was liquefied in different solvents under 400–540 °C without H_2 and catalyst used. The influences of solvent and temperature on the liquefied products were investigated by combination with the characterization of FTIR, TG and element analysis, and the hydrogen donoration was discussed in order to explore its high-efficiency utilization technology.

2. Experimental

2.1. Materials

Xilinguole lignite (XL) used in this study was obtained from Inner Mongolia, China. It was pulverized to pass through a 200 mush sieve (< 74 μm) followed by desiccation in a vacuum at 353 K overnight before use. Table 1 lists the ultimate and proximate analyses of XL. All solvents used are commercially purchased reagents without further purification.

2.2. Liquefaction procedure

TL was carried out in a batch 150 ml autoclave. 8 g coal and 40 ml solvent were charged. The autoclave was purged with N_2 (99.999%) or H_2 (99.99%) for three times and pressurized to the desired initial pressure. It was heated to required temperature at a rate of 15 °C/min with stirring, and maintained at the temperature for 1 h. Then the autoclave was quenched to ambient temperature in a water bath, and the head pressure was released slowly. The gas product was simultaneously collected for GC analysis.

The autoclave was thoroughly washed with tetrahydrofuran (THF) solvent to recover the liquefied product. The following procedure was used to separate the recovered product. Firstly, the liquefied product was separated into THF soluble (THFS) and THF insoluble (THFI) by extraction with THF solvent. The conversion was calculated by the THFI mass. Secondly, THFS was successively extracted with n-hexane and toluene into hexane soluble (oil + solvent), hexane insoluble/toluene soluble (asphaltene, AS) and toluene insoluble (preasphatlene, PA). Yields of AS and PA was calculated by the obtained AS and PA masses, and the yield of Gas + oil was obtained by difference between conversion and AS + PA yields. Liquefaction conversion and all product yields were based on dry and ash-free basis coal. Most of the runs were made in duplicate and the reproducibility was better than ± 2.5%.

Table 1
Ultimate and proximate analyses of XL.

Sample	Proximate analysis (wt%)			Ultimate analysis (wt%, daf)				
	M_{ad}	A_d	V_{daf}	C	H	N	S	O[a]
XL	15.77	11.01	40.34	69.2	4.1	1.1	0.6	25.0

[a] By difference.

2.3. Characterization of liquefaction derivatives

The compositions of N_2, H_2, CH_4, CO, CO_2, and C2–C4 in collected gases were simultaneously analyzed by GC with a thermal conductivity detector (5A molecular sieve packed column) and a flame ionization detector (Porapak-N packed column and 30 × 0.53 × 25 μm KCL capillary column). IR spectra were measured by a Nicolet 6700 spectrometer at ambient temperature. About 10 mg of sample was mixed with 200 mg of KBr, and the mixture was pressed into a pellet. TG curve was recorded with a NETZSCH STA-449-F3 thermogravimetry in 30 ml/min nitrogen (99.99%) at a rate of 10 °C/min. Element analysis was carried out using an Elementar Vario EL III.

3. Results and discussion

3.1. TL in toluene solvent

In order to investigate the hydrogen donatability of lignite self, XL was liquefied in toluene under 0.1 MPa (initial pressure) N_2 atmosphere at the range of 400–540 °C. In present work, it is unexpectedly found that all liquefied products obtained in toluene mainly consist of the fractions of gas + oil and THFI, and the sum of AS and PA yields is < 1%. Experiment results in Fig. 1 display that the conversion of XL increases with the raising of temperature up to 480 °C, at which the highest conversion of 25.8% is obtained. Further raising the temperature to 540 °C, the conversion gradually decreases to 11.8%. In the range of 420–510 °C, TL conversions all are over 23.2%. It reveals that only a small part of free radicals convert into small oil and gaseous hydrocarbon by the abstraction of hydrogen from lignite matrix or the disproportionation, and most of pyrolytic free radicals form THFI by regressive reaction due to poor hydrogen donor ability in toluene. Further, the analysis results of the gas products formed at 450 °C show that the yields (wt%, daf) of H_2, CO, CO_2, CH_4, and C_2–C_3 hydrocarbon are 1.16, 0.08, 0.14, 1.03 and 1.71%, respectively. It is noted that there is a significant amount of H_2 to be formed, suggesting that the matrix of XL happened obviously dehydrogenation in process of TL. However, poor swelling and dissolving capacity of toluene is not advantageous to the diffusion of pyrolytic free radicals, so that only small free radical can capture the hydrogen to form small molecular gas and oil, and most

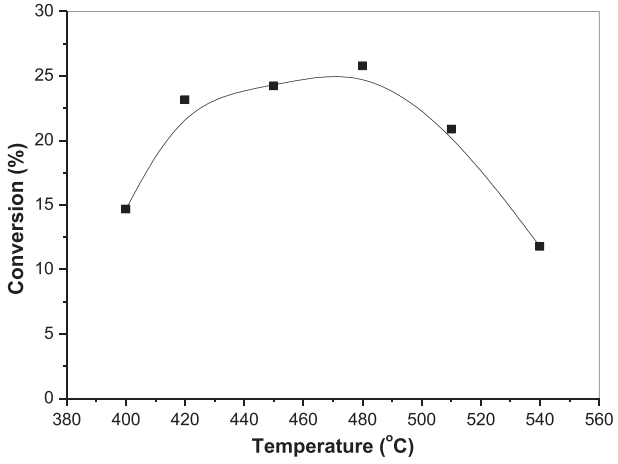

Fig. 1. TL conversion of XL at different temperatures in toluene under 0.1 MPa N_2.

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