



Torrefaction: Mechanistic study of constituent transformations in herbaceous biomass



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ABSTRACT

Several improvements in biomass properties due to torrefaction can be attributed to a chemical transformation of its constituents. This study focusses on investigating the nature of these transformations along with their association with mass and energy yields for varying conditions of torrefaction temperatures and times for verge grass and bagasse. Torrefaction was carried out in a 0.87 l bench-top fixed bed reactor convectively heated with a nitrogen flow. Chemical analysis of the products was carried out using high performance liquid chromatography (HPLC) following a two-step acid hydrolysis, whereas the applied thermal analysis techniques included differential thermogravimetry and bomb calorimetry. It was seen that for a torrefaction temperature of 290 °C at a residence time of 15 min, approximately 23% glucan and 82% xylan in bagasse is converted as compared to 96% glucan and 97% xylan that is converted in verge grass. In addition to the degradation of structural carbohydrates, the extent of formation of acid insoluble residue (char) was also seen to differ with the choice of feedstock. As a consequence, within the range of torrefaction conditions, a comparable reduction in mass yield is found to lead to a drop in energy yield that is 25% less in the case of verge grass as compared to bagasse.

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1. Introduction

Torrefaction has been widely studied as a pre-treatment for biomass feedstock towards enabling their use as fuels in thermal conversion processes. It involves thermally treating raw biomass in non-oxidizing conditions at temperatures of 230–300 °C, leading to a formation of a fuel into a more coal-like solid. Even as the net energetic benefits of torrefaction can only be ascertained following a complete mass and energy balance of the torrefaction process, it is the improvements in fuel quality that can, in several cases, enable widespread utilization of biomass as a fuel. The advantages of torrefaction range from improved grindability and hydrophobicity, higher energy density and calorific value as well as reduced vulnerability to biodegradation [1,2]. The resulting relative ease of storage and cost-effectiveness in transportation may enable the adoption of biomass as a commodity fuel. In general, torrefaction is reported to result in energy yields ranging from 75 to 90% for mass yields around 50–70%, depending on the severity of torrefaction [3] with temperatures being more critical than time.

The added value of torrefaction might be even more necessary in enabling the utilization of herbaceous (non-woody) biomass for thermochemical conversion. Several studies have been performed in the past to study torrefaction of herbaceous biomass [4–9], including grasses and agricultural residues. The objective of most of these studies has been to quantify the mass and energy yields of torrefaction within a range of process conditions and to study the effects of treatment on certain fuel characteristics such as elemental composition, volatile/fixed carbon ratio and calorific value. These studies have involved torrefaction being carried out typically with a few grams of biomass heated in a sample tube placed in an oven subjected to a certain time/temperature configuration. All research generally indicates decreasing O/C and H/C ratios, with reducing volatile yields and an increase in calorific value on account of torrefaction with higher severities leading to greater deviations from the raw biomass properties. The weight loss in torrefaction and improvement in properties have previously been attributed to the devolatilisation of the hemicellulose fraction (and possibly a partial degradation of cellulosic and lignin fractions) of biomass. It has been seen that for biomass types with high hemicellulose contents, the weight loss is also higher (and especially prominent at higher temperatures) [5,6], indicating that hemicelluloses is the least thermally stable structural constituent of biomass, followed by cellulose and lignin.

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Rationalization of the improvement in biomass properties due to torrefaction has been performed at the fundamental level of chemical bonding and functional groups as well as on the basis of chemical transformation of the constituent carbohydrates. The commonly applied techniques at the fundamental level include solid state ^{13}C NMR spectroscopy, FTIR spectroscopy as well as dedicated chemical tests for certain organic functional groups. It has been seen that even at temperatures of 240°C , there is a significant decrease in the acetyl groups, which can be attributed to the de-acetylation of hemicelluloses [10–12]. Higher torrefaction temperatures also indicate a decrease in crystallinity of cellulose [10]. At lower temperatures, there is evidence of demethoxylation of syringyl to guaiacyl groups within lignin [12]. However, at higher temperatures (exceeding 270°C), torrefaction was also found to increase the intensity of the aromatic C–C and C–H bonds, postulated to be a result of formation of condensed lignin structures following the cleavage of ether bonds ($\beta\text{--O--}4$) in lignin [13]. These studies are however aimed at giving a qualitative assessment of chemical transformations, and are usually limited to the study of woody biomass.

Some studies further characterize the biomass with respect to the unreacted structural constituents following torrefaction. A commonly applied technique involves the use of differential thermogravimetry to obtain characteristic weight loss peaks in the devolatilisation of biomass. It has been observed that with increase in torrefaction temperature the hemicellulose “shoulder” adjoining the cellulose peak in the differential thermogram disappears, indicating its decomposition [5,13,14]. At higher torrefaction temperatures, the cellulose peak is also seen to reduce in magnitude indicating its decomposition. It has, however, also been shown that mineral content in biomass can play a significant role in affecting the reactivity of the biopolymer leading to a further overlapping of the cellulose degradation peak with that of hemicellulose [15]. Also biomass may contain more than one type of hemicellulose, with several kinds of hemicelluloses (including xylan) containing more than one characteristic peak [16]. This leads to difficulties in peak deconvolution and identification of the effect of torrefaction on the hemicellulose content of the fuel based on TGA data alone.

