



Full Length Article

Acid-catalysed cellulose pyrolysis at low temperatures



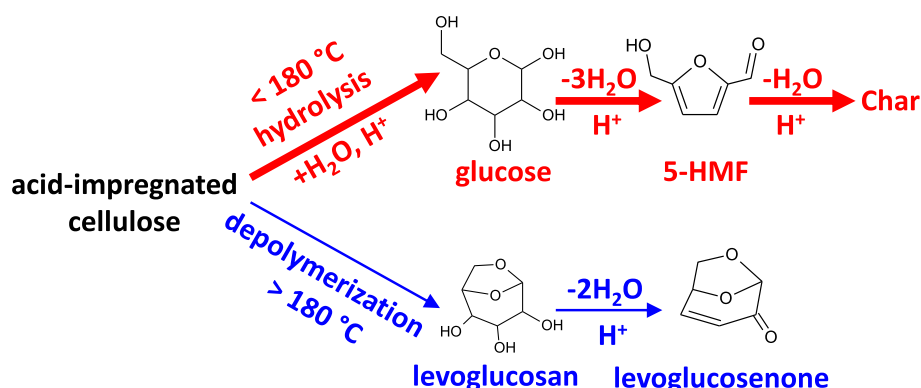
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HIGHLIGHTS

- The pyrolysis of the acid-impregnated cellulose is studied at 50–325 °C.
- Dehydration reactions are dominant during acid-catalysed cellulose pyrolysis.
- Acid catalyses the formation of glucose oligomers as reaction intermediates.
- Hydrolysis produces glucose as a key reaction intermediate at low temperatures.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 3 October 2016

Received in revised form 18 December 2016

Accepted 20 December 2016

Available online 3 January 2017

Keywords:

Biomass

Cellulose

Fast pyrolysis

Acid-catalysed pyrolysis

Mechanism

ABSTRACT

This study reports the pyrolysis of the acid-impregnated cellulose at 50–325 °C. The presence of acid is found to significantly change cellulose pyrolysis mechanism. While the pyrolysis of raw cellulose mainly proceeds with depolymerisation reactions, the pyrolysis of the acid-impregnated cellulose is dominantly contributed by dehydration reactions. The acid impregnation process seems to weaken the hydrogen bonding networks in cellulose, promoting the formation of glucose oligomers as reaction intermediates. Due to the presence of acid in the reaction intermediates, the glucose oligomers are rapidly hydrolysed to glucose, especially at low temperatures (i.e., 100 °C) where the evaporation of produced water (via dehydration) is slow. The results also suggest that glucose is subsequently dehydrated to low molecular weight compounds at increased temperatures. The highly dehydrated cellulose further suppresses the depolymerisation reactions, resulting in a low levoglucosan yield during acid-catalysed pyrolysis of cellulose. The highly dehydrated cellulose also favours char formation likely via furanic structures which are finally transformed into aromatic structures at temperatures >300 °C.

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1. Introduction

Pyrolysis is an important process for converting the abundant biomass resource into biofuels such as bio-oil and biochar at optimal pyrolysis conditions [1,2]. For example, pyrolysis at a fast heating rate and medium temperatures (i.e., 450–550 °C) maximises

bio-oil production, but favours biochar production at a slow heating rate and low temperatures (i.e., 250–350 °C) [3]. While extensive research was conducted on biomass/cellulose pyrolysis, there are still considerable scope in understanding biomass/cellulose pyrolysis reactions [4–8]. For example, β -elimination mechanism [9] is believed to be a competitive pathway leading to the formation of low molecular weight products [10–12]. Via this mechanism, organic acids may play an important role in cellulose pyrolysis [9]. Therefore, it is of critical importance to understand

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the role of acid during cellulose pyrolysis. It was reported that acid-catalysed cellulose pyrolysis promotes the formation of char and some dehydrated products at the expense of levoglucosan [13–15]. Especially, the pyrolysis of acid-loaded cellulose can produce significant amount of levoglucosone [13], which is one of the value-added biochemicals with functional groups suitable for organic synthesis [16]. Acid impregnation is also considered as an effective strategy to passivate the inherent inorganic species in biomass to increase the yield of pyrolytic sugars in bio-oil from biomass fast pyrolysis [17–19]. However, there are still considerable scope in understanding the effect of acid on biomass or cellulose pyrolysis. Therefore, this study reports a set of systematic study on acid-catalysed cellulose pyrolysis at 50–325 °C.

