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Research Paper

A novel and efficient process for lignin fractionation in biomass-derived glycerol-ethanol solvent system

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ABSTRACT

Glycerol, as a nontoxic, biodegradable and sustainable solvent, together with biomass-derived ethanol was employed in this work to fractionate and purify enzymatic hydrolysis lignin (EHL) from enzymatic hydrolysis residue (EHR). Detailed characterizations, including GPC, FTIR, ^{13}C and 2D-HSQC NMR and Py-GC/MS analysis were conducted to provide a broad evaluation of the obtained lignin fractions. The GPC analysis revealed that the proposed method could realize the efficient fractionation of EHL with relatively narrow polydispersity, and three lignin fractions (F1, F2 and F3) with gradually increased molecular weight ($\overline{M}n$ from 8690 to 20110 g mol^{-1}) and reduced polydispersity were obtained. The structural characterization (FTIR, NMR and Py-GC/MS) indicated that with the increase of molecular weight, G unit content in lignin fractions increased due to the more stable C—C bond formed by C5 in G unit. Besides, F1 contained highest phenolic acids, which indicated the potential application of F1 in bioactive products. The study of glycerol recycle showed that glycerol could be recycled with high recovery rate and re-employed to fractionate lignin efficiently. Consequently, the study indicated that compared with traditional dissolving by multiple organic solvents, the sequential dissolution in glycerol-ethanol solvent was a novel, green, and efficient way to fractionate EHL and reduce its molecular weight and structural heterogeneity.

1. Introduction

Lignin, consisting of three phenypropanoid units with various degrees of oxygenation/substitution on the aromatic ring, is the most abundant natural renewable aromatic material (Jääskeläinen et al., 2017; Wang et al., 2010). From the view of chemical structure, lignin is an amorphous polyphenolic polymer formed by the polymerization of three monomers, namely syringyl alcohol (S), guaiacyl alcohol (G) and *p*-coumaryl alcohol (H) (Vanholme et al., 2010; Wang and Chen, 2013a). As the organic constituent of photosynthesized plant biomass, the annual production of lignin on Earth has been approximated in the range of 5–36 × 10^8 tons (Gellerstedt and Henriksson, 2008). Moreover, with the rise of lignocellulosic ethanol production obtaind by enzymatic hydrolysis and fermentation, the yield of lignin as the by-product will reach to 62 million tons by 2022 (Ragauskas et al., 2014). The efficient use of renewable biopolymers products (such as lignin, starch, etc) fits well into the concept of sustainability, therefore, more and more attention is paid to study the application of the natural material (Fan et al., 2017; Stewart, 2008).

As is known to all, lignin is a heterogeneous material including complex chemical structure and high polydispersity of molecular weight (Li and McDonald, 2014). The chemical structure of lignin as well as the content of functional groups had been found to change with molecular weight (Sun et al., 2000). Consequently, the molecular weight has a vital effect on the structure and functional group of lignin and, to a great degree, on the performance of lignin for subsequent application. Therefore, to achieve efficient and comprehensive utilization of lignin with different molecular weight, lignin upgrade by fractionation seems to be a prior way because it can obtain particular molecular lignin fractions with certain properties. Due to the solubility differences of lignin with different molecular weight, dissolution of lignin in variant solvents have been employed to obtain lignin with low polydispersity. Several dissolution fractionation ways composed of intricate solvents have been developed to fractionate lignin including ether, methanol, methane chloride, dichloromethane, acetic ether, *n*-butyl alcohol, etc. (An et al., 2017; Li et al., 2017; Thring et al., 1996;

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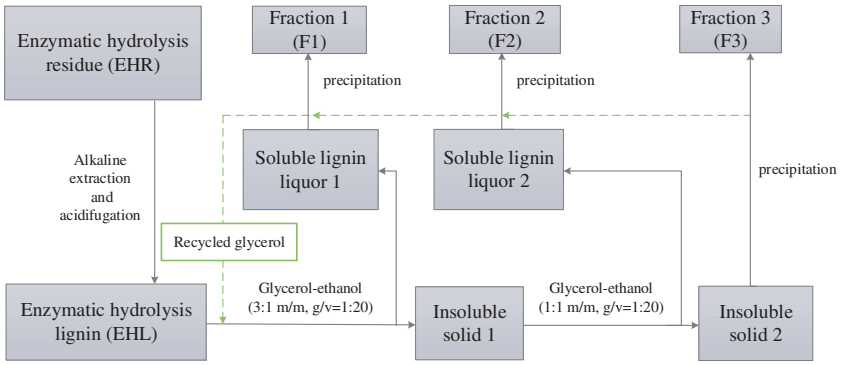

Fig. 1. Scheme for fractionation of lignin from EHR.

