Fuel 137 (2014) 375–383

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Effects of wet torrefaction on reactivity and kinetics of wood under air combustion conditions

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HIGHLIGHTS

- Torrefaction temperature and holding time significantly influence the combustion reactivity and kinetics of woody biomass.
- The effect of torrefaction pressure is insignificant.
- Mass fraction and activation energy of hemicellulose are reduced by wet torrefaction.
- Activation energy of cellulose is increased by wet torrefaction.

ARTICLE INFO

Article history:
Received 24 March 2014
Received in revised form 18 June 2014
Accepted 5 August 2014
Available online 19 August 2014

Keywords:
Wet torrefaction
Wood reactivity
Combustion kinetics
Kinetic modelling
Biofuel pretreatment

ABSTRACT

This work continues our assessment of wet torrefaction for energy applications, looking at effects of the process parameters (temperature, holding time and pressure) on the reactivity and intrinsic kinetics of wood under air combustion conditions. Woody materials, Norway spruce and birch, were wet torrefied in various conditions (temperature: 175, 200, 225 °C; holding time: 10, 30, 60 min; and pressure: 15.54, 70, 160 bar). The reactivity of the treated and untreated woods was thermogravimetrically examined under a synthetic air environment (21% O_2 and 79% N_2 in volume). A four-pseudo-component model with different reaction orders was adopted for kinetic modelling and extracting the kinetic parameters. The results showed that when increasing either torrefaction temperature or holding time, the torrefied woods behaved more char-like than the raw fuels. However, pressure did not show significant effect on the reactivity. Relatively longer char combustion stages and higher conversion rates (up to $0.5 \times 10^{-3}\ s^{-1}$) were observed for the woods after torrefaction. The activation energy was decreased for hemicellulose and char, but increased for cellulose after torrefaction, whereas the trend for lignin is not clear. In addition, the hemicellulose mass fraction decreased after torrefaction (from 0.15 to 0.05 for spruce and from 0.23 to 0.06 for birch). The amount of char in the torrefied woods increased gradually with increasing torrefaction temperature or holding time (from 0.24 to 0.40 for spruce, and from 0.18 to 0.34 for birch).

1. Introduction

Wet torrefaction (WT), which may be defined as treatment of biomass in hydrothermal media (HM) or hot compressed water (HCW) at temperatures within 180–260 °C [1–5], is a promising method for production of high quality solid fuels from low cost wet biomass resources such as forest residues, agricultural waste, aquatic energy crops, and sewage sludge. The concept of WT is very similar to "hydrothermal carbonization" (HTC) [6–15] and sometimes is discussed under the general term "hydrothermal conversion" [15–19] or "hydrothermal treatment" [20–25]. Although the terminologies of WT and HTC have sometimes been used interchangeably, there is a significant difference between them. While WT aims at producing upgraded solid fuels for energy applications only, HTC is employed mainly for producing charcoal, with much higher carbon content, which can be used not only as fuel but also as activated carbon, soil enhancer, fertilizer, etc. Clearly, energy efficiency of the process, fuel properties and combustion properties of the product are more critical for WT than for HTC, and thus the former tends to be performed at lower temperatures (180–260 °C) than the latter (from 300 °C).

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http://dx.doi.org/10.1016/j.fuel.2014.08.011

Like dry torrefaction (DT), which may be defined as thermal treatment of biomass in an inert environment at atmospheric pressure and temperatures within the range of 200–300 °C [26–28], WT results in the following main improvements in the fuel properties of biomass: (1) increased heating value due to a reduction in the O/C ratio; (2) intrinsic transformation from hygroscopic into hydrophobic nature of biomass; (3) better grindability coupling with less energy requirement for size reduction of the fuel. After WT, the wet hydrophobic solid product can be effectively made dry by mechanical and/or natural dewatering, which is an attractive option capable of dramatically reducing the energy requirement for the post-drying step. In addition to the solid fuel product, many valuable organic compounds including acetic acid, formic acid, lactic acid, glycolic acid, levulinic acid, phenol, furfural, HMF, and sugars are found in the aqueous phase products of WT, making up approximately 10 wt% of the feedstock [4,6]. The potential use of these water-soluble organic fractions for production of valuable products may contribute to further improving the economy of the WT process.

Recently, an assessment of WT for energy applications (combustion, gasification, and pyrolysis) in comparison with DT has been reported by our research group [1]. The assessment includes a literature review of past studies relevant to WT, which will not be repeated in this present work. A core theme of the assessment was to investigate the effects of process parameters including pressure, reaction temperature, holding time, and feedstock particle size on the yield and fuel properties of the solid product. For reaction temperature and holding time, positive trends of their effects on the yield and fuel properties of the solid products were observed, which are similar to those for DT. However, pressure and feedstock particle size only have minor effects. More interestingly, the ash content of biomass fuel is significantly reduced by WT. This suggests that WT can be employed to produce “cleaner” biomass solid fuels as well, with respect to inorganic elements. In addition, a comparison between WT and DT supported by regression analyses and numerical prediction showed that WT can produce solid fuel with greater heating value, higher energy yield, and better hydrophobicity at much lower temperatures and holding times than DT [1].

