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Transformation of potassium and sodium in lignite during the supercritical water gasification process

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ABSTRACT

Supercritical water gasification (SCWG) has been shown to be one of the most potential technologies for lignite utilization. The transformation characteristics and reaction mechanisms of potassium and sodium in lignite during SCWG were studied. Experiments were conducted in a batch autoclave under different reaction conditions. By sequential extraction, potassium and sodium in lignite were classified as follows: the soluble fraction (A1), the carboxylic matrix-associated fraction (A2), the macromolecular organic group-associated fraction (A3), and the inorganic silicate mineral fraction (A4). After SCWG, the residue contained decreased amounts of the A1 and A2 fractions but increased amounts of the A3 and A4 fractions, corresponding to reduced risks posed by potassium and sodium. Additionally, the potassium and sodium concentrations in the liquid products varied significantly and were closely related to the amount of water and the solubilities of the different fractions. Potassium and sodium were not detected in the gas phase. The transformation pathways of potassium and sodium during SCWG were deduced. A1 was soluble in water, and A2 and A3 decomposed to release potassium and sodium, which reacted with organic groups or SiO_2 to form more stable fractions. A4 was stable and did not decompose under the experimental conditions used here.

1. Introduction

Lignite is difficult to use because of its low calorific value, high moisture, large volatile component, and high ash content. However, lignite is a good raw material for gasification, which is considered the technology with the greatest potential for lignite utilization. Lignite exhibits high reactivity and low viscosity and contains a large volatile component, which facilitate gasification [1]. Despite these attractive features, high moisture content of lignite not only leads to its low calorific value but also removes a substantial amount of heat during gasification. Thus, lignite must be dried in advance, which is an energy-intensive process. A method for converting coal to gas with a high calorific value in supercritical water (SCW) was proposed by Modell in 1978 [2]. Many studies investigating the supercritical water gasification (SCWG) of lignite have demonstrated that gases with high hydrogen yields can be obtained and that, using SCWG, complete gasification can be achieved at a lower temperature than required for conventional gasification [3–12]. In SCWG, gasification occurs in SCW, and, thus, there is no need to dry the lignite. Organic matter and O_2 can be completely dissolved in SCW, facilitating a homogeneous and rapid reaction.

Previous studies have concentrated on improving the H_2 yield, and pollutant emission and the transformation process of lignite in SCWG have been ignored. Several pollutants are produced during coal utilization, including particles, sulfur and nitrogen oxides, heavy metals, and alkali metals. We previously investigated the sulfur transformation in lignite during SCWG [13]. Alkali metals in coal not only cause fouling and corrosion, which affect safe operation, but also lead to pollution to the environment [14]. Researches by has been performed to avoid the negative effects of alkali metals, but they remain important pollutants that are difficult to handle. A number of studies have reported the emission characteristics and fraction transformations of alkali metals during coal combustion, pyrolysis, and gasification [15–23], and their results constitute a basis for alkali metal control. The reaction medium of SCWG is water, unlike conventional lignite-utilization processes; thus, the reaction mechanisms and emission characteristics of alkali metals during lignite SCWG will likely be completely different. Previous

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Table 1
Analysis of lignite.

Industrial analysis wt.%				Ultimate analysis wt.%				K (mg/kg)	Na (mg/kg)
M_{ad}	A_{ad}	V_{ad}	FC_{ad}	C_{ad}	H_{ad}	N_{ad}	S_{ad}	1657	3654
11.25	18.98	48.44	21.33	49.51	4.42	0.84	0.58		

studies of alkali metals in SCW reactions have focused on promoting fuel conversion by adding alkali salts as catalysts [5–8,24–27]. However, the transformation characteristics and reaction mechanisms of alkali metals, which are important for the implementation of lignite SCWG, have not yet been addressed.

In this research, the transformations of potassium and sodium were studied to elucidate the reaction mechanisms and transformation characteristics during lignite SCWG.

2. Material and methods

2.1. Materials

The lignite employed in this investigation was obtained from Inner Mongolia. The lignite was broken and ground to obtain particles smaller than 0.2 mm. The lignite characteristics are shown in Table 1. Distilled water, hydrogen peroxide (reagent grade), and nitrogen (99.99% pure) were used in the experiments.

