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A co-production of sugars, lignosulfonates, cellulose, and cellulose nanocrystals from ball-milled woods

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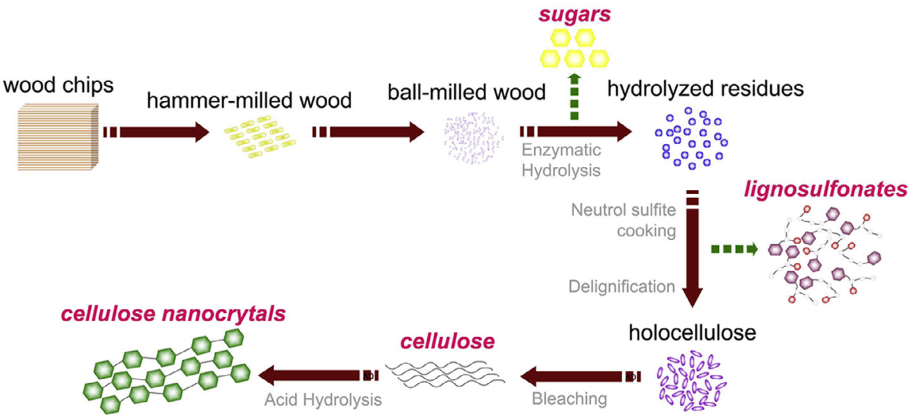
HIGHLIGHTS

- Micronized wood facilitates the co-production procedures.
- The mass balance points out the potential of cellulose and lignin recovery.
- Holistically, the study demonstrated the concept of co-production would be realizable.

GRAPHICAL ABSTRACT



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ABSTRACT

This study demonstrated the technical potential for the large-scale co-production of sugars, lignosulfonates, cellulose, and cellulose nanocrystals. Ball-milled woods with two particle sizes were prepared by ball milling for 80 min or 120 min (BMW_{80}, BMW_{120}) and then enzymatically hydrolyzed. 78.3% cellulose conversion of BMW_{120} was achieved, which was three times as high as the conversion of BMW_{80}. The hydrolyzed residues (HRs) were neutrally sulfonated cooking. 57.72 g/L and 88.16 g/L lignosulfonate concentration, respectively, were harvested from HR_{80} and HR_{120}, and 42.6 ± 0.5% lignin were removed. The subsequent solid residuals were purified to produce cellulose and then this material was acid-hydrolyzed to produce cellulose nanocrystals. The BMW_{120} maintained smaller particle size and aspect ratio during each step of during the multiple processes, while the average aspect ratio of its cellulose nanocrystals was larger. The crystallinity of both materials increased with each step of wet processing, reaching to 74% for the cellulose.

1. Introduction

Lignocellulosic biomass is an abundant and sustainable, carbon-neutral resource. It can be converted into biofuels as a promising

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renewable energy alternative to fossil fuels (Wyman, 1999). The biochemical conversion of biofuel production from lignocellulosic biomass includes the pretreatment of biomass feedstock, enzymatic hydrolysis of disrupted carbohydrates (saccharification), and the fermentation of sugars by microbes. Since upstream progresses, i.e. pretreatment and saccharification, are the key technological barriers for industrial production of cellulosic ethanol, substantial research efforts have been made in pretreatment of biomass feedstock to improve the cellulose-to-glucose conversion. The versatile pretreatment methods are classified into physical (grinding and milling) (Alvira et al., 2010; Barakat et al., 2014), chemical (acids, alkalis, oxidizing agents, sulfites, sulfates, and organic solvents) (Zhang et al., 2006; Sun and Cheng, 2002; Liu et al., 2016a; Yang et al., 2013), physico-chemical (steam explosion) (Cantarella et al., 2004), biological (bacterial) (Itoh et al., 2003), and a combination of these pretreatment methods (Pan et al., 2004; Zhu et al., 2009). Finally, an over 90% of cellulose-to-glulose conversion was reachable after the above pretreatments. However, these pretreatments to overcome the recalcitrance of biomass require more energy consumption, chemical usage, or damage to residual carbohydrate components and lignin (Agarwal et al., 2013; Miao et al., 2011). For example, physical treatment for the size reduction consumed $0.2–3.1 \times 10^3$ MJ/ton wood with various milling types, species, and conditions (Zhu et al., 2015). Organic solvent treatment or sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL) consumed $1.6–1.8 \times 10^3$ MJ/ton wood based on sugar yields at 65% carbohydrate equivalent with the optimal conditions, and the consumption in steam explosion with the same sugar yields was as much as 2.0×10^3 MJ/ton wood (Zhu and Pan, 2010; Zhu et al., 2015). Therefore, the complicated procedures to produce biofuels as a single-product are currently not cost-competitive for large consumption. To solve this problem, a further biorefinery concept should be designed with processes that produce additional high value-added products from lignocellulosic biomass, generating the maximum value by balancing multi-products distribution.

