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Short communication

Association of inorganic species release with sugar recovery during wood hydrothermal processing

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HIGHLIGHTS

- Significant water-insoluble Mg and Ca are released during hydrothermal processing.
- The release of Mg and Ca in biomass is in good correlation with the arabinose recovery.
- Organically-bound Mg and Ca are likely associated with hemicellulose side chains.

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ABSTRACT

Over 90% of the inherent Mg and Ca in wood can be released during wood hydrothermal processing in a semi-continuous flow reactor at 10 MPa and 150 °C. An increase in temperature to 180 °C results in rapid release of Mg and Ca, but a further increase in temperature has little effect. The release of Mg and Ca is associated with the conversion of organic matter during hydrothermal processing. In particular, the release of water-insoluble Mg and Ca correlates well with the arabinose recovery, suggesting that these species are bound to carboxylic acid functional group on hemicellulose side chains and their release requires the cleavage of these side chains.

1. Introduction

Hydrothermal processing is an important technical route for pretreating or processing of biomass and other feedstock for producing biofuels and biochemicals [1–11]. Biomass such as mallee may contain abundant inorganic species, especially alkali and alkaline earth metallic (AAEM) species [12]. During hydrothermal processing, at least part of these inorganic species, which are known to potentially catalyse the undesired decomposition of sugar products [13–15], may potentially be released into the aqueous phase. Thus far, little attention has been paid on the release characteristics of these inorganic species from biomass during hydrothermal conversion. Therefore, this study deploys a semi-continuous reactor to investigate the release of inorganic species during hydrothermal processing of wood.

2. Experimental section

Wood was sampled from mallee (*Eucalyptus loxophleba*, subspecies *Lissophoia*) in Western Australia. The sample was prepared using a cutting mill (model: Fritsch Pulverisette 15) and sieved to the size fraction of 150–250 μm. The prepared sample was then frozen at −9 °C prior to experiments. The structural carbohydrate composition (expressed as arabinan, galactan, glucan, xylan, mannan) of the biomass sample was analysed via acid hydrolysis based on a NREL method (see more details in the Supplementary Material) [16]. The arabinan, galactan, glucan, xylan and mannan contents determined are 1.06, 2.21, 40.66, 17.95 and 0.38 wt% on a dry basis, respectively. The contents of AAEM species in the biomass sample were quantified following the procedure detailed elsewhere [17]. The contents of Na, K, Mg and Ca are 0.024, 0.066, 0.033 and 0.128 wt% on a dry basis, respectively. More detailed properties of the wood sample used in this study can be found in Table S1 of the Supplementary Material.

A semi-continuous flow reactor system (detailed elsewhere [18]) was employed. Briefly, ~50 mg of the biomass sample was

