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Hydrothermal extraction and hydrothermal gasification process for brown coal conversion

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Abstract

A novel coal conversion process was proposed: the method combines "a hydrothermal extraction of brown coal (HT-Extraction)" and "a catalytic hydrothermal gasification of the extract (CHT-Gasification)" both of which are performed under the exactly same conditions of less than 350 °C and less than 20 MPa. Organic compounds in the aqueous phase, extracted from brown coal, was gasified using a novel Ni-supported carbon catalyst developed by the authors, producing combustible gas rich in CH_4 and H_2. Through this process performed at 350 °C and 18 MPa, an Australian brown coal was almost perfectly converted into 53% of upgraded coal, 23% of methane, and 24% of carbon dioxide on carbon basis. Simultaneously, 4.4 mol of hydrogen was generated from 100 mol of carbon of the coal. This process transferred 97% of energy involved in the raw coal to the products, indicating its effectiveness.

Keywords: Coal upgrading; Hydrothermal extraction; Hydrothermal gasification

1. Introduction

Brown coal and/or lignite must be important energy resources in the near future because of their worldwide abundant minable reserves. Brown coal contains a large amount of water (~60%) in general, resulting in its low calorific value. This means that dewatering or drying is essential when brown coal is transported to be utilized [1]. On the other hand, dewatered brown coal tends to have high spontaneous combustion tendency as compared with raw brown coal, which causes serious problems for storage and transportation. Since the spontaneous combustibility of brown coal is associated with its high oxygen content coming from oxygen functional groups, it is required to reduce the amount of oxygen functional groups to suppress the spontaneous combustibility. The process to reduce the oxygen functional groups is called upgrading. Therefore, both dewatering and upgrading are necessary to utilize brown coal more effectively.

Conventional evaporative drying processes are effective to remove water from brown coal, but they cannot upgrade brown coal. In addition, the evaporative drying is highly energy intensive process. On the other hand, non-evaporative dewatering process such as Fleissner process [2] and MTE (mechanical thermal expression) process [3,4] are less energy intensive processes. These processes are operated under hydrothermal conditions at 200–300 °C to remove the water as liquid. Hydrothermal treatment is very promising because it decomposes part of oxygen functional groups of brown coal, which not only increases the heating value but suppresses the spontaneous combustibility. It is preferable to employ higher temperatures for the hydrothermal treatment to be more effective, but the amount of organic compounds leached out from coal into the aqueous phase increases with increasing temperature [5]. This causes loss of combustible organic matter on one hand, and necessitates wastewater treatment on the other hand [6,7]. Another problem associated with the hydrothermal treatment is that the treatment is not economical when it is solely used as a coal dewatering/upgrading process.

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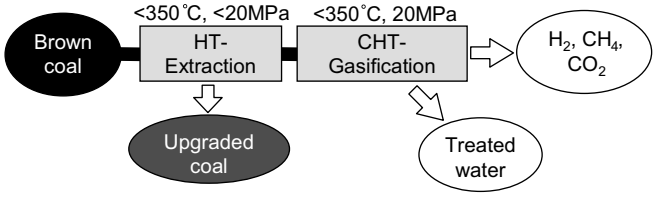

Fig. 1. A schematic illustration of the new brown coal utilization process proposed.

To rationally overcome these problems, a concept combining the dewatering/upgrading process and the wastewater treatment process is proposed here based on our recent investigations, as shown in Fig. 1. We have proposed that various coals including brown coal can be extracted by up to 80% in flowing non-polar solvent at less than 350 °C [8,9]. We have also developed a novel Nickel/Carbon catalyst that can completely gasify organic compounds dissolving in water at less than 350 °C and 20 MPa, producing fuel gas consisting of hydrogen and methane [10,11]. The catalyst has been successfully applied to gasify organic compounds dissolving in an industrial wastewater and to gasify organic compounds leached out from a brown coal through hydrothermal dewatering [12]. Our idea is to extract brown coal by coal inherent water or water containing its extract as the first stage of process (HT-Extraction) to increase the amount of organic compounds leaching out into aqueous phase [13] and to ensure the upgrading of coal (see Fig. 1). Then the organic compounds (extract) dissolving in water is directly supplied to the second stage of the process consisting of a reactor packed with the novel Nickel/Carbon catalyst, where all extract is expected to be gasified to produce hydrogen and methane (CHT-Gasification). The products obtained from this process are expected to be upgraded coal, fuel gas rich in hydrogen and methane, and treated water. Furthermore, the first and the second stage are operated under exactly the same conditions: less than 350 °C and less than 20 MPa, which will facilitate the design and operation of the proposed process. These great merits of the process will surely make the proposed process environmentally benign as well as economical.