The traditional biorefinery reported in the literature have focused on only improving the percentage of cellulose-to-glucose conversion. The hydrolyzed residues or unemployed components has been overlooked. Enzymes digest cellulose and hemicellulose into monomeric sugars. Generally, with a physical treatment of feedstock, the integrated lignin and partly recalcitrant cellulose with high crystalline structure are still remained in the hydrolyzed residues. A considerable amount of lignin can be recovered in chemical pretreatment and partly recalcitrant cellulose is remained in hydrolyzed residues. Therefore, a potential to transfer the unemployed components into value-added products is existent. The significant profitability improvement in biorefinery operations is possible.

It is well known that lignin derivatives are popular used in the practical application, since natural lignin is difficult to be isolated from lignocellulosic biomass. Sulfonated lignin (lignosulfonate) is a commercial value-added product, which is widely used in construction, animal feed, drilling, packaging, leather, and agriculture (Cheng et al., 2015; Aitcin, 2000; Suparno et al., 2005; Lora et al., 2008). The sulfonation is performed under alkaline or acid conditions, and a over 50% conversion of lignin was obtained (Xu et al., 2015; Liu et al., 2016a). Nevertheless, the usage of alkaline or acid is inconsistent with the minimizing environmental risk. An alternative milder method was developed to use hydrolysis and neutral sulfite processes, reported by Liu et al. (2016a) Liu et al. (2016b). Unlike the traditional approach of alkaline and acid sulfite cooking by the extraction of lignin at the cost of the degradation of a considerable amount of another components, this neutral sulfite process may maintain cellulose and hemicellulose and produce non-toxic byproducts, like furfural, acetic acid (Prusas, 1984; Zhu et al., 2009; Jin et al., 2013; Gu et al., 2012). This treatment can be acted as an optimization to recover lignosulfonates in biorefinary.

The other potential recalcitrant cellulose in hydrolyzed residuals can be also theoretically and practically co-produced. Enzymes hydrolyze the amorphous cellulose and then crystalline cellulose, finally remaining crystalline cellulose in hydrolyzed residuals. Their properties are similar to the cellulose in pulping (Frederick et al., 2008; Filson et al., 2009). For economic assessment, the cellulose nanofibers/nanocrystals are highly value-added and achievable in a biorefinery. They can be survived in diluted acid with mechanical force or concentrated acid. In fact, Oksman et al. (2011) isolated cellulose nanocrystals and nanofibers from the industrial biofuel residuals, which exhibited a more thermal stability with a lower surface charge than commercial cellulose nanocrystal isolated from cotton (Herrera et al., 2012). A handful researches have paid attention on co-producting biofuels and biomaterials. The approaches recover only lignin or cellulose combined with the biofuels, and do not recover other components. Therefore, at present, no research attempted to recover sugars, lignin and recalcitrant cellulose in a biorefinary progress.

The aim of this study was to transfer the traditional biorefinery for a single-product to a new biorefinery for producing multi-products. We demonstrate the feasibility of maximizing total value by co-producing multiple products through utilizing all components of a lignocellulosic material. This new biorefinery is designed by using ball milling pretreatment, neutral sulfite delignification, and cellulose upgradation, generating four target products (sugars, lignosulfonates, cellulose, and cellulose nanocrystals). The product yields are balanced to provide an intuitive view of the integrated profitability of multi-products. In order to co-produce more products and maximize their values of these products, recent advances in bioprocessing through medium ball milling pretreatment allows the improved co-production and less energy consumption. Because 92% of sugar conversion spent over 50 days for ball milling, which was a low-efficiency and high energy-consuming process (Agarwal et al., 2013). A moderate/mild mechanical energy may release most accessible cellulose in a low-cost pathway, and balance the remaining intact lignin and less accessible cellulose, which are further chemically processed into value-added products (Zhu et al., 2011; Jiang et al., 2016). Furthermore, we evaluated the effects of micronized wood (ball-milled wood) on the facilitation of co-production and the balance of each product distribution in this study. Neutral sulfite treatment are introduced to recover lignosulfonates in an environmental way. The loosened lignin generated from the medium ball milling pretreatment is also prone to extraction during the neutral sulfite treatment (Lawther et al., 1996; Lu and Ralph, 2003). Cellulose and cellulose nanocrystals are obtained by common bleaching method to accurately learn the product yield. Douglas-fir wood chips were used as a model biomass feedstock to demonstrate the utility of the micronized wood for co-production of multiple products in a biorefinery. The wood chips were first micronized by a pilot planetary ball mill and were further subjected to a sequence of fractionation procedures that were designed to maximize product yield with minimal energy consumption. The mass balance of products or residuals was monitored in each step. This biorefinery can be improved or optimized on an industrial scale based on the best current technologies. Different methods may generate a slightly different balance of materials and products, but the general trend should be the same.

2. Materials and methods

2.1. Ball-milled wood preparation

The preparation of milled wood was subjected to a two-stage milling. Fresh Douglas-Fir wood chips were hammer-milled to