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Fluidized bed pyrolysis of distilled spirits lees for adapting to its circulating fluidized bed decoupling combustion

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ABSTRACT

Distilled spirits Lees, rich in cellulose, water and N element, are difficult to burn efficiently and cleanly in grate chain stock boiler. The circulating fluidized bed decoupling combustion (CFBDC) was therefore proposed to burn the distilled spirits lees efficiently and with low-NOx emission. The pyrolysis behavior of the distilled spirits lees was investigated in a fluidized bed reactor for optimizing the pyrolysis conditions of the pyrolyzer in CFBDC. The results showed that the distilled spirits lees began to devolatize at 250 °C and at 350–450 °C the tar yield reached its maximum of about 16.3 wt.% (dry base). The chemical oxygen demand (COD) value of the condensed liquid reached its maximum of about 50,000 mg/L at 450 °C. With raising temperature the pyrolysis gas tended to contain more CO and H_2 and less CO_2. The functional groups H-O, aliphatic C-H, aromatic ring, C=O and C-O were all presented in the char generated at low-temperatures, while only the C-O group was identified for the char from the pyrolysis at 650 °C. The article suggested that the pyrolysis for the CFBDC was better around 500 °C so that certain volatiles could remain in the char to sustain stable combustion.

1. Introduction

In China, the distilled spirits lees generated in the unique solid-state fermentation process producing distilled spirits represent a kind of special biomass resource, which contains about 60 wt.% water and is rich in cellulose. The total amount of the lees is up to 15 million tons per year [1]. Traditionally, the distilled spirits lees have sufficiently high nutrition content for being feedstuff or protein substrate of animals such as pig. With progress in the biotechnology, the digestible nutrition in the lees becomes so low that it cannot meet the requirement of animal feedstuff. Nowadays, except for a part used as the filler material for animal feedstuff or as fertilizer, the distilled spirits lees are mainly disposed as waste causing serious environmental pollution [2–4]. Meanwhile, even for the uses as feedstuff filler and fertilizer, the drying of the lees leads to high energy consumption and high cost so that these utilizations can hardly be widely applied. Highly reliable technologies for rapid and large-scale utilization of the distilled spirits lees are thus in a great demand in China, especially for large distiller factories. This kind of technologies can also be applied to many other lees and residues such as vinegar lees and Chinese herb residues generated in various light industrial processes.

The nature of rich in cellulose in the distilled spirits lees makes them hardly treated via biological conversion technologies. The thermal conversion of the lees into the energy usable in the fermentation process, such as steam or fuel gas, is thus considered to be viable. By now, the consumed steam in the Chinese manufacturers of distilled spirits is generally produced by burning fossil fuel. Burning the distilled spirits lees to produce steam not only alleviate the pollution problem caused by the lees but also substitute for a part of the fossil fuel consumed in the production process. Wuliangye Co. Ltd. has tried to chain grate boiler for combusting the distilled spirits lees [5]. This practice showed that the distilled spirits lees cannot completely burn off in the stock boiler, while deep predrying of the lees was also required. The NOx emission in the stock boiler is also high because of the high N content in the lees and the high combustion temperature in the boiler. Thus, the technology of chain grate boiler combustion is not widely applied in China.

Circulating fluidized bed combustion is more suitable for low-rank fuels such as city garbage and lignite. Nonetheless, Permchart et. al [6] still failed to burn bagasse with 48.8 wt.% water in a conic fluidized bed. Patumsawad et. al [7] investigated the maximal moisture content of the municipal solid waste (MSW) that allowed its efficient burning in a fluidized bed. They found that the temperature in their fluidized bed was lower than 600 °C when the fuel water content was above 20 wt.%. Although the sludge with 65 wt.% water was co-fired with coal in a 103 MW Foster Wheeler CFB boiler [8], the high moisture

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content obviously decreased the combustor temperature. Therefore, the traditional CFB still has difficulty in burning efficiently and stably the biomass containing high water content.

The so-called circulating fluidized bed decoupling combustion (CFBDC) under development in Institute of Process Engineering (IPE), Chinese Academy of Sciences (CAS) intends to provide an improvement on the preceding inefficiency of the conventional CFB combustor [9]. The CFBDC is based on a dual bed system, and composed of a fluidized bed pyrolysis reactor and a riser combustor, as is conceptualized in Fig. 1. The fuel, such as the distilled spirits lees, is fed into the fluidized bed reactor to be dried and pyrolysed first through interacting with the hot heat carrier particles (HCPs) circulated between the two beds of the system. The solid residue of the pyrolysis (i.e., char) mixed with HCPs and then forwarded to the bottom of the riser to undergo combustion there. The pyrolysis gas, with steam as well, from the pyrolyzer is sent to an intermediate position of the riser to cause its co-firing with the char inside the riser. The combustion heat in the riser not only generates the desired energy product, such as steam, but also heats up the circulated HCPs. In this CFBDC process, the fuel water is completely removed in the pyrolyzer to ensure the highly efficient and stable combustion of the high water content fuel. Meanwhile, the reduction effects on NOx of both char and the combustible gas species in the pyrolysis gas (H_2, CO, CH_4) can lead to low NOx emission [10–13]. In comparison with the traditional CFB combustion, the CFBDC is thus more adaptive to high-water content fuel and enables low NOx emission.

