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# Effect of torrefaction on structure and fast pyrolysis behavior of corncobs

Anqing Zheng, Zengli Zhao *, Sheng Chang, Zhen Huang, Xiaobo Wang, Fang He, Haibin Li

*Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Science, Guangzhou 510640, PR China*

## HIGHLIGHTS

- ▶ Torrefaction as pretreatment prior to fast pyrolysis can improve bio-oil quality.
- ▶ The structure change of torrefied corncob was quantitatively characterized by $^{13}$C NMR.
- ▶ Bio-oil yield penalties were attributed to cross-linking and charring of corncobs.

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## ABSTRACT

Pretreatment of corncobs using torrefaction was conducted in an auger reactor at 250–300 °C and residence times of 10–60 min. The torrefied corncobs were fast pyrolyzed in a bubbling fluidized bed reactor at 470 °C to obtain high-quality bio-oil. The heating value and pH of the bio-oil improved when the torrefaction as pretreatment was applied; however, increasing bio-oil yield penalties were observed with increasing torrefaction severity. Fourier transform infrared Spectroscopy (FTIR) and quantitative solid $^{13}$C nuclear magnetic resonance spectrometry (NMR) analysis of torrefied corncobs showed that the devolatilization, crosslinking and charring of corncobs during torrefaction could be responsible for the bio-oil yield penalties. Gas chromatography-mass spectrometry (GC–MS) analysis showed that the acetic acid and furfural contents of the bio-oil decreased with torrefaction temperature or residence time. The results showed that torrefaction is an effective method of pretreatment for improving bio-oil quality if the crosslinking and charring of biomass can be restricted.

## 1. Introduction

Biomass is the only renewable energy source that can be used as an alternative to fossil fuel for producing liquid fuel. Moreover, biomass conversion is considered as being environmentally friendly since it has a negligible sulfur, nitrogen, and metal content and is $CO_2$ neutral (Sharma and Bakhshi, 1993). Several processes are being studied to convert solid biomass into liquid fuel, including fermentation of biomass to ethanol, biomass gasification followed by Fischer–Tropsch or methanol synthesis, and aqueous phase reforming and so on (Carlson et al., 2008; Zhang et al., 2012). In comparison to these processes, fast pyrolysis of biomass provides for the highest yield of liquid products (as high as 70–80 wt.%) and lowest cost (Vispute et al., 2010; Zheng et al., 2012). Biomass fast pyrolysis is a thermal decomposition process that occurs in an inert atmosphere using high heating rates ($10^3$–$10^4$ K/s) and short residence times (<2 s) at about 450–550 °C to maximize liquid production with solid char and non-condensable gas as low yield co-products (Bridgwater, 1999; Garcia-Perez et al., 2008b). The liquid products, known as bio-oil, are a low-quality fuel that has a complex composition, high acid and high water contents, low heating value and storage instability (Czernik and Bridgwater, 2004; Mohan et al., 2006). Pretreatment of biomass prior to fast pyrolysis has been identified as one of the most promising methods to improve the quality of bio-oil (de Wild et al., 2009b; Meng et al., 2012).

Biomass has a complex composition, mainly comprised of hemicellulose, cellulose, lignin, extractives (tannins, fatty acids, resins), and ash. Pretreatment can alter the composition and structure of biomass leading to a change in the mechanism and product distribution of biomass fast pyrolysis (Hassan et al., 2009). Several pretreatment methods prior to fast pyrolysis have been investigated, including water leaching, pretreatment with dilute acid and alkali, and hot compressed water treatment. Water leaching removes alkali metals and alkaline earth metals, thus inhibiting their catalytic function during fast pyrolysis, resulting in a high yield of levoglucosan (Scott et al., 2001). Pretreatment with dilute acid and hot compressed water treatment can cause decomposition of hemicellulose, a decrease in the degree of polymerization (DP) and crystallinity of cellulose, resulting in a high yield of anhydrosugar (Chaiwat et al., 2008; de Wild et al., 2009b; Dobele et al., 1999). Pretreatment with dilute alkali can lead to the solubilization of hemicellulose and the disruption of the lignin structure (Alvira

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* Corresponding author. Tel.: +86 02087057721; fax: +86 02087057737.
*E-mail address:* zhaozl@ms.giec.ac.cn (Z. Zhao).

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et al., 2010; Misson et al., 2009; Wang et al., 2011b). In addition to these methods, torrefaction can also been considered as a potential pretreatment prior to fast pyrolysis of biomass (Meng et al., 2012; Zheng et al., 2012). Torrefaction is a low-temperature pyrolysis process carried out at the temperature ranging from 200 to 300 °C to liberate water and release volatile organic compounds, primarily through the devolatilization of the hemicelluloses (de Wild et al., 2009a; Prins et al., 2006a). Torrefaction is an effective method to reduce the water, acid and oxygen contents of bio-oil to improve its heating value and pH (Meng et al., 2012; Zheng et al., 2012); however, the effects of torrefaction severity on the structure of torrefied biomass and its corresponding fast pyrolysis behavior, and especially the pyrolysis mechanism are currently not well understood. In the present study, torrefaction of corncobs was conducted in an auger reactor at 250, 275 and 300 °C and residence time of 10, 20 and 60 min. The torrefied corncobs were fast pyrolyzed in a bubbling fluidized bed reactor at 470 °C to obtain bio-oil. Solid $^{13}$C NMR and FTIR were used to characterize the structural changes of the torrefied corncobs. The compositional analysis of the bio-oil was performed with GC–MS. The effects of torrefaction temperature and residence time on the change in fast pyrolysis behavior of torrefied corncobs are described and discussed and a mechanism is proposed.

