Fuel 113 (2013) 379–388

Contents lists available at SciVerse ScienceDirect

Fuel

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

Torrefaction of woody biomass (Juniper and Mesquite) using inert and non-inert gases

Dustin Eseltine, Siva Sankar Thanapal, Kalyan Annamalai, Devesh Ranjan *

Department of Mechanical Engineering, MS 3123 Texas A&M University, College Station, TX 77843, United States

HIGHLIGHTS

- Encroachment of woody biomass in rangelands and grasslands of central Texas.
- Torrefaction as viable pretreatment option for Mesquite and Juniper.
- Effect of carbon dioxide as medium for torrefaction.
- Increased weight loss and improved grindability on using CO_2 for torrefaction.

ARTICLE INFO

Article history:
Received 30 May 2012
Received in revised form 25 April 2013
Accepted 29 April 2013
Available online 29 May 2013

Keywords:
Torrefaction
Carbon-dioxide
TGA

ABSTRACT

Torrefaction has been shown to be a viable pre-treatment process for thermally upgrading biomass and making it better suited for use as a fuel. Results are presented here from the torrefaction of two different woody biomass (Mesquite and Juniper) using thermogravimetric analysis (TGA). Samples were torrefied in two different mediums (Nitrogen and Carbon-dioxide) to investigate the impact of inert and non-inert gases on the thermal degradation of the biomass, specifically mass loss as well as the breakdown of hemicellulose, cellulose, and lignin. A wide range of torrefaction temperatures ranging from 200 to 300 °C was investigated at a single residence time. TGA thermograms showed increased amounts of weight loss when the biomass was torrefied in a Carbon-dioxide environment compared to inert environments, while derivative thermogravimetric analysis (DTA) showed a drop in the peak rate of hemicellulose and cellulose weight loss when using Carbon-dioxide as the torrefaction medium. Fuel properties analysis of samples subjected to a mild torrefaction process (240 °C) showed increases in ash and fixed carbon content of the biomass, independent of torrefaction medium. Furthermore, comparison of the grindability of raw and torrefied samples showed torrefaction in a Carbon-dioxide environment further improved the grindability of the torrefied biomass. The effect of inert and non-inert torrefaction mediums on the volatile species (CO_2, CO, CH_4, and C_2H_6) released from torrefied Mesquite during pyrolysis was further investigated via TGA–FTIR analysis.

1. Introduction

The continued use of fossil fuels worldwide has lead to increased research in the area of non-conventional energy technologies. Of the different non-conventional energy sources available (wind, solar, tidal, nuclear), biomass is a widely available energy source which is considered to be carbon neutral as well as renewable. The energy stored within the biomass can be extracted through different techniques which include biochemical (such as anaerobic digestion producing biogas) and thermo-chemical methods. Thermo-chemical ways of extracting the energy from the biomass includes pyrolysis, gasification, co-combustion and reburning. Pyrolysis is a process of treating the biomass at very high temperatures (temperatures greater than 300 °C) in an inert environment which results in the production of fuel in all three phases oil (l), char (s) and gases (g) which are combustible. Gasification and combustion of raw biomass are direct combustion techniques which involve the use of air. Gasification is carried out in fuel rich conditions (Equivalence ratio (ER) > 1; partial oxidation) and combustion is carried out in fuel lean condition (ER < 1, excess air) [1]. Ash fouling [1–3], poor grindability [4], and lower heat value of raw biomass makes it difficult to burn the raw biomass directly in coal fired boilers. The overall conversion efficiency of raw biomass is limited by its high moisture content which can also have significant effects on grindability [5] and energy yield [6]. It has been noted that biomasses with high moisture contents are better suited for biological conversion processes [7] (anaerobic digestion) unless they undergo some pre-treatment process that

---

* Corresponding author. Tel.: +1 979 458 3580; fax: +1 979 458 3081.
E-mail addresses: eseltined@tamu.edu (D. Eseltine), sivsan.siva@tamu.edu (S.S. Thanapal), kannamalai@tamu.edu (K. Annamalai), dranjan@tamu.edu (D. Ranjan).

0016-2361/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2013.04.085

reduces the moisture content, such as drying. Torrefaction is one of the techniques which has been studied recently to improve the grindability and energy density or heat value (HV) of biomass. It involves the partial pyrolysis of biomass in order to improve its fuel properties [8–14]. Torrefaction is similar to pyrolysis, with the heat treatment being carried out in a lower temperature range (200–300 °C) and the resulting product biomass having a higher energy density.

Torrefaction mainly removes moisture in the biomass and causing it to become hydrophobic [14–16] due to destruction of hydroxyl (OH) groups in the biomass [17] allowing for easier storage and transportation. Furthermore, the destruction of OH groups results in a biomass with a larger heating value due to a decrease in oxygen content. The hydrophobic nature of torrefied biomass also results in less energy being required to process the biomass. The improved properties of torrefied biomass suggest that it is viable as a renewable energy source that is better suited for use in co-firing and gasification applications [17–19] when compared to virgin (untreated) biomass. Further studies [20] have shown that gasification of torrefied woody biomass produces more usable CO and H_2 than raw biomass. A simplistic rationale for explaining the improved HV of biomass is to use empirical Boie equation for HV of biomass [21].

