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Short communication

Suppressed char agglomeration by rotary kiln reactor with alumina ball during the pyrolysis of Kraft lignin

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ABSTRACT

In this study, the pyrolysis of Kraft lignin was conducted in a rotary kiln reactor using rotating alumina balls as a filler to achieve a continuous pyrolysis process by the suppression of char agglomeration. Temperature variation experiments showed that the gas yield increased and the char yield decreased with an increase in the pyrolysis temperature from 550 °C to 650 °C. The maximum oil yield was obtained at a reaction temperature of 600 °C. Compared to a fixed bed reactor, a rotary kiln reactor using alumina balls produced the higher quality oil containing larger amount of organic phase oil and higher selectivity to aromatic hydrocarbons. At all temperatures, no lignin char agglomeration occurred inside the reactor due to the effective collision of lignin char intermediates and alumina balls, allowing a continuous pyrolysis process without reactor plugging.

Introduction

The worldwide demand for renewable energy has increased due to the energy crisis, environmental contamination, and climate change caused by intensive use of fossil fuels [1]. Biomass is an alternative energy source that can potentially replace fossil fuels. Among the various kinds of renewable energy sources, the importance of biomass has been emphasized because it is the only carbon source that can produce both energy and carbon-based chemical feedstock [2]. Thermal treatment of biomass is being investigated intensively because value-added chemicals can be produced using the appropriate thermal conversion technology [3–8]. Pyrolysis, a thermal decomposition technology performed under a non-oxygen atmosphere at temperatures between 400 and 600 °C, is a proper method which can produce the large amount of bio-oil from biomass. Recently, different kinds of pyrolysis, such as microwave-assisted pyrolysis [9], was also reported as an effective method for the production of high-quality oil from biomass.

Lignin, a main lignocellulosic component of wood biomass, is a cross-linked phenolic polymer forming the support tissues of wood and bark [10]. A large amount of lignin is released to the environment as waste mainly from the pulp manufacturing process. Lignin has high potential to become an alternative source of petroleum-derived aromatic chemicals. The market value of aromatic chemicals, such as phenol, is also very high. On the other hand, a considerable amount of lignin is classified as waste and is incinerated [11].

The pyrolysis of lignin is a promising technology for decomposing the polymeric structure of lignin and converting it to a liquid fuel, called bio-oil, which contains large quantities of valuable phenolic compounds, in a simple one-step process [12]. On the other hand, research on the pyrolysis process of lignin is still in its initial stages using laboratory-scale batch-type reactors [13]. Several technical barriers need to be overcome before the lignin pyrolysis process can be scaled up [14]. One of the most difficult problems is that the stable and continuous operation of the reactor is quite challenging during lignin pyrolysis due to the large amount of lignin char accumulating inside the reactor. Nowakowski et al. [15] recommended that less pure lignin samples, such as lignin isolated by acid hydrolysis, which contain some sugary components, are better than pure lignin when a conventional continuous

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lignin pyrolysis system is used. In the case of pure lignin, they recommended the use of a new reactor system, such as entrained-flow, high temperature, long residence time, etc. The large agglomerates and swelling of char produced during the pyrolysis of lignin can cause a blockage of the reactor, requiring additional reactor maintenance to repeat the pyrolysis. Recently, several studies reported a method to minimize char agglomeration and swelling by the mechanical modification of the reactor or the pretreatment of lignin [16–18]. For example, modification of the reactor feeding system was effective in reducing the level of char agglomeration but it could not prevent the reactor from plugging completely. The co-feeding of lignin with calcium hydroxide was reported to be quite effective in preventing agglomeration of char inside the reactor because calcium hydroxide pretreatment can decrease the amounts of phenolic hydroxyl, carboxylic acid, and aldehyde groups, which cause the severe agglomeration of lignin during pyrolysis [19]. They also indicated that this pretreatment process enables us to carry out the pyrolysis of lignin in a conventional fluidized bed reactor without reactor modification, even though additional processes, such as char burning and leaching ash with water, are needed to recycle calcium hydroxide. In another study, Zhou et al. [20] reported the continuous pyrolysis of lignin derived from a bioethanol pilot plant in a PCR (pyrolysis centrifuge reactor), which has a continuous char removal function under the mechanical action of rotating vanes.

Another possible method to minimize char agglomeration is to use alumina ball as a packing material of the reactor during the pyrolysis of lignin. Alumina ball has been used as an effective grinding media in ball milling due to its thermal resistance and mechanical strength. Therefore, these properties of alumina ball can reduce the char agglomeration when it is used for lignin pyrolysis by providing the mechanical grinding effect.

