



Modelling the reactions of cellulose, hemicellulose and lignin submitted to hydrothermal treatment

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ABSTRACT

The main compounds of plant biomass, i.e., cellulose, lignin and hemicellulose, were submitted to hydrothermal carbonisation (HTC) in ranges of temperature and time of 140–240 °C and 0.5–24 h, respectively. Those parameters were combined into a single one, the severity factor, and its effect on hydrochar yield on the one hand, and on pH, yield and composition of the liquid fraction on the other hand, was investigated in depth. The production of furanic and phenolic compounds was correlated with both severity and pH. The kinetics of furfural (FU) and 5-hydroxymethylfurfural (5-HMF) production and consumption were also investigated and modelled, and the results were compared to those reported in the literature. The production of nine phenolic compounds from lignin HTC was also considered.

1. Introduction

Hydrothermal carbonisation (HTC), whose history dates from the early 1900's (Bergius, 1915), is a very simple process by which a bioresource is submitted to mild temperatures (130–250 °C) in a pressurised liquid medium (generally pure water) using a closed reactor, i.e., an autoclave. In the latter, the pressure is self-generated and allows obtaining both solid and liquid products (Borrero-López et al., 2017).

HTC is cost-effective as it does not require chemicals and avoids costs related to materials drying, and it perfectly allows biomass conversion into high added-value organic compounds through hydrolysis and subsequent dehydration and fragmentation (Braghiroli et al., 2015). Cellulose, hemicellulose and lignin are the main macromolecular compounds of wood and plant biomass in general, and the former two macromolecules are well-known precursors of furfural (FU) and 5-hydroxymethylfurfural (5-HMF), respectively, when submitted to HTC. HTC of lignin can also provide some valuable compounds like vanillin, used for cosmetics and flavouring, or syringaldehyde, used as ingredient for food and flavour (Onwudili, 2015; Zhou, 2014), amongst others.

However, a solid carbonaceous residue, called hydrochar, is also obtained in the same process, having many interesting features such as porosity and functional groups like hydroxyls, carbonyls, etc. (Chen et al., 2017). Hydrochars are interesting by-products as they present higher heating values (Basso et al., 2015) than their corresponding

biomass precursors, and have been proposed for soil amendment (Steinbeiss et al., 2009), for CO₂ capture (Jatzwauck and Schumpe, 2015) or as precursors of carbon materials (Borrero-López et al., 2017; Braghiroli et al., 2012, 2015b).

Extensive work has been carried out on HTC of many kinds of bioresources, like wheat straw (Reza et al., 2015), plant biomass wastes (Fang et al., 2015), loblolly pine (Lynam et al., 2011), soft rush (Jatzwauck and Schumpe, 2015) as well as on each individual major compound of such biomass (Lu et al., 2013; Gao et al., 2012; Pińkowska et al., 2011; Wang et al., 2015). However, only a few works combined the studies of cellulose, hemicellulose and lignin. For instance, Kang et al. (2012) previously focused on HTC of the latter compounds, amongst others, but only a rather narrow temperature range was investigated and no detailed studies of the liquid products was performed. As far as we know, no research related to the liquid and solid fractions obtained from cellulose, hemicellulose and lignin submitted together to HTC has been published.

In the recent past, the kinetics of FU production/decomposition competitive reactions (Marcotullio et al., 2009) were thoroughly studied for several biomasses or biomass-derived molecules such as wheat straw (Yemiş and Mazza, 2012) and xylose (Liu et al., 2014) submitted to HTC. Most works generally focused either on production or on decomposition reactions separately (Liu et al., 2014; Danon et al., 2014; Kim et al., 2011). Simple consecutive reaction models as well as models taking into account side reactions have been developed (Jing and Lü,

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2007; Liu et al., 2014) and are in agreement with published studies on degradation compounds from sugars (Rasmussen et al., 2014; Yang et al., 2012; Chen et al., 2012). An intermediate between xylose and furfural has also been proposed for explaining the kinetics of FU production (Marcotullio, 2011; Chen et al., 2015).

Regarding the kinetics of reaction of 5-HMF, Chen et al. (2010) studied its production whereas Girisuta et al. (2006) studied its decomposition to levulinic acid, but again there was not too much work related with these two competitive processes in the same study (Jing and Lü, 2008; Shen and Wyman, 2012). The case of 5-HMF is more complex than that of FU, because some degradation products are known to decompose afterwards, such as levulinic acid.

The main purpose of the present work was to assess the effect of HTC conditions on lignin, cellulose and hemicellulose in a broad range of temperatures (140–240 °C) and time (0.5–24 h), by studying the production of FU, 5-HMF and up to nine aromatic compounds as a function of HTC severity, and to apply simple models for describing the observed kinetics. Relationships between the latter and pH, and yields of resultant liquid and solids, were also looked for.

