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Improvement in coal content of coal–water slurry using hybrid coal impregnated with molasses

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ABSTRACT

To improve the efficiency of the gasification process of coal slurry, it is very important to determine the characteristics of coal–water slurry (CWS) and increase the coal content of CWS. If CWS is produced from low rank coal, the gasification efficiency will be diminished due to the difficulty of generating CWS with high coal content. Against this backdrop, studies have been conducted on the use of chemicals to improve slurry viscosity. However, to the best of our knowledge, few publications have reported on the modification of coal characteristics for CWS ability using biomass. Preparing high coal content CWS with low rank coal is generally difficult due to the outstanding water absorptive ability from its numerous hydrophilic pores. Therefore, we suggest hybrid coal slurry and demonstrate that hybrid coal, where surface and pore characteristics were modified by using molasses, makes it possible to prepare high coal content CWS with low rank coal.

1. Introduction

Despite growing worldwide interest in renewable energy, we are still largely dependent on fossil fuels as a main energy source. Among them, coal is more abundant and evenly distributed in comparison with other fossil fuels. However, there is an unstable supply of high rank coal for coal-fired electrical power plants. Another problem is that CO_2 emissions will continue to rise as the utilization of low rank coal gradually increases in the near future [1,2]. Recently, researchers have focused on improving the efficiency of power plants and reducing the emission of CO_2 and other harmful substances, such as NO_X and SO_X, by using an integrated gasification combined cycle (IGCC) [3,4].

Gasification processes, the core technology of IGCC and coal-to-liquid (CTL) processes, are classified into fixed-bed, fluidized bed, and entrained flow gasifiers according to the reaction configurations. Entrained flow gasifiers are classified into dry coal gasification and coal slurry gasification according to the fuel type [5–7]. In particular, coal-slurry-type entrained flow gasifiers are favorable to a large scale process due to the short residence time of coal. Accordingly, demonstration scale IGCC plants in the United States, China, and Europe are equipped with entrained flow gasifiers of coal slurry type [8]. Consequently, for the improvement in gasification efficiency, it is important to identify the characteristics of CWS and try to raise the coal content of CWS in entrained flow gasifiers.

In a coal-slurry-type gasification process, the heat emitted by oxidation of CWS is supplied to endothermic gasification reaction in an autothermal manner [9]. To improve the efficiency of gasification reactions, CWS with high coal content and a high heating value should be prepared. Since the coal content of CWS is inversely proportional to the slurry viscosity, it is difficult to increase the coal content of CWS while maintaining its viscosity [10]. Past studies have increased the packing density by decreasing the void fraction between particles through mixing small-particle-sized and large-particle-sized coal [11], and prepared CWS with high coal content through the addition of surfactants [12–14]. However, to the best of our knowledge, there has been no research on improvement in the coal content of CWS by controlling the pore characteristics of coal with biomass.

In our previous study, we developed HCK (Hybrid Coal by Korea Institute of Energy Research) to upgrade low rank coal with bioliquids and comply with regulations, such as the renewable portfolio standard (RPS) and the cap-and-trade system. Hybrid coal is a new fuel produced from diffusion of bioliquids (such as molasses and sugar cane juice) into the pores of low rank coal, followed by pre-carbonization at low temperature. After diffusion and carbonization, the bioliquid embedded in the coal pores is converted to artificial carbon and volatile matter, resulting in a two-in-one fuel combining biomass and coal [15]. In this study, CWS was prepared using hybrid coal fabricated with different coal types, and its characteristics were investigated.

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2. Experimental section

2.1. Preparation of hybrid coal

For the preparation of CWS, hybrid coal was prepared from Shenhua coal (SHC) supplied by Shenhua Group Corporation of China, Indonesian coal (IC) by Glencore, and Shievee Ovoo coal (SOC) by Shievee Ovoo mines of Mongol. Lump coals were subject to coarse crushing via a jaw crusher, and fine grinding with a pin mill type crusher. And then particles smaller than 75 μm were sorted. Before producing hybrid coal, raw coal was dried in a 105 °C oven to empty the coal pores filled with water and accelerate the impregnation of coal pores with molasses provided by Evermiracle of Korea. Molasses, amounting to 10 wt.% of dried coal, was dissolved in water to produce a coal-molasses solution paste. It was aged for 12 h in an air atmosphere and then placed in a 105 °C oven to promote the impregnation of coal pores. Finally, molasses impregnated coal was pre-carbonized at 250 °C to produce the hybrid coal. The characteristics of the hybrid coals and raw coals are shown in Table 1.

2.2. Preparation and viscosity measurement of CWS

Before the CWS preparation, agglomerated hybrid coal was crushed to a particle diameter of below 75 μm, and a solution was prepared by adding 10 wt.% ethanol without any surfactant. The finely-crushed raw coal and hybrid coal were added into the ethanol solution with an increase in coal content, and then stirred vigorously to obtain a homogeneous coal slurry with a mechanical stirrer. The viscosity of CWS was measured using a viscometer (TVC-5, Toki Sangyo Co.) at a temperature of 20 °C and a rotor rotation rate of 20 rpm.

