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Research paper

Combustion behavior of low-rank coal impregnated with glycerol

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ABSTRACT

The addition of biomass to an existing coal-fired boiler has emerged as a prospective option for reducing CO_2 emissions to mitigate the problems associated with excess global warming. However, the cost associated with retrofitting an injection system and the unstable combustion hinder the use of this option. Therefore, we propose the use of coal impregnated with glycerol as fuel that can be directly injected into an existing boiler. This is a two-in-one fuel that combines a low-rank coal (LRC) with bio-liquid matter extracted from biomass such as molasses or sugarcane juice. In this study, for the first time, we used glycerol, which is a low value co-product of biodiesel production, as the bio-liquid, because the use of molasses or sugar-cane juice raises food ethical issues. The aim of this study was to investigate the combustion behavior of coal impregnated with glycerol, using experimental and numerical methods. The results showed that the calorific value of coal impregnated with glycerol increased, and the combustibility at low and high temperatures was improved by impregnation of low-rank coal with up to 20% glycerol. We also confirmed that the combustion performance of coal impregnated with glycerol was unaffected and was identical to that of original coal. However, excess glycerol (more than 20%) led to oxygen deficiency near the burner and thermal expansion, which reduced the combustibility. The results of this study therefore suggest that less than 20% glycerol is the optimal condition for low-rank coal impregnated with glycerol.

1. Introduction

Biomass, recognized as a leading candidate among renewable energy sources, represents 10–14% of the world's total fuel stream and is the fourth largest global energy resource [1,2]. Substituting biomass for traditional fossil fuels in large-scale combustion facilities is not only very important for meeting societal energy needs but also has the potential to contribute greatly toward the reduction of greenhouse gases emitted into the atmosphere [3]. Therefore, biomass has been considered a potential feedstock for power station co-firing options, and the co-firing of coal and biomass fuels is currently being considered as an alternative means of reducing CO_2 emissions. The co-firing rationale is based on the fact that the thermal utilization of biomass can contribute to the reduction of CO_2 emissions because the same amount of CO_2 is extracted from the atmosphere during the growth period of the plants as is released by combustion [4,5]. Currently, co-firing coal with a limited amount of biomass, typically 2–20%, has been widely implemented in power plants. However, co-firing with biomass has attracted considerable attention because much of the predicted combustion behavior is nonlinear. Such co-firing presents unstable situations in a coal-combustion environment because of the dissimilar types or different reactivities of biomass [6,7].

Recently, hybrid coal, which is a combination of low-rank coal (LRC) and bio-liquid matter, have been developed, and its features have been analyzed [8]. It is a two-in-one fuel produced by impregnating the coal pores with the bio-liquid matter extracted from biomass, such as molasses and sugarcane juice, instead of impregnating with moisture. Specifically, during hybrid coal preparation, the paste produced by mixing crushed raw coal with bio-liquid aqueous solution is aged for 12 h and dried at 378 K for 6 h to improve the diffusion of the carbon precursor into the

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inherent-moisture-filled coal pores. Consequently, the calorific value is improved because of the artificial volatile/carbon matrix formed by bio-matter.

Currently, upgrading technologies for LRCs are being developed worldwide. Typically, these upgrading processes involve the upgrading of brown coal (UBC) and hot-water drying (HWD). The UBC process developed by Kobe Steel upgrades LRC to a fuel with a high calorific value by slurry dewatering with no chemical reaction. In the UBC process, LRC is first crushed and mixed with oil, and a small amount of asphalt is added to the slurry. This coal–oil slurry is heated under pressure to dewater it because the oil soaks into the pores of the coal, thus removing its water. The produced UBC adsorbs little moisture, because the asphalt can deactivate the active sites [9–11].

In the HWD process, the pulverized raw coal is mixed with water and heated at 573 K for 1 h to achieve the optimum processing conditions. The autoclave atmosphere in the HWD is purged, and 1 MPa of pressure is provided by N_2. The autoclave is heated at a rate of 66 mK s^{-1} to 573 K under high pressure [12,13]. The coal-upgrading processes mentioned above require fossil fuel-derived additives, such as bunker oil, and harsh operating conditions (UBC: 676 K–726 K, 0.35 MPa; HWD: 543 K–603 K, 15 MPa). Thus, they face the some problems because of operational difficulties and economic constraints.

However, Lee et al. reported that the hybrid coal produced using bio-liquid matter, such as molasses and sugarcane juice, is improved in terms of calorific value and reactivity by a simple production process [8]. Moreover, the hybrid coal has single coal combustion patterns unlike a simple blend of biomass and coal. If hybrid coal (biomass/coal ratio = a mass fraction of 28%) is used as a fuel to generate 500 MW of power, the net CO_2 emission is 21.2%–33.1% lower than that for LRC. Namely, this not only improves the combustibility but also simultaneously reduces the CO_2 emissions. Nevertheless, hybrid coal produced from molasses and sugarcane juice used in previous studies raises economic and food ethical issues [14].