2. Material and methods

2.1. Raw material

Cellulose was Type 102 VIVAPUR (high-purity) microcrystalline cellulose provided by JRS Pharma (Rosenberg, Germany). Hemicellulose was high-purity xylan extracted from beech wood and supplied from Roth (Karlsruhe, Germany). Lignin used was lignin powder Lignine PROTOBIND 1075 (Asian Lignin Manufacturing India Private Limited), which is soda lignin. All compounds used for identification and quantification of phenolic and furanic compounds by HPLC were analytical grade and purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Hydrothermal carbonisation (HTC)

HTC experiments were performed in 100 mL Teflon[®]-lined autoclaves. The liquid to solid (L/S) weight ratio was 8 (16 g/2 g) where L stands for liquid (i.e., pure water) and S for the considered biomass compound (BC) on dry basis. BC and distilled water were thus weighed and introduced in a glass insert so as to protect the PTFE liner of the autoclave from any contamination. Autoclaves were next hermetically closed and placed in a ventilated oven preheated at the desired temperature (160, 170, 180, 200, 220 or 240 °C) for the required reaction time (from 0.5 to 24 h). Afterwards, the autoclaves were removed from the oven and let to cool down to room temperature for several hours before opening.

Since both time (t) and temperature (T) produce changes in the results of the HTC process, their effect was investigated through the severity factor ($\log R_0$) which was introduced to combine these two parameters into a single one (Overend and Chornet, 1987). Indeed, $\log R_0$ takes into account the different significances of these two parameters through an exponential factor for the temperature, and through a proportional factor for time. It reads:

$$\log R_0 = \log \left[t \cdot \exp \left(\frac{T-100}{\omega} \right) \right] \quad (1)$$

where t is the residence time (min), T the working temperature (°C) and ω is an HTC parameter. The initial value for lignocellulosic materials that was suggested for ω was 14.75, since it corresponds to the activation energy of a first-order hydrolytic process (Xu et al., 2011). As it remains an empirical parameter, ω was sometimes changed when using other bioresources and different temperature ranges, as did Ko et al. (2015) for glucose by using the value 4.6.

2.3. Liquid/solid separation and analysis

After HTC, liquid and solid products obtained together in the autoclave were separated by vacuum filtration. The amount of liquid was weighed immediately after filtration, whereas solids were placed in a vacuum oven for 6 h at 60 °C for complete drying and subsequent weighing.

Qualitative identification of the main volatile compounds in the liquid phase was carried out by gas chromatography coupled with mass spectrometry (Clarus 500 GC/MS). Regarding quantitative analyses, furanic and phenolic compounds were determined using an Ultimate 3000 high-performance liquid chromatograph equipped with auto-sampler, diode array and fluorescence detectors, and columns described below.

A Hypersyl Green PAH column was used for FU, 5-HMF and 5-MF quantification. Four UV absorption wavelengths were used, i.e., 220, 276, 284 and 291 nm. Doing so, fluorescence and emission occurring at wavelengths of 360 nm and 443 nm, respectively, could be avoided. Water and acetonitrile were used as mobile phases and the acetonitrile/water ratio was changed from 5/95 to 100/0 during the 35 min of the total analysis time as follows: in the first 1.5 min, the 5/95 ratio was maintained; from 1.5 to 15 min, acetonitrile increased linearly up to a 50/50 ratio; from 15 to 20 min, the acetonitrile again increased up to 100/0 and this ratio was maintained for 5 min more. From 25 to 30 min, acetonitrile decreased until the initial ratio, i.e., 5/95, and it was maintained 5 min until the end of the analysis.

Phenolic compounds were quantified with a Pinnacle DB BiPh 5 μ m column, and UV absorption wavelengths of 195, 201, 231 and 300 nm were used. Mobile phases were water and acetonitrile too. The program started with an acetonitrile/water ratio of 10/90 during the first 3 min. Later, the acetonitrile content increased up to 15/85 at min 5, and remained constant until min 13. From 13 to 15 min, acetonitrile increased up to the ratio 20/80 and was kept constant 13 min more. From 28–33 min, the acetonitrile concentration increased up to the ratio 100/0, which was kept for 5 min more. From 38–43 min, acetonitrile concentration decreased to 90/10 ratio, and remained constant for 7 min more, until the end of the experiment at 50 min. Again, all the aforementioned changes of the acetonitrile/water ratio were linear.

The yield of each considered organic molecule X, Y_X , was calculated according to the following equation:

$$Y_X (\%) = \frac{[X] V}{W_{BC}} \times 100 \quad (2)$$

where $[X]$ is the concentration (g mL^{-1}) of each soluble organic compound within the volume V of liquid (mL) obtained after HTC, and W_{BC} is the mass (g) of the biomass component studied on dry basis.

The hydrochar yield, Y_{HC} , was determined from Eq. (3):

$$Y_{HC} (\%) = \frac{W_{HC}}{W_{BC}} \times 100 \quad (3)$$

where W_{HC} is the mass of dry hydrochar after HTC.

The liquid yield from HTC, LY_{HC} , was calculated as follows:

$$LY_{HC} (\%) = \frac{LW_{HC}}{LW_0} \times 100 \quad (4)$$

where LW_{HC} is the amount of liquid weighed after filtration, and LW_0 is the initial amount of liquid added in the autoclave.

2.4. Kinetics

The fits to experimental kinetic data was carried out with OriginPro 8.5.1 software by minimising χ^2 through the Levenberg-Marquart algorithm. Simple models considering successive decomposition reactions either without or with side reactions, herein called A and B models, respectively (Perez and Fraga, 2014; Marcotullio, 2011) were applied to the data, and allowed deriving kinetic parameters for each temperature

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