



Structural and chemical modifications of typical South African biomasses during torrefaction



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HIGHLIGHTS

- Different fibre composition between woods and sweet sorghum bagasse.
- Higher surface area increases after torrefaction for bagasse than wood.
- Torrefaction reduced significantly hemicelluloses than cellulose.
- Formation of acid-resistant was observed with torrefaction of bagasse.
- Torrefaction treatment increases average crystallite diameter of biomass.

ARTICLE INFO

Article history:

Received 13 October 2015

Received in revised form 1 December 2015

Accepted 9 December 2015

Available online 14 December 2015

Keywords:

Biomass
Torrefaction
CP-MAS ¹³C NMR
XRD

ABSTRACT

Torrefaction experiments were carried out for three typical South African biomass samples (softwood chips, hardwood chips and sweet sorghum bagasse) to a weight loss of 30 wt.%. During torrefaction, moisture, non-structural carbohydrates and hemicelluloses were reduced, resulting in a structurally modified torrefaction product. There was a reduction in the average crystallite diameter (L_c) (XRD), an increase in the aromatic fraction and a reduction in aliphatics (substituted and unsubstituted) (CPMAS ¹³C NMR). The decrease in the aliphatic components of the lignocellulosic material under the torrefaction conditions also resulted in a slight ordering of the carbon lattice. The degradation of hemicelluloses and non-structural carbohydrates increased the inclusive surface area of sweet sorghum bagasse, while it did not change significantly for the woody biomasses.

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1. Introduction

Biomass utilization, either as a precursor for electricity generation or biofuel production, has received a lot of attention in the last decade in the wake of increasing calls for renewable energy utilisation. Waste biomass is of great interest as it avoids the competition between energy and food crops, which may assist with food security in the world (Aboyade et al., 2013). South Africa, amongst other African countries, produces large amounts of waste biomass from the paper industry, sugar industry as well as municipal wastes (Damm and Triebel, 2008). These biomasses include wood chips (softwood and hardwood), sugarcane bagasse, sweet

sorghum bagasse, dried corn cobs and corn stover (Aboyade et al., 2013; Damm and Triebel, 2008), having a large lignocellulosic content, offering potential in thermochemical applications.

Pre-treatment methods are often used to beneficiate the biomass, e.g. to ensure a reduction in oxygen, moisture, and smoking propensity of the generated fuel (Yang et al., 2014). Many pre-treatment methods have been studied to provide this highly sought 'new biomass' and the specific application seems to determine the preferred pre-treatment method (Tumuluru et al., 2011). Often referred to as mild pyrolysis, torrefaction is most suited for thermochemical applications and is reported to upgrade biomass by producing a more hydrophobic fuel with an increased fixed carbon content (Chen et al., 2015; Tumuluru et al., 2011; Wannapeera and Worasuwannarak, 2012; Yang et al., 2014). Torrefaction does not only reduce bulk and oxygenated discharges but torrefied biomass also has a higher energy yield and mass energy density

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than raw biomass resulting from the degradation of mostly hemicelluloses and to a lesser extent celluloses and lignins (Kim et al., 2012; van der Stelt et al., 2011).

The chemical and structural characteristics of biomass are mainly dependent on the fibre composition i.e. the amount of hemicellulose, cellulose and lignin and these vary for each biomass family. For instance, woody biomass records highest lignin amounts whilst it is adequately reported that bagasse (sugarcane or sweet sorghum) is rich in hemicelluloses and non-structural carbohydrates (Carrier et al., 2013; Wannapeera and Worasuwannarak, 2012). The amounts of each of the fibre components contribute to process products in any application, for instance: higher lignin biomasses are suitable for thermochemical applications for their higher solid yield after pyrolysis (Wang et al., 2008; Wannapeera and Worasuwannarak, 2012). In the case of thermochemical applications, char properties are frequently investigated, mostly to explain observed pyrolysis or gasification kinetics (Cao et al., 2014; Guerrero et al., 2008).

Recent research on the characteristics of torrefied biomass focuses on the change in elemental compositions, C/O and H/O ratio, fibre composition, thermal stability, hydrophobicity and grindability (Phanphanich and Mani, 2011; Tumuluru et al., 2011; Wannapeera and Worasuwannarak, 2012). There is only limited reporting on structural changes by torrefaction as investigated by solid state NMR, XRD as well as explanations of surface area changes in relation to the lignocellulosic compositional alterations by torrefaction. A detailed evaluation of these structural changes could be beneficial to understanding the torrefied material's reactivity towards pyrolysis, combustion and/or gasification (van der Stelt et al., 2011; Xue et al., 2014).

