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Short communication

Catalytic depolymerization of coal char over iron-based catalyst: Potential method for producing high value-added chemicals

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ABSTRACT

This study examined the feasibility of catalytic depolymerization of coal char obtained from the pyrolysis of low-rank coal at low temperature over iron-based catalyst to produce valuable chemicals. The depolymerization with or without the addition of ferric nitrate in a Gray-King assay reactor from 150 to 600 °C was performed. Compared with 0.2% of organic liquid products generated from the depolymerization without catalyst, the liquid yield increased to 1.61% (more than 7 times) when 1 wt% of catalyst was added. The GC × GC–MS analyses of the de-watered liquid products from depolymerization with catalyst showed that nitro-substituted phenols and alkyl-substituted naphthalene occupied the main contents, which were approximately 54.67% and 36.53%, respectively, and the rests were aliphatic hydrocarbons. An obvious DTG peak was observed from depolymerization with catalyst at 150–400 °C interval. The FTIR spectra analysis showed that the percentage of ether bond of the remained char with catalyst decreased compared with that of raw char without catalyst, reflected that the catalyst facilitates the breaking of ether bond of the raw char to produce more smaller fragments so that more liquid organic products were produced. This research provides a novel method for clean and efficient utilization of coal char and a potential way to produce high value-added chemicals.

1. Introduction

Pyrolysis is generally considered as a preferred way for low-rank coal utilization to produce char, tar and fuel gas [1,2]. Coal char is a major by-product during low-temperature pyrolysis of coal, which occupies more than half amount of product in the pyrolysis of brown coal. It is a disordered carbonaceous material with highly polycyclic aromatic structures linked together by some bridge bonds with heteroatoms such as oxygen, sulfur and nitrogen functional atoms distributed at the edge or basal plane of the molecule, in which some inorganic matters are trapped [3]. As a solid fuel, char is generally used as an alternative fuel to supply energy [4] or as a raw gasification material to produce syngas [5]. Owing to the porous structure, the coal char is extensively used as low-cost absorbent for removing contaminants in industrial sewages and gases. Also, the coal char can be used as catalysts or catalyst supports for tar upgrading or tar elimination [6,7]. Compared with raw coal, the coal char becomes more regular and structured. Moreover, for the chars obtained from the pyrolysis of low-rank coal at low temperature, it is possible to crack the relative weak chemical bonds in the char to produce high value-added liquid chemicals with smaller molecular weight. However, to date, little information on this topic can be found in the literature.

Theoretically, application of catalysts can significantly affect the pathway of related reactions and selectively break down the chemical bonds. However, the catalysts used for the coal conversion should be cheap and effective. To date, iron-based catalysts have been widely studied in different coal thermal conversion processes due to the benefits of low-cost, availability and environmental friendliness [8]. In our previous work [9], it has been proved that the tar yield increased and the concentration of aromatic nucleus decreased via the depolymerization of lignite by the addition of iron-based catalyst [10,11]. In this work, the feasibility of catalytic depolymerization of the coal char in a Gray-King assay reactor to produce valuable chemicals was evaluated, in which $Fe(NO_3)_3{\cdot}9H_2O$ was employed as the iron-based catalyst. The liquid product was analyzed by a comprehensive two-dimensional gas chromatography combined with a mass spectrometry (GC × GC–MS). Thermogravimetric analysis (TGA) and fourier transform infrared (FTIR) spectra analysis were also performed for the raw and yielded char. The catalytic depolymerization mechanism was proposed based on these experimental results.

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2. Experimental

2.1. Preparation of raw char

One lignite, produced from Yunnan Province, China, was chosen as the feedstock of char sample. Coal depolymerization was performed in a Gray-King assay reactor [12]. In brief, 20 ± 0.1 g coal sample (mesh: 80–100) was placed in a horizontal quartz tube. When the temperature of an electric furnace reached 150 °C, the coal sample loaded tube was put into the furnace and heated the determined temperature of 600 °C with a heating rate of 5 °C/min, and then stayed at 600 °C for 15 min. Finally, the tube was taken out of the furnace and the char was collected as raw char sample, which is noted as R-char, and the yield of R-char is 62.96% (ad).

2.2. Pretreatment and experimental methods

Catalyst loading procedure has been introduced in our previous work [9]. In brief, 10 g of R-char was sprayed with 6 mL of accessory ingredient [13] containing 1 wt% (metal salt content to dry coal basis) $Fe(NO_3)_3 \cdot 9H_2O$, and then stayed 30 min. The catalyst loaded sample was dried at 115 °C for 2 h.

