Separation and Purification Technology 191 (2018) 250–256

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Separation of aromatic monomers from oxidatively depolymerized products of lignin by combining Sephadex and silica gel column chromatography

Ying Zhao[a], Xinping Ouyang[a,*], Jing Chen[a], Lisha Zhao[a], Xueqing Qiu[a,b,*]

[a] School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China
[b] State Key Laboratory of Pulp & Paper Engineering, South China University of Technology, Guangzhou 510640, PR China

ARTICLE INFO

Keywords:
Oxidative depolymerization
Lignin
Separation
Column chromatography
Aromatic monomers

ABSTRACT

The conversion of lignin into value-added aromatic monomers has attracted much attention as these monomers can be potentially used to prepare liquid fuel rather than heavy oil by further hydrodeoxygenation. A new process combining Sephadex and silica gel column chromatography was employed to obtain aromatic monomers with higher purity. It was found that pH and polarity of mobile phase were the most important factors affecting the separation effect for Sephadex G-10 and silica gel column chromatography, respectively. When the pH of mobile phase reached 10.5, the ionization of hydroxyl together with carboxyl groups resulted in electrostatic repulsion between the aromatic compounds and Sephadex G-10 gel, which counteracted the adsorption caused by hydrogen bond between aromatics and gel, causing the increase of the separation effect. Under the condition of pH above 10.5, Sephadex gel column chromatography gave 78.1% of purity of aromatic monomers (PAM) and 99.5% of recovery of aromatic monomers (RAM) due to the elimination of non-size exclusion effect. Silica gel column chromatography was further conducted to obtain 99.8% of PAM and 73.9% of RAM. The polar mobile phase was favorable for eluting aromatic monomers, while the non-polar mobile phase was beneficial to remove oligomers and increasing the PAM.

1. Introduction

Lignin is one of the abundant renewable raw materials in nature, and it is generally considered to be consisted of three phenylpropane units (syringyl, guaiacyl and p-hydroxyphenyl) linked by C−C and C−O bonds [1,2]. Therefore, lignin can be depolymerized into aromatic compounds [3] to prepare liquid bio-fuel by the further hydrodeoxygenation [4]. Currently, the depolymerization of lignin into value-added aromatic monomers has attracted a lot of attention in view of the fast consumption of fossil resource and energy [5]. However, the depolymerized products of lignin (DPLs) are complicated mixture containing aromatic monomers, dimers, trimers, oligomers and other organics, which makes the DPLs difficult to be upgraded. Moreover, considering the length of carbon chain, aromatic monomers are most likely suitable for preparing liquid fuel. Therefore, it is necessary to separate aromatic monomers from the complex DPLs.

Vacuum distillation [6] and Molecular distillation [7] were reported to separate DPLs. However, the boiling-points of DPLs are relatively high due to the oxygenous groups in the DPLs. Consequently, a high temperature or vacuum is needed to get a good separating effect, resulting in a high energy input.

Extraction is one of the widely used separation methods. Kang et al. [8] reported that the DPLs were separated into four main types of substances (benzenediols, monophenolic hydroxyl products, weak-polar products, and water-soluble products) with ethyl acetate and methylene dichloride as extractant at different acidity. However, the main objective of the work was to explore the mechanism for decomposition of lignin rather than the separation of aromatic monomers. Li et al. [9] reported that a new process for the separation of phenols obtained by depolymerization from cotton stalk under vacuum distillation, followed by the extraction with dichloromethane. This process gave 93.89% of relative content of phenol derivatives, but it did not mention the recovery ratio. Generally, organic solvent is utilized in liquid-liquid extraction resulting in the possibly environmental pollution. Supercritical carbon dioxide extraction was adopted to the separation of DPLs to collect methyl dehydroabietate and concentrate vanillin and methyl vanillate [10], which may be a promising approach to get aromatic monomers from DPLs. However, the separation efficiency of aromatic monomers containing more polar functional groups still faces the great challenge. Ultrafiltration and nanofiltration were also reported for separating aromatic monomers and oligomers from lignin degradation products [11]. Werhan et al. [12] used nanofiltration

* Corresponding authors at: School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China
E-mail addresses: ceouyang@scut.edu.cn (X. Ouyang), xueqingqiu66@163.com (X. Qiu).

http://dx.doi.org/10.1016/j.seppur.2017.09.039
Received 15 July 2017; Received in revised form 5 September 2017; Accepted 19 September 2017
Available online 21 September 2017
1383-5866/

membranes with molecular weight cut-offs ranging 280–900 g/mol to separate aromatic monomers from DPLs. While 98% of aromatic monomers permeated through membranes, the filtrate contained 65.7% of dimers, 35.0% of trimers and 28.9% of oligomers at the same time. This report was to obtain two fractions considerably enriched in monomers and high molecular weight products, respectively, that can further be processed and purified.

Column chromatography has been widely used for the separation of organic molecules and macromolecules [13], and silica gel column chromatography is based on different adsorption capabilities of the substances on silica gel [14]. Yang et al. [15] found that combination of extraction and liquid column chromatography was effective for isolating the phenol derivatives from bio-oils, in which phenol derivatives was concentrated up to 100%. However, it did not mention the recovery ratio of phenol derivatives.

Up to now, there were few references available on the separation of aromatic monomers from degradation products of lignin. Sephadex gel column chromatography has excellent separation and batch to batch reproducibility on the basis of molecular size [16]. In our previous work, lignosulfonate fractions with high purity were separated by combining Sephacryl S-100 with Sephadex LH-20 column chromatography [17]. To further realize the high-value utilization of these aromatic monomers to refined chemicals and high quality bio-fuel, the DPLs deserve purification [18]. In the present work, a separation process combining Sephadex and silica gel column chromatography was used to separate aromatic monomers from the oxidative DPLs to get high purity of aromatic monomers (PAM) and relatively higher recovery of aromatic monomers (RAM) for further producing liquid fuel by hydrodeoxygenation of these aromatic monomers.