Debate regarding the ethical issues of biofuels has occurred over the past few decades. Biofuels appeared to be very promising, and, indeed, the expectation of certain researchers was that they would solve many great challenges all at once, i.e., provide a new source of income for farmers and revenue from clean technology, as well as renewable endless sources of fuel, thus leading to far less greenhouse gas (GHG) emissions than fossil fuels [15]. The food versus fuel argument calls into question the ethics of diverting land from food to energy production, and has two key facets: first, that demand for biofuels has an impact on food prices, which disproportionately affects poor people in the global South, and second, that it leads to competition with existing food production in established agricultural areas or requires expansion into new environs [16].

To secure this fuel diversity that is the center of ethical questions, in this study, glycerol was used instead of molasses or sugarcane juice as the bio-liquid matter for impregnation. Glycerol is generally formed as a waste product from biodiesel production. As worldwide production of biodiesel fuel increases, a growing concern is the abundance of waste glycerol as the expansion of biodiesel production may lead to overproduction of glycerol wastes [17]. As a by-product, 1 mol of glycerol is produced for every 3 mol of biodiesel, which is equivalent to a mass fraction of approximately 10% of the total product. Glycerol markets have reacted strongly to the increasing availability of glycerol; although the global production of biodiesel is still very limited, the market price of glycerol has dropped rapidly [18].

However, clean combustion of glycerol is difficult because of concerns related to hazardous emissions. In particular, most in the biodiesel-producing community share a fear that burning glycerol could produce acrolein, an aldehyde that is a thermal decomposition product of glycerol and is toxic at very low concentrations [19]. According to Bonnardeaux, acrolein formation occurs only when the burning of glycerol is conducted at temperatures lower than 673 K [20]. For this reason, glycerol presents desirable combustion properties for heating purposes, and it can be one of the alternatives to diversify the bio-liquid matters that could solve the known economic and ethical difficulties [21].

The purpose of this study was therefore to analyze the fundamental properties of coal impregnated with glycerol and to examine closely the combustion behavior using experimental and numerical methods.

2. Experimental section

2.1. Production process of coal impregnated with glycerol

We have developed a method of producing coal impregnated with molasses and sugarcane juice, which was described in detail in a previous paper [8]. In this study, we produced coal impregnated with glycerol instead of molasses or sugarcane juice. Fig. 1 shows a schematic diagram of coal impregnated with glycerol. Mongolian Shivee Ovoo raw coal (SOCR) was used, and glycerol (extra pure grade produced from Duksan, South Korea) was used as the biomass-based carbon precursor. The specific properties of the glycerol were as follows: flash point, approx. >453 K; vapor density, 3.1; molecular weight, 92.09; boiling point, approx. 563 K; specific gravity, 1263 kg m^{-3}; solubility, soluble in water. The as-received lumps of SOCR were crushed to a particle diameter ranging from 75 μm to 90 μm. In a typical preparation, a glycerol aqueous solution was prepared by mixing a certain amount of glycerol (glycerol/coal weight ratio on a dry basis), which was determined to ensure that the coal particle paste could be soaked with the solution. The crushed SOCR was impregnated with the as-prepared carbon precursor aqueous solution. The paste was then aged for 24 h to impregnate the glycerol well into the coal pores and dried at 378 K for 5 h to improve the evaporation of moisture remaining in the coal particles and accelerate glycerol impregnation.

2.2. Experimental apparatus

A thermogravimetric analyzer (TGA 701, LECO) was used for proximate analysis (moisture, fixed carbon, volatile matter, and ash content), which was carried out under ASTM-specified conditions. Thermogravimetric analysis/differential thermogravimetry (TGA/DTG) was carried out at a heating rate of 0.16 K s^{-1} with 1.6 cm^3 s^{-1} of air using a TGA Q500. The mesopore properties were determined using nitrogen sorption tests (all samples were degassed for 7 h at 373 K) with a Micromeritics ASAP 2020, which is a physisorption analyzer that measures the Brunauer–Emmett–Teller (BET) surface area, pore size, and pore volume in a non-destructive format. Surface area was calculated from the slope and intercept of the BET equation. A scanning electron microscope (SEM, HITACHI S3500N) was used to visualize the pore structure. A portable gas analyzer (Eurotron GreenLine 9000) was used to measure the flue gas concentration (O_2, CO, CO_2 NOx, SO_2).

High-temperature experiments (approximately 1500 K in the reactor) were conducted in an entrained-flow drop tube reactor (DTR), which is a useful device for investigating coal combustion. The DTR used in this study, which was designed at the Pusan Clean Coal Center, Korea, was 30.0 cm long and had an internal diameter of 7.0 cm. A detailed description of the experimental setup for the DTR is provided elsewhere [15]. In the experiments, the coal injection rate was 3.3 mg s^{-1}, the particle size ranged from 75 μm to 90 μm (based on the Rosin–Rammler distribution), and the particle