2. Experimental section

2.1. Materials and pyrolysis experiments

A raw cellulose sample was prepared via sieving microcrystalline cellulose (Avicel PH-101, Sigma-Aldrich) to the size fraction of 75–106 μm. Acid-impregnated cellulose samples were prepared from the raw cellulose at two acid loading levels of 0.5 and 1 mmol g⁻¹. Briefly, an acid solution was prepared by diluting appropriate amount of sulfuric acid in water to a total volume of 25 ml. Then ~5 g of raw cellulose was added into the acid solution to form a slurry mixture. The slurry mixture was stirred in an automatic shaker for 15 min and then dried in an oven at 30 °C for 48 h to remove excess water in the slurry, yielding the acid-impregnated cellulose sample. Fast pyrolysis experiments were conducted at 50–325 °C in a drop-tube/fixed-bed reactor equipped with a pulsed feeder similar to the one used previously [20]. The detailed descriptions of the experimental setup and procedure can be found in the [Supplementary material](#). Briefly, in a pyrolysis experiment, the reactor was preheated to a pyrolysis temperature using argon (ultra-high purity) as carrier gas. Approximately 0.4 g of cellulose sample was then fed into the reactor for pyrolysis in a single pulse, followed by a further holding at the pyrolysis temperature for 15 min. Upon the completion of a pyrolysis experiment, the reactor was immediately lifted out of the furnace and cooled down rapidly to room temperature with argon continuously flowing through the reactor. After the tar condensed on the wall of the reactor outlet was burned, the reactor was weighted before and after the experiment for determining cellulose conversion based on weight (see more discussion in Section 2.3). After weighing the reactor, the char was collected for further analysis. It is noted that the volatiles at the reactor outlet were not collected for analysis because these products experienced significant secondary reactions thus do not represent the primary products of cellulose pyrolysis.

2.2. Sample characterisation and analyses

Each char sample was extracted using deionised water to yield a solution containing water-soluble intermediates generated during cellulose pyrolysis. The carbon content of the solution was analysed using a total organic carbon analyser (Shimadzu TOC-V_{CPH}) for determining the yield of the water-soluble intermediates. The solution was also analysed by high performance anion exchange chromatography with pulsed amperometric detection and mass spectrometry (HPAEC-PAD-MS) to characterise the sugar products in the solution, using an ion chromatography (IC) system (Dionex ICS-3000). The sugar and anhydro-sugar oligomers with degrees of polymerization (DPs) of 1–5 were identified using available standards. Other high-DP (up to 8) sugar and anhydro-sugar oligomers were analysed by mass spectrometry [21]. The C, H, O and S

contents of char sample were determined using an elemental analyser (PerkinElmer 2400 series II CHNS/O). Post hydrolysis [22] was also carried out to convert all sugars in the char sample to mono-sugars for quantifying the total sugar content of the sample using the HPAEC-PAD. The functional groups of the char sample were characterised by Fourier transform infrared (FTIR) spectroscopy (Perkin-Elmer Spectrum 100 ATR-FTIR). Nuclear magnetic resonance (NMR) spectroscopy (Varian 400 NMR spectrometer) was used to obtain the solid state ¹³C NMR spectra of the char samples.

2.3. Calculation of cellulose conversions based on weight, carbon and sugar

Cellulose conversion during pyrolysis can be calculated on a basis of either weight, carbon or sugar. To determine the cellulose conversion based on weight, the reactor weight before and after the experiments were determined. Then, the cellulose conversion based on weight (C_{weight}) is calculated using the following equation:

$$C_{weight} = \frac{W_{cellulose} - W_{char}}{W_{cellulose}} \quad (1)$$

where W_{char} (g) and $W_{cellulose}$ (g) are the weight (daf) of char and cellulose fed into the reactor, respectively. The sulfur content of char sample is analysed to obtain the weight (daf) of char.

To determine the cellulose conversion based on carbon, the carbon contents of char and cellulose were measured. The cellulose conversion based on carbon (C_{carbon}) is calculated as:

$$C_{carbon} = \frac{W_{cellulose} \times C_{cellulose} - W_{char} \times C_{char}}{W_{cellulose} \times C_{cellulose}} \quad (2)$$

where C_{char} (%) and $C_{cellulose}$ (%) are the carbon content (daf) of char and cellulose, respectively.

To determine the cellulose conversion based on sugar, post hydrolysis experiments were carried out to quantify the total sugar contents of char samples. The sugar content of a solid sample (S_{sample}) is determined using the following equation:

$$S_{sample} = \frac{W_{sugar}}{W_{sample}} \quad (3)$$

where W_{sugar} (g) is the recovery of sugar products from post hydrolysis using W_{sample} (g, daf) of solid sample. Then, the cellulose conversion based on sugar (C_{sugar}) is calculated using the following equation:

$$C_{sugar} = \frac{W_{cellulose} \times S_{cellulose} - W_{char} \times S_{char}}{W_{cellulose} \times S_{cellulose}} \quad (4)$$

where S_{char} (%) and $S_{cellulose}$ (%) are the sugar content of char and cellulose, respectively.

3. Results and discussion

3.1. Cellulose conversion during acid-catalysed cellulose pyrolysis

Cellulose conversion during pyrolysis can be calculated on weight, carbon and sugar bases (with the detailed methods for calculations given in Section 2.3). Similar conversions on three different bases indicate that cellulose pyrolysis mainly takes place via depolymerisation reactions at the glycosidic bonds to release levoglucosan [23]. This is exactly the case for the raw cellulose pyrolysis, as shown in Fig. 1a. The reaction during the raw cellulose pyrolysis at temperatures <250 °C is slow but becomes rapid at temperatures >300 °C. This is because the evaporation of levoglucosan as the pyrolysis product is slow at temperatures below its boiling point (~300 °C [9]). The results in Fig. 1a also suggest that

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