



## Short communication

# Formation of organic acids during cellobiose decomposition in hot-compressed water

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## ABSTRACT

This paper systematically reports the major organic acids produced during cellobiose decomposition in hot-compressed water (HCW) at 200–275 °C and a residence time of 8–66 s. Saccharinic, formic, lactic and glycolic acids are identified and quantified using high-performance anion exchange chromatography with conductivity detection and mass spectrometry (HPAEC-CD-MS). Among the identified organic acids, saccharinic acid, which is reported for the first time in the field under non-catalytic conditions, has the highest yield (i.e., ~5.8% at 275 °C and ~66 s) on a carbon basis, but formic acid has the highest contribution to total hydrogen ion in the liquid product due to its high molar concentration and high dissociation constant. The results also show that the hydrogen ion concentrations contributed by the identified organic acids agree well with those calculated from the measured pH of the solutions after the reaction, especially at cellobiose conversions < 80%. The reaction pathways for the production of these organic acids during cellobiose decomposition in HCW are also summarised and discussed.

## 1. Introduction

Biomass is considered as a promising feedstock for sustainable production of biofuels and platform biochemicals such as sugars, furans, polyols, and organic acids [1]. Among the technologies for biomass utilisation, hydrothermal conversion in hot-compressed water (HCW) has received increasing attentions because of the unique properties of HCW [2–4]. For example, the high ion product in HCW can enhance both acid- and base-catalysed reactions [5]. However, the products from biomass hydrothermal conversion are complicated; furthermore, catalysts and solvents are generally required to improve the selectivity for efficient production of biochemicals [6–8].

Due to the complex structure of lignocellulosic biomass, various model compounds including cellulose [9–12], cellobiose [13–15] and glucose [16,17] have been employed to understand the mechanism of biomass hydrothermal conversion. In HCW, cellulose is primarily decomposed into glucose oligomers with a wide range of degrees of polymerisation (DPs), which are then converted into low-molecular-weight compounds via a series of reactions such as isomerisation, hydrolysis, *retro*-aldol and dehydration reactions [9,18]. Recently, a series of systematic investigations was carried out to understand the primary reactions of cellobiose (the simplest oligomer linked by glycosidic bond) under various catalytic or non-catalytic hydrothermal conditions [15,19–21]. The pH value of the liquid product decreases substantially

(i.e., from ~7 to ~4) as cellobiose conversion increases under non-catalytic conditions [15,19,21,22]. It was evident that some organic acids appear to be produced even at the early stage of cellobiose conversion [21,22]. While the formation of various organic acids (i.e., formic, acetic, glycolic, lactic, levulinic and saccharinic acids) from carbohydrate decomposition under non-catalytic and catalytic hydrothermal conditions were reported previously [23–25], there has been no studies on the nature and quantity of organic acids produced during cellobiose decomposition under non-catalytic hydrothermal conditions. Particularly, the formation of saccharinic acid from cellobiose decomposition under hydrothermal conditions is poorly understood.

It is known that saccharinic acid has three isomeric forms: isosaccharinic, metasaccharinic and parasaccharinic acids [26]. Saccharinic acid is one of the important organic acids produced under alkaline degradation of cellulose, and its formation is strongly affected by reaction conditions such as alkali metal cation and pH [26–33]. During alkaline degradation of cellulose, it was widely accepted that two types of reactions compete to form different saccharinic acids: end-wise degradation (peeling) and termination (stopping) reactions, which produce isosaccharinic and metasaccharinic acids, respectively [26,29,33–35]. For example,  $\beta$ -alkoxy-carbonyl elimination leads to splitting off the reducing end group and generates isosaccharinic acid, while the formation of metasaccharinic acids is the consequence of the  $\beta$ -hydroxy-carbonyl elimination at C3 atom at reducing end group and

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subsequent rearrangement of the enol through keto-enol tautomerisation [26,33,35]. So far, there is no systematic study on the formation of saccharinic acid from carbohydrate decomposition under non-catalytic hydrothermal conditions. Moreover, our previous study indicates that the initial pH can significantly influence the primary reactions of carbohydrate decomposition in HCW [21]. It is expected that the formed organic acids may further catalyse the primary decomposition of carbohydrate in HCW. Therefore, this communication aims to identify and quantify the formation of various organic acids during cellobiose decomposition in HCW at 200–275 °C. It is noteworthy that this study has successfully identified the formation of two saccharinic acids, which were seldom reported under non-catalytic conditions.

