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Torrefaction of agriculture straws and its application on biomass pyrolysis poly-generation

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HIGHLIGHTS

- Torrefaction darkend the color and improved the grindability of agricultural straws.
- Torrefaction had different effects on char, liquid oil and biogas during pyrolysis.
- Char yield of pyrolysis torrefied straw increased and its fuel property not changed.
- Liquid oil is upgraded and concentrated phenols with less water content below 40 wt.%.
- Biogas is concentrated H_2 and CH_4 with higher LHV up to 15 MJ/nm^3.

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ABSTRACT

This study investigated the properties of corn stalk and cotton stalk after torrefaction, and the effects of torrefaction on product properties obtained under the optimal condition of biomass pyrolysis polygeneration. The color of the torrefied biomass chars darkened, and the grindability was upgraded, with finer particles formed and grinding energy consumption reduced. The moisture and oxygen content significantly decreased whereas the carbon content increased considerably. It was found that torrefaction had different effects on the char, liquid oil and biogas from biomass pyrolysis polygeneration. Compared to raw straws, the output of chars from pyrolysis of torrefied straws increased and the quality of chars as a solid fuel had no significant change, while the output of liquid oil and biogas decreased. The liquid oil contained more concentrated phenols with less water content below 40 wt.%, and the biogas contained more concentrated H_2 and CH_4 with higher LHV up to 15 MJ/nm^3.

1. Introduction

An efficient, clean, and renewable energy source with near-zero emission of CO_2 and low pollutants emission, biomass has recently attracted increasing research attention. As an agricultural country, China generates a large amount of agricultural straw wastes annually, and over 703 million tons of straw were produced in 2007 alone (Shi, 2011), over half of which could be utilized as energy source. However, the low bulk density, high moisture content, degradation during storage, and low energy density of raw lignocellulosic biomass are critical challenges in using agricultural residues as cellulosic feedstock. Thus, the pretreatment of biomass is necessary to improve its quality for efficient energy conversion.

Torrefaction, also known as a mild-pyrolysis for the pretreatment of biomass, is a thermal process that occurs at 200–300 °C under an inert atmosphere and at low heating rates (Prins, 2005). During the torrefaction process, biomass is dried, releasing a large amount of CO (~20%) and CO_2 (~80%) and small amount of volatile organics simultaneously (Prins et al., 2006b). The volume of the original material can be reduced by 30–70%, and the material retains over 90% of the original energy in the biomass (Medic et al., 2010). Torrefaction not only upgrades the fuel properties of biomass, but also increases the grindability of biomass (Kokko et al., 2012; Ohliger et al., 2013; Van Essendelft et al., 2013). Phanphanich and Mani (2011) showed that the energy consumed in milling torrefied sawdust decreased from 237 kWh/t to 23 kWh/t. In terms of molecule mechanism, torrefaction increases the amount of atomic carbon and decreases that of atomic hydrogen and oxygen, making agricultural straws suitable for thermal conversion into energy (Medic et al., 2010; Uemura et al., 2013). Pimchuai et al. (2010) investigated the combustibility of torrefied rice husk in the spout-fluid bed combustor and found that torrefied husks ignited faster and raised the bed temperature to a higher level because of

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its low moisture content. Couhert et al. (2009) investigated the effect of torrefaction on syngas products, and observed that torrefied beech wood produced approximately the same quantities of CO_2, 7% more H_2 and 20% more CO compared with the parent wood.

Compared with products from combustion and gasification, the properties of products obtained from pyrolysis are more likely to be influenced by the chemical compositions of feedstock (van der Stelt et al., 2011). Torrefaction can affect the properties of pyrolytic products by changing the chemical composition of biomass. Meng et al. (2012) analyzed the composition of oils from fast pyrolysis of torrefied and raw loblolly pine chips and found that bio-oils from torrefied samples became more concentrated in pyrolytic lignin with less water content than that from raw samples. Zheng et al. (2013) reported that the acetic acid and furfural content of the bio-oil decreased with the increase of torrefaction temperature or residence time. And several other studies suggested that torrefaction could reduce the yield of bio-oil, carbon conversion efficiency and energy conversion efficiency of fast pyrolysis (Boateng and Mullen, 2013; Liaw et al., 2013; Zheng et al., 2012). Ren et al. (2013) investigated the microwave pyrolysis of torrefied Douglas fir sawdust pellet and found that in the pyrolysis oil from torrefied biomass the concentrations of phenols and sugars increased while the concentrations of guaiacols and furans were reduced. In addition, torrefaction also altered the compositions of syngas by reducing CO_2 and increasing H_2 and CH_4.

Despite the theoretical findings reviewed above, the utilization of bio-oil is currently limited in China because of the relatively poor economic efficiency (Hu et al., 2010), even though bio-oils from torrefied feedstocks contain concentrated phenols and sugars. In our previous works (Chen et al., 2012), the biomass-based pyrolytic polygeneration system was put forward to generate solid char, liquid oil, and biogas from biomass compared with fast pyrolysis for bio-oil alone. The polygeneration system demonstrates high potential for industrial utilization and several demonstration projects have been built and in operation in China. Because of the huge demand and the high quality of biogas and char, these demonstration projects had gained more profits than projects adopting other technologies such as gasification for biogas and combustion for electricity.

