



## Full Length Article

# Polymerization of glucose during acid-catalyzed pyrolysis at low temperatures

Yu Long, Yun Yu\*, Bing Song, Hongwei Wu\*

Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia



## ARTICLE INFO

**Keywords:**  
Biomass  
Glucose  
Pyrolysis  
Acid catalysis  
Polymerization

## ABSTRACT

This study reports the importance of polymerization reactions during the pyrolysis of acid-impregnated glucose at 60–150 °C. The experimental results demonstrate that polymerization reactions are the dominant reactions to produce oligosaccharides of various linkages and degrees of polymerization (DP) during acid-catalyzed glucose pyrolysis at low temperatures. The maximal DP of the oligosaccharide products depends on pyrolysis temperature, i.e., from ~4 at 60 °C to ~18 at 120 °C. As the major primary products, the disaccharides of various  $\alpha$  and  $\beta$  linkages (including 1,6-, 1,4-, 1,3-, 1,2- and 1,1-glycosidic bond) have been successfully identified, indicating that mutarotation reactions also play important roles in acid-catalyzed glucose pyrolysis. Due to the high reactivity of the hydroxyl group on C6, disaccharides with 1,6-glycosidic bond (i.e., gentiobiose and isomaltose) are more favorably formed with high initial selectivities, i.e., ~27 and ~20% for gentiobiose and isomaltose at an acid loading of 0.5 mmol/g, respectively. The formation of  $\alpha$ -linkage disaccharides follows an order of 1,6-glycosidic bond > 1,4-glycosidic bond > 1,3-glycosidic bond > 1,2-glycosidic bond > 1,1-glycosidic bond. An increase in acid loading enhances the formation of disaccharides, especially those with 1,6-glycosidic bond. The experimental results reported in the study provide new insights into acid-catalyzed glucose pyrolysis mechanism for the development of advanced pyrolysis technologies to produce biofuels and biochemicals.

## 1. Introduction

Fast pyrolysis converts biomass into high-energy-density renewable biofuels (i.e., bio-oil, bio-char and/or bioslurry [1–3]), which can partly replace the traditional fossil fuels (i.e., crude oil and coal) for stationary combustion applications [3–5]. However, biomass pyrolysis bio-oil suffers from some undesired properties (i.e., high water content, high acidity, high viscosity, low heating value, poor phase stability), which have hindered its further commercial applications. The poor quality of bio-oil is at least partially due to the presence of inherent alkali and alkaline earth metallic (AAEM) species present in biomass, which catalyze the fragmentation and dehydration reactions to produce low-molecular-weight products, such as formic acid and hydroxyacetaldehyde [6–8]. To improve the quality of bio-oil, various acid pretreatment methods (i.e., acid leaching [9], acid impregnation [10–12], or a combination of both) have been proposed to suppress the catalytic effect of AAEM species on biomass pyrolysis. However, the acid loading needs to be optimized since overloading of acid may lead to additional reactions catalyzed by extra acid. Previous studies [13,14] have shown that the loaded acid enhances the formation of dehydrated

products (i.e., levoglucosenone) and char from cellulose pyrolysis. Therefore, it is of critical importance to understand the effect of acid loading on biomass pyrolysis.

The mechanism of biomass or cellulose pyrolysis under acidic conditions have been studied in the literature [14–16]. Recently, it was reported [17] that acid loading could significantly change the cellulose pyrolysis mechanism via enhancing the formation of reaction intermediates even at 100 °C. During acid-catalyzed cellulose pyrolysis, glucose instead of levoglucosan was identified as an important intermediate at temperatures < 180 °C. It is clear that acid-catalyzed glucose pyrolysis plays an important role in cellulose pyrolysis under acidic conditions. However, the fundamental reaction mechanisms governing the effect of acid loading on glucose pyrolysis are largely unclear, especially the roles of polymerization reactions under acidic conditions. It is known that polymerization reactions take place during the pyrolysis of levoglucosan [18] or glucose under non-catalytic or acidic conditions, contributing substantially to char formation. However, previous studies on glucose pyrolysis mainly focus on the decomposition reactions to produce levoglucosan and 5-hydroxymethylfurfural at temperatures > 200 °C [19]. There has been no investigation into the

\* Corresponding authors.