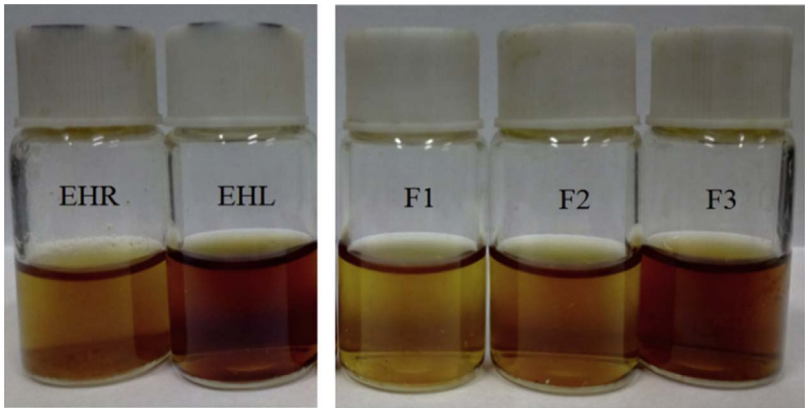

Fig. 2. Photos of EHR, EHL and the lignin fractions in weakly basic solution (5 mg/mL in 1% NaOH solution).

Table 1
Yield and chemical compositions of EHR, EHL and lignin fractions.

	Yield (%)	Lignin purity				
		AIL (%)	ASL (%)	Glucose content (%)	Xylose content (%)	Ash content (%)
F1	18.87 ± 0.56	87.08 ± 0.30	2.98 ± 0.28	0.83 ± 0.18	0.75 ± 0.12	3.02 ± 0.23
F2	28.80 ± 0.43	85.73 ± 0.43	3.12 ± 0.31	1.06 ± 0.24	0.87 ± 0.19	3.48 ± 0.19
F3	45.34 ± 0.67	80.67 ± 0.36	3.18 ± 0.20	1.65 ± 0.12	1.43 ± 0.20	4.39 ± 0.30
EHL	–	83.47 ± 0.55	3.69 ± 0.18	1.38 ± 0.34	0.96 ± 0.11	3.58 ± 0.24
EHR	–	56.86 ± 0.38	2.92 ± 0.11	18.15 ± 1.28	9.77 ± 0.43	7.90 ± 0.36

F1:fraction 1.
F2:fraction 2.
F3:fraction 3.
EHL: enzymatic hydrolysis lignin.
HER: enzymatic hydrolysis residue.

Yuan et al., 2009). Although the effect of selective lignin fractionation is striking, the tedious process of organic solvent extraction is nocuous for environment and increase the cost of lignin production. Therefore, it is natural that a facile and green method for lignin fractionation should be explored to enlarge lignin application.

With the rapid development of biodiesel, glycerol, as the by-product of the biodiesel, is readily acquired, cheap, poisonless and biodegradable compared with other green solvents such as ionic liquids. Moreover, glycerol possesses other properties including low vapor pressure, high boiling (290 °C), easily recyclable and sustainable (Liu et al., 2017). These properties for glycerol conform to the demand of the green solvents and the sustainable chemical processes. Some researchers had utilized glycerol as a promoting solvent for organic synthesis to enhance reaction selectivity (Gu et al., 2008; Wolfson et al., 2006). In the recent literatures, glycerol as a sustainable solvent was recovered and reused for the further reaction process, such as regioselective β,β-diarylation of alkenes and copper-catalyzed cross-coupling reactions (Delample et al., 2010; Ricordi et al., 2012). However, glycerol is still not used as solvent for lignin fractionation. Therefore, considering of the advantageous of glycerol (stable and recyclable), this work attempts to value the novel process utilizing glycerol-ethanol solvent, instead of toxic and multi-organic solvent such as ether, methane chloride and acetic ether, as the solvent for lignin fractionation.

Thus, in this work, glycerol was innovatively applied as a solvent to achieve effective fractionation process for enzymatic hydrolysis lignin (EHL). By this method, the obtained lignin fractions were subsequently characterized by the following analysis technology: GPC, FTIR, ^{13}C and 2D-HSQC NMR and Py-GC/MS analysis. In addition, the glycerol recovery and reuse for lignin fractionation were further studied.

2. Materials and methods

2.1. Materials

Enzymatic hydrolysis lignin (EHL) was obtained from enzymatic