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.

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.

© 2012 Elsevier Ltd. All rights reserved.

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 ($10^5$–$10^6$ 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 crystalinity 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...