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Structure and morphology variation of solid residue from co-liquefaction of lignite and Merey atmospheric residue

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ABSTRACT

Structural features of the co-liquefaction solid residue (CLSR) from the co-liquefaction of lignite and Merey atmospheric residue (MRAR) were analyzed to investigate the internal correlation relevant to the hydro-conversion process of the reaction system. The feedstocks were loaded by using different catalysts, which resulted in a series of CLSRs with different hydroconversion degree after co-liquefaction. The experimental results showed that the carbonaceous solid conversion efficiency was related to the H/C atomic ratio and O content of the CLSR. X-ray diffraction (XRD) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis were used to study the structural parameter changes of the CLSRs from co-liquefaction with different catalysts. Experimental data of the selected analytical parameters exhibited credible relationship with the carbonaceous solid conversion efficiency. Considering the structure variation of CLSRs was clearly associated with the conversion of co-liquefaction, the utilization of linear fitting for the approximate evaluation of carbonaceous solid conversion efficiency was suggested. A comparison of the particle-size distribution and microscopic morphology of different CLSRs showed that the small mean particle diameter and a fragmented CLSR shape resulted as distinctive features for the high hydroconversion of co-liquefaction. Besides, the microscopic feature variation indicated the inhibition of coke formation in the reaction system was crucial to improve the hydroconversion degree of co-liquefaction of lignite and heavy oil.

1. Introduction

Developments in clean-coal utilization, including a significant focus on coal liquefaction, are aimed at enhancing product value and reducing environmental contamination [1,2]. Indirect coal liquefaction has a commercial global application, whereas industrial applications of direct coal liquefaction have stagnated for decades because of technical problems and investment issues [3]. Recently, the co-liquefaction of coal and heavy oil have attracted researcher interest in coal-rich countries, especially China, because of the one-unit technical features of the simultaneous processing of coal and heavy oil [4,5].

In general, highly volatile coal and heavy oil with enriched aromatics are considered to be suitable components for hydroconversion in co-liquefaction. Unlike conventional direct coal liquefaction with the use of specific hydrogen-donor solvents [6], the co-liquefaction of coal and heavy oil requires a higher catalytic activity for the applied catalysts [7,8]. Highly dispersed catalysts have exhibited a favorable efficiency for coal conversion, and include supported catalysts, water-

soluble catalysts, and oil-soluble catalysts [9–12]. An activity evaluation for coal liquefaction in literature indicates that molybdenum and iron are the most common transition metals for catalysis, and that the hydrogenation reaction is discussed most frequently [13–15]. An application of desirable hydrogenation catalysts could saturate numerous molecular fragments or free radicals that are derived from coal pyrolysis in the reaction of solvents at a high temperature, and contribute to improve the overall conversion and oil yield [16].

Because of limitations in feedstock properties and catalytic activity, a large amount of co-liquefaction residues, and in particular, the in-extractable parts, namely, the co-liquefaction solid residue (CLSR), have resulted, which prevents further processing [17]. CLSR is the final residue from the successive reactions of pyrolysis, hydrogenation, and condensation of co-liquefaction feedstocks. The contained structural information of the CLSR may reflect the conversion extent of coal and the reaction processes directly [18]. A sequential extraction is used frequently to separate different polarity fractions from the coal liquefaction residues for sophisticated characterization [19], and complex

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mixtures of minerals, unreacted organic constituents, and condensation products concentrate in the CLSR. The complicated composition of CLSR makes it difficult to study its chemical and structural properties compared with asphaltene and preasphaltene.

Previous literature has addressed many qualitative or quantitative methods for the structural characterization of raw coal by various analytical techniques [20–26], and has included mainly Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), thermogravimetry (TG), and electron microscopy. Reports exist on a thorough analysis of the relationship between the coal structure and the reaction behaviors [27,28]. Sun et al. proved that the co-liquefaction of coal and petroleum residues is improved after the mechanical activation of coal as was consistent with the coal characterization [29], but changes in the liquefaction residue were not discussed. Wang et al. [30] suggested that the mass loss of tetrahydrofuran in the insoluble coal liquefaction residue resulted mainly from carbonate decomposition and dehydrogenation. Absorption bands of aliphatic CH stretching and oxygen-containing functional groups appeared to weaken after the liquefaction of sub-bituminous coal and lignite according to changes in the FTIR spectra [31]. However, a quantitative or semi-quantitative analysis of CLSR and the corresponding parametric variation during coal liquefaction are unclear, especially for the co-liquefaction of coal and petroleum residues. Since the analytical data of CLSR are potential to reflect or to evaluate the reaction process of co-liquefaction system, the investigation of convenient analytical methods of CLSR is of great importance, especially for the industrial application.

We investigated the CLSRs from the co-liquefaction of Mery atmospheric residue (MRAR) and lignite loaded with different catalysts by various analytical methods and discussed the correlation between the characterization features and the reaction results. A comparison of the analytical data from the raw coal and different CLSRs allowed for a study of the influence of catalytic activity on the conversion of the reaction system. The possible role of applied catalysts during the co-liquefaction process of lignite and MRAR was proposed.

