



Research article

Distribution coefficient of products from lignin oxidative degradation in organic-water systems

Jingying Pan^{a,b}, Jie Fu^{a,*}, Shuguang Deng^{b,*}, Xiuyang Lu^a^a Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou, 310027 Zhejiang, China^b Chemical & Materials Engineering Department, New Mexico State University, Las Cruces, NM 88003, USA

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ABSTRACT

A study on extraction of 15 kinds of possible lignin degradation products from aqueous solutions was performed by evaluating the distribution coefficients of five different organic-H₂O systems under different conditions. The experimental results show that the extraction of lignin degradation products from aqueous solutions achieved equilibrium within 30 min; the concentration of the extracted materials and the amount of extractant had a negligible effect on the distribution coefficients. Among the five kinds of extractants investigated in this work, n-butanol was the best solvent for extracting the lignin degradation products, and chloroform had a good selectivity for the extraction of aldehyde. The temperature greatly influenced the distribution coefficients because the distribution coefficients decreased considerably with the extraction temperature. These results provide insights for the degradation of the lignin in a two-phase system.

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1. Introduction

As the development of the world, the demand for new energy becomes more and more urgent [1]. Lignin is the second most abundant renewable biomaterial in the world and lignin is a complex three-dimensional polymer of phenylpropane units [2] linked together by carbon-carbon and ether bonds [3,4], indicating that lignin is a promising raw material for high-value aromatic compounds. However, lignin receives less attention compared to cellulose and hemicellulose because of the complex structure and resistance to be degraded [5,6]. Previous reports show that combustion is still the most common way of lignin utilization [1,4,7]. Therefore, an efficient way to convert lignin to aromatic compounds attracts much attention.

Currently, there are several technologies to convert lignin to aromatic compounds such as hydrolysis, pyrolysis and oxidation [8]. The traditional method of lignin degradation involves a base (e. g. NaOH) [9,10], or an acid (e. g. H₂SO₄) as the catalyst [11], or using high temperature and high pressure [4,7,12–14]. Wahyudiono et al. [13] studied the degradation of lignin in near- and super-critical water at temperatures from 623 to 673 K using a batch type reactor. The main products were catechol (28.4 wt.%), phenol (7.5 wt.%), m, p-cresol (7.9 wt.%) and o-cresol (3.8 wt.%). The oxidation method used oxidants in a relatively mild condition [15]. Crestini et al. [16] summarized oxidation degradation as a new environmental friendly method in biofuel applications because of the green catalyst, relatively mild conditions of the reaction. Zhou [17] studied the oxidation of kraft lignin over zeolite-encapsulated Co(II)

[H₄] salen and [H₂] salen complexes. 2-Methoxy phenol, 2-hydroxy benzaldehyde, and 4-hydroxy-3,5-dimethoxyphenyl ethanone were the major products in the study. In some other cases, the main products in lignin oxidation degradation are vanillin and syringaldehyde [8].

Yoshikawa et al. [18] explored a two-phase method to degrade lignin. In the step of depolymerization, lignin was degraded in an n-butanol-H₂O system. The hydrolysis occurred in the aqueous phase, and then the degradation products (included carboxylic acids) were extracted to the organic phase and esterified with n-butanol. The yield of lignin-derived liquid product reached 85–88 C-mol% under appropriate reaction conditions. Both esterification and extraction of phenols can accelerate the degradation. If a solvent can extract the products very efficiently, the degradation would be accelerated greatly. So a proper extractant is very important for the two-phase degradation.

In this study, the extraction behaviors of 15 kinds of aromatic compounds which were reported as the products from lignin degradation products were investigated. Ethyl acetate, chloroform, n-butanol, cyclohexane and n-hexane were used as extractants to extract the products from aqueous solutions. The effect of different conditions on the extraction was evaluated; the difference between different products in the extraction was discussed. These results provided insights for the degradation of the lignin with the extractant existing in the reaction system.

2. Experimental section

2.1. Materials

Vanillin (≥99% AR), o-dihydroxybenzene (≥99.5% GC), salicyl alcohol (≥98% AR), salicylal (≥99% AR), salicyl acid (≥99% AR), P-hydroxy

* Corresponding authors.

E-mail addresses: jiefu@zju.edu.cn (J. Fu), sdeng@nmsu.edu (S. Deng).

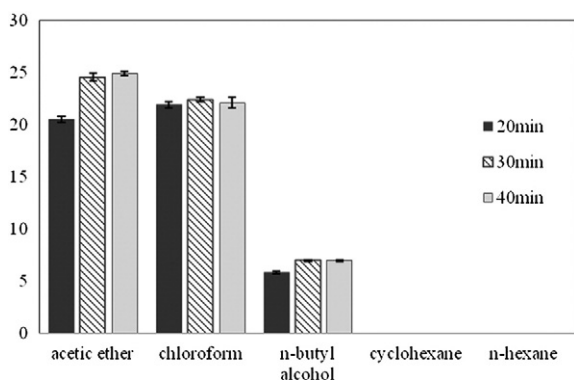


Fig. 1. Distribution coefficient of vanillin in five extraction systems with different vibration times.

benzyl alcohol ($\geq 97\%$ AR), P-hydroxybenzaldehyde ($\geq 99\%$ AR), P-hydroxybenzoic acid ($\geq 99\%$ AR), guaiacol ($\geq 99\%$ AR), syringaldehyde ($\geq 98\%$ AR), and ethyl vanillin ($\geq 98\%$ AR) were obtained from Aladdin Industrial Inc., China. Ethyl acetate ($\geq 99.5\%$ AR), chloroform ($\geq 99\%$ AR), n-butanol ($\geq 99\%$ AR), cyclohexane ($\geq 99\%$ AR), n-hexane ($\geq 99\%$ AR), phenol ($\geq 99.5\%$ AR), benzyl alcohol ($\geq 99\%$ AR), benzaldehyde ($\geq 98.5\%$ AR), and benzoic acid ($\geq 99.5\%$ AR) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the chemicals were used as received without any purification or pretreatment. The chemical purity of composition is defined by mass fraction.