Even as carbohydrate analysis is commonly performed on raw biomass samples, there are a few instances of it being used to analyze torrefaction products for unconverted constituents. Shoulaifar et al. [11] used a combination of acid methanolysis (for non-cellulosic carbohydrates), acid hydrolysis (for cellulose) and Klason lignin methods for samples of birch wood torrefied in the range of $240\text{--}280^\circ\text{C}$. It was observed that at a torrefaction temperature of 255°C there was a 71% pentose degradation with only around 11% degradation of cellulose. The torrefaction led to an increase in the acid insoluble residue (acid insoluble lignin + torrefaction char) of 49% as compared to the original value. Ben and Ragauskas [10] and Park et al. [13] both used a two-step acid hydrolysis method for analysing torrefied loblolly pine over a range of torrefaction times and temperatures. Both found a similar trend in the rapidly decreasing fraction of pentoses, a gradual decrease in hexoses and increasing quantities of acid insoluble residue. However, there is scant literature available with respect to studying the effect of torrefaction on herbaceous biomass. One such study performed by Shang et al. [17] used a two-step hydrolysis with torrefied wheat straw, indicating a near total conversion of hemicellulose and cellulose. However, the study only considered a single torrefaction condition of 300°C with a torrefaction time of 2 h (parameters which are probably too severe for industrial applications).

The present paper is based on a study of the constituent transformations in two kinds of biomass: verge grass and sugarcane bagasse processed using a range of torrefaction temperatures and residence times. One of the objectives of the study is to quantify the torrefaction yields for various feedstocks over a range of tempera-

tures and residence times and to rationalize the difference in yields with respect to biomass constituents. This can enable an a priori assessment of mass yields in torrefaction based on the compositional data of the biomass feedstock. As compared to carbohydrate analysis, differential thermogravimetry is a much more convenient technique for analysing biomass constituents; hence it is also an objective of this study to validate its applicability to analysing torrefied herbaceous biomass. Herbaceous biomass is often characterized by the presence of a large quantity of extractives. Along with the structural carbohydrates, these extractives also contribute to the solid yield in torrefaction, a phenomenon that shall also be studied as a part of this work. Lastly, it is an objective to analyse the progressive effects of the loss of the various components on the calorific value (HHV) of the torrefied biomass product.

2. Methodology

2.1. Biomass feedstock and preparation

The present study concerns the comparative study of torrefaction of verge grass and sugarcane bagasse. Verge Grass (V.G.) used in the experiment can be more specifically described as verge grass trimmings, and do not include the root of the plant. The verge grass used in this study was harvested in September 2014 in Delft, The Netherlands. The sugarcane bagasse (henceforth referred to as ‘bagasse’) used in this study was procured from a sugar mill in the district of Satara (Maharashtra), India following processing in August–September 2014. The average moisture contents (as received on wet basis) are 72% for verge grass and 16% for sugarcane bagasse. The average ash contents (dry basis) are 10% for verge grass and 6% for sugarcane bagasse. Prior to torrefaction, the biomass samples were oven dried at 105°C for 24 h, to enable accurate estimation of mass yields on a dry basis. For the purpose of drying, approximately 100 g of biomass is spread out on to a perforated aluminum foil tray before being placed in a drying oven. When the drying protocol was first established, hourly weight measurements (at each hour) were performed that indicated that there was practically no weight loss (less than 1% of previous reading) after 5 h of drying. However, since widely used drying protocols recommend a drying time of around 24 h, this is what was followed.

2.2. Production of torrefied biomass

The biomass torrefaction setup consists of a vertically disposed stainless steel tube with a volume of 0.87 l. The tube itself is divided into three equal compartments (referred to as the *bottom*, *middle* and *top*) by means of perforated dividers to allow for the flow of convective media. Each compartment is packed with 25–30 g of oven-dried biomass (the range being a consequence of the difference in packing densities of verge grass and bagasse), leading to a total loading of 75–90 g of biomass per batch of production. Heat is convectively transferred to the biomass packed inside the tube volume using an electrically heated inert gas (nitrogen) flow of 60 normal liters per minute ($\text{L}_n \text{min}^{-1}$). Each compartment is equipped with a thermocouple measuring the temperature in the core of that section. The desired *torrefaction temperature* is reached using a ramping rate of approximately $7\text{--}8^\circ\text{C min}^{-1}$, following which the temperature is maintained for a period referred to as the *torrefaction time*. An important objective in carrying out experiments with this particular setup was, in fact, to try to approach ‘realistic’ cases of convective heat transfer in a packed bed. The tube that contains the biomass has a significant thermal inertia and even as the tube is isolated, it is not electrically traced. Consequently there exists a temperature gradient between the bottom and top of the reactor; meaning that the biomass contained in the different sections

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