Biomass characterization using WA-XRD-CFA (Wide angle X-ray Diffraction carbon fraction analysis) and CP-MAS ^{13}C NMR (cross polarization Magnetic Angle Spinning ^{13}C solid state Nuclear Magnetic Resonance spectroscopy) has been receiving much attention in the past 5 years. The effect of comminution on raw biomass samples has been investigated using powder WA-XRD-CFA (Murillo et al., 2014; Zhao et al., 2013), and char comparisons (Guerrero et al., 2008) were also established whilst crystallinity and mineralogy changes during pyrolysis are reported elsewhere (Cao et al., 2014; Guerrero et al., 2008). Crystallinity may also be quantified by CP-MAS ^{13}C NMR, as shown by Foche et al., (2001), for differently sourced celluloses. Even though raw biomass structure is complicated to understand, CP-MAS ^{13}C NMR has been reported and peak positions were assigned to the main groups found. Degradation of lignocellulosic components either by torrefaction or pyrolysis have also been tracked by CP-MAS ^{13}C NMR experiments (Freitas et al., 2001; Melkior et al., 2012; Park et al., 2013; Wikberg and Maunu, 2004). Park et al., (2013) reported insightful findings on the transformation of biomass by heat treatment structures using both CP-MAS and DP-MAS ^{13}C NMR (direct polarization ^{13}C solid state Nuclear Magnetic Resistance spectroscopy) and noted the superiority of DP-MAS in quantifying non-protonated carbons. Ben and Ragauskas (2012), elaborated on how torrefaction affects raw pine carbohydrate composition and also conclusions on how heat disrupts the binding that binds the macro-components together using CP-MAS ^{13}C NMR. However, lattice parameters and carbon type changes due to torrefaction as determined by WA-XRD-CFA and CP-MAS ^{13}C NMR, respectively, have yet not received considerable attention.

In coal characterization, parameters from WA-XRD-CFA, HR-TEM (high resolution transmission electron microscopy) and CP-MAS ^{13}C NMR provided insight in the structural arrangement of the material in relation to gasification kinetics (Okolo et al., 2015; Roberts et al., 2015a). A similar approach to raw and torrefied biomass is currently lacking and forms part of the motivation of this paper. The overall purpose is to establish the properties

of the torrefied biomass to be used for evaluation of gasification kinetics. The effect of torrefaction on the structural and chemical characteristics of three (3) biomass samples abundantly available in South Africa; SB (sweet sorghum bagasse), SW (softwood chips) and HW (hardwood chips) is studied.

2. Methods

2.1. Materials

SW and HW were supplied by the South African Pulp and Paper Industries Limited (Pretoria, Republic of South Africa) and SB was obtained from the Agricultural Research Council (ARC), Potchefstroom (Republic of South Africa). All samples were air-dried for a week, ground to ~5 mm using a hammer mill (TRF-70) and milled to <500 μm using a ball mill. Nitrogen (purity $\geq 99.999\%$) and carbon dioxide (purity $\geq 99.998\%$) were supplied by Africa Oxygen Limited (Afrox).

2.2. Torrefaction

Torrefaction experiments were performed in a thermogravimetric analyser (TA-SDTQ 600). The samples were heated at 10 $^{\circ}\text{C}/\text{min}$ from 30 $^{\circ}\text{C}$ to 260 $^{\circ}\text{C}$, in 100 Nml/min N_2 . The samples were kept at 260 $^{\circ}\text{C}$ until a loss of 30 wt% of the air dried material was obtained. This mass loss was obtained after 110, 100 and 20 min heating at the maximum temperature for SW, HW and SB respectively. These conditions were then used for bulk torrefaction which was carried out in a tube furnace from Elite Thermal Systems Limited (Model TSH12/75/610), where 15 g of biomass was torrefied. In this communication, RSW, RHW and RSB denote raw SW, raw HW and SB respectively, whilst TSW, THW and TSB refer to torrefied SW, HW and SB, respectively.

2.3. Characterization of biomass samples

2.3.1. Ultimate and proximate analysis

The carbon, hydrogen, oxygen and nitrogen contents were determined on a CE 440 elemental analyser using the ASTM D 5373 method, for both the raw and torrefied material, and the oxygen content was calculated by difference. Proximate analysis was performed using a U-Therm TGA. Standard methods of analyses used are shown in Table 1, while the fixed carbon content was determined by difference. Calorific value measurements were performed using an oxygen bomb calorimeter (IKA 500).

2.3.2. Composition analysis

Adopting the 'food industry' method (Carrier et al., 2011), acid detergent lignin (ADL), acid detergent fibre (ADF), neutral detergent fibre (NDF) and non-structural carbohydrates were determined at ARC-Analytical services, Republic of South Africa. Eqs. (1) and (2) were used to determine the hemicellulose and cellulose fractions of the samples. It should be noted that the ADL value was assumed to be the total lignin mass percentage in the samples (Phanphanich and Mani, 2011).

$$\text{Hemicelluloses}(\text{wt.}\%) = \text{NDF} - \text{ADF} \quad (1)$$

$$\text{Cellulose}(\text{wt.}\%) = \text{ADF} - \text{ADL} \quad (2)$$

2.3.3. Thermogravimetric analysis (TGA)

Pyrolysis experiments, for both the raw and torrefied biomass, were carried out in a thermogravimetric analyser (SDTQ 600), using approximately 15 mg of sample, and ramping the temperature from 30 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$ under N_2 (100 Nml/min) at 10 $^{\circ}\text{C}/\text{min}$.

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