



Impact of the lignocellulosic material on fast pyrolysis yields and product quality



Marion Carrier*, Jan-Erns Joubert, Stephen Danje, Thomas Hugo, Johann Görgens, Johannes (Hansie) Knoetze

Department of Process Engineering, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

HIGHLIGHTS

- Fast pyrolysis of South African feedstocks.
- Overlap of chemical and transfer phenomena in the bubbling fluidized bed reactor.
- Key role of the hemicelluloses content on the quality of fast pyrolysis bio-oil.
- Dependence of biochars' properties with the carbohydrates content.

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ABSTRACT

The paper describes the fast pyrolysis conversion of lignocellulosic materials inside a bubbling fluidized bed. The impact of biopolymers distribution in the biomass feed, namely hemicelluloses, cellulose and lignin, on the yields and properties of pyrolytic bio-oils and chars was investigated.

Although it is not possible to deconvolute chemical phenomena from transfer phenomena using bubbling fluidized bed reactors, the key role of hemicelluloses in biomass feedstocks was illustrated by: (i) its influence on the production of pyrolytic water, (ii) its impact on the production of organics, apparently due to its bonding relationship with the lignin and (iii) its ability to inhibit the development of chars porosity, while the cellulose appeared to be the precursor for the microporous character of the biochars. These results are of interest for the selection of suitable feedstocks aimed at producing bio-oil and char as fuels and soil amendment, respectively.

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1. Introduction

Plant biomass has potential to be a sustainable energy source and could become a viable alternative to the use of fossil resources. It is of particular interest to researchers and policy-makers in South Africa where CO₂ emissions are a problem (Tomaschek et al., 2012). The assessment of existing and available biomass for bioenergy applications is a critical issue for optimization biomass utilization. The Council for Scientific and Industrial Research (CSIR) developed an analytical frame-work and decision-support tools to assist in assessing, managing and monitoring the sustainability of bioenergy (Von Maltitz and Stafford, 2012). This work mapped the woody biomass distribution in South Africa. The outcomes of the work were a national resource map for woody biomass projecting the growth and the estimation of potential quantities. Resources such as the invasive alien plants and bush encroachment, which have the highest potential as biomass

sources, are only available for a defined period of time, estimated to be 20 years. Substantial amounts of waste biomass from agriculture (11.8 Mton per year), wood and forestry residues (9.2 Mton per year) and sugar cane bagasse (7.5 Mton per year) can also be used for bioenergy purposes (Vosloo, 2013). Conversion of South African forest and agricultural residues through thermochemical processes is not only considered as a potential source for the production of heat, electricity and transport fuels, but can also produce added-value materials and chemicals, e.g. activated carbon and biochar as a soil amendment (Uras et al., 2012; Carrier et al., 2012).

Lignocellulosic plant biomasses such as forest and agricultural wastes are composed mainly of carbohydrates (i.e. hemicelluloses and cellulose) and lignin. The proportion of these basic polymer blocks varies according to the origin and the type of biomass (Carrier et al., 2011). In addition to the major components, minor amounts of extractives, inorganics and water made up the final composition. The impact of lignocellulosic composition on the quantity and quality of pyrolysis products has often been reported at the milligram scale using a pyrolyzer oven or a microbalance

* Corresponding author. Tel.: +27 21 808 9485; fax: +27 21 808 2059.

E-mail addresses: carrier@sun.ac.za, marion_carrier@msn.com (M. Carrier).

coupled with gas chromatography or/and mass or infrared spectrometry. These studies described the chemistry behind fast pyrolysis degradation of individual and pure compounds, to identify the major chemical degradation mechanisms (Shen et al., 2010; Hosoya et al., 2007). Recently, additional milligram scale studies showed the limitations in using model lignocellulosic compounds to predict yields (Pasangulapati et al., 2012; Couhert et al., 2009). These studies showed the significant role of the chemical composition of the lignocellulosic feedstock on the composition and yields of gases generated by pyrolysis processes. They demonstrated that it is not possible to predict pyrolysis gas yields from a recombined mixture with model compounds representing the lignocelluloses feedstock. This failure could be explained by the lack of interactions between the biopolymers and the absence of ash intimately linked to the lignocellulosic structure, which influences pyrolysis (Pasangulapati et al., 2012; Couhert et al., 2009). The use of native lignocellulosic biopolymers is then critical to fully understand the role of lignocellulosic composition on pyrolysis reactions and products.

The influence of the original lignocellulosic composition on fast pyrolysis (FP) products obtained from kilogram scale plants (approx. 1 kg/h) is not well reported. Previous investigations mainly focused on the yields and the quality of the products: liquids (moisture, pH, density, viscosity, high heating values, elemental analysis and organics composition), solid residue (pH, surface area, moisture content) or non-condensables (gas composition) (Oasmaa et al., 2010; Mullen, 2010). Only Oasmaa et al. (2010) conducted a full analysis of the lignocellulosic composition of feedstocks to point out the impact of this on yields and the quality of products from the 20 kg/h FP conversion. They concluded that the higher content of hemicelluloses in grass and straw feedstocks, compared to woody biomass, resulted in higher gas yields, in particular higher CO₂ amounts. The bio-oil analyses suggested that no clear difference between grassy and woody biomass could be made in terms of cellulose degradation into a mixture of sugars and water (levoglucosan and hydroxyacetaldehyde). Mullen (2010) suggested that hemicelluloses were degraded mainly into acids and gases during fast pyrolysis, while the decomposition of the lignin resulted in the production of phenolic compounds condensed in the pyrolytic liquid. They also described the properties of biochar, where adsorptive capacity was mainly affected by the presence of inorganics in the raw lignocellulosic material.