In this study, the pyrolysis of lignin was conducted in a rotary kiln reactor with alumina ball as a rotating filler to prevent or minimize lignin char agglomeration, thereby achieving a continuous pyrolysis process. To accomplish this, a new rotary kiln reactor, in which the rotation speed and slope of the reactor can be controlled, was designed, and alumina balls were used as the filler inside the reactor. The yields of the liquid products produced from the pyrolysis of Kraft lignin at different temperatures were evaluated, and the level of char formation after the reaction was monitored and compared with that obtained from a conventional fixed-bed reactor. Gas chromatography/mass spectrometry (GC/MS) analysis of the liquid product was also performed to examine the chemical composition of the product oil.

Materials and methods

Lignin and alumina ball

The powder form of Kraft lignin (Sigma-Aldrich) was used as a sample for the pyrolysis of lignin in this study. The lignin was sieved to make a particle size smaller than 300 μm and dried at 80 °C for 6 h to eliminate the residual water. Proximate, ultimate, and gel permeation chromatography (GPC) analysis were performed to determine the physico-chemical properties of lignin [21]. Proximate and ultimate analysis were performed according to the standard methods, ASTM D 7582 (2015) and ASTM D 5373 (2014) using an elementary analyzer (Flash EA 1113, CE). The gel permeation chromatography (GPC) experiments were carried out to know the average molecular weight distribution of lignin using a Waters 2695 instrument. For this, 100 μL of lignin solution diluted in tetrahydrofuran was injected to GPC Column (Styragel HR2/Styragel HR4/Styragel HR5) at 30 °C. Thermogravimetric analysis (TGA Pyris Diamond; Perkin–Elmer) of Kraft lignin was also carried out. For TGA, 5 mg of Kraft lignin was heated non-isothermally from ambient temperature to 700 °C at 10 °C/min, 20 °C/min and 30 °C/min under 20 mL/min in a nitrogen atmosphere. Alumina ball (diameter: 5 mm), purchased from a local supplier, was used to provide the stable temperature and physical collision with lignin pyrolysis intermediates. X-ray diffraction (XRD) measurement of alumina ball was performed to identify its crystal phase on a X′pert PRO X-ray diffractometer (Panalytical) with Cu Kα radiation (λ = 0.15406 nm).

Rotary kiln reactor

Fig. 1 shows a schematic diagram of the rotary kiln type pyrolyzer designed for the rapid pyrolysis of lignin. The rotary kiln

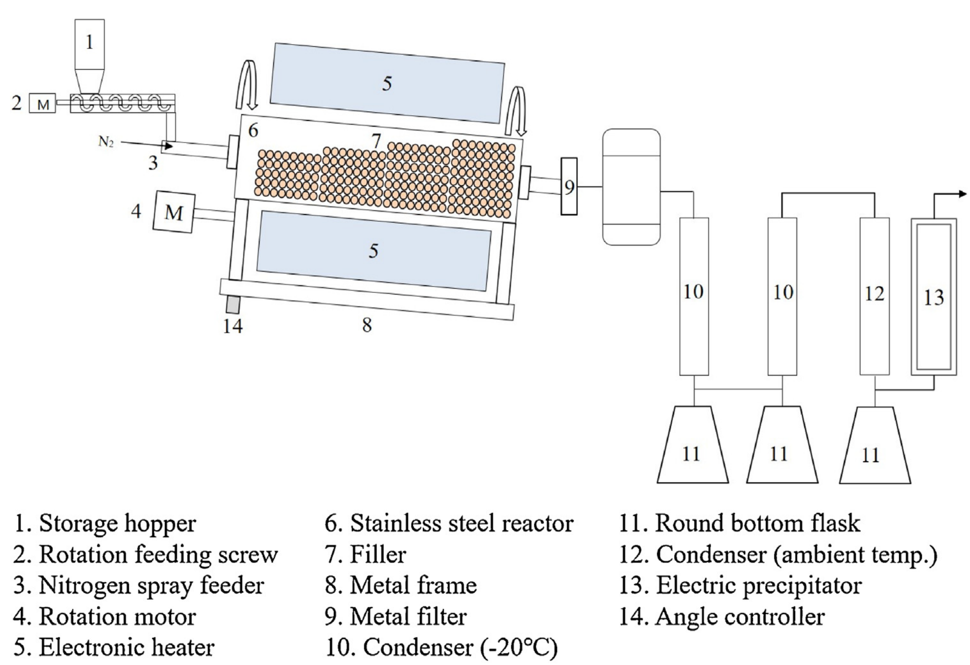

Fig. 1. Schematic diagram of rotary kiln reactor system.