The depolymerization of R-char with or without catalyst was conducted following the same procedure as the preparation of the raw char sample shown above. The condensable liquid products were collected in a conical flask placed in an ice-salt bath with a temperature below −10 °C. The liquid products were weighed, and then dissolved in dichloromethane (CH_2Cl_2). The anhydrous Na_2SO_4 was added into the solution to remove the water. Thereafter, Na_2SO_4 was washed by CH_2Cl_2 followed by drying to a constant weight in a vacuum drying oven at 50 °C. The remained solid char, noted as Y-char, was also collected and weighed. The tar yield is deduced by the yield of liquid product minus the water. The yields of tar, char and water were calculated using the weight percentage on the dry base. The ultimate and proximate analysis of raw coal, R-char and Y-char with/without catalyst are shown in Table 1. The product yields are defined as follows:

$$Y_{water} = \frac{W_{water} - W_0 \times M}{W_0 \times (1-M)} \times 100\%$$

$$Y_{tar} = \frac{W_{liquid} \text{-} W_{water}}{W_0 \times (1-M)} \times 100\%$$

$$Y_{char} = \frac{W_{char}}{W_0 \times (1-M)} \times 100\%$$

where Y_{water}, Y_{tar} and Y_{char} is the yield of water, tar and char in dry base; W_{water}, W_{liquid}, W_{char} is the weight of water, liquid products and char, respectively; W_0 and M is the weight of sample and content of moisture in dry base.

Table 1
Proximate and ultimate analysis of samples.

Sample	Proximate analysis (wt%)			Ultimate analysis (wt%, daf)				
	M_{ad}	A_d	V_{daf}	C	H	N	S	O
raw coal	27.87	8.72	54.77	65.94	4.79	3.51	0.66	23.96
R-Char[a]	1.46	21.34	32.71	72.07	2.52	6.07	0.99	15.77
Y-Char without Cat.[b]	1.31	21.17	28.59	73.75	2.34	6.01	1.17	14.51
Y-Char with Cat.[c]	1.09	24.31	21.01	73.97	2.95	6.16	1.09	11.13

[a] Raw char.
[b] Yielded char without catalyst.
[c] Yielded char with catalyst.

2.3. GC × GC-MS analysis

In this work, the liquid products were analyzed by a comprehensive two-dimensional gas chromatography combined with mass spectrometry (GC × GC–MS), in which a ZX10542 thermal modulator (ZOEX Corporation, USA) and an Agilent 7890B chromatograph equipped with 5977A mass spectrometer (Agilent Corporation, USA) were included. The detailed operational procedure was following: the oven temperature in the GC increased to 300 °C with a rate of 5 °C/min and the temperature of modulator increased to 300 °C with a rate of 3 °C/min. The injector temperature was 300 °C and a split ratio was 50:1. The carrier gas was helium (purity 99.999%) with a constant flow rate 1 mL/min. One general set of column was used: DB-1 column (nonpolar, 15 m × 0.25 mm, 1 μm film thickness) connected with BPX-50 column (medium polar, 2.75 m × 0.1 mm, 0.1 μm film thickness). Data acquisition was done by using "MS hunter" software (Agilent Corporation) and analysis was conducted by employing "GC image" software (ZOEX Corporation). Detected compounds were identified using NIST08 mass library.

2.4. FTIR analysis

The measurement was conducted with a Bruker FTIR spectrometer using pellet technique. Here, 1 mg sample was mixed with 100 mg KBr and milled in an agate mortar. The spectra was recorded by collecting 50 scans at a resolution of 8 cm^{-1} with measuring regions of 4000–400 cm^{-1}.

2.5. TG analysis

TG analysis was carried out using a thermalgravimetry analyzer (SETSYS Evolution, SETARAM). Approximately 10 mg sample was heated from ambient temperature to 650 °C with a heating rate of 10 °C/min using argon as carrier gas with a flow rate of 100 mL/min.

3. Results and discussion

3.1. Product distribution and GC × GC-MS analysis

A comparison of the color of liquid products derived from raw char depolymerization in the cases with and without catalyst, which were dissolved in dichloromethane, is presented in Fig. S1. When the catalyst was added, it is obvious that yellow product was produced. Furthermore, as shown in Fig. 1, the yield of liquid product increased about 7 times (from 0.21% to 1.61%) while the Y-char yield decreased from 96.31% to 94.06%. Here, in the presence of catalyst, the chemical bonds in the raw char could be broken much more easily, and more liquid organic products were generated under the experimental conditions.

Fig. 2 illustrates a three dimensional (3D) total intensity chromatogram (TIC) images of the products from the depolymerization of R-char with catalyst. Here, the X-axis of GC × GC chromatogram is the volatility-based retention time (min), the Y-axis is the polarity-based retention time (s), and the Z-axis is the MS response. Based on the NIST library and peak volume, the proportions of the detected components in the liquid products were determined and the results are shown in Table S1. It can be seen that nitro-substituted phenols and alkyl-substituted naphthalene occupied the most in the products, which were approximately 54.67% and 36.53%, respectively, and the rest was mainly aliphatic hydrocarbons, nearly 7.8%. However, only a little aliphatic hydrocarbons, as shown in Fig. S2 and Table S2, were detected by the GC × GC–MS under the same conditions from the products derived from the depolymerization of R-char in the absence of catalyst. Therefore, the catalyst is necessary for the depolymerization of R-char in order to get more high-value-added liquid products.