



Influence of lignocellulose thermal pretreatment on the composition of condensable products obtained from char devolatilization by means of thermogravimetric analysis–thermal desorption/gas chromatography–mass spectrometry

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ABSTRACT

Four lignocellulosic biomass types, i.e. pine, bamboo, corn cob and corn stover were converted at varying temperatures (250–400 °C) and hold times (30 or 60 min). Chars produced were devolatilized in a thermogravimetric analyser (TGA) and evolved condensable volatile products were captured and quantified by thermal desorption/gas chromatography–mass spectrometry. Based on the mass loss rate curves (dTG), char devolatilization products distribution was consistent with the extent of biomass modification by thermal pretreatment. It was evident that pretreatment at 250 and 275 °C led to significant conversion of hemicelluloses, the latter resulting in a 2–3 factor decrease in acids yield from char devolatilization. Except for pine (with more crystalline structure), significant cellulose conversion was achieved at 300 °C resulting in a decreased levoglucosan yield and at least a 10 factor reduction in furans production from char devolatilization compared to raw biomass. Most of the oxygenated groups were converted during pretreatment at a temperature of 350 °C while the char became a more condensed aromatic structure. Therefore the condensable organic products were obtained in low yields (< 1 wt%) and were characterized by a majority of aromatic hydrocarbons and the absence of most of the oxygenated compounds, except for the phenolic products.

1. Introduction

Fossil-based fuels play a major role in the global energy supply chain. However, the use of such fuels poses environmental problems such as air pollution and global warming [1]. In addition these fuels are non-renewable and hence, the need for an alternative fuel source that is both renewable and environmentally friendly. Lignocellulosic biomass has the potential to replace fossil-based fuels, given that it is a renewable carbon carrier and offers environmental benefits such as CO₂ neutrality, and low SO_x and NO_x emissions [2,3].

Several methods exist for the conversion of biomass into energy and/or energy carriers. Prominent among these are the thermochemical processes such as gasification, combustion and pyrolysis generating energy products including bio-fuels and power from biomass [4,5]. However untreated lignocellulose exhibits characteristics such as high moisture content, high oxygen content, heterogeneity, low bulk and energy density, hydrophilicity, susceptibility to microbial decay and difficulty in grinding [3,6,7]. These characteristics impact adversely on the processing/conversion efficiency and the quality of the products

obtained when lignocellulose is utilized in the above mentioned processes. Improvement of the characteristics of untreated lignocellulose would ensure more efficient utilization in energy conversions.

Torrefaction and slow pyrolysis are among the thermal pretreatments used to improve biomass properties for energy conversions [8]. Torrefaction is a mild form of pyrolysis usually in the temperature range of 200–300 °C [9,10], while slow pyrolysis is typically undertaken between 300 and 500 °C [11], in an inert atmosphere. Compared to other thermochemical processes they are characterized by low heating rates (< 50 °C) and long volatiles residence time. Thermal pretreatment processes provide lignocellulose with several added advantages such as reduced moisture content [8,12], reduced O/C ratio [13], hydrophobicity [14,15], increased energy density [16], improved grindability [9,17] and uniformity of the solid fuel product [18]. Due to the above advantages research on thermal pretreatment has increased over the last few decades [2]. Most of these studies, however, have focused on the impact of thermal pretreatment conditions (temperature and hold time (HT)) on the mass yield [19,20], heating value [20] and grindability [9,21] of the solid product. Temperature is usually

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reported to be the factor with the most pronounced effect. Char yields ranging from 75 to 90 wt% with an HHV increase of 1–3 MJ/kg have been reported for torrefied biomass at 250 °C, while char yields of 40–60 wt% and an HHV increase of 3–7 MJ/kg were obtained at 300 °C [3,13]. At higher temperatures, for instance 400 °C and above char yields of less than 40 wt% [22] and an HHV greater than 25 MJ/kg [23] have been reported. The effect of HT had been observed, especially during torrefaction, with longer HT resulting in improved HHV and reduced char yields. For instance a 13.5 wt% reduction in char yield and 2.6 MJ/kg increase in HHV were obtained for wood at 280 °C when HT was increased from 25 to 80 min [20].

Depending on the lignocellulosic composition of biomass, the yield and fuel properties of the char product as influenced by temperature during thermal pretreatment can vary significantly. For example using two woody biomasses (*Lantana Camara* and *Mimosa Pigra*) with similar initial HHV (≈ 18 MJ/kg), Mundike et al. [20] obtained 43.4 wt% char yield and 27.1 MJ/kg HHV for *Lantana Camara* and 52.1 wt% char yield and 24.5 MJ/kg HHV for *Mimosa Pigra* when both were torrefied at 303 °C. This difference was attributed to the relatively high hemicellulose content in *Lantana Camara*. While hemicellulose conversion occurs at 200–350 °C, lignin conversion occurs at a slow rate over a wide range (200–600 °C) with the maximum rate usually at 400 °C [24,25].