The pyrolysis of distilled spirits lees in fluidized bed constitutes one of the important technical aspects of the CFBDC system. However, very few literature studies have ever investigated the pyrolysis behavior of biomass lees, although some studies have been conducted to make porous carbon materials by carbonizing and activating the waste lees [14–17]. Especially, there was almost no study regarding the direct pyrolysis of high moisture content biomass lees. This work is thus devoted to investigating the pyrolysis behavior of distilled spirits lees in a fluidized bed reactor. It is expected to gain a thorough insight into the characteristics of pyrolysis products at different temperatures, and thereby to optimize the pyrolysis conditions adaptive to CFBDC in terms of realizing stable combustion and low NO emission for burning the high water-content and N-content distilled spirits lees.

2. Experimental section

2.1. Apparatus and test approach

Experiments were carried out in the setup shown in Fig. 2, which was composed of a fluidized bed reactor (30 mm in ID and 450 mm high), a gas supply system, an electrically heated furnace, and a tar and gas collection system. In the fluidized bed reactor, a quartz porous plate was mounted around the longitudinally middle point of the reactor so as it becomes also the gas distributor for the reactor. A K-type thermocouple measured the temperature inside the fluidized particles and the temperature was treated as the reaction temperature. The pyrolysis was tested in N_2 atmosphere and the flow of N_2 was controlled with mass flow meter. In each test about 2.0 g distilled spirits lees was fed into the reactor from its top when the reactor temperature reached its preset value.

The generated tar was collected in a system consisting of three condensing tubes (in series) cooled with 5 °C water and three acetone-washing bottles immersed in an ice-water bath (see Fig. 2). Following the system layout in Fig. 2, the liquid from condensing the pyrolysis gaseous product (mainly water) in the first three condensers was collected in a flask to test the soluble chemicals and their resulting COD. The gas after removing tar was metered in a wet gas flow meter and passed through a silicone gel column to remove the residual moisture in the gas. The clean gas was totally collected with gas bags for GC analysis.

In this work, the pyrolysis of distilled spirits lees was studied at 250–650 °C. Each test lasted for 30 min from fuel feeding to complete pyrolysis. It was shown that this time allowed all volatile gasses to be released. The N_2 velocity in the reactor varied with tested temperature in a range of 0.017–0.024 m/s under cold condition. After each pyrolysis test, the reactor was taken out of the electric furnace and cooled to room temperature in the N_2 flow and then the residual carbon (i.e., char) was measured by weight.

The distilled spirits lees from Luzhoulaojiao Corporation Ltd, China, were tested in this work and Table 1 shows the major fuel properties. The lees tested in this work contained about 60 wt.% water and had a relatively high content of N, say, 3.9 wt.% in the dry and ash free (daf) base. The sizes of the distilled spirits lees were in 2.0–5.0 mm. The used bed material was quartz sand in sizes of 0.12–0.2 mm and the static bed height of sand in the reactor was about 10 mm.

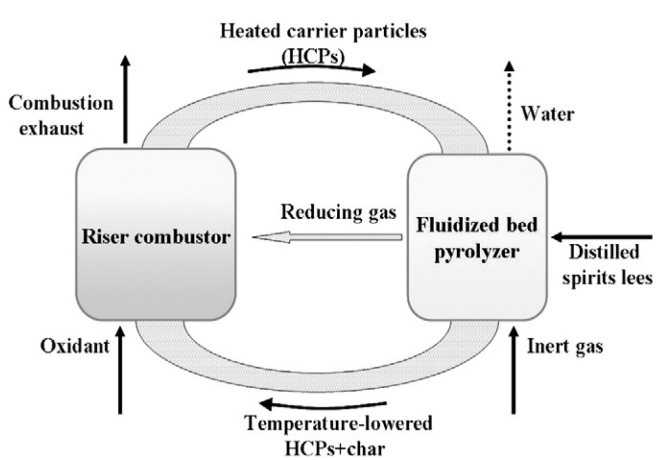

Fig. 1. Conceptual plot of circulating fluidized bed decoupling combustion (CFBDC).

2.2. Data analysis

The mass of char was measured by weighing directly the solid residual in the cooled reactor, while the mass of pyrolysis gas was calculated with Eq. (1) according to the measured gas volume and volumetric composition, as

$$m_{gas} = \sum_{j=1}^{n} VC_j / 22.4 \times M_j, \tag{1}$$

where, V is the measured gas volume; C_j is the volume concentration of the gas species j; and M_j is the molar mass of the gas species j.

After each pyrolysis test, all the condensing and connection tubes and the washing bottles were washed with acetone and the obtained washing acetone was mixed with the tar-dissolved acetone from the washing bottles to form the raw liquid for tar recovery. The tar was recovered by evaporating first the acetone in a rotary evaporator at 45 °C and 40 kPa and then drying the evaporation-left liquid in a vacuum drier working at 40 °C and 50 kPa. The weight that eventually varied little with the drying time was taken as the tar weight presented herein. The water amount generated in pyrolysis was estimated through mass balance.

The mass yield of each individual pyrolysis product was calculated according to Eq. (2) shown below, where Y_i is the yield of product i (wt.%); m is the mass of pyrolyzed distilled spirits lees (g) and m_i is the mass of product i (g).

$$Y_i = \frac{m_i}{m} \times 100\% \tag{2}$$