## 2. Experimental section

Cellobiose (purity  $\geq 98\%$ ), formic acid (purity  $\geq 95\%$ ) and glycolic acid (purity  $\geq 99\%$ ) used in this study were purchased from Sigma-Aldrich. Lactic acid stock standard solution (2 g/L) was sourced from Australian Chemical Reagent (Australia). The standards of  $\alpha$ -metasaccharinic acid (3-deoxy-D-ribo-hexono-1,4-lactone) and  $\beta$ -metasaccharinic acid (3-deoxy-D-arabino-hexonic acid, calcium salt) were synthesized by Synthos Inc. (Canada) and  $\alpha$ -isosaccharinic acid was purchased from Carbosynth Ltd (UK). The experiments of cellobiose decomposition in HCW were carried out in a continuous flow reactor system which was used and described in a previous study [36]. Briefly, cellobiose solution with a concentration of 3 g/L fed by an HPLC pump at 10 mL/min was mixed with 20 mL/min of water delivered by a second HPLC pump. The water was preheated in a sand bath to rapidly heat the solution to a desired reaction temperature (200–275 °C). A thermocouple was placed at the inlet of the stainless steel (SUS 314) tube reactor to monitor the reaction temperature. The residence time ( $\tau$ ) of the reaction was controlled by varying the tube length according to  $\tau = V\rho/F$ , where  $V$  is reactor volume ( $\text{m}^3$ ),  $\rho$  is water density at the reaction temperature ( $\text{kg}/\text{m}^3$ ), and  $F$  is total mass flow rate ( $\text{kg}/\text{s}$ ). The reaction effluent was rapidly quenched in an ice water bath to stop the reactions immediately, and then sampled for further analysis. The reaction pressure was maintained at 10 MPa using a back-pressure regulator.

The organic acids in liquid sample were analysed using high performance anion exchange chromatography with conductivity detection and mass spectrometry (HPAEC-CD-MS, model: Dionex ICS-5000). The system is equipped with a Dionex ATC-3 trap column for removal of carbonate in the eluent, a Dionex IonPac AS11-HC analytical column for separation and a Dionex AERS 500 suppressor for removal of eluent prior to analysis by CD and MS. A gradient program consists of initial elution of 1 mM NaOH for 8 min, followed by a linear increase of NaOH concentration to 60 mM for 20 min then holding at 60 mM NaOH for 20 min for adequate separation of organic acids. Selected ion monitoring (SIM) scanning mode is used for detection and quantification of organic acids. The yield ( $Y_i$ ) and selectivity ( $S_i$ ) of the organic acids (on a carbon basis) are calculated by  $Y_i = (c_i \times a_i) / [C(0) \times a]$  and  $S_i = (c_i \times a_i) / [(C(0) - C(t)) \times a]$ , respectively, where  $c_i$  is the concentration of an organic acid  $i$  in product,  $C(0)$  is the initial cellobiose concentration in reactant,  $C(t)$  is the cellobiose concentration in product at reaction time  $t$ ,  $a_i$  and  $a$  are the carbon content (mass fraction) of organic acid  $i$  and cellobiose, respectively.

## 3. Results and discussion

Fig. 1 presents a typical HPAEC-CD-MS chromatogram of the liquid sample from cellobiose decomposition at 275 °C and a residence time of 66 s. Various organic acids including saccharinic ( $m/z = 179$ ), formic ( $m/z = 45$ ), lactic ( $m/z = 89$ ) and glycolic ( $m/z = 75$ ) acids can be clearly detected in the liquid sample. It is noteworthy that two saccharinic acids are detected in this work. To the authors' knowledge, this is the first time in the field that the formation of saccharinic acid is