The extent of cellulose conversion has a critical influence on char yield and composition as cellulose is the main lignocellulose constituent. While slow conversion can occur for temperatures lower than 300 °C, cellulose depolymerization becomes very fast at higher temperatures as evidenced by the presence of a narrow peak with a maximum usually observed between 320 and 380 °C on the dTG curve of thermogravimetric analysis (TGA) [26]. The main factors identified as influencing the maximum temperature are the cellulose crystallinity [27,28], the catalytic effect of inorganics [26] and some interactions due to the decomposition of the other constituents [29]. An interesting illustration is a study of the conversion of washed and unwashed grasses [26]. As a consequence, in case a significant conversion of the cellulose constituent is required, the temperature of the thermal pretreatment must be adapted to the type of biomass considered. The temperature of the thermal pretreatment is thus based on a compromise. Increasing temperature leads to more extensive conversion which results in higher char heating value, but lower char yield. For temperatures higher than 400 °C, the conversion of the lignocellulosic constituents is more limited, thus such temperatures are avoided in order to limit the energy demand of pretreatment.

The use of biomass char as substitute fuel for coal in combustion and gasification processes is envisioned to increase in the future as research strives towards sustainable and environmental friendly sources of energy. For such applications, a critical factor is the composition of the volatile organic compounds released from biomass char during the devolatilization step. For combustion, the presence of reactive volatiles can significantly modify the combustion performance of a fuel [30,31]. In the case of gasification applications, some volatiles called tar cause several operational problems such as corrosion or deactivation of catalysts used during syngas conversion [32]. While several studies about the composition of volatiles released during biomass torrefaction or pyrolysis can be found (though it is still a challenge due to the complexity of bio-oil), similar studies about char devolatilization are limited. Previous work [33,34] reported torrefaction of biomass up to 290 °C with subsequent pyrolysis of the torrefied biomass (char) to study the effect of the pretreatment on the bio-oil and concluded that the bio-oil properties were greatly improved. Regarding thermal pretreatment to produce char for combustion and gasification applications a more severe pretreatment temperature is required. For such experiments, especially when thermal pretreatment was realized at relatively high temperature, low yields of organic compounds are expected. As a consequence, the use of a solvent to recover the organic compounds is not recommended and an analytical method such as thermogravimetric

analysis with quantification of captured evolved volatile products by thermal desorption/gas chromatography–mass spectrometry (referred to as TGA–TD/GC–MS) recently developed [35] appears as particularly suitable.

In the current work, the influence of thermal pretreatment on the characteristics of four different lignocellulosic feedstocks was explored. The aim of the study was to assess the impact of torrefaction and slow pyrolysis on the chemical properties of biomass, and the effect of pretreatment conditions on the mechanisms of devolatilization of the generated chars, evaluated through analysis of the volatile products' chemical composition. Thermal pretreatment experiments and the subsequent devolatilization of the chars were performed at milligram-scale in TGA. The volatiles products from devolatilization of chars were captured onto thermal desorption tubes and analyzed by thermal desorption/GC–MS for identification and quantification by internal calibration. The combination of thermal degradation with compositional analysis of volatile products provided insights into the mechanisms and pathways for specific volatiles evolution.

2. Materials and methods

2.1. Feedstock

Four types of biomass from different provinces of South Africa were used for this study. These include two corn (*Zea mays*) residues; corn stover (CS) and corncob (CC), pine (*Pinus radiata*) (PN) and bamboo (*Bambusa balcooa*) (BB), which were obtained from the Northern, Eastern and Western provinces, respectively. Prior to further analysis, sub-samples of each feedstock for experiments were obtained by the standard method DD CEN/TS 14780:2005. The biomass feedstocks were ground and sieved to a particle size range of 250–450 μm using Retsch mill (model ZM100) and a vibratory sieve shaker (model AS200). Both corn residues had a moisture content of less than 7 wt% (as received), while PN was obtained in the form of pellets (5–25 mm length and 6–12 mm diameter, EC Biomass Fuel Pellets (Pty) Limited, Eastern Cape, South Africa) and had a moisture content of 4–8 wt%. BB was air dried to less than 10 wt% moisture and cut into chips (about 2 cm \times 0.5 cm).

2.2. Chemical analysis

The lignocellulose chemical composition (extractives, acetyl, lignin and structural carbohydrates) of raw biomass feedstocks were determined according to the standard laboratory analytical procedures (LAPs) 002, 003, 017 and 019, as developed by the National Renewable Energy Laboratory (NREL) (http://www.nrel.gov/biomass/analytical_procedures.html). Proximate analysis was conducted to determine the percentages of ash, fixed carbon (FC) and volatile matter (VM) present in feedstock according to ASTM method E1131, by means of thermogravimetric analysis (TGA) (TGA/DSC 1-LF1100 system, Mettler Toledo). Elemental analysis was determined using a Leco TruSpec Micro elemental analyzer.

2.3. TGA thermal pretreatment

The thermal pretreatment (torrefaction or slow pyrolysis) of biomass samples was achieved by the use of TGA (TGA/DSC 1-LF1100 system, Mettler Toledo). About 180–400 mg per sample of raw biomass (depending on the bulk density of biomass feedstock) was pretreated in an inert atmosphere at an argon (baseline 5.0, Afrox SA) flow rate of 70 mL/min. The following heating program was followed: dynamic heating at 10 °C/min from 30 °C to the appropriate pretreatment temperature, followed by isothermal condition for a specific hold time. The pretreatment temperatures were 250, 275, 300, 350, and 400 °C, while the hold times were fixed at 30 min or 60 min. Biomass pretreatment was performed in at least triplicate to generate sufficient quantities of

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