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Article

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Partial oxidation of synthesized wastewater containing lignin to vanillin and phenol under mild conditions

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Abstract

Partial oxidation of synthesized wastewater containing lignin to form phenol and vanillin was investigated. The reactions were carried out in a high-pressure reactor at various temperatures in the range of 140–200 °C and under the air atmosphere with the initial air pressure of 2 bar for 75 min. The addition of NaOH has a strong effect on the formation of vanillin and phenol. The results showed that the highest vanillin concentration of 23.4 ppm and the highest phenol production of 30 ppm were obtained at a temperature of 140 °C and 200 °C, respectively. The vanillin and phenol can be produced from the partial oxidation of wastewater containing lignin at mild conditions.

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Keywords: Phenol; Vanillin; Hydrothermal; Waste management

1. Introduction

Lignin has been reported as a natural resource that is rich in aromatic structure. It has a high potential to use as an alternative source for the production of fuel and high-value products [1]. Wastewater discharged from the pulping process is typically rich in lignin that may cause the undesired color of treated wastewater. There are many researchers report that lignin in the liquid phase can be converted into high value-added compounds such as phenol and vanillin. However, the main problem for the utilization of lignin is poor reactivity due to the condensed structure

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of lignin [2]. Therefore, the reactivity of lignin can be increased by degrading it into phenolic compounds. The degradation of lignin is widely studied, including biodegradation [3], pyrolysis [4], and oxidation [5,6]. Phenol and vanillin which have significant applications in the chemical, pharmaceutical, food, and fuel industries can be produced from lignin degradation by partial oxidation method [7]. Phenol is one of the productions of lignin oxidation, which was proposed to form by two reaction steps; firstly, lignin is depolymerized into lower molecular weight compounds and partly into lignin constituent monomer, dimers, and oligomers. For the second step, the depolymerized products were oxidized into phenolic compounds [8]. NaOH has been reported that it can catalyze the decomposition of carbonyl compounds in partial oxidation of lignin in supercritical water [9]. However, it can occur at severe conditions, high temperature and high pressure that cause high-energy consumption to maintain a high rate of lignin degradation. It is interesting to use the NaOH as a catalyst for the decomposition of lignin; it may reduce the severe condition to a mild condition. Thus, this study aims to investigate the influence of NaOH on the production of vanillin and phenol by partial oxidation at mild conditions using the hydrothermal process.

2. Materials and methods

2.1. Partial oxidation of lignin

The partial oxidation of lignin was performed in a batch high-pressure reactor. Kraft lignin solution was prepared by dissolving 1 g of lignin powder (AR grade) purchased from Sigma-Aldrich in 1 l of distilled water and adjusted the solution pH to 10 by adding 1N sodium hydroxide purchased from Loba Chemie PVT.Ltd., India. Then poured 400 ml of lignin solution into the reactor and fed air to increase the pressure of the reactor to an initial value of 2 bars. After that, the reactor was heated to elevated reaction temperature (160–200 °C) and kept it constant for 75 min. During the reaction, 5 ml of samples were drawn from the reactor every 15 min.

The next series of experiments for studying the effect of adding more NaOH followed the same steps as described before except the preparation of lignin solution prepared by dissolving 1 g of lignin and 2 g of NaOH in 1 l of distilled water.

2.2. Sample analysis

The sample was filtered through a 0.22 µm syringe filter (Lubitech). Phenol and vanillin concentrations were analyzed using High-Performance Liquid Chromatography, HPLC (HPLC Alliance waters e2695, USA) equipped with an entafluorophenyl C18 column (250 mm × 3.0 mm, five µm, KNAUER). The gradient elution was performed using a solvent system comprising solvent A (water with 0.1% acetic acid) and B (99.9% methanol) with a constant flow rate of 0.8 ml/min during the 35 min analysis. A linear gradient programming was carried out with an initial composition of 90% A, gradually changing to 77% A in 30 min, then kept it constant for 5 min. The peaks of vanillin and phenol were detected using a UV/Visible detector (Water 2489 UV/Visible, USA) at wavelengths of 274 nm.