E-mail addresses: [Yun.Yu@curtin.edu.au](mailto:Yun.Yu@curtin.edu.au) (Y. Yu), [h.wu@curtin.edu.au](mailto:h.wu@curtin.edu.au) (H. Wu).

polymerization reactions of glucose during pyrolysis at temperatures < 200 °C, especially under acidic conditions. At low temperatures, the intermediates formed from the primary reactions can be identified to reveal the underlying mechanisms. Therefore, this paper reports a systematic study to understand the polymerization of glucose during acid-catalyzed pyrolysis at 60–150 °C.

## 2. Experimental section

### 2.1. Materials and sample preparation

Glucose and disaccharide standards were purchased from Sigma-Aldrich. Sulfuric acid (98 wt%) was purchased from Thermo Fisher Scientific. Acid-impregnated glucose samples were prepared at two acid loading levels of 0.25 and 0.5 mmol/g by dissolving suitable amounts of glucose in a total volume of ~25 ml of diluted acid solutions containing appropriate amounts of sulfuric acid, followed by continuous stirring for 5 min at room temperature. The final solution was kept in a freezer at a temperature of -20 °C for 2 h, before drying in a freeze dryer (Alpha 2-4 LDplus) for 48 h. The acid-impregnated glucose samples were stored in the freezer at -20 °C prior to pyrolysis experiments.

Pyrolysis experiments were performed at 60–150 °C in a drop-tube/ fixed-bed reactor equipped with a pulsed feeder (details given elsewhere [20]). Briefly, the reactor was preheated to the desired pyrolysis temperature in a vertical furnace, with argon continuously flowing through the reactor at ~1.1 L/min. Once the pyrolysis temperature was reached, ~0.4 g of acid-impregnated glucose was fed into the reactor in one shot, followed by a further holding of 0–15 min at the temperature. Upon the completion of the experiment, the reactor was immediately lifted out of the furnace and cooled down to room temperature, with argon continuously flowing through the reactor. For experiments at zero holding time, the preheated reactor was immediately lifted out of the furnace and cooled down by continuous argon once the sample was injected and heated to the desired reaction temperature. The solid products were obtained and stored in a freezer at -20 °C for further analysis.

### 2.2. Sample analysis

To determine the unreacted glucose and other sugar products in the solid sample, the solid sample after pyrolysis was dissolved in deionized water, followed by filtration to obtain a water-soluble sample. The water-soluble sample was then analyzed by a high-performance anion-exchange chromatography with pulsed amperometric detection and mass spectrometry (HPAEC-PAD-MS) via an ion chromatography (Thermo Fisher ICS-5000) to identify and quantify the sugar products (i.e., glucose, disaccharides) in the liquid sample according to a previous method [21].

The liquid sample was also analyzed by gel permeation chromatography (GPC) with a column (PL aquagel-OH 20 5 μm 300 × 7.5 mm) to detect the formation of oligosaccharides with higher degrees of polymerization (DP of molecule weight from 21,040 to 180) using a high-performance liquid chromatography (Varian 380-LC) equipped with an evaporative light scattering detector (ELSD). Deionized water was used as the mobile phase at a flow rate of 1 ml/min. The temperatures of evaporation and nebulizer were set at 80 °C and 40 °C in ELSD, respectively. The carbon content of the liquid sample was quantified using a total organic carbon analyzer (Shimadzu TOC-VCPH). The total sugar content of the solid sample was analyzed via post-hydrolysis [22], and the moisture content of the solid sample was analyzed by a Karl Fisher Titration (Mettler V30).

