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A promptly approach from monosaccharides of biomass to oligosaccharides via sharp-quenching thermo conversion (SQTC)

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ABSTRACT

In this study, a novel and facile approach of conversion monosaccharides (glucose and xylose) to oligosaccharides (Cello-oligosaccharides and Xylo-oligosaccharides) was demonstrated. The approach did not introduce any chemical reagent and the preparation process could be environmentally friendly. Identification and quantification by ion chromatography (IC) and high performance liquid chromatography (HPLC) showed that the yields of COS and XOS reached to 44.62% (38 s) and 47.09% (30 s) respectively at 500 °C reaction temperature coupled with sharp-quenching method. Structural characterization indicated that such oligosaccharides showed a degree of polymerization (DP) with 2–6, and the units mainly linked by β-(1 → 4)-glycosidic bond.

1. Introduction

Increasing interest has been devoted in recent years to convert the monosaccharides of biomass into various functional products and chemical platforms (Wei and Wu, 2016; Li, Pan, Wu, & Xie, 2016). Monosaccharides especially derived from biomass were one of the most hopeful biomass-related chemicals, and could be used as the raw material for further synthesis of various high-value chemicals. Therefore, as a representative of monosaccharides, glucose and xylose are significant platform chemicals for manufacturing biochemical and have been applied in many fields (Choudhary, Pinar, Sandler, Vlachos, & Lobo, 2011; Huber, Chheda, Barrett, & Dumesic, 2005).

Oligosaccharide, a derivative of natural components, has been usually defined as saccharides including anyone from 3 to 10 sugar moieties (Mussatto & Mancilha, 2007). Consequently, oligosaccharides are small molecular weight carbohydrates. Based on the physiological properties, the oligosaccharides can be classified to non-digestible and digestible (Voragen, 1998). The consumption of non-digestible oligosaccharides (NDOs) comes along with many benefits such as helping maintain a fine gastrointestinal environment and increasing intestinal bifidobacteria. Moreover, they restrain pathogen colonization, growth and results in systemic effects which can be benignant to health (Crittenden & Playne, 1996; Voragen, 1998). The effective and light daily ingestion of arabinoxylan-oligosaccharides, xylo-oligosaccharides and cello-oligosaccharides are known to positively influence the physiological functions on human health (Broekaert et al., 2011; Akpinar & Penner, 2015). Cello-oligosaccharides (COS) and Xylo-oligosaccharides (XOS) are generally defined as saccharides composed of 2–6 glucose or xylose by β-1, 4-linkages, which have many practical applications in pharmaceuticals, feed formulations and food applications (Vázquez, Garrote, Alonso, Domínguez, & Parajó, 2005; Chu et al., 2014).

The means of production of COS or XOS were mainly from cellulose or xylan rich biomass and included autohydrolysis, chemical methods and direct enzymatic hydrolysis (Vázquez et al., 2005; Aachary & Prapulla, 2009; Billès, Onwukamike, Coma, Grelier, & Peruch, 2016). Autohydrolysis could be used as a first step in produce oligosaccharides which usually required extra treatment or specialized equipment (Zhu et al., 2006). Chemical methods may include an acid hydrolysis or alkaline extraction. Alkaline hydrolysis was likely the efficient method but could lead to corrosion of the equipment and produced excess monosaccharides in the hydrolysate (Otieno & Ahring, 2012). Acid hydrolysis may generated undesirable by-products, such as furfural and hydroxymethylfurfural, which finally gave rise to monosaccharides released rapidly (Carvalho, Oliva Neto, Silva, & Pastore, 2013). In addition, enzymatic hydrolysis is considered more feasible because of the relatively mild reaction condition and more easily controlled. However, enzymatic hydrolysis may not be economically viable at commercial scale of production (Otieno & Ahring, 2012). Furthermore, the yields of oligosaccharides synthesized in various common methods were summarized and compared in supplementary data (Table S1). Therefore, the raw materials of oligosaccharides were mainly from biomass in recent years and there were still shortcomings of different traditional methods to some extent. In consideration of the high cost and long reaction time of the enzymatic methods as well as environmental pollution of chemical methods, a rapid, efficient and environmentally-friendly method (sharp-quenching thermal conversion (SQTC)) for