In this paper, the validity of the proposed concept is examined through systematic experiments. The HT-Extraction behavior of an Australian brown coal in flowing water is investigated at temperatures of 300 and 350 °C to examine the validity of the first stage. Next, experiments combining the HT-Extraction and the CHT-Gasification are performed to examine the validity of the whole process.

2. Experimental

2.1. Coal sample

An Australian brown coal, Loy Yang (LY), was used. Table 1 shows elemental composition, ash content, and water content of raw LY coal. LY has high oxygen and water contents, but contains a very small amount of mineral matters.

Table 1
Ultimate analysis and contents of ash and moisture of coal used

Coal	Ultimate analysis (wt% d.a. f)					Ash (wt% d.b.)	Moisture (wt%, a.r.)
	C	H	N	S	O (diff.)		
Loy Yang (LY)	66.9	4.7	0.7	0.3	27.5	1.5	57.8

2.2. Preparation of Ni/Carbon catalyst

A methacrylic acid type resin (Mitsubishi Chemical, WK-11) which has carboxyl groups as ion exchange sites was used as a starting material. It was spherical in shape and its diameter was about 0.5 mm. The resin was treated in an ammonium complex ion aqueous solution of $NiSO_4$ at room temperature to exchange H^+ by Ni^{2+}. The amount of Ni^{2+} exchanged was controlled by changing the $NiSO_4$ concentration. The resin ion-exchanged was then washed by deionized water followed by vacuum drying at 70 °C for 24 h. The dried resin was heated at the rate of 10 K/min to 500 °C in a nitrogen stream to prepare a Ni-supported catalyst. Fig. 2 shows a SEM image of the catalyst prepared. It was very hard spherical particle of 0.3 mm in diameter. Fig. 3 shows the TEM image of the catalyst. It is clearly shown that Ni particles of around 4 nm in diameter are highly dispersed in the catalyst. The amount of Ni supported by this method reached as high as 47%, which was estimated from the amount of ash formed on combusting the catalyst. The BET surface area was measured to be 170 m^2/g, and most of pores were 1–10 nm in diameter. Thus, the catalyst prepared here was hard spherical particle, supporting lots of Ni in highly dispersed state in porous carbon support. This catalyst was expected to be effective for treating organic compounds soluble in water, judging from the peculiarities of the catalyst.

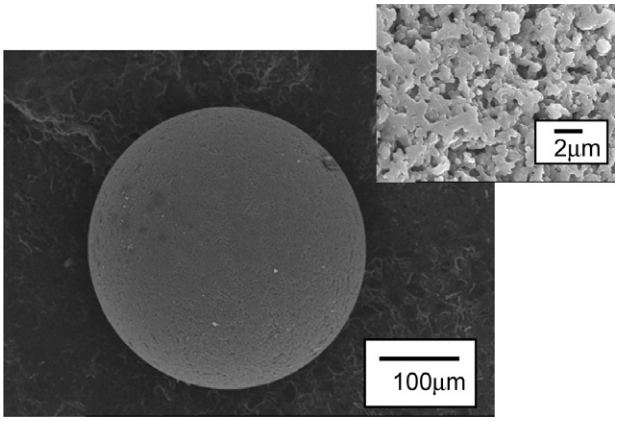

Fig. 2. SEM image of the Ni-supported carbon catalyst.