



One-pot lignin depolymerization and activation by solid acid catalytic phenolation for lightweight phenolic foam preparation



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ARTICLE INFO

Keywords:

Enzymatic hydrolysis lignin
Solid acid catalytic phenolation
Lignin depolymerization
Lignin reactivity
Phenolic foam characterization

ABSTRACT

Lignin valorization offers a significant opportunity for the commercial operation of a cellulosic ethanol-derived biorefinery. In this work, a novel solid acid catalytic phenolation (SACP) process was employed to treat enzymatic hydrolysis lignin (EHL) and the obtained product was further applied to prepare lightweight phenolic foams ($\rho = 30\text{--}40 \text{ kg/m}^3$). The changes of the molecular weight and structure of lignin under the SACP treatment were investigated by GPC, Py-GCMS, and 2D-NMR analyses. The results indicated that under the optimized SACP conditions (140 °C, 4% HZSM-5, and 2 h), the molecular weight (\bar{M}_w) of EHL sharply decreased from 6695 to 2418 g/mol without condensation. The Py-GCMS and 2D-NMR analyses suggested that phenol was incorporated at the C_α position through a nucleophilic reaction and this reaction inhibited the lignin condensation during the acidic treatment. Due to the simultaneous depolymerization and phenolation, the treated lignin showed noticeable increase in phenolic hydroxyl content and reactivity with formaldehyde. The further characterization of lignin-based phenolic foams showed that the treated lignin could replace 50% phenol to prepare phenolic foams with satisfactory thermal insulation and compression strength properties. Consequently, this work demonstrates that SACP is effective to depolymerize and activate lignin for high lignin content phenolic foam preparation and offers a value-added way of lignin application as heat-insulating foam materials.

1. Introduction

The high processing costs of producing cellulosic ethanol from agricultural and forestry residues have obviously limited the widespread industrial operation of cellulosic ethanol. Derived from the petroleum refinery, a multi-product lignocellulose biorefinery is proposed to revive the economic efficiency of cellulosic ethanol through the auxiliary profits of by-products (Melero et al., 2012). Due to the totally different chemical structure with the other two main components in lignocelluloses, lignin is usually considered as an underused residual in a cellulosic ethanol plant. In order to make the biorefinery approach economically viable, the issue about lignin valuable utilization must be addressed (Doherty et al., 2011; Ragauskas et al., 2014).

Lignin is a cross-linking aromatic polymer composed of three different phenylpropane monomers. Because of the similar cross-linked networking structure with phenolic resin, the replacement of the petroleum-derived phenol for phenolic resin preparation has been considered as one value-added option for lignin applications (Kai et al., 2016; Yang et al., 2014). Phenolic resin foam exhibits exceptional flame

retardance, low thermal conductivity, high thermal stability compared with other polymeric foams and has been widely used as insulating materials in fields where flame resistance is crucial, such as high-rise buildings, aircraft, and chemical pipelines (Shen and Nutt, 2003). So far, several attempts have been made to use lignin as phenol substitution for phenolic foam preparation (Carvalho and Frollini, 2002; Del Saz-Orozco et al., 2012; Hu et al., 2011b; Li et al., 2017; Zhuang et al., 2011). However, lignin is generally less reactive than phenol due to the fewer positions available for the methylation reaction that is crucial for lignin to be incorporated into the phenolic resin (Tejado et al., 2007; Wang and Chen, 2014a). Therefore, the improvement of lignin reactivity is a critical upgrade process to prepare phenolic foam with acceptable properties (Hu et al., 2011a).

According to the previous studies, low molecular weight lignin shows higher content of phenolic groups than high molecular weight lignin (An et al., 2017; Wang and Chen, 2013). It is suggested that lignin with higher content of phenolic groups performs better in preparing foam materials due to more crosslinking points (Doherty et al., 2011; Tejado et al., 2007). Besides, low molecular weight lignin has low

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Table 1
Formula for lignin-based phenolic form preparation with different substitution rates.

Substitution Rate (S, %)	Lignin (g)	Phenol (g)	37% Aqueous formaldehyde (g)			20% Aqueous NaOH (w/v, ml)			Additives (g) for 100 g resol foaming ^a		
			Consumed by lignin	Consumed by phenol	Total	Consumed by lignin	Consumed by phenol	Total	Tween-80	n-pentane	HCl
0	0	100	0.0	138.0	138.0	0.0	42.6	42.6	7.5	10.0	15.0
30	30	70	10.1	96.6	106.7	15.0	29.8	44.8			
40	40	60	13.5	82.8	96.3	20.0	25.5	45.5			
50	50	50	16.9	69.0	85.9	25.0	21.3	46.3			
60	60	40	20.3	55.2	75.5	30.0	17.0	47.0			

^a The additive compositions are same for all the five different substitution rates.

viscosity, which is conducive to mixing with a foaming agent and generating uniform bubbles during the foaming process (Hu et al., 2013; Pan and Saddler, 2013). Therefore, lignin depolymerization is proposed as a modification way before phenolic foam preparation. Currently, some depolymerization processes, such as pyrolysis (Sukhbaatar et al., 2009), hot-compressed water liquefaction (Wang et al., 2009) and catalytic hydrothermal treatments (Cheng et al., 2013), are applied to obtain depolymerized lignin for phenolic resin synthesis. However, the conditions of these depolymerization processes are always harsh (> 200 °C). Besides, an auxiliary purification process of depolymerized products is normally necessary, which increases the operating costs.