However, the high energy consumption of feedstock pretreatment, especially the grinding of biomass, and the waste of liquid oil due to the high water content, prevent further enhancement of economic efficiency of these demonstration projects. Torrefaction has the potential of reducing grinding consumption of feedstocks and improving the utilization quality of products from biomass pyrolysis. Therefore, introducing torrefaction into biomass pyrolytic polygeneration may offer a new path to enhance the economic efficiency. But little research attention is paid to investigate the influence of torrefaction on biomass pyrolytic polygeneration, especially how to optimize torrefaction conditions when it is introduced to the pyrolytic polygeneration system.

In this study, the properties of two typical Chinese agricultural straws after torrefaction (cotton stalk and corn stalk) were firstly investigated, and four torrefaction conditions in varied temperatures were discussed. The subsequent pyrolysis based on the optimum condition of biomass pyrolytic polygeneration was carried out for the raw and torrefied stalks to investigate the influence of torrefaction on the yield and composition of pyrolysis products. An optimal torrefaction condition to biomass pyrolytic torrefaction was found.

2. Methods

2.1. Materials

The agricultural straws used were cotton stalk and corn stalk, which were collected from Wuhan and Xiaogan, Hubei province, respectively. All the straws were naturally dried after being reaped. Then, the collected straws were stored in a wareroom with good ventilation.

2.2. Physico-chemical property measurement of torrefied straws

Straws were torrefied using a fixed bed to investigate the effects of torrefaction on its physico-chemical properties. Fig. 1 in Supplementary material (Fig. 1S) shows the fixed-bed torrefaction system composed of a vertical tube (I.D.: 38 mm and H: 600 mm), an electrical furnace, a gas condensing system, and an incondensable gas collection and analysis system. The tube was pre-heated to a preset temperature (200, 230, 260 or 290 °C). After the temperature stabilized, the sample (5 g, particle size: 2–3 cm) was quickly placed in the center of the reactor and kept for 30 min. The heating rate measured was up to 20–35 $°C\,min^{-1}$ which would not influence the products (Deng et al., 2009). Pure N_2 (99.99%) was purged continuously to maintain an inert atmosphere. After pretreatment under an N_2 atmosphere, the solid products were cooled to ambient temperature in approximately 25 min and were subsequently collected for further analysis.

The grindability experiments on the raw and torrefied straws were conducted based on the previous study (Abdullah and Wu, 2009), but a cutting mill (Taiwan Chyun Tseh Industrial Co., Ltd., output of 0.75 kW) was used instead of the laboratory ball mill. To calculate the energy consumption during the grinding, the instantaneous output of the power of the mill was collected by a multi-function transducer (HarnWell, D800) connected to a computer where the time-power data was stored. The raw and torrefied samples (particle size: 2–3 cm) were placed into the cutting cell, and the cutting mill operated at a rotating speed of 2850 r/min. In each experiment, the same volume of raw or torrefied samples (approximately 30 ml) were placed in the cell to ensure consistent energy consumption for the cutting mill. The grinding duration was sufficiently long to ensure that all output particles could pass the 100 mesh sieve (<0.152 mm). The particle size distribution was measured using a British particle size analyzer (Master Min, MALVERN2000, British). Five trials were performed for each sample, and the results were averaged.

The proximate and elemental components of the torrefied straws were measured using SDTGA-2000 (Las Navas Company, Spain) and an elemental analyzer (Vario EL II CNHS/O, Germany). The higher heating value (HHV) of the raw and torrefied samples was measured using an oxygen bomb calorimeter (Parr 6300, American).

2.3. Pyrolysis and the characteristic of products

The raw and torrefied straws were pyrolyzed in the same fixed bed described in Section 2.2. In our previous works (Chen et al., 2012), the optimum temperature for obtaining high-quality pyrolytic products from the biomass polygeneration system was 550–650 °C. Therefore, the selected pyrolysis temperature of raw and torrefied biomass in the fixed bed was 550 °C. For each trial, about 3 g of sample was loaded into the sample carrier and placed on the top of the reactor before heating. A flow of preheated nitrogen (99.99%, 1 L/min) was used to provide an inert atmosphere in the reactor. When pyrolyzing the cotton stalks, the reactor was heated to the experimental temperature from the ambient temperature by the furnace at a rate of 30 °C/min. After the experimental temperature was reached, the sample carrier was moved rapidly from the top to the heated zone of the reactor. The samples were rapidly heated and decomposed, and the volatiles were purged out by N_2. Subsequently, the condensable volatiles were collected in an ice-water condenser, whereas the non-condensed parts were filtered through a glass wool filter and cleaned. The gaseous product