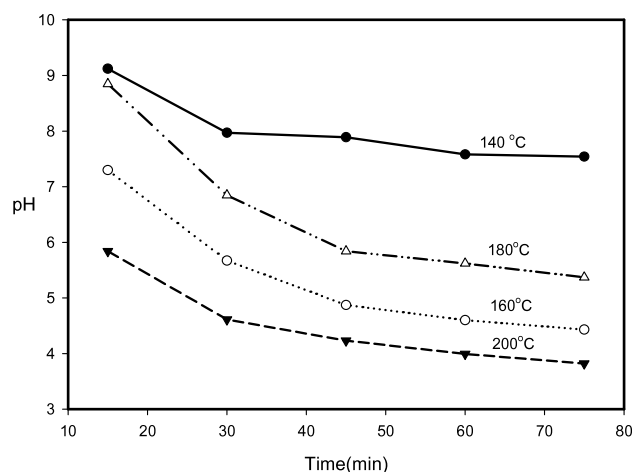
3. Results and discussion

The objective of this work was to determine proper operating conditions for partial oxidation of lignin to produce vanillin and phenol. The effects of temperature, reaction time, and NaOH concentration on the formation of vanillin and phenol were studied. The results of partial oxidation of an aqueous lignin solution with various NaOH concentrations at the temperature of 140 °C, 160 °C, 180 °C, and 200 °C for 75 min shows in Table 1. The results indicate that the presence of NaOH shows a higher concentration of vanillin and phenol than that of the lignin solution without the adding of NaOH. The pH of the treated mixture collected during the reaction at various temperatures shows in Fig. 1. It shows that the long reaction time gives the high formation of acid products. According to the decrease of pH, it was correlated with the decrease of vanillin concentration in alkaline oxidation [10]. Moreover, the presence of carboxylic acid may cause the precipitation of lignin in the acidic region, which affects the depolymerization of lignin. The presence of NaOH can neutralize the acid compounds and keep the pH of the solution in the alkaline region. These phenomena can support the data shown in Table 1.

Lignin was oxidized in a conventional batch reactor under the initial air pressure of two bars. The total pressure was increased during the heating-up period and then constantly due to the reaction temperature was constant.

Table 1. Vanillin and Phenol concentrations after the oxidation of lignin solution at the initial air pressure of 2 bars for 75 mins.

Reaction temperature (°C)	Lignin solution (not adding of NaOH)		Lignin solution (adding of NaOH)	
	Vanillin concentration (ppm)	Phenol concentration (ppm)	Vanillin concentration (ppm)	Phenol concentration (ppm)
140	1.5	1.8	23.4	24.4
160	2.6	1.7	10.8	21.3
180	4.2	3.8	17.2	24.1
200	0.3	1.2	14.9	29.0

**Fig. 1.** Changes of pH solution during the partial oxidation of lignin solution absence of NaOH.

Dissolved oxygen in the liquid phase increase with an increase of initial pressure and may cause further oxidation to acid compounds and carbon dioxide, as reported in our previous work. Sriprom et al. reported that wet air oxidation removed 75% of chemical oxygen demand in an aqueous lignin solution at the temperature of 200 °C and under an initial air pressure of 10 bars [11]. It suggests that dissolved organic compounds can be converted to lower molecular weight substances and some volatile products at high pressure and high temperature.

To study the influence of temperature and reaction time on vanillin production at 140 °C, 160 °C, 180 °C and 200 °C while keeping the initial air pressure of 2 bar and the initial lignin concentration of 1 g/L. As shown in Fig. 2, the highest vanillin concentration of 23.4 ppm was obtained at the temperature of 140 °C while vanillin produced from partial lignin oxidation was around 10.8 ppm at 160 °C, 17.2 ppm at 180 °C and 14.9 at 200 °C. The results indicate that the functional group was cleaved to give low molecular weight products at high temperatures. Therefore, vanillin production decreased with an increase in the reaction temperature.

Fig. 3 shows yields of phenol increased with an increase of temperature in the range of 140 °C to 200 °C, while the yields of phenols obtained around 20–30 ppm. The highest produced phenol was 30 ppm at a temperature of 200 °C. The result showed that the increase of temperature would catalyze the oxidation of lignin to form some low molecular weight products such as phenolic compounds and phenol.

As shown in Figs. 2 and 3, the yield of vanillin and phenol by lignin oxidation increased from 15.5 ppm to 23.4 ppm by extending the time from 15 min to 75 min at 140 °C. The yield of oxidation began to decline with a further increase in reaction time. The yield of vanillin and phenol reduced to 10.8 ppm for 160 °C, 17.2 ppm for 180 °C, and 14.9 ppm for 200 °C by extending the time from 15 min to 75 min. It was mainly due to the generation of decomposed products by the further oxidation of lignin-derived aromatic compounds to carbon dioxide.

4. Conclusions

The oxidation of lignin to produce vanillin and phenol by the hydrothermal technique in a batch reactor was studied. The reactional system includes a step of vanillin and phenol were formed from lignin oxidation and other reaction where vanillin and phenol were oxidized. Experiments using high-molecular weight lignin were achieved

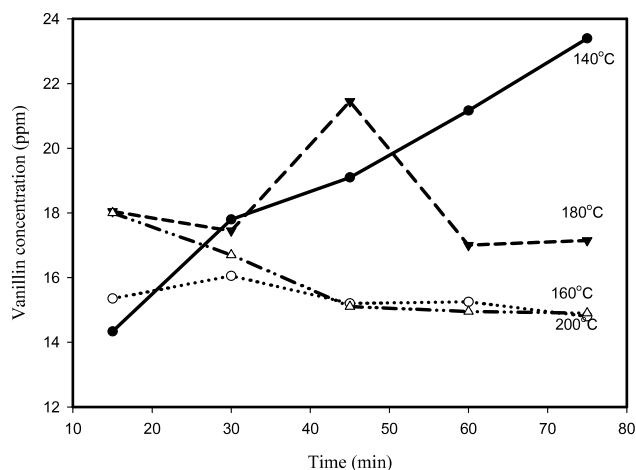


Fig. 2. Vanillin concentration during the partial oxidation of lignin under an initial air pressure of 2 bars and NaOH of 2 g.

