Biomass and Bioenergy 104 (2017) 17–35

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Chemical and morphological evaluation of chars produced from primary biomass constituents: Cellulose, xylan, and lignin

Matthew W. Smith [a, b], Brennan Pecha [a, b], Greg Helms [c], Louis Scudiero [d], Manuel Garcia-Perez [a, *]

[a] *Department of Biological Systems Engineering, Washington State University, Pullman, WA 99164, USA*
[b] *Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Pullman, WA 99164, USA*
[c] *Center for Nuclear Magnetic Resonance Spectroscopy, Washington State University, Pullman, WA 99164, USA*
[d] *Department of Chemistry and Materials Science and Engineering Program, Washington State University, Pullman, WA 99164, USA*

ARTICLE INFO

Article history:
Received 24 January 2017
Received in revised form
26 May 2017
Accepted 30 May 2017

Keywords:
Char
Biochar
Pyrolysis
NMR
Raman
XPS

ABSTRACT

The effect of pyrolysis temperature on the morphology, bulk and surface chemistry of cellulose, xylan and lignin chars has been examined. Chars were produced between 300 and 700 °C. Raman, X-ray photoelectron, nuclear magnetic resonance spectroscopic techniques, scanning electron microscopy and surface area analysis were used to characterize each sample. Formation of polyaromatic structures were found to be prevalent at 400 °C for both cellulose and lignin chars, and showed development at 300 °C for Xylan. The low A bands identified in the lignin char produced at 400 °C indicate that crosslinking at low temperatures preferentially forms hexagonal or larger rings. Aromatic condensation increased until 500 °C, and remained stable up to 700 °C. The sharp drop in oxygen content as temperature is increased up to 500 °C and the formation of ether (C-O-C) groups indicates that oxygen is a primary reaction component for crosslinking and polycondensation. Despite the considerable increase in ring size for char produced at 700 °C compared to 500 °C, only very mild loss of oxygen is identified, suggesting that C-C bonds are forming with minimal oxygen mediation The increased broadness of the NMR peak and the Raman G band suggest that at these temperatures the increase in ring size occurs largely in a 3 dimensional manner rather than planar with contributions from non-hexagonal rings and out-of-plane distortion. By comparing the NMR dephasing data to the I(D)/I(G) ratio an approximate relation between this Raman data and cluster size has also been derived.

1. Introduction

Pyrolysis of biomass has proven to be a promising technology for production of chars and biofuels [1–6]. The products are the result of a complex thermochemical reaction pathway that occurs when lignocellulosic materials are heated over 300 °C in the absence of oxygen. Chars formed under high temperature pyrolysis (above 600 °C) contain large fractions of highly stable aromatic compounds, similar to high grade coals, that are resistant to microbial attack [6], and make pyrolysis a possible technology for carbon storage. Studies of anthorosols have shown evidence that char-like materials substantially alter the physical and chemical properties in ancient Terra Preta soils [7,8], leading to long lasting carbon storage and improved crop production. Char is hypothesized to have potentially positive effects on both physical and chemical soil properties such as aeration, cation exchange capacity, and water holding capacity [6,9,10]. While excellent results have been observed from these ancient soils, results with virgin chars produced under laboratory conditions have resulted in less certain results, with authors finding chars to improve crop performance, hinder performance or have little to no effect [9,11]. Though the source of char is known to affect application outcome [12], detailed analysis of materials used in these studies is often lacking, leaving uncertainty regarding the chemical and physical comparability of the materials tested.

A number of tools are available to assess bulk physical and chemical properties, as well as adsorbed compounds that may impact soil quality. Analysis of the underlying chemical structure of the char has also been evaluated using a host of spectroscopic

---

* Corresponding author. Biological Systems Engineering, WSU, LJ Smith, Room 205, Pullman, WA 99164-6120, USA.
E-mail address: mgarcia-perez@wsu.edu (M. Garcia-Perez).

http://dx.doi.org/10.1016/j.biombioe.2017.05.015
0961-9534/

techniques; however, interpretation is often difficult due the broad, poorly defined peaks that are often obtained. A recent series of methods to interpret nuclear magnetic resonance (NMR) [13], X-ray photoelectron (XPS) [14] and Raman spectra [15] of chars has yielded promising results for chars from cellulose, however more work is required to determine if these methods are applicable to other biomass constituents as well as whole biomass. To better address the design and application of char based products from lignocellulosic feedstock, the development of correlations between biochar properties, production conditions and end-use effectiveness is critical.

Lignocellulosic material is composed of three main polymers; cellulose, hemicellulose and lignin [9–14]. The distribution of these polymers is a critical factor controlling pyrolysis product distribution. Previous work has also shown that the composition of chars can be modelled accurately using a non-interacting assumption [16]. Carbonization of lignocellulosic material proceeds initially via depolymerization, dehydration, cross-linking and condensation reactions [17–20]. Volatile compounds formed by the initial primary reactions may also undergo secondary heterogeneous reactions with char along the diffusion path out of the particle [21,22]. A liquid intermediate can also form as the molecules shrink that can also undergo secondary heterogeneous and homogenous reactions to form a highly stable polyaromatic moieties that makes up the backbone of char [1].