### 2.3. Data processing

Glucose conversion ( $C$ ) during pyrolysis was calculated on a carbon basis using Eq. (1):

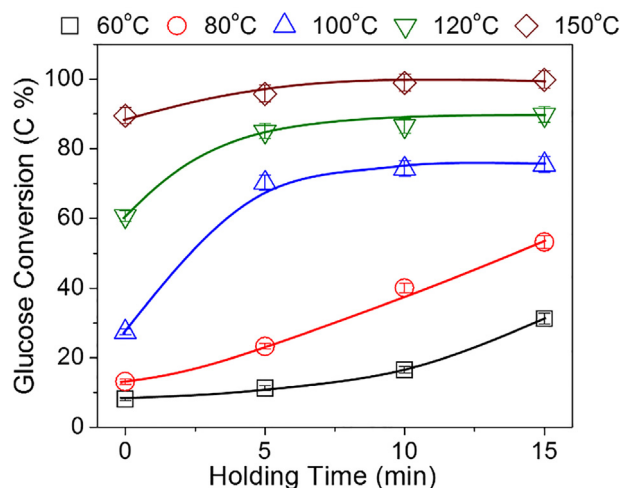


Fig. 1. Glucose conversion as a function of holding time at 60–150 °C and an acid loading of 0.25 mmol/g.

$$C = \frac{W_{\text{glucose}} \times c_{\text{glucose}} - W_{\text{glucose, solid}} \times c_{\text{glucose}}}{W_{\text{glucose}} \times c_{\text{glucose}}} \quad (1)$$

where  $W_{\text{glucose}}$  (g) and  $W_{\text{glucose, solid}}$  (g) are the weight of the glucose in the reactant and solid product after pyrolysis, respectively, and  $c_{\text{glucose}}$  (%) is the carbon content of glucose.

The yield ( $Y_i$ ) and selectivity ( $S_i$ ) of product  $i$  are calculated as below:

$$Y_i = \frac{W_i \times c_i}{W_{\text{glucose}} \times c_{\text{glucose}}} \quad (2)$$

$$S_i = \frac{W_i \times c_i}{(W_{\text{glucose}} - W_{\text{glucose, solid}}) \times c_{\text{glucose}}} \quad (3)$$

where  $W_i$  (g) is the weight of qualified product  $i$  in the solid product after pyrolysis, and  $c_i$  (%) is the carbon content of product  $i$ .

## 3. Results and discussion

### 3.1. Glucose conversion during acid-catalyzed pyrolysis

Fig. 1 presents the glucose conversion during the pyrolysis of the acid-impregnated glucose with an acid loading of 0.25 mmol/g at temperatures of 60–150 °C and holding times of 0–15 min. Although glucose is stable at 150 °C under acid-free conditions [23], Fig. 1 shows that glucose conversion under acidic conditions already takes place even at 60 °C. Glucose conversion increases with holding time and reaches ~31% after 15 min holding at 60 °C. The results in Fig. 1 further show that glucose conversion is strongly dependent on temperature. Even without holding, the glucose conversion increases rapidly from ~28% at 100 °C to ~90% at 150 °C. Therefore, the presence of acid significantly enhances glucose conversion even at such low temperatures.

However, it can be seen that the glucose conversion becomes slow as the holding time increases at high temperatures (> 100 °C). This is likely due to the reduced water content in the pyrolysing sample, since water can assist the formation of C1-carbocation in glucose to facilitate the polymerization reactions [24]. The moisture content of the acid-impregnated glucose sample after freeze drying is ~10%, due to the formation of glucose monohydrate [25]. The moisture content of the solid samples after pyrolysis at 120 and 150 °C were analyzed and presented in Fig. S1 of the Supplementary Material. It can be seen that the moisture content reduces as the holding time increases, and a higher pyrolysis temperature leads to an increased reduction in the moisture content of the solid sample. For example, the moisture content

Download English Version:

<https://daneshyari.com/en/article/6630607>

Download Persian Version:

<https://daneshyari.com/article/6630607>

[Daneshyari.com](https://daneshyari.com)