2.2. Experimental procedure.

In a typical experimental run for the extraction, 0.025 g of compound, 25 mL of H₂O and 25 mL of extractant were added to a 150 mL conical flask. The vibrator was set at 30 °C, and then the flask was placed on the vibrator and vibrated for 30 min. The product was moved to a separating funnel. After standing, the organic layer and aqueous layer were separated into two volumetric flasks. The product samples were filtered by 0.45 μ m filter membrane and analyzed by a high-pressure liquid chromatograph (HPLC).

In the experimental runs for the effect of vibration time on the extraction, the vibrator was hold for 20 min, 30 min or 40 min at 30 °C. The other conditions were the same as the typical experimental run. In the experimental runs for the effect of concentration of extracted material on the extraction, the amount of vanillin was 0.025 g, 0.05 g or 0.075 g. The other conditions were the same as the typical experimental run. In the experimental runs for the effect of amount of extractant on the extraction, the extractant volume was 12.5 mL, 25 mL, 37.5 mL or 50 mL. The other conditions were the same as the typical experimental run. The treatment of the product was the same as the typical experimental run.

2.3. Analysis

The product samples were analyzed by an Agilent HPLC 1100 equipped with a variable wavelength detector. The column was 4 mm ID \times 250 mm KNAUER C18 reverse-phase column; the temperature of column was set at 35 °C; the mobile phase consisted of 0.2 wt.% acetic acid aqueous solution (A) and methanol (B) with a rate of 0.5 ml min⁻¹

Table 1
Distribution coefficient of vanillin in five extraction systems with different vibration times.

	Acetic ether	Chloroform	n-Butyl alcohol	Cyclohexane	n-Hexane
20 min	20.5 ± 0.2	21.9 ± 0.2	5.83 ± 0.11	0.021 ± 0.002	0.049 ± 0.002
30 min	24.6 ± 0.3	22.4 ± 0.2	6.99 ± 0.06	0.019 ± 0.001	0.05 ± 0.003
40 min	24.9 ± 0.2	22.1 ± 0.4	7 ± 0.06	0.02 ± 0.002	0.048 ± 0.002

Table 2
Dipole moment and dielectric constant of the extractants [21].

	Dipole moment	Dielectric constant, D
Ethyl acetate	1.78	6.081 (20 °C)
Chloroform	1.04	4.807 (25 °C)
n-Butanol	1.66	17.84 (20 °C)
Cyclohexane	0	2.02 (25 °C)
n-Hexane	0	1.89 (20 °C)

Table 3
Distribution coefficient of vanillin in five extraction systems with different concentrations of vanillin.

	Acetic ether	Chloroform	n-Butyl alcohol	Cyclohexane	n-Hexane
0.5 g · L ⁻¹	22.7 ± 0.4	21.9 ± 0.2	7.2 ± 0.2	0.02 ± 0.004	0.054 ± 0.003
1 g · L ⁻¹	22.2 ± 0.2	22.4 ± 0.3	7.1 ± 0.1	0.019 ± 0.002	0.049 ± 0.001
1.5 g · L ⁻¹	22.8 ± 0.3	22.1 ± 0.2	6.9 ± 0.3	0.021 ± 0.001	0.049 ± 0.002

and a gradient elution: 0 min (20% B) → 40 min (90% B) → 50 min (20% B); the flow rate was 0.5 mL min⁻¹.

In the cyclohexane-H₂O system and n-hexane-H₂O system, the samples were analyzed by gas chromatography (Agilent GC 7890A) equipped with a flame ionization detector (FID), and a 30 m \times 320 μ m \times 0.25 μ m HP-5 column from Agilent, China. The initial temperature of the GC was set at 50 °C for 3 min, and then the oven temperature was increased at a rate of 10 °C min⁻¹ until reaching 300 °C which was maintained for another 5 min. The detector and injector temperature was set at 300 °C. The injection volume was 0.5 μ L.

3. Results and discussion

3.1. Effect of vibration time on the distribution coefficient

The results in the figures and tables were got by averaging three testing values of repeated measurements. The standard deviation, "s" was calculated by the following formula:

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2}$$

The standard uncertainty $u(x)$ is the standard deviation of the mean, which is:

$$u = s(x) = \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^n (x_i - \bar{x})^2} = \frac{s}{\sqrt{n}}$$

The uncertainty would be the standard uncertainty multiply by a factor. When the measurement was carried on for three times, for level of confidence of approximately 68%, the factor is 1.32.

The results were written as $x \pm \frac{s}{\sqrt{3}} \times 1.32$, the level of confidence was approximately 68%.

Fig. 1 shows the distribution coefficients of vanillin in five extraction systems with different vibration times. At 20 min, the distribution coefficients of vanillin in the five extraction systems were smaller than those

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