The carbonization of cellulose competes with both depolymerization [23–26] and fragmentation reactions [17,18,23,27–29]. A detailed mechanism reaction mechanism has been proposed by Wang et al. [30] detailing these pathways. Cellulose begins to degrade between 250 and 300 °C, forming an “active cellulose” phase (crystalline depolymerized cellulose) via cleavage of weak glycosidic bonds resulting in short chains of 200–300 glucose units [23,27,31–35], with sufficiently low melting point to allow a molten phase to form prior to carbonization. NMR studies by Pastorova et al. [36] suggest that by this stage in pyrolysis a variety of rearrangement and fragmentation products are also present, including furans, hydroxyaromatics, unsaturated hydrocarbon chains, and new oxygenated groups including carboxyls and carbonyls. The molten cellulose phase depolymerizes to form monomeric and oligomeric sugars [37], the oligomeric sugars undergoes a variety of dehydration, cross-linking, and fragmentation reactions as pyrolysis continues [34,35,38,39]. The volatile monomeric compounds can be easily evaporated at pyrolysis temperatures, the oligomeric products can be removed by thermal ejection [40]. Finally, the oligomers in the liquid intermediate poly-condense to form the aromatic carbon structures typical of charcoal [16,32,41–44]. Pastorova et al. [36] provide a detailed explanation of the crosslinking mechanism of cellulose. In this model, the active or molten cellulose products are hypothesized to react through aldol type reactions with ring fragments and cleaved rings, causing randomized three dimensional growth of the condensed phase. In addition to aldol condensation, at temperatures above 200 °C, electro-spin resonance (ESR) studies have identified the formation of radical sites from homolytic cleavages [45]. These free-radicals are expected to further promote crosslinking and condensation reactions.

Char formation mechanisms from lignin have also received considerable attention in the literature. Cleavage of lignin bonds during pyrolysis is predicted to proceed via homolytic cleavage, substitution, and hydrogen transfer-induced bond scission reactions [46,47]. These reactions tend to favor decomposition of the ether bonds, as demonstrated by Kawamoto [48]. Model compounds studies have shown that groups containing phenolic structures are considerably more reactive than groups without, showing increased yields of both char (from polycondensation) and guaiacol (from β-ether cleavage) [48]. Lignin depolymerization mechanism depends on the number of monomer units linked by C-C bonds [49,50]. Clusters with more than 3 units are likely to pass through a melt phase during pyrolysis [40]. Once in this state polycondensation tends to increase the average molecular weight of the clusters [51–54]. Lignin oligomers integration into biochar structure has been hypothesized to proceed via a series of aldol condensation [46] and radical induced crosslinking [55].

The decomposition of hemicellulose is the least studied of the primary biomass components [56,57]. Degradation is often assumed to follow similar reaction pathways as that of cellulose; however, the amorphous nature of the polymer may facilitate more rapid decomposition, as demonstrated by Wang et al. [30] in an investigation of the effect of crystallinity on cellulose pyrolysis. Thermogravimetric studies have demonstrated that primary decomposition begins at a temperature as low as 250 °C and is nearly complete by 350 °C, with only slight mass loss associated with further heating to 700 °C. These results indicate that far more extensive crosslinking occurs in the hemicellulose structure at low temperatures, stabilizing much of the residual char structure, even before polycondensation occurs. Analysis of the products from hemicellulose pyrolysis indicates substantially higher furanic type compounds than typically obtained from cellulose [56].

There are very few studies in the literature on the differences in composition of the chars produced from cellulose, hemicellulose and lignin. Previous analyses of the pyrolysis of mixed components has shown that while substantial deviations in the yield of both liquids and gases occurs when assuming a non-interacting model, char yields are highly predicable by the additive contribution of each of the polymers in the feedstock [16]. What is not known is if the composition of each of the biomass constituents contributes separately to form distinct structures.

Thus, the main objective of this paper is to study how the individual biomass components (cellulose, hemicellulose and lignin) and the pyrolysis temperature impact the bulk, surface and morphological properties of the resulting chars. Recently proposed Raman [15], XPS [14] and NMR schemes [13] are employed with scanning electron microscopy, surface area analysis and chemical analysis to better define the char structures that form from a thermoseries of each material.

2. Materials and methods

2.1. Avicel cellulose and xylan

Avicel Cellulose was purchased from Sigma Aldrich (product# 11365)) and used as received for all studies. Xylan produced from beechwood has been used a surrogate for hemicellulose (Sigma Aldrich, product# X4252) and was used as received.

2.2. Milled wood lignin purification

Milled wood lignin (MWL) was produced from hybrid poplar wood following a modified Bjorkman Method [58,59]. In this method ~200 g of wood are first extracted using a 9:1 (v:v) acetone water solution followed by a 2:1 (v:v) ethanol benzene mixture. Each extraction is performed for a minimum of 8 h using a Soxhlet extraction system. The extracted wood fiber is then dried at 80 °C overnight. Dried wood fiber was then milled for 50 h using a ball mill (Across International) with alumina jars and zirconia balls. Milling was performed at 10 Hz with a 15 min on/15 min off cycle. After milling, the wood flour was extracted using a 96% dioxane solution, and solids were separated by centrifugation and re-extracted. A total of 3 extractions were performed on the wood flour. To obtain the crude wood lignin the dioxane was evaporated using a rotary evaporator. To reduce the carbohydrate content of