2. Experimental

2.1. Materials

Anhui coal, a Chinese lignite, was used as received, ground and sieved to less than 200 mesh, before being dried under vacuum at 110 °C overnight. MRAR, the atmospheric residue of a naphthenic heavy oil from Venezuela, was used as the heavy oil with which to conduct the liquefaction experiments with coal. The coal and oil characteristics are shown in Table 1.

The coal was pretreated in an aqueous solution with a certain amount of ferrous sulfate, nickelous nitrate, cobaltous nitrate, or ammonium molybdate by isometric impregnation, and the mass ratio of added metal salt to coal was 4000 $\mu\text{g}\cdot\text{g}^{-1}$ (calculated by metal content as shown below). Then the coals impregnated with different metal salts as catalysts were dried under vacuum at 110 °C overnight. The industrial analysis of every sample was conducted to determine the moisture and ash content in different pretreated coal samples.

2.2. Liquefaction experiments

A slurry mixture of lignite and MRAR (1:3 by mass ratio, 150 g), and sulfur of 0.5 g as a promoter, were loaded into a 500-mL stirred autoclave for the liquefaction experiments, with a catalyst concentration of 1000 $\mu\text{g}\cdot\text{g}^{-1}$ based on the total mass of coal and oil. The autoclave was charged with hydrogen to 8.0 MPa at room temperature, and heated to 400 °C at 3.33 °C/min with stirring. After 1 h at the reaction temperature of 400 °C, the autoclave was cooled rapidly with water. Every experiment was repeated at least three times. The gas composition and an elemental analysis of the coal-oil slurry and product were obtained to

Table 1
Characterization of the dried Anhui lignite coal feed and the MRAR solvent.

Description	Properties	
	Lignite	MRAR
<i>Proximate analysis (wt%)</i>		
moisture	0.72	–
volatile matter	53.6	–
fixed carbon	41.71	–
ash	3.97	–
<i>Ultimate analysis (wt%, daf)</i>		
carbon	71.78	84.82
hydrogen	6.3	10.87
nitrogen	0.62	0.63
sulfur	0.43	2.89
oxygen (by difference)	20.87	0.79
H/C molar ratio	1.05	1.54
aluminum, (wt%)	0.499	–
silicon, (wt%)	0.444	–
iron, (wt%)	0.358	–
magnesium, (wt%)	0.226	–
calcium, (wt%)	0.163	–
density, 20 °C ($\text{g}\cdot\text{cm}^{-3}$)	–	0.9976
viscosity, 100 °C ($\text{mm}^2\cdot\text{s}^{-1}$)	–	290.2
condensation point (°C)	–	22
carbon residue (wt%)	–	15.33
saturate (wt%)	–	31.49
aromatics (wt%)	–	39.44
resin (wt%)	–	19.36
C7-asphaltene (wt%)	–	9.71

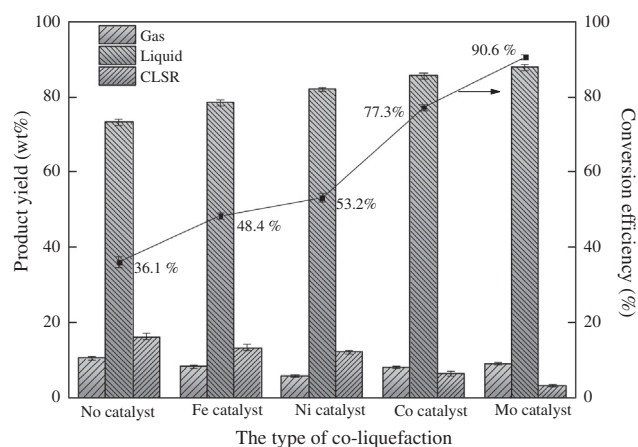


Fig. 1. Product distribution with different catalysts from co-liquefaction of lignite and MRAR.

calculate the hydrogen consumption according to reported literature [32,33]. The total feedstock was the sum of hydrogen consumption and coal-oil slurry, and the gas product mass was calculated from the mass difference between the liquid and solid product and the sum of the total feedstock.

The solid product (namely the CLSR) inside the autoclave was collected and separated by Soxhlet extraction with toluene, which could be considered to be unreacted coal and formed coke [34]. The solid yield was the mass percentage ratio of solid product to the total feedstock, and the liquid yield was obtained from the difference between the feedstock and the gas and solid product. Because the mass of the formed coke could not be determined directly, the dry-ash-free carbonaceous solid conversion efficiency (labeled $Con_{(daf)}$) was calculated based on the dry-ash-free weight of insoluble toluene to evaluate the hydro-conversion degree of co-liquefaction system, from Eq. (1) [35]:

$$Con_{(daf)} = \frac{m_{coal} \times (1 - M_{ad} - A_{ad}) - M \times w_{CLSR} \times (1 - w_{ash})}{m_{coal} \times (1 - M_{ad} - A_{ad})} \times 100\% \quad (1)$$

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