## 2. Experimental

### 2.1. Preparation of torrefied corncob

Corncob was provided by the Baodi feed mill in Tianjin, China. The corncobs were ground, sieved to a particle size range of 0.25–0.40 mm, and dried at 105 °C for 8 h before torrefaction. The ultimate analysis and chemical composition analysis of corncob are shown in Table 1. The elemental analysis of corncob was performed on a Vario EL (Elementar Analysensysteme, Hanau, Germany). The chemical composition of the corncobs was analyzed according to the standard Laboratory Analytical Procedures (LAP) for “Determination of Structural Carbohydrates and Lignin in Biomass” provided by the National Renewable Energy Laboratory (NREL).

Torrefied corncobs were prepared in an auger reactor system. The schematic of the system is given in Fig. 1(a). The auger reactor was 100 mm in diameter and 0.6 m in length, and heated by an 3.5 kW electrical furnace. Temperature was controlled by a temperature control unit. The reaction temperature was set to 250, 275, or 300 °C, while the residence time was 20 min. The reaction residence time were controlled with a motor to maintain 10, 20 or 60 min when the reaction temperature was kept constant at 275 °C. Nitrogen flow was used to maintain an inert atmosphere and to remove volatile products from the reactor. The corncobs were moved through the heating reactor by the action of a rotating screw to obtain solid and volatile products. The solid products, known as torrefied corncobs, were collected in a collection bin. Each experiment was repeated twice under the same conditions.

### 2.2. Fast pyrolysis of torrefied corncob

Fast pyrolysis of torrefied corncobs was conduct in a 10 kg/h fluidized bed reactor system. The schematic of the system is shown in Fig. 1(b). It consisted of a gas pre-heater, screw feeder, fluidized bed reactor, two gas–solid cyclones, heat exchanger, two gas–liquid cyclones and cotton filter. The fluidized bed was 219 mm in diameter. Silica sand was used as bed material and to a height of 12 cm. Nitrogen was used as fluidizing gas at a flow rate of 12 Nm$^3$/h. The reaction temperature was 470 °C. The char was separated and collected by two gas–solid cyclones in series. These cyclones were maintained at 300 °C with heating tapes. The bio-oil was cooled and collected in a heat exchanger maintained at around −10 °C followed by two gas–liquid cyclones. The uncollected aerosol was absorbed by a cotton filter at the end of the system. Total liquid products included the liquid collected by heat exchanger, gas–liquid cyclones and weight gained by the cotton filter. The char products involved the char collected by two gas–solid cyclones and char in bed material. The char in the bed material was determined by oxidation at 650 °C for 5 h in a muffle furnace and measuring the weight loss. Each experiment was performed twice under the same conditions.

### 2.3. Characterization of torrefied corncob and bio-oil

The $^{13}$C solid NMR spectra of torrefied corncobs, using a combination of cross-polarization (CP), magic angle sample spinning (MAS) and high-power proton decoupling, were obtained on a Bruker AV-300 solid NMR spectrometer operating at a proton frequency of 300 MHz (carbon frequency at 75 MHz) at room temperature. Acquisition was performed with a CP pulse sequence using a 2 ms proton 90° pulse of 2.4 µs. The MAS speed was 10.5 kHz, and the relaxation delay was 5 s. The solid $^{13}$C CP/MAS NMR can be employed to obtain high-resolution solid NMR spectra in acceptable time consumed. However, one of the major drawbacks of CP/MAS NMR is that the present technique cannot be applied to directly obtain quantitative results. Two obstacles should be overcome prior to quantitative analysis using CP/MAS NMR. One is the overlapping of signals in spectra. Another one is that different carbons in spectra have different cross-polarization dynamic. Hence, in order to obtain quantitative results from the CP/MAS NMR experiments, all the signals in spectra were deconvolved into individual lines using Gaussian–Lorentzian fitting prior to integration. And then all the integrals were corrected by a factor taking into account the cross-polarization dynamics, which obtained by variable contact-time experiments according to literature works (Davis et al., 1994; Kolodziejski and Klinowski, 2002).

The Fourier transform infrared Spectroscopy (FTIR) analyses of torrefied corncobs were carried out on a Bruker TENSOR27 in order to characterize the main functional groups of the torrefied corncobs. KBr discs were prepared by mixing about 2 mg of sample with 200 mg of KBr.

The GC–MS analysis of bio-oil obtained from fast pyrolysis was performed on a Agilent 7890 GC followed by an Agilent 5973 mass selective detector (MSD). The GC column used was an HP-INNO-Wax column (30 m × 0.25 mm, 0.25 µm film thickness). The oven was programmed to hold at 50 °C for 2 min, then increased at 10 °C/min to 90 °C, followed by an increase at 4 °C/min to 120 °C, and an increased at 8 °C/min to 230 °C and holding there for 10 min. Helium was used as carrier gas. The injector temperature was 250 °C. The injector split ratio was set at 20:1. The ion source temperature was 240 °C for the mass spectrometer detector. The

**Table 1**
Ultimate analysis and chemical component analysis of corncob.

| Sample | Ultimate analysis/wt.%, daf[a] | | | | | Chemical component analysis/wt.% | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C | H | O[b] | N | S | Extractive | Hemicellulose | Cellulose | Lignin |
| Corncob | 43.87 | 6.06 | 49.50 | 0.53 | 0.04 | 8.10 | 33.31 | 36.26 | 13.51 |

[a] daf: Dry ash free basis.
[b] The oxygen content was calculated by difference.