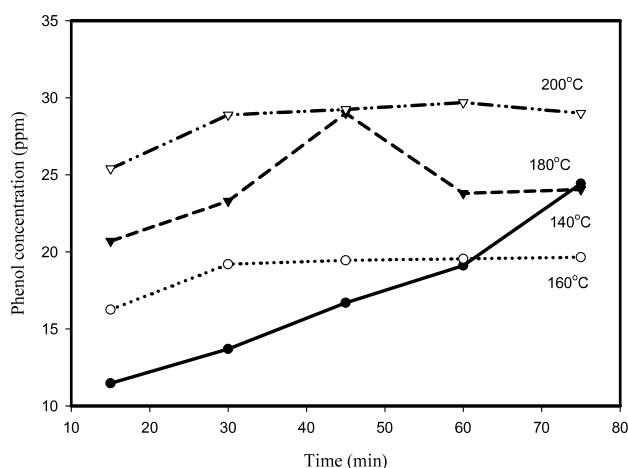


Fig. 3. Phenol concentration during the partial oxidation of lignin under an initial air pressure of 2 bars and NaOH of 2 g.

showing a lower conversion to vanillin and phenol when compared with low-molecular-weight lignin. A maximum of vanillin concentration of 23.4 ppm and a maximum of phenol concentration of 30 ppm were obtained. The highest produced vanillin and phenol were obtained at a temperature of 140 °C and 200 °C, respectively. The addition of NaOH is the most important factor in the partial oxidation of lignin to yield vanillin and phenol products. The presence of NaOH catalyzes this reaction to form high value-added product from lignin oxidation; however, the production rate of those products are quite low. For further study, the screening of a new catalyst should perform to give more yield of vanillin and phenol.

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References

- [1] Pouteau C, Dole P, Cathala B, Averous L, Boquillon N. Antioxidant properties of lignin in polypropylene. *Polym Degrad Stab* 2003;81(1):9–18.

- [2] Xiao B, Sun XF, Sun RunCang. The chemical modification of lignins with succinic anhydride in aqueous systems. *Polym Degrad Stab* 2001;71(2):223–31.
- [3] Bugg Timothy DH, Ahmad Mark, Hardiman Elizabeth M, Rahmanpour Rahman. Pathways for degradation of lignin in bacteria and fungi. *Nat Prod Rep* 2011;28(12):1883–96.
- [4] Collard François-Xavier, Blin Joel. A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses, and lignin. *Renew Sustain Energy Rev* 2014;38:594–608.
- [5] Das Lalitendu, Kolar Praveen, Sharma-Shivappa Ratna. Heterogeneous catalytic oxidation of lignin into value-added chemicals. *Biofuels* 2012;3(2):155–66.
- [6] Lange Heiko, Decina Silvia, Crestini Claudia. Oxidative upgrade of lignin—Recent routes reviewed. *Eur Polym J* 2013;49(6):1151–73.
- [7] Pacek Andrzej W, Ding Ping, Garrett Mark, Sheldrake Gary, Nienow Alvin W. Catalytic conversion of sodium lignosulfonate to vanillin: engineering aspects. Part 1. Effects of processing conditions on vanillin yield and selectivity. *Ind Eng Chem Res* 2013;52(25):8361–72.
- [8] Lora Jairo H, Glasser Wolfgang G. Recent industrial applications of lignin: a sustainable alternative to nonrenewable materials. *J Polym Environ* 2002;10(1–2):39–48.
- [9] Watanabe Masaru, Inomata Hiroshi, Osada Mitsumasa, Sato Takafumi, Adschiri Tadafumi, Arai Kunio. Catalytic effects of NaOH and ZrO_2 for partial oxidative gasification of n-hexadecane and lignin in supercritical water. *Fuel* 2003;82(5):545–52.
- [10] Fargues Claire, Mathias Álvaro, Rodrigues Alfrío. Kinetics of vanillin production from kraft lignin oxidation. *Ind Eng Chem Res* 1996;35(1):28–36.
- [11] Sriprom Pongsert, Neramittagapong Sutasinee, Lin Chitsan, Wantala Kitirote, Neramittagapong Arthit, Grisdanurak Nurak. Optimizing chemical oxygen demand removal from synthesized wastewater containing lignin by catalytic wet-air oxidation over CuO/Al_2O_3 catalysts. *J Air Waste Manage Assoc* 2015;65(7):828–36.