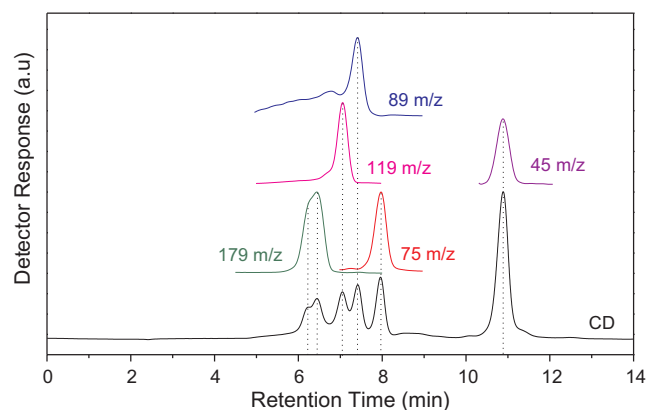


Fig. 1. HPAEC-CD-MS chromatogram of a typical sample from cellobiose decomposition at 275 °C and a residence time of 66 s. MS detection mode: negative ion; needle voltage:  $-4$  kV; ESI probe temperature: 450 °C; cone voltage: 45 V.

reported under non-catalytic conditions. It is known that there are three types of saccharinic acids (i.e., isosaccharinic, metasaccharinic and parasaccharinic acid), but the formation of parasaccharinic acid is rarely reported from carbohydrate decomposition in HCW. To further identify the saccharinic acids from cellobiose decomposition, we have purchased three different saccharinic acids:  $\alpha$ -isosaccharinic,  $\alpha$ -metasaccharinic and  $\beta$ -metasaccharinic acids. As shown in Figure S1 of the Supplementary Material, both  $\alpha$ - and  $\beta$ -metasaccharinic acids match well with Peak 2, while  $\alpha$ -isosaccharinic acid doesn't match with Peak 1. Thus, it is very likely that Peak 1 is  $\beta$ -isosaccharinic acid. However, this study didn't identify Peak 1 due to the unavailability of standard. Further analysis of the calibration curves for the three saccharinic acids indicates that the saccharinic acids have almost same response for MS detection with SIM scan mode at  $m/z = 179$ . This enables us to quantify the total saccharinic acid produced from cellobiose decomposition.

The concentrations of four major organic acids (i.e., saccharinic, formic, lactic and glycolic acids) in liquid products from cellobiose decomposition in HCW at 200–275 °C were quantified via HPAEC-CD-MS. The yields and selectivities of those organic acids on a carbon basis are presented in Fig. 2. The results clearly indicate that the yields of organic acids are low at 200 °C, i.e.,  $\sim 0.53\%$  for saccharinic acid,  $\sim 0.07\%$  for formic acid,  $\sim 0.02\%$  for glycolic acid and almost no lactic acid after a residence time of  $\sim 66$  s. However, the yields of organic acids increase with reaction temperature. For example, the yields of saccharinic, formic, lactic and glycolic acids at 275 °C and  $\sim 66$  s residence time substantially increase to  $\sim 5.8\%$ ,  $\sim 2.5\%$ ,  $\sim 0.8\%$  and  $\sim 0.8\%$ , respectively. Based on the concentrations of organic acids in the products, the selectivities of organic acids were further calculated and plotted as a function of cellobiose conversion in Fig. 2. It can be seen that the selectivities of organic acids are initially zero and the organic acids only start to appear after a conversion of 5–10%, indicating that the organic acids are unlikely to be the primary products during cellobiose decomposition in HCW. The selectivities of organic acids increase with cellobiose conversion, and the maximal selectivities achieved in this study are  $\sim 5.8\%$  for saccharinic acid,  $\sim 2.0\%$  for formic acid,  $\sim 1.0\%$  for lactic acid and  $\sim 0.9\%$  for glycolic acid at 275 °C and  $\sim 66$  s. Among the organic acids quantified in this study, saccharinic acid has the highest yield and selectivity on a carbon basis. However, formic acid is the most abundant acid due to its high molar concentration, thus contributing significantly to the hydrogen ion in the liquid product.

Fig. 3 shows the contributions of saccharinic, formic, lactic and glycolic acids to the total  $\text{H}^+$  dissociated from the quantified organic acids at 200–275 °C. The total dissociated  $\text{H}^+$  concentration was calculated based on the dissociation constants ( $K_a$ ) of the acids at room temperature (see more details in the Supplementary Material). The data indicate that the total dissociated  $\text{H}^+$  is mainly contributed by formic

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