In the present work, we proposed a novel lignin depolymerization process by solid-acid catalytic phenolation (SACP) in phenol/water solvent under moderate temperature (≤ 160 °C). After removal of the solid-acid catalyst, the products were used for phenolic resin synthesis without any further processing. The hypothesis here is that lignin is phenolated and depolymerized simultaneously to enhance the activity of lignin in the following resin synthesis process. As a result, it is expected that the treated products will exhibit preferable performance as phenol substitution for phenol-formaldehyde foam preparation under high substitution rate. Enzymatic hydrolysis lignin (EHL) as the raw material was treated by SACP and further applied to prepare phenolic foam. The morphology, density, thermal conductivity, and compression strength properties of lignin-based phenolic foams with different substitution rates were compared. In addition, the lignin properties after SACP treatment were characterized by the phenolic hydroxy content, the reactivity with formaldehyde, and the uncombined lignin content in the cured resin.

2. Materials and methods

2.1. Experimental materials

EHL from corn stalk was obtained according to the process described by Liu et al. (2018), which was consisted by 83.47% Klason lignin (w/w), 3.69% acid-soluble lignin (w/w), 2.34% carbohydrates (Glucosan and xylan, w/w), and 3.58% ash (w/w). Solid acid (HZSM-5) was purchased from the catalyst plant of Nankai University (Tianjin, China). All laboratory reagents were chemically pure.

2.2. Solid-acid catalytic phenolation (SACP) treatment of lignin

EHL and melting phenol were added into a batch pressure-tight reactor equipped with a thermocouple and a mechanical stirrer. The mass ratio of EHL to phenol was calculated according to the substitution rate *S*.

$$S = \frac{L}{(L + P)} \times 100\% \quad (1)$$

Where *S* was the substitution rate of lignin, *L* was the mass of lignin added and *P* was the mass of phenol. After sufficient mixing at 50 °C for

10 min, distilled water (10% of phenol mass) and solid acid with 0%, 2%, 4% and 6% (to the total mass of lignin and phenol) were added. The resulting mixture was then stirred and heated at different temperatures (100, 120, 140 and 160 °C) for desired time (0.5, 1.0, 2.0 and 3.0 h). After the reaction, the mixture was filtered through a 10 mesh metal filter to remove the solid acid catalyst. The treated products were collected and stored at 4 °C for subsequent characterization and phenolic foam preparation.

2.3. Preparation of lignin-based phenolic foam

The 37% aqueous formaldehyde solutions used for resin synthesis included two parts: one was consumed by lignin with the mass ratio of 1:8 (formaldehyde/lignin) and the other was consumed by phenol according to the molar ratio of 1.6:1 (formaldehyde/phenol, shown in Table 1). The amount of NaOH added was also the sum of two parts: one was consumed by lignin with the mass ratio of 1:10 (NaOH/lignin) and the other was used as catalyst with a molar ratio of 1:5 (NaOH/phenol, shown in Table 1). After the addition of formaldehyde and NaOH and mixing at 50 °C for 10 min, the mixture was then heated at 65 °C for 1 h and 92 °C for 1 h, respectively. The synthesized resol was cooled down to 40 °C and neutralized by 4 mol/L HCl to pH 8.0–8.5 with vigorous stirring. After that, the resin was dehydrated to the solid content (about 70%) by a vacuum rotary evaporator (Wang and Chen, 2014b).

The obtained lignin-based resol, surfactant (Tween-80) and foaming agent (*n*-pentane) were weighted in a papery container according to the formula given in Table 1 and thoroughly mixed using a glass rod to disperse foaming agent in the resin (Wang and Chen, 2014b). 37% Hydrochloric acid (wt%), as a curing agent, was added with vigorous stirring to form a homogeneous mixture. The papery container with the resultant mixture was immediately placed in a pre-heated oven at 80 °C for 1 h to complete the foaming and curing process. All the foam samples were prepared in three duplicates.

2.4. Characterization of lignin treated by SACP

1.0 g treated product was dissolved in 2 ml 95% ethanol solutions followed by addition of 20 ml 80 °C distilled water for lignin precipitation. The mixture was centrifuged at 8500 × *g* for 10 min. After discarding the supernatant, the precipitated lignin was re-dissolved in 95% ethanol solutions and precipitated in 80 °C distilled water again. After centrifugation, the precipitated lignin was collected and then washed by 80 °C distilled water to sufficiently eliminate the free phenol. Finally, the treated lignin used for characterization was dried by freeze dehydration.

The reactivity of lignin with formaldehyde was analyzed by the following procedure. 0.1 g dried treated lignin was dissolved in 2 ml 10 g/l NaOH solutions and then diluted to 10 ml by distilled water. 0.054 g formaldehyde (37%) was added into the lignin solutions and the mixture was placed in a shaking bath at 80 °C with a rotation rate of 150 rpm (Wang and Chen, 2014a). After reaction for 2 h, the lignin was

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