$$\mathrm{HHV}_f\ (\mathrm{kJ/kg}) = 35,160 * Y_C + 116,225 * Y_H - 11,090 * Y_O + 6,280 * Y_N + 10,465 * Y_S \quad (1)$$

where Y_C, Y_H, Y_O, Y_N and Y_S denote the mass fractions of carbon, hydrogen, oxygen, nitrogen and sulfur respectively. Increasing the carbon percentage and lowering the oxygen percentage results in increases in the HV of fuel. Increases in heating value with increasing pyrolysis temperature are due to the almost complete removal of oxygenated compounds [9,17]. Studies conducted by Bridgeman et al. [9] on the torrefaction of canary grass, wheat straw, and willow observed that the moisture, oxygen, and hydrogen percentages decreased while carbon percentage increased with increases in the torrefaction temperature. The decrease in oxygen percentage coupled with the increase in carbon percentage thereby resulted in higher heating values. The mass and energy yields of willow (a woody biomass) were also noticeably higher when compared to that of canary grass and wheat straw. Similar research by Sadaka et al. in 2009 [22] on the torrefaction of wheat straw, rice straw, and cotton gin waste observed that the heating value increased with increasing residence temperature and residence time. However, increasing torrefaction temperatures resulted in higher amounts of mass loss during the torrefaction process. Furthermore, it has been shown that torrefaction temperature has a much greater effect on mass loss and energy yield than residence time by Pimchuai et al. and others [23,14]. The lower limit is set by the devolatilization temperature of hemicellulose which is below 250 °C [9]. Hemicellulose and cellulose have been found to devolatilize before lignin in biomass. The devolatilization of hemicellulose beginning around 200 °C with complete devolatilization occurring by 350 °C. Also cellulose exhibits devolatilization beginning at 250 °C [24–29]. Although the upper temperature limit of torrefaction does not allow for the full devolatilization of cellulose and hemicellulose, depolymerization has been shown to occur. Furthermore, recent studies by Chen and Kuo [26] have concluded that there are no apparent interactions between the three basic constituents of biomass (hemicellulose, cellulose, and lignin).

Woody biomass is a particular type of biomass that could benefit greatly from a pre-treatment process such as torrefaction given that it is initially very difficult to grind due to its fibrous nature. Furthermore, woody biomass has invaded grasslands and rangelands causing a reduction in herbaceous plant life [30,31]. Ansley et al. [32] have pointed out that using woody biomass as a source of bioenergy could not only provide an alternative energy source but also reduce the impact of woody plants on grasslands and rangelands. Mesquite and Juniper wood are two specific types of woody biomass found abundantly in Texas that could be used for such a purpose.

The effect of residence time (t_{res}) and residence temperature (T) on the properties of various biomass using nitrogen as the torrefaction medium has been widely documented. However, despite large amounts of research on the torrefaction of biomass it appears that there is scant literature on investigating the effect of non-inert gases upon the weight loss characteristics and thermal degradation of torrefied biomass. Given that Carbon-dioxide is one of the main emissions from fossil fuel combustion, recycling of CO_2 to thermally upgrade biomass could improve the overall efficiency of either process. This coupled with the fact that biomass is a source of energy that is carbon neutral make Carbon-dioxide an intriguing alternative to Nitrogen as a torrefaction environment. The present study focuses on investigating the effect CO_2 has upon the thermal degradation of two woody biomass during torrefaction and pyrolysis using a thermogravimetric analyzer. By studying a wide range of torrefaction temperatures the effect of temperature can be seen upon the weight loss characteristics of both biomass. Furthermore, an optimal torrefaction temperature can be determined from mass loss data and estimated heating values. For the present study the optimal torrefaction temperature is utilized to further study the effect of Carbon-dioxide as a torrefaction medium upon the fuel properties, grindability, and emissions profile of torrefied biomass.

2. Experimental procedure

2.1. Thermal degradation analysis via TGA

The torrefaction characteristics of the Mesquite and Juniper wood were investigated using a TGA (TA Instruments Q600). During experiments the flow rate of the purge gas was controlled and regulated via the internal mass flow controller within the TGA with the purge gas having a flow rate of 200 ml/min. Samples were loaded into TGA at ambient temperatures; roughly 10 mg of sample were used for each test. Once the samples had been loaded the furnace was purged. Samples were then heated at a constant heat rate of 20 °C/min from an ambient temperature to the torrefaction temperature, where the biomass was torrefied for 1 h at that fixed temperature. This residence time was chosen based upon the mass loss during torrefaction of biomass torrefied between 30 min and 3 h being extremely similar [8]. After torrefaction of the biomass was completed the furnace was heated from the torrefaction temperature to 1000 °C at a rate of 20 °C/min. The entire process served to torrefy the biomass and then pyrolyze the torrefied biomass. Samples were torrefied between 200 and 300 °C in 20 °C increments to investigate a wide range of torrefaction temperatures.

2.2. Batch torrefaction

A laboratory oven was used to torrefy larger amounts of biomass for fuel property analysis. For batch torrefaction in the laboratory oven the initial particle size of 2–4 mm was used. Samples were initially placed in 5 ml ceramic crucibles and the crucibles were put into the oven at room temperature. The purge gas flow was started and maintained at 6 LPM by an external flow meter. Once the oven had been purged the samples were heated from ambient temperatures to the torrefaction temperature at a rate of 20 °C/min. The samples were then held at the torrefaction temperature for 1 h, removed from the oven, and placed in a dessicator to cool.