In general, the conclusions around the influence of the lignocellulosic biomass composition on the chemical reactions and composition of products in a 1 kg/h fast pyrolysis plant are limited. Indeed, the design of a fast pyrolysis reactor, in particular bubbling fluidized bed reactor type, is not well adapted to control the regime of the pyrolytic reaction (Mettler et al., 2012) as the transport and chemical-controlled pyrolysis mechanisms are numerous and interconnected, which does not allow deconvolution of chemical and transport phenomena (Di Blasi, 2008).

Therefore the present work introduces the chemical and structural influence of lignocellulosic composition of feedstocks on the yield and quality of fast pyrolysis products by describing the basic bio-oil and char characteristics and heat and mass transfer limitations within the raw biomass and a 1 kg/h fast pyrolysis unit.

2. Methods

2.1. Materials and preparation

Sugar cane bagasse (BG) from the Kwazulu-Natal area of South Africa was provided by the Sugar Milling Research Institute (Durban, South Africa). Corn cobs (CC) and corn stover (CS) were collected in the Lichtenburg area in the Northwest province of South Africa. *Eucalyptus grandis* (EC) woodchips were provided by

Mondi from the Kwazulu-Natal coastline. A corn residues mixture combining 70 wt.% of corn stover with 30 wt.% of corn cob was also prepared. All feedstocks (40 kg) were air-dried and stored in an outdoor shed and milled using a SM 100 Retsch mill, first with a 4 mm sieve and then with a 2 mm sieve. An AS 200 Retsch shaker was used to remove the fines (<250 μm) and oversize (>2000 μm) fractions. The mass median particle diameter (dp₅₀) was calculated for the log-normal distribution dataset, and was found to be 408, 1129, 868 and 573 μm for CS, CC, BG and EC, respectively (results not shown). The shape of CS, BG and EC particles was considered as cylindrical, while CC particles were considered as spherical.

2.2. Analytical methods

Sub-samples were taken from the individual batches of lignocellulosic biomass according to the cone and quartering technique (DD CEN/TS 14780:2005) and subjected to a series of physico-chemical characterizations. Water content (ASTM E871/Metrohm KF Titrino), higher heating value (HHV) (IKA C200 Bomb calorimeter) and pH (509900 Utech Instruments) were determined for the liquid phase. The analytical strategy to characterize the initial biomass and solid residue included water content (Technical Association of the Pulp and Paper Industry (TAPPI) T264 and ASTM D-871–82), ash content (TAPPI T211), proximate analysis (ASTM E11311/Mettler Toledo TGA/DSC 1 – LF 1100), HHV (IKA C5000 bomb calorimeter) and elemental analysis (TruSpec[®] Micro Series Analyser) (Table 1). The characterization of CC, CS and EC biochars encompassed a series of analyses such as the determination of pH_{KCl} and pH_{H₂O} (Titrator IKA[®]KS 260), cation exchange capacity (CEC) (Ion chromatography-Dionex DX-120 Ion Chromatograph), citric acid digestible nutrients (Macro-element/ICP-MS Agilent 7700-Micro-element/Varian Liberty II Radical ICP instrument) and inorganics content (XRF/PANalytical HighScore Plus Software, Axios 2.4 kW instrument with Rh Tube) (Table 2).

The BET surface area of chars was measured by using a Micro-metrics ASAP 2010. The porous structure was described using a method previously developed and presented in Carrier et al. (2012), which has been found to be adequate for the microporosity and mesoporosity evaluation of pyrolysis chars containing little organic material. However, the large standard deviation obtained (Table 3) indicated that a more rigorous sampling procedure should be established in order to take into account the heterogeneity of solid residues and then identify the inconsistencies between sub-samples.

2.3. Determination of the lignocellulosic composition

Sub-samples of lignocellulosic feedstocks were milled and sieved as mentioned in Section 2.1, isolating the biomass particle size range +250 μm and –425 μm for the lignocellulosic characterisation. Analyses were done in accordance with the Technical Association of the Pulp and Paper Industry (TAPPI) standard methods for characterizing woody biomass (T264 om-88, T211 om-85) used in the pulp and paper industry (Sluiter et al., 2010). As the optimization of the extraction methods was not within the scope of this study, the same extraction methods have been applied to the different feedstocks to compare holocellulose, α-cellulose and lignin contents between feedstocks. Experimental errors of 2 wt.%, 5.7 wt.%, 5 wt.% and 2 wt.%, respectively, for the determination of lignin, hemicelluloses, cellulose and extractives contents have been found.

2.3.1. Extractives

The biomass extractives content was determined in accordance to T264 om-88 of the TAPPI standard methods (Preparation of wood for chemical analysis). Approximately 5 g of biomass was

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