2.3. Characteristics of raw coal and hybrid coal

For the characteristics of raw coal and hybrid coal, a proximate analysis, elemental analysis, higher heating value, thermal gravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDS) with X-ray dot mapping, mesopore property analysis, particle size analysis, contact angle analysis and water re-adsorption test were conducted. A proximate analysis and an elemental analysis were carried out by using a TGA-701 (LECO) and TruSpec Elemental Analyzer (LECO) and a SC-432DR Sulfur Analyzer (LECO), respectively. A higher heating value was obtained by using A Parr 6320EF Calorimeter (PARR). In order to observe the characteristics of combustion, DTG was carried out at a heating rate of 10 °C/min and 100 mL/min of air using a TGA Q500. For investigation of the distribution of components (Al, Si, C and O) on the surface, EDS and X-ray dot mapping analyses were conducted by using a HITACHI S-4700 instrument. In order to observe characteristics of mesopore properties of raw coal, hybrid coal and swollen hybrid coal, nitrogen sorption tests (all samples were degassed for 7 h at 100 °C) were carried out by using a Micromeritics ASAP 2020 instrument. Particle size was measured by using HELOS (H1433) & RODOS.

Table 1
Proximate and ultimate analysis of the raw coal and hybrid coal samples.

Samples	Proximate analysis (Dry basis, wt.%)			Ultimate analysis (Dry ash free basis, wt.%)					HHV (kcal/kg)
	VM	Ash	FC	C	H	N	O	S	
SHC-R	39.60	10.20	50.20	77.26	4.94	1.47	15.56	0.76	6330
SHC-H	38.59	10.52	50.89	79.46	5.02	0.95	13.81	0.76	6370
IC-R	46.97	8.82	44.21	68.52	5.41	1.24	24.16	0.66	5760
IC-H	45.14	8.85	46.01	74.60	5.04	0.80	18.94	0.63	6040
SOC-R	39.57	24.20	36.23	60.30	4.10	1.17	33.05	1.38	4300
SOC-H	37.85	24.10	38.05	73.65	3.86	0.18	20.49	1.82	4670

(R: raw coal, H: hybrid coal, VM: volatile matter, FC: fixed carbon and HHV: higher heating value).

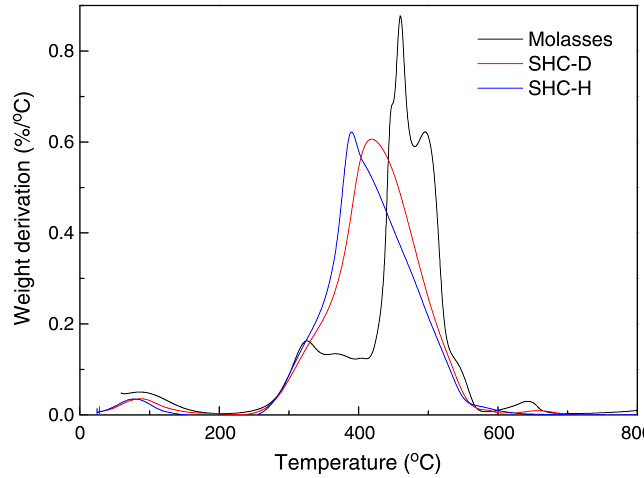

Fig. 1. DTG curves of molasses, SHC-D and SHC-H.

For investigation of the water adsorption in coal pores, the contact angle was measured by using a PHODNIX-300 (SEO, Korea) instrument and water re-adsorption test was conducted. To measure the contact angle, dried raw coal and hybrid coal powder were compressed under pressure of 5 MPa to prepare 25 mm diameter and 4 mm thick discs, and then 10 μL water droplets were deposited on the coal discs using a micro-syringe. To confirm the re-adsorption rate of water, dried coal and hybrid coal were swollen in excess water and filtered for 15 min. Re-adsorption rate of water can be described as

$$\text{Re}-\text{adsorption rate of water}\,(\%) = \frac{(W_i - W_d)}{W_i} \times 100 \qquad (1)$$

Where, W_i is coal weight after swelling in excess water and then filtering, W_d is coal weight after drying filtered coal at 105 °C for 24 h.

3. Results and discussion

3.1. Fuel characteristics of hybrid coal

Proximate, ultimate and a higher heating value analyses were performed on hybrid coal impregnated with molasses and its raw coal. The results are shown in Table 1. In the case of the proximate analysis

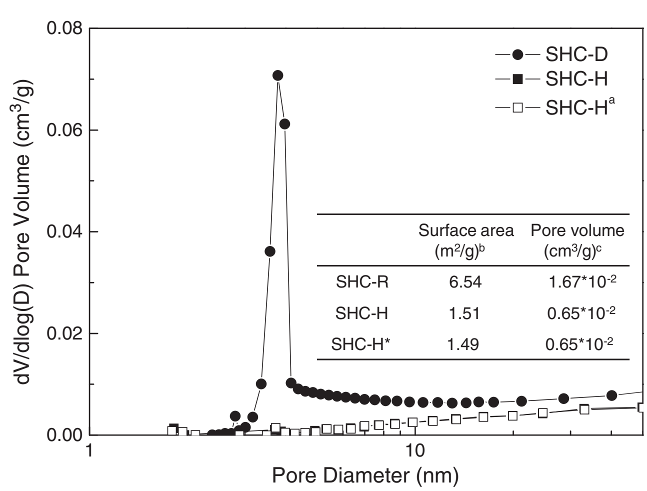

Fig. 2. Pore size distribution, surface area and pore volume for SHC-D, SHC-H and SHC-H[a]. [a]Swollen and washed sample. [b]BET surface area calculated from the slope and intercept of the BET equation. [c]Single point total pore volume taken from the volume of N_2 adsorbed at P/Po = 0.995.