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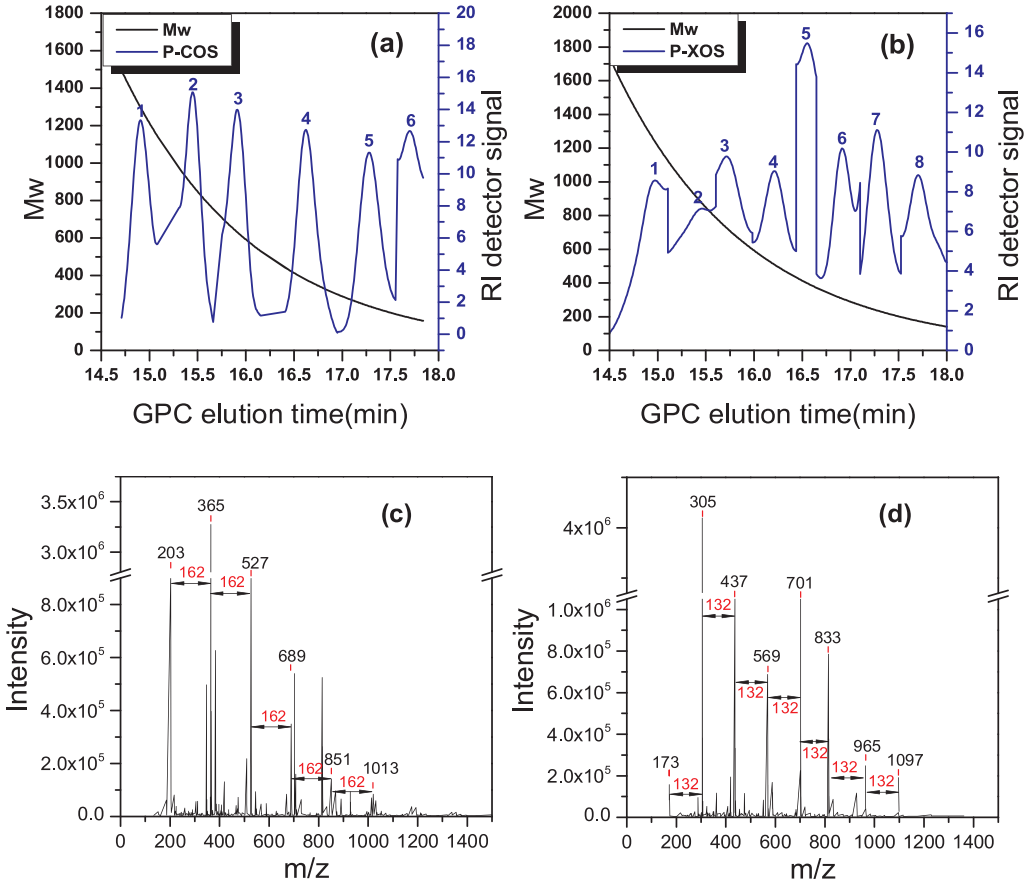

Fig. 1. Molecular weight distribution and analysis of precursor oligosaccharides. (a) GPC of cello-oligosaccharides, (b) GPC of xylo-oligosaccharides (c) Positive ion mode HRMS of P-COS (d) Positive ion mode HRMS of P-XOS.

manufacture oligosaccharides from monosaccharides of biomass have been proposed in this study. The oligosaccharides yields of this approach may be not higher than traditional methods now. But using such approach, the oligosaccharides could be obtained directly within few seconds without introduce any chemical reagent and environmentally friendly in preparation process. This approach has revealed, for the first time, the preparation of oligosaccharides from sustainable monosaccharides and supplements the insufficient of traditional methods to a certain extent. Moreover, this method may give more information available for the large-scale and continuous production of oligosaccharides.

Different from the traditional pyrolysis that convert lignocellulosic biomass into liquids, gases and chars (Chen, Liang, & Wu, 2016; Wang, Dai, Yang, & Luo, 2017), the objective of this study was to design a thermo-chemical conversion approach (SQTC) which reacted rapidly at designed temperature and followed by a sharp quenching for oligosaccharides production from monosaccharides. Firstly, the precursor oligosaccharides (PO) which contains a certain amount of oligosaccharides were produced by SQTC using a self-made static tube furnace (see Fig. S1 in supplementary data). And then the composition and chemical structure of producing PO were investigated. In addition, the possible mechanisms of monosaccharides to oligosaccharides by SQTC were also proposed in this study. According to our knowledge, no reports to indicate oligosaccharides production from monosaccharides of biomass, especially by such a new method of thermo-chemical conversion.

2. Materials and methods

2.1. Materials

The samples of glucose and xylose with the purity of 99% were purchased from Sigma-Aldrich Co.,Ltd. Formic acid (≥98%), acetic acid (≥98%), hydroxymethylfurfural (HMF, ≥98%) and furfural (FF, ≥98%) were all supplied by Sinopharm Chemical Reagent Co.,Ltd., China. Standard reagents of cellobiose (≥98%), cellotriose (≥95%), cellotetraose (≥95%), cellopentaose (≥95%), xylobiose (≥98%), xylotriose (≥98%), xylotetrose (≥95%) and xylopentaose (≥95%) were purchased from Tokyo Chemical Industry (Japan). All reagents were used without further purification.

2.2. Preparation methods

With a U type quartz tube as the carrier, the monosaccharides (about 0.5 g) were separately fed in a tubular furnace reactor and reacted in an N_2 atmosphere at designed temperatures. When the samples boiled apparently and generated a pale yellow liquid, the U type quartz tube was removed into liquid nitrogen rapidly and quenched sufficiently. Monosaccharides of biomass turned into precursor oligosaccharides (PO) which were highly soluble in water. Precursor oligosaccharides were dissolved in demineralized water, freeze-dried, and refrigerated until used. Samples were processed at least ten times and use randomized as well as repeated in the subsequent tests to reduce the errors.

2.3. Analytical methods

The molecular weight distribution and analysis of precursor