Despite various advantages of WT over DT, only a few studies on WT have been reported [1–5] compared to a sharply increasing number of studies on DT during the last few years [26–34]. In addition, most WT studies focused on the effects of process parameters on the yield and fuel properties of the solid product. To our knowledge, no study of using solid fuel obtained from WT for energy applications has been reported so far. Combustion is currently the most important energy application of biomass solid fuel, considering its contribution to more than 90% of the global bioenergy deployment [35–39]. It is therefore important and necessary to investigate into the effects of WT on combustion reactivity and kinetics of biomass solid fuels.

Several studies on combustion of dry torrefied biomass have been reported [30,40–43], which would be beneficial for studying combustion behavior of wet torrefied biomass fuel. Pimchuai et al. [40] and Bridgeman et al. [30], for example, studied the combustion of biochars obtained from DT of different biomass materials. They found that the combustion of dry torrefied husks and herbaceous biomass released more heat than that of the raw materials due to the higher fixed carbon content of the biochars. However, no kinetic data was reported from these studies. Arias et al. [41] applied a simple first-order kinetic model to estimate the activation energy and pre-exponential factor of raw and dry-torrefied eucalyptus samples in a two-stage combustion process (devolatilization followed by combustion). The results showed that both kinetics parameters (the activation energy and pre-exponential factor) increased in stage 1 and decreased in stage 2 after DT. Nevertheless, the model was based on an empirical method which was not validated because the model itself could not either reproduce simulated curves or give any information about the fit quality between the predicted and experimental data. Recently, studies on the combustion kinetics of dry torrefied woody biomass materials using multi pseudo-component models have been reported by Broström et al. [42] and Tapasvi et al. [43]. The former employed a global kinetic model and the latter employed a distributed activation energy model (DAEM). The results from the two approaches showed that DT had little effect on the kinetic parameters of the torrefied biomass regardless of the treatment conditions. Broström et al. [42] reported that the activation energy values of hemicellulose, cellulose and lignin were constant at 100.6, 213.1, and 121.3 kJ/mol, respectively for both raw and dry-torrefied spruce. Tapasvi et al. [43] found that the activation energy values for cellulose, non-cellulosic part and char remained at 135, 160 and 153 kJ/mol, respectively for different types of feedstock and DT conditions.

This present study is a follow-up of our first assessment of WT for energy applications [1], which has been published as mentioned earlier. The objective of the present work was to assess the effects of WT conditions (temperature, holding time and pressure) on the combustion reactivity and kinetics of biomass solid fuels. Thermogravimetric analysis (TGA) was employed for this work as it is a proven method for studying devolatilization and combustion of biomass in the kinetic regime [44,45].

2. Materials and methods

2.1. Materials

As mentioned in the introduction, the present work is a follow-up of our first report on comparative assessment of WT for energy applications. The biomass materials used for this work were obtained from the previous work, in which the full details about materials and experimental methods were presented and can be found elsewhere [1]. For a convenience, a brief extraction is imported in this present work.

Stem wood from Norway spruce (softwood) and birch (hardwood) were selected as feedstock for the study since they are the main wood species in Norwegian forests. The samples were cut into 1 cm cubes for WT in hot compressed water, using a 250 ml Parr reactor series 4650 (Parr Instrument, USA) at different temperatures (175, 200, 225 °C), pressures (15.54, 70, 160 bar) and holding times (10, 30, 60 min). The corresponding vapour pressures of water at 175, 200, and 225 °C are 8.93, 15.54, and 25.50 bar, respectively. However, in order to keep more water in the liquid phase, the pressure of 70 bar was used for all of the WT experiments, except for the investigation of the pressure effect at 200 °C [1]. For this investigation, the pressures of 15.54, 70 and 160 bar were employed. Distilled water was used as the reaction media. The ratio of dry feedstock over water was 1:5 by weight.

After WT, the wet solid products were dried at 105 °C for 48 h and then stored in a desiccator for further analyses. The proximate and ultimate analyses of the samples used for this work are presented in Table 1. The proximate analyses were performed according to ASTM standards: ASTM E871, ASTM E872 and ASTM D1102 for moisture content, volatile matter and ash content, respectively. The ultimate analyses were determined (on a dry basis) by means of an “EA 1108 CHNS-O” elemental analyzer (Carlo Erba Instruments). The higher heating values (HHVs) were calculated on dry and ash free basis, according to Channiwala and Parikh [46].

2.2. Thermogravimetric analysis method and procedure

A thermogravimetric analyzer (Mettler Toledo TGA/SDTA851e) was employed for this study. The biomass solid fuels were first