2.2. Apparatus and experimental methods

The internal volume of the reactor was 100 mL, and the temperature and pressure were 600 °C and 30 MPa, respectively. The flow diagram of the experimental apparatus is presented in Fig. 1. The experimental process was described in detail previously [13]. Gaseous fractions were absorbed by two-stage 5% aqueous HNO_3, and liquid fractions were collected via outlets at the bottom of the reactor. The solid residue was collected from the reactor and cooled to room temperature.

1-Temperature-controlling instrument; 2-N_2 high-pressure gas cylinder; 3-heating furnace; 4-thermocouple; 5-autoclave; 6-pressure gauge; 7- gas-liquid separator; 8-gas flowmeter

Table 2
Percent of potassium and sodium fractions in lignite and solid products.

Sequence number	Experimental conditions	Fractions	K (%)	Na (%)
1	lignite	A1	11.5	21.6
		A2	26.3	38.0
		A3	17.9	2.9
		A4	44.3	37.5
2	t = 450 °C P = 25 MPa ER = 0.2	A1	0.7	2.1
		A2	9.7	31.6
		A3	37.5	16.3
		A4	52.1	50.0
3	t = 600 °C P = 25 MPa ER = 0.2	A1	1.3	2.6
		A2	2.9	15.8
		A3	37.8	35.5
		A4	58.1	46.1
4	t = 600 °C P = 19 MPa ER = 0.2	A1	1.4	3.2
		A2	16.4	19.1
		A3	35.3	33.4
		A4	46.9	44.3
5	t = 600 °C P = 25 MPa ER = 0	A1	1.0	2.3
		A2	7.3	25.9
		A3	37.5	27.2
		A4	54.2	44.6
6	t = 600 °C P = 25 MPa ER = 0.4	A1	1.9	2.7
		A2	14.5	9.4
		A3	39.5	38.6
		A4	57.1	49.3

2.3. Analytical methods

The total concentrations of potassium and sodium in the solid, liquid, and gas phases were determined as follows.

Lignite and residue samples were pretreated by microwave digestion. Then, 5 mL of HNO_3, 2 mL of HCl, and 1 mL of HF were added to 0.1-g samples of lignite or residue. The digestion tank was sealed and placed in a microwave digestion apparatus. The contents were heated to 230 °C within 25 min and insulated for 20 min. Then, 0.2 g of HBO_3 was added to the digestion tank. The contents were heated to 180 °C within 18 min and insulated for 15 min. Subsequently, the contents were cooled, evaporated and diluted to the necessary volumes for analysis.

Liquid fractions were heated in a water bath and evaporated to near dryness. Then, 5 mL of HNO_3 and 2 mL of 30% H_2O_2 were added to the residues, and the digestion tank was sealed and placed in a microwave digestion apparatus. The contents were heated to 200 °C within 25 min and insulated for 15 min. Finally, the contents were cooled, evaporated and diluted to the necessary volumes for analysis.

Gaseous fractions were absorbed by two-stage 5% aqueous HNO_3 and analyzed without pretreatment.

Chemical extraction was used to selectively extract different forms of potassium and sodium.

1. Water-soluble fraction (A1): first, 50 mL of distilled water was added to 1 g of sample. Then, this solution was heated in a water bath for 24 h at a constant temperature (60 °C). Finally, the mixture was filtered and diluted to 100 mL for analysis.
2. Carboxylic matrix-associated fraction (A2): the residue obtained in step (1) was washed and then dried for 2 h. Next, 50 mL of 1-M aqueous NH_4AC was added to the dried residue, and the resulting solution was heated in a water bath for 24 h at a constant temperature (60 °C). The mixture was then filtered and diluted to 100 mL for analysis.
3. Macromolecular organic group-associated fraction (A3): the residue obtained in step (2) was washed and then dried for 2 h. Next, 50 mL of 1-M aqueous HCl was added to the dried residue, and the resulting solution was heated in a water bath for 24 h at a constant temperature (60 °C). The mixture was then filtered and diluted to 100 mL for analysis.
4. Inorganic silicate mineral fraction (A4): the residue obtained in step (3) was washed and dried for 2 h. Then, the residue was subjected to microwave digestion.

The potassium and sodium concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, OPTIMA 7000DV, PerkinElmer).

3. Results and discussion

3.1. Fraction transformations of potassium and sodium

Alkali metals exist as inorganic and organic forms in lignite. Inorganic alkali metals include hydrated ions, soluble inorganic