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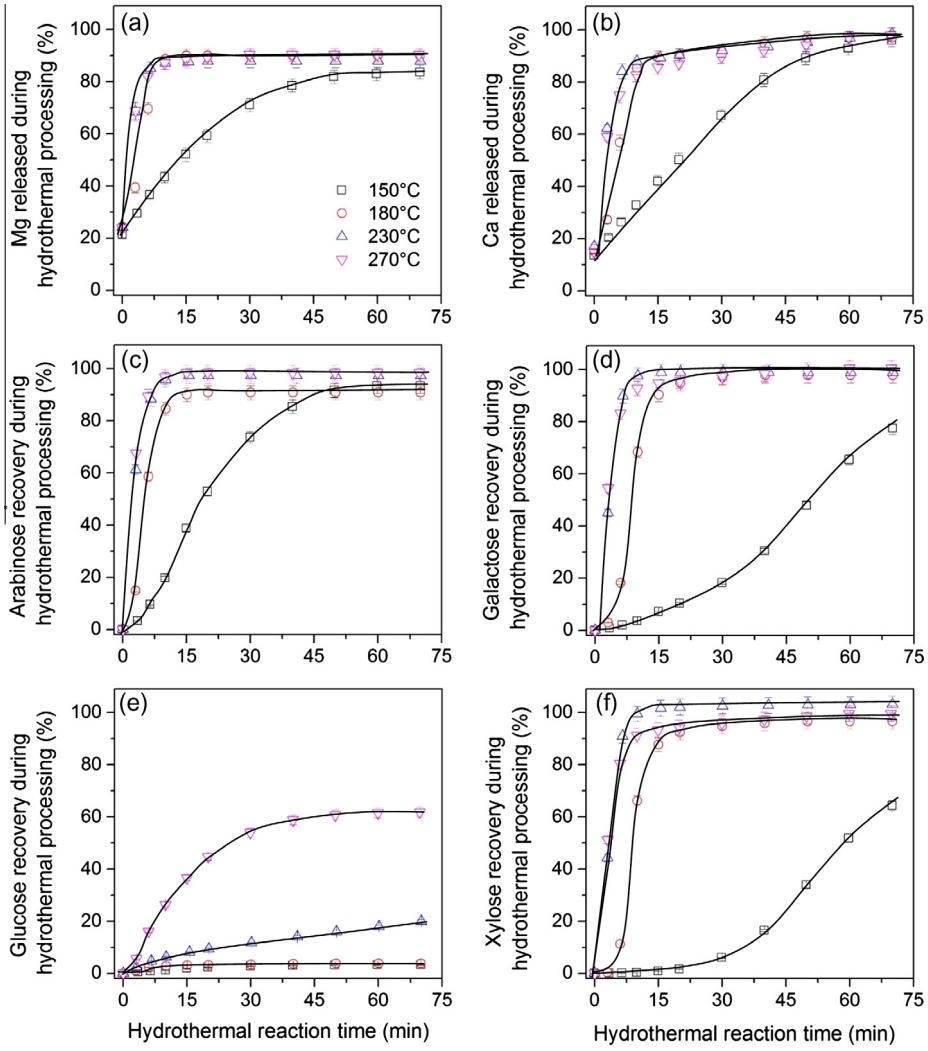

Fig. 1. (Panel a and b) Amount of Mg and Ca released from wood as a function of reaction time during hydrothermal processing at 150–270 °C, expressed as % of the total Mg and Ca in biomass, respectively. (Panel c–f) The recovery of arabinose, galactose, xylose and glucose during hydrothermal processing at 150–270 °C quantified through post-hydrolysis, expressed as % of the respective total sugars in the wood.

loaded into the reactor cell. Prior to experiment, the sample was leached with ultrapure water for 30 min at room temperature to remove water-soluble inorganic and organic matter in biomass. The reactor system was then rapidly heated (1–2 K/s) to reaction temperature (150–270 °C) and held for 70 min. The pressure of the reactor was controlled at 10 MPa using a back pressure regulator. The reactor effluent was immediately quenched with ice water bath to minimise subsequent secondary reactions of the liquid product. The liquid product is sampled at designated time intervals.

The total sugars and the AAEM species in the liquid product were analysed immediately after each experiment. The total sugars (i.e., arabinose, galactose, glucose, xylose and mannose) were quantified after post-hydrolysis (see more details in the Supplementary Material) by a high performance anion exchange chromatography with a pulsed amperometric detector (HPAEC-PAD) via a Dionex ICS-3000 ion chromatography (IC) system equipped with CarboPac PA20 analytical and guard columns. For adequate separation of arabinose, galactose, glucose, xylose and mannose, a gradient program was developed, consisting of initial elution of water for 20 min, regeneration with 0.3 M sodium acetate in 0.1 M NaOH for 2.5 min then 0.3 M NaOH for 6 min before equilibration with water for 10 min. The total flow rate of the eluent was 0.5 mL/min. Post column addition of NaOH was required to ensure sufficient linearity of the PAD detector response. The sugar recovery used in this paper is defined as total amount of sugar monomer and oligomers in the liquid products (quantified via post-hydrolysis) normalised to total sugar in biomass. The AAEM species in liquid sample were quantified using another Dionex ICS-3000 system equipped with IonPac CS12A analytical and guard columns. The eluent was 0.02 M methanesulfonic acid. All the analyses were done at least in duplicate with the average values and standard error reported.

3. Results and discussion

The water-soluble inorganic and organic matter in the wood sample were first leached with ultrapure water at room temperature. About 90% of the Na and K in the wood sample can be removed via water washing (see Fig. S1 of the Supplementary Material), while only ~21% of the Mg and ~14% of the Ca are water-leachable. The remaining AAEM species in the wood sample are likely to be organically bound thus cannot be leached by room temperature water [17]. A small amount of organic matter (~2% on a carbon basis) was also leached from the wood sample at room