2. Material and methods

2.1. Chemicals and reagents

Wheat straw alkaline lignin (WAL) purchased from Shandong Quanlin Paper Industry Company (Gaotang, Shandong, China) was purified by acidulation precipitation and ultrafiltration [18], therefore the purity of WAL is 85.31%. Sephadex G-10 gel and silica gel were purchased from General Electric Company (Fairfield, Connecticut, USA) and Qingdao Marine Chemical Factory (Qingdao, Shandong, China), respectively. All other chemicals were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China).

2.2. Depolymerization of lignin

The process for oxidative depolymerization of lignin was optimized as published before [18], in which 0.3 g lignin, 20 mL methanol-water (1:1, v/v), 0.08 g CuO, 0.004 g $Fe_2(SO_4)_3$ and 2 mL H_2O_2 (30% wt) were placed in a 100 mL of stainless steel autoclave (Beijing Shijishenglang Chemical Machinery Co., Ltd., China). The depolymerization reaction was carried out at 150 °C for 60 min with a stirring speed of 400 rpm. The oxidative DPLs contained 9 kinds of identified aromatic monomers by LC-MS analysis, as shown in Fig. 1, and the overall yield of these aromatic monomers was 17.92%.

2.3. Sephadex G-10 gel column chromatographic separation

The separation of DPLs by Sephadex G-10 gel column chromatography was conducted in an AKTA Prime chromatography system (General Electric, USA). 0.5–4 mL of the depolymerized liquid was injected into a column (70 × 1.6 cm i.d.) packed with Sephadex G-10 gel, and eluted with aqueous solution of different pH (3.6–10.5) at flow rate of 0.1–2.0 mL/min. Eluates were collected in test tubes (5.0 mL/tube) by an automatic distribution collector. The obtained samples in each tube were acidified with sulfuric acid to pH 2 for HPLC analysis. Then the collected samples in certain tubes containing aromatic monomers were combined and concentrated to 5.0 mL for HPLC analysis.

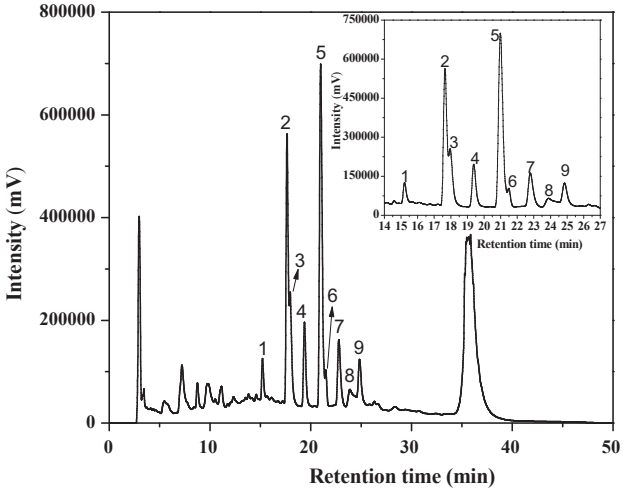

Fig. 1. The HPLC chromatogram of oxidative DPLs1: p-hydroxybenzoic acid; 2: vanillic acid; 3: p-hydroxybenzaldehyde; 4: syringyl acid; 5: vanillin; 6: p-hydroxyacetophenone; 7: syringaldehyde; 8: p-coumaric acid; 9: acetovanillone.

2.4. Silica gel column chromatographic separation

27 g of silica gel activated at 110 °C for 1 h [19] were added into a silica gel column (40 × 2 cm i.d.). Then the concentrate collected after separation by Sephadex G-10 gel column chromatography was eluted with different organic solvent as the mobile phase at a flow rate of 0.5 mL/min. The eluates were collected and then identified by HPLC.

2.5. Characterization of separated products

The DPLs were analyzed on Shimadzu LC-20A liquid chromatography (Japan) equipped with a ZORBAX SB-C18 column (250 × 4.6 mm, 5 μm particle size) and a maXis impact tandem mass spectrometer (Bruker Daltonics, USA). The separation was carried out on the ZORBAX SB-C18 column. The mobile phase used a binary system consisting of phosphoric acid aqueous solution (pH at 2) (A) and methanol (B) for a total running time of 45 min, and the gradient changed as follows: 90% A/10% B for 2 min, 73% A/27% B in 8 min, 65% A/35% B in 10 min, 57% A/43% B in 10 min, 10% A/90% B in 15 min until the end of running. 20 μL of the samples were injected in the column, and the eluates were detected at 280 nm at 40 °C. The aromatic monomers were identified from their mass spectra followed by comparing their retention time with those of the standard compounds. The yields of resulting aromatic monomers were determined by standard curves [18]. The PAM and RAM were calculated by the following equations respectively, based on their different peak areas [20].

$$PAM(\%) = A_1/A_2 \times 100 \quad (1)$$

$$RAM(\%) = m_1/m_2 \times 100 \quad (2)$$

where A_1, A_2, m_1, and m_2 were the peak area of aromatic monomers after separation and the total peak area of the degradation products, weight of aromatic monomers before and after column chromatographic separation, respectively.

High resolution mass spectrometry (HRMS) was recorded on a Bruker maXis impact mass spectrometer (Germany) equipped with an ESI source. Scans acquired positive ion mode from *m/z* 50–1000 with formate solution as an internal standard to correct the molecular weight. The pressure of the nebulizer was set at 0.3 bar. The temperature and flow rate of the dry gas was 180 °C and 4 mL/min, respectively.

The surface charges of Sephadex G-10 gel were determined by a