Technical Report

Optimization of Lignin Conversion by Hydrothermal Method for Recovery of Vanillin

Pongsert SRIPROM^{*1※2}, Pornyamon LEEPHISUTH^{*2※3※4}, Arthit NERAMITTAGAPONG^{*2※3※4},
and Sutasinee NERAMITTAGAPONG^{*2※3※4†}

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This work aimed to optimize lignin conversion to vanillin by hydrothermal method. An experiment was designed by Box-Behnken Design (BBD). Temperature, NaOH concentration, and reaction time were chosen as independent parameters for achieving the optimum reaction condition. The reaction products were analyzed by high-performance liquid chromatography. Based on the experimental results, the optimum condition for the hydrothermal process was predicted using the response surface method. The maximum vanillin production of 18.1 mg/L was predicted at the optimum condition given by the temperature of 142 °C, NaOH concentration of 9.2 g/L, and reaction time of 32 min. The conversion of lignin to vanillin was experimented using the predicted optimal condition to verify the prediction. It was found that the hydrothermal method at the optimum condition yielded 18.1 ± 2 mg/L of vanillin, which was in good agreement with the predicted value. It was also found that the yield of vanillin was influenced by temperature, NaOH concentration, and the interaction of both parameters, whereas the reaction time was much less influential.

Key Words

Lignin conversion, Vanillin, Hydrothermal

1. Introduction

Lignin is the main pollutant in pulp and paper wastewater, causing high color and organic concentrations. It has a large and stable polymer structure, which is detrimental to the environment^{1) 2)}. Some researchers reported that lignin in the liquid phase could be converted to high value-added compounds such as phenol and vanillin³⁾. The most commonly used method for the purpose is the hydrothermal decomposition technique. Hydrothermal

technologies are mostly described as chemical and physical conversions using high temperature and pressure. Several researchers have provided a positive assessment of hydrothermal conversion technology to be an effective technology to decompose polymer derived from plants. Thus, the hydrothermal technique was used for lignin conversion by several researchers^{4) ~ 8)}.

The aims of this study were to optimize the condition of lignin conversion for recovery of vanillin by the hydrothermal method and to assess the individual effects of lignin conversion parameters (temperature, NaOH concentration, and reaction time), and their interaction effects on the yield of vanillin.

2. Experiment

The optimization of experimental conditions for lignin conversion by the hydrothermal method was designed using Box-Behnken design (BBD) technique⁹⁾. The experimental results were then treated by the Regression Analysis to obtain the model for predicting the vanillin yield as a function of the condition parameters. The model was used to generate data to be used in the response surface

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- ※1 Program of Food Process Engineering,
Faculty of Agro-Industry,
King Mongkut's Institute of Technology Ladkrabang
Bangkok, 10520, Thailand
 - ※2 Research Program on Development of Appropriate
Technologies for Coloring Agent Removal from Textile
Dyeing, Pulp & Paper, Sugar Industries for Sustainable
Management, Center of Excellence on Hazardous Substance
Management (HSM)
Pathumwan, Bangkok, Thailand
 - ※3 Department of Chemical Engineering,
Faculty of Engineering, Khon Kean University
Khon Kean, 40002, Thailand
 - ※4 Research Center for Environmental and Hazardous
Substance Management (EHSM), Khon Kean University
Khon Kean, 40002, Thailand

† Corresponding author: sutasineene@kku.ac.th

methodology (RSM) to determine the optimal condition. The software MINITAB version 17.0 [Minitab Pty Ltd, Australia] was used for the experimental design, data analysis, quadratic model building, and graph plotting. A total of 15 experiments were conducted, and the conditions are shown in Table 1. The independent variables were, based on our preliminary experimental trials, reaction temperature (140 - 180 °C), NaOH concentration (4-20 g/L), and reaction time (15-45 min). In the table, -1 and +1 represented the lower and the upper limits, respectively, whereas 0 represented the mid-point of the ranges.

The hydrothermal process was carried out in a high-pressure batch reactor. 1000 mg/L of 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 sodium hydroxide pellet purchased from Loba Chemie PVT.Ltd., India. Four hundred milliliters of lignin solution was poured into the 1000 ml tubular reactor, and air from a pressure cylinder was used to increase the pressure of the reactor to an initial value of 2 bars. After that, the reactor was heated using a temperature controlled electric heater to an elevated reaction temperature at a rate of 5 °C/min and kept at the temperature for 75 min. During the reaction, 5 ml of samples were drawn from the reactor every 15 min for the concentration analysis of vanillin. Vanillin concentrations were analyzed using high-performance liquid chromatography (HPLC Alliance waters e2695, USA) equipped with a pentafluorophenyl C18 column (250 mm × 3.0 mm, 5 µm, KNAUER). The mobile phase was a mixture of 30% v/v methanol/water and 1% v/v acetic/water with the volumetric ratio of methanol solution to acetic acid of

30:70. The flow rate of mobile phase was kept constant at 0.75 ml/min. Vanillin was detected using a UV/Visible detector (Water 2489 UV/Visible, USA) at wavelengths of 274 nm.

3. Results and Discussion

The experimental results of vanillin concentration are also shown in Table 1. An approximate regression model of the vanillin concentration based on the experimental results can be expressed by the following polynomial equation:

$$Y = 17.1507 - 2.4764X_1 + 0.8622X_2 + 0.0325X_3 - 1.8962X_1^2 - 1.0545X_2^2 - 1.5574X_3^2 + 2.0X_1X_2 - 0.9029X_1X_3 + 0.9034X_2X_3 \quad (1)$$

where Y is the yield of vanillin in mg/L.

The linear-model term of temperature (X_1) and NaOH concentration (X_2) and the second-order terms of temperature(X_1^2), reaction time (X_3^2), were found to have a significant effect on vanillin concentration (all 95% confidence levels having a P-value <0.05). A study was also conducted of the interaction effects of variables, and it was found that only temperature and NaOH concentration (X_1X_2) had a significant interaction effect. Based on this discussion, the model can now be reduced to be,

$$Y = -63.1 + 1.178X_1 - 1.892X_2 + 0.396X_3 - 0.00454X_1^2 - 0.00656X_3^2 + 0.01250X_1X_2 \quad (2)$$

Adequacy check of the proposed model is an important part of the analysis. Good adequacy can ensure that the approximating model provides an adequate approximation to the real system. The diagnostic plots (the actual vanillin concentration vs. the predicted vