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# Short communication

# Electrocatalytic degradation of aspen lignin over Pb/PbO<sub>2</sub> electrode in alkali solution



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# A R T I C L E I N F O

ABSTRACT

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Keywords: Aspen lignin Electrocatalytic degradation 4-Methylanisole Pb/PbO<sub>2</sub> electrodes Alkaline water electrolysis A novel procedure about electrochemical catalysis degradation of aspen lignin with Pb/PbO<sub>2</sub> anode in the threedimensional electrode (TDE) reactor was investigated. SEM, XRD and cyclic voltammogram tests were employed to study the surface morphology, composition and the electrochemical redox performance of the fabricated Pb/ PbO<sub>2</sub> electrode. The lignin was cracked by 'OH and hydrogenated by [H] atom generated from alkaline water electrolysis, leading to the production of 4-methylanisole and other products. Raw material lignin concentration, current density, temperature and time were optimized. The pathway of electrocatalytic degradation and hydrogenation process of lignin in alkaline solution was also discussed.

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# 1. Introduction

As a kind of renewable resource of organic carbon, lignin accounts for about a quarter in woody plants. Lignin is considered to be, after cellulose, the second most abundant natural polymer. However, lignin has been regarded as a waste byproduct of the lignocellulosic biomass conversion processes despite that it is composed of valuable aromatic monomers [1]. For exploring the specific structure of lignin and getting valuable refine chemical, many efforts have been paid to degrade lignin such as fast pyrolysis, hydrothermal degradation, photodegradation and electrochemical degradation.

In recent years, owing to its ease of operation and environmental friendliness, electrocatalytic oxidation has been employed for the degradation of lignin [2]. The variety and yields of products obtained from lignin oxidation varied according to the nature of the anode. B. Mahdavi [3] studied the degradation of lignin model compounds in aqueous ethanol at Raney nickel electrodes, showing the efficiency of hydrogenolysis of the C–O bond can be optimized to 100% at proper condition.

We had previously reported the degradation of lignin to BHT by electrocatalytic reaction in 2D electrode system [4], however there was a problem of the electrochemical impedance as the case for the strong adsorption of hydroxyl group in lignin. The TDE reactor based on electrochemical catalysis has been employed in this research work. Because there are a large number of the particle electrode materials placed into the TDE reactor to form charged microelectrodes and increase its large specific surface areas in connection with the reactant. The reactivity of electrochemical oxidation in TDE reactor can be improved. By contrast with 2D electrode, the addition of granular activated carbon may enhance the conductivity and mass transfer or the adsorption of reactant [5], 3D electrode has greater advantage in degrading organics [6,7].

4-Methylanisole, also known as 1-methoxy-4-methyl benzene, belongs to methoxybenzene derivatives. It mainly applies in food flavor, inedible essence, and pharmaceutical intermediate. 4-Methylanisole is an edible spice (as seen in FDA104-93-8), especially in the preparation of walnut, hazelnut and other nut essence. It had been achieved by upgrading of bio-oil in a catalytic pulsed dielectric barrier discharge plasma reactor [8].

# 2. Materials and experimental methods

#### 2.1. Materials

Aspen lignin was supplied by Luohe Huadong Lignin Company, Henan Province, China. Elemental analysis (C, H, N) of aspen lignin was conducted using a FlashEA 1112 Series element (Thermo Electron Corporation). The contents of carbon and hydrogen in aspen lignin were 59.7% and 5.94%, respectively. Lead chips and stainless steel wire mesh (purity  $\geq$  99.99%) were purchased from Tianjin Guangfu Fine Chemical Research Institute, China. The granular activated carbon with particle sizes in range of 1.40–3.35 mm provided by Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd, China. All of the solutions were prepared using deionized water.

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Fig. 1. SEM images of the Pb/PbO2 electrode before (a) and after (b) electrolysis in 1 mol/L NaOH solution.

# 2.2. Preparation of the Pb/PbO<sub>2</sub> electrode by electrodeposition

The Pb/PbO<sub>2</sub> electrode was prepared by electrodeposition [9]. The pretreatment of lead sheet included following steps: burnish the surface of lead sheet with sandpaper (P 120), impregnate into acetone, clean by mixture solution (Na<sub>2</sub>CO<sub>3</sub> 20 g/L, Na<sub>3</sub>PO<sub>4</sub> 20 g/L, NaOH 50 g/L), acidic clean by mixed acid solution (HNO<sub>3</sub> 400 g/L, HF 5 g/L) for 2 min and boil for 5 min in oxalic acid solution (100 g/L). The pure lead sheet, about 12 (2 × 6) cm<sup>2</sup>, was sited in an electrolytic cell which composed of anode, copper sheet of the same size used as cathode and 0.86 mol/L H<sub>2</sub>SO<sub>4</sub> electrolyte solution. The electrodeposition was performed with 50 mA/cm<sup>2</sup> controlled by a DC regulated power supply (ss1792c, Shijiazhuang KeHeng Electronic Company, China) at room temperature for duration 1 h. Then the Pb/PbO<sub>2</sub> electrode was obtained.

# 2.3. Electrocatalytic degradation of aspen lignin to chemicals based on three-dimensional electrodes

The experiments were carried out in three-dimensional electrode reactor [10]. Particle electrode was filled between Pb/PbO<sub>2</sub> electrode (anode) and stainless steel wire mesh (5 \* 5) electrode (cathode). Sodium hydroxide (1 mol/L) solution was used to dissolve lignin and gave the concentrations of lignin solution of 40 g/L in the electrolytic cell. The DC regulated power supply provided current 20–90 mA/cm<sup>2</sup> for the electrocatalytic degradation of lignin. The lignin alkali solution was stirring by magnetic stirring for mass transfer uniform. The reaction temperature and time were controlled within 30–90 °C and 0–8 h, respectively.

#### 2.4. The analysis and separation of the degradation products

The degradation liquid of lignin was extracted with the same volume ethyl acetate and acidified to pH 2–3 by  $0.86 \text{ mol/L} \text{ H}_2\text{SO}_4$  solution to



Fig. 2. XRD patterns of Pb/PbO<sub>2</sub> before and after electrolysis in 1 mol/L NaOH solution.

precipitate unreacted lignin residua simultaneously. The mixed liquor of organic solvent and water phase was sufficiently stirred until the lignin residue flocculation. The extract liquor and unreacted lignin residue were separated by the vacuum filter. The filter cake was dried to calculate the lignin degradation rate and the filtrate was separated by separatory funnel into water and extractive phase.

The crude products of lignin degradation were got by reduced pressure distillation to evaporate and recover the solvent. The separation and purification of products depended on thin layer chromatography and column chromatography separation (silica 200–300 mesh, eluent, n-hexane: ethyl acetate = 6:1, v/v). The main product was 4-methylanisole and its chemical structure was confirmed by GC–MS, NMR spectra. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  6.789 (s, 1H, CH),  $\delta$  6.81 (s, 1H, CH),  $\delta$  7.069 (s, 1H, CH),  $\delta$  7.090 (s, 1H, CH),  $\delta$  2.97 (s, 3H, CH<sub>3</sub>),  $\delta$  3.769 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  157.45, 129.877, 129.808, 113.672, 55.249, 20.442; MS: 123(7), 121(46), 107(30), 79(20), 77(34), 51(9), 50(4). The other degradation products such as acetovanillone, toluene, vanillin, syringaldehyde, 2,6-dimethoxyphenol and styrene were confirmed by GC with internal standard methods.

The products were qualitatively and quantitatively measured by internal standard method on the gas chromatography (GC) instrument (SHIMADIU, GC-2010) equipped with a FID detector and an Agilent J&W GC column (DB-FFAP, length 30 m, diameter 0.32 mm, film 0.25  $\mu$ m). The temperature of injection inlet, column and detector was 240 °C, programming 50 °C–220 °C and 280 °C respectively. The flow rate of carrier gas, high purity nitrogen (purity of 99.99%), was controlled with 38.7 mL·min<sup>-1</sup> and injecting volume of sample solution was 1  $\mu$ L for split sampling program of split ratio 20.0.



Fig. 3. CV curve recorded for the Pb/PbO<sub>2</sub> electrode without and with lignin in the threedimensional electrochemical reactor.



Fig. 4. CV curves recorded for the  $Pb/PbO_2$  electrode before (a) and after electrolysis 4 h (b) in 1 mol/L NaOH solution.

#### 3. Results and discussion

#### 3.1. Characterization of the prepared Pb/PbO<sub>2</sub> electrode

SEM images (seen in Fig. 1) were used to characterize morphology and coating surface structure of  $Pb/PbO_2$  electrode. The surface of the original  $Pb/PbO_2$  electrode was uniform and the crystal size was very fine. By contrast, after electrolysis 4 h, the electrode was not such a uniform crystal size and the electrode surface became rough and had many "cracks". This might be attributed to the generation of dioxygen on the anode surface resulting in the crystal structure change [11] in the process of electrochemical reaction.

Fig. 2 showed the XRD pattern of the internal PbO<sub>2</sub> layer deposited in the alkaline solution. Comparison of electrode XRD spectra before and after electrolytic reaction indicated that  $\alpha$ -PbO<sub>2</sub> crystal was easier to transform into  $\beta$ -PbO<sub>2</sub>, as  $\beta$ -PbO<sub>2</sub> had stronger stability, the effective constituent to the benefit of electrochemical degradation of lignin in the alkaline solution was  $\beta$ -PbO<sub>2</sub> crystal structure.

The cyclic voltammogram tests were conducted in a three-electrode system. In Fig. 3, the cyclic voltammogram tests in 1 mol/L NaOH solution with 40 g/L lignin and without lignin were carried out. Fig. 4(a) indicated a Pb/PbO<sub>2</sub> before electrolysis, the anodic peak corresponding to the formation of PbO<sub>2</sub> and was followed by vigorous oxygen evolution on the surface of PbO<sub>2</sub>, the cathode peak might be assigned to the reduction of PbO<sub>2</sub> to Pb [12]. In Fig. 4(b), after electrolysis 4 h, an anodic peak was observed at E + 0.3 V which might be due to the oxidation of lignin by 'OH generated from water electrolysis (as seen in Eq. (1)) [13].

Meanwhile, the reduction potential value -2.5 V was obviously lower than equilibrium potential [14] (1.459 V) of Pb/PbO<sub>2</sub> electrode, the generation of hydrogen atoms (as seen in Eq. (2)) on the surface of cathode could be carried out by alkaline water electrolysis [15,16].

$$Pb/PbO_2 \text{ anode} : H_2O - e^- \rightarrow OH + H^+$$
(1)

$$Fe-Cr-Mn-Cu \text{ cathode}: H_2O + e \rightarrow [H] + OH$$
(2)

$$\mathbf{R}...\mathbf{R}' + \mathbf{OH} + [\mathbf{H}]/\mathbf{alloy} \rightarrow \mathbf{ROH} + \mathbf{R}'\mathbf{H}$$
(3)

# 3.2. Electrochemical degradation of lignin in the three-dimensional electrode reactor

As shown in Fig. 5, two different analysis methods by GC were applied to analyze the samples. It was found that the main product 4-methylanisole, and coproducts 2,6-dimethoxyphenol, vanillin, acetovanillone, syringaldehyde, toluene as well as styrene were confirmed by internal standard method which corresponded with the retention time at 8.39, 2.07, 3.02, 3.28, 5.67, 2.77 and 5.30 min respectively. Some other unidentified products were also observed.

The electrochemical oxidation of lignin was conducted at 50 mA/cm<sup>2</sup>. The residual amount of lignin and the products yield of lignin degradation were shown in Fig. 6. About 88% lignin had been decomposed within first 5 h. At the end of degradation 8 h, lignin was almost completely degraded, the residual lignin was only 1.5 g/L and the cumulative yield of main product 4-methylanisole reached 343.3 (g/kg lignin). Other coproducts yield, such as vanillin and syringaldehyde, was shown in the micro-enlarge figure of Fig. 6.

# 3.3. Optimization of operating parameters for electrocatalytic degradation of lignin

Because the effective content of products was comparatively high in first hour and second hour, the operating parameters for electrocatalytic degradation of lignin were therefore optimized in unit hour, and the maximum yield of seven kinds of products was listed in Table 1.

All experiments were carried out with aspen lignin dissolving in the concentration 1 mol/L of NaOH solution to give a homogeneous system. As shown in Table 1, it was found that in unit time the maximum yield of main product 4-methylanisole (64.9 g/kg lignin) was achieved in run 1 as following optimal operations: the content of aspen lignin dissolving in alkali liquid 40 g/L, current density 50 mA/cm<sup>2</sup>, temperature 50 °C, in 2nd hour, the volume ratio of extraction solvent ethyl acetate to lignin degradation liquid (R) was 1. Similar with this operations, the maximum yield of coproduct styrene was 1.8 g/kg lignin at 60 mA/cm<sup>2</sup> (as



Fig. 5. Lignin degradation products (black line) and standard substance (red line) gas chromatograms with column temperature constant method (M) and temperature programming method (N).



Fig. 6. Effective content of lignin and products during the lignin degradation.

seen in run 3), and 2,6-dimethoxyphenol was 9.48 g/kg lignin at temperature 50 °C (as seen in run 4). The selection of the extraction solvent affected the extraction efficiency of lignin degradation products. For example, if the extraction solvent was chloroform instead of ethyl acetate as shown in run 8, not only didn't get the styrene, but also the extraction efficiency of other products reduced obviously. Other extraction solvents, 1,1,1-trichloroethane and anisole, seemed don't fit for extraction yet.

Fig. 7(I) showed that the maximum yield of 4-methylanisole appeared in the lignin concentration of 40 g/L, beyond that the yield was no longer enhanced with the raw material lignin concentration increased. Because lignin was one of the antioxidants [17], excessive lignin had made the antioxidation increase greatly so that the effect of the raw material lignin concentration on the yield of 4-methylanisole was not crucial.

The impact of current density on the electrochemical oxidation of lignin was presented in Fig. 7(II). For 40 g/L lignin mentioned above, lignin oxidation was accelerated with an increase of the applied current density from 20 to 50 mA/cm<sup>2</sup>. The extra current density over 50 mA/cm<sup>2</sup> exhibited indistinctive contribution to the oxidation of lignin. According to the theory proposed by Scialdone [18], higher values of current density resulted in a marked decrease of the faradic efficiency of the electrolysis process [19]. It was revealed in Fig. 7(III) that the yield of 4-methylanisole increased with temperature rising from 30 to 50 °C. Because the 'OH radical was one of oxidants, if the temperature continuously increased, oxidants would be decomposed [20,21]. Therefore, part of the 'OH was broken when temperature was higher than 50 °C, which leaded to the reduction of 4-methylanisole.

# 4. Conclusion

In this study, we have put forward a novel preparation of 4methylanisole from aspen lignin in alkali solution by threedimensional electrode reactor. The  $\beta$ -PbO<sub>2</sub> crystal on the surface of Pb/PbO<sub>2</sub> electrode played an effective role on providing 'OH radical for lignin oxidation degradation. And the [H] atom was supplied with the electrolysis of water molecule while the cathode potential became lower than the equilibrium potential. Lignin was firstly cracked to intermediates by 'OH radical oxidation, and then hydrogenation by [H] atom made the intermediates molecular bond saturation so that new compounds were given. The cumulative yield of main product 4methylanisole reached 343.3 (g/kg lignin) at the end of degradation 8 h with the optimal conditions as following: aspen lignin content 40 g/L, current density 50 mA/cm<sup>2</sup>, temperature 50 °C. By the end of 8 h

Run	Reaction phase	Extraction phase	R	Current	Т	Time	Product yie	lds (Y, g/kg lignin h <sup>-</sup>	(1				
	(lignin, g/L NaOH lignin)			density (mA/cm <sup>2</sup> )	(°C)	(h)	Vanillin	Syringaldehyde	Toluene	Styrene	Acetovanillone	4-Methylanisole	2,6-Dimethoxyphenol
1	40	Ethyl acetate	1	50	50	2nd	31.80	11.90	2.14	1.63	4.60	64.90	7.43
2	40	Ethyl acetate	2	50	50	2nd	23.50	12.40	2.60	2.53	2.10	69.20	9.60
ŝ	40	Ethyl acetate	1	60	50	2nd	11.30	6.50	1.90	1.80	2.17	40.00	9.20
4	40	Ethyl acetate	1	60	50	1st	4.25	13.75	1.90	1.20	4.02	40.25	9.48
5	50	Ethyl acetate	1	50	40	1st	33.30	12.20	1.63	0.70	2.18	39.25	6.93
9	50	Ethyl acetate	1	50	60	1st	12.00	6.78	1.88	1.48	4.68	33.30	7.10
7	50	Ethyl acetate	1	50	70	2nd	11.50	9.48	2.33	1.15	2.18	33.25	6.98
8	40	Chloroform	1	50	50	2nd	8.80	4.00	1.78	0.00	2.16	34.75	5.60
6	40	1,1,1-Trichloroethane	1	50	50	2nd	4.75	5.00	1.15	0.00	0.00	23.75	0.00
10	40	Anisole	1	50	50	2nd	3.38	0.00	0.00	0.00	2.10	33.00	4.50
R stands	for the volume ratio c	of extraction solvent to lignin e	degradat	ion liquid.									

**Table 1** 



Fig. 7. The effects of reaction factors on yield of 4-methylanisole. (I) Raw material lignin concentration, (II) current density, (III) temperature.

of lignin degradation, most of aspen lignin had been decomposed. Other coproducts such as vanillin, syringaldehyde, 2,6-dimethoxyphenol, acetovanillone, toluene, and styrene were also achieved. In summary, the electrocatalytic degradation of lignin is a promising approach for the conversion of lignin into valuable products such as 4-methylanisole, which not only enhances the potential utility of lignin but also produces fine chemicals instead of the fossil raw materials.

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# References

- [1] C.R. Lee, J.S. Yoon, Y.W. Suh, J.W. Choi, J.M. Ha, D.J. Suh, Catal. Commun. 17 (2012)
- 54 P. Parpot, A.P. Bettencourt, E.M. Belgsir, J. Appl. Electrochem. 30 (2000) 727.
   B. Mahdavi, A. Lafrance, A. Martel, Appl. Electrochem. 27 (1997) 605.

- [4] Y.M. Zhang, Y. Peng, X.L. Yin, Zh.H. Liu, G. Li, J. Chem. Technol. Biotechnol. 89 (2014).
- L. Wei, S. Guo, G. Yan, C.M. Chen, Electrochim. Acta 55 (2010) 8615. [5]
- L. Xu, H.Z. Zhao, S.Y. Shi, Dyes Pigments 77 (2008) 158. [6] X.B. Wu, X.Q. Yang, D.C. Wu, Chem. Eng. J. 138 (2008) 47.
- T. Hmed, K. Mahsa, G. Mohammad, R. Parisa, C.G. Bruce, Energy Fuel 28 (2014) 4545. [8]
- X. Li, D. Pletcher, F.C. Walsh, Chem. Soc. Rev. 40 (2011) 3879. [9]
- L. Xu, H. Zhao, S. Shi, G.Z. Zhang, J.R. Ni, Dyes Pigments 77 (2008) 158. [10]
- [11] Y. Zheng, W. Su, S. Chen, X.Z. Wu, X.M. Chen, Chem. Eng. J. 174 (2011) 304.
- [12] P. Veluchamy, M. Sharon, J. Electroanal. Chem. 361 (1993) 261.
- M.A. Quiroz, S. Reyna, C.A. Martinez-Huitle, S.A. Ferro, Appl. Catal. B Environ. 59 [13] (2005) 259.
- [14] D. Claus, O.B. Jurgen, John Wiley & Sons, Germany, 2011 p.169.
- [15] K. Jurewicz, E. Frackowiak, F. Beguin, Appl. Phys. A 78 (2004) 981.
- A. Manabe, M. Kashiwase, T. Hashimoto, T. Hayashida, A. Kato, K. Hirao, Electrochim. [16] Acta 100 (2013) 249.
- [17] K. Toh, H. Yokoyama, H. Noda, Y. Yuguchi, J. Food Biochem. 34 (2010) 192.
- [18] O. Scialdone, A. Galia, C. Guarisco, S. Randazzo, Electrochim. Acta 53 (2008) 2095.
- C. Tang, W. Yan, C. Zheng, Front, Environ, Sci. Eng, China 8 (2014) 337. [19]
- F.L. Souza, J.M. Aquino, D.W. Miwa, M.A. Rodrigo, J. Environ. Chem. Eng. 2 (2014) [20] 811.
- [21] M. Panizza, G. Cerisola, J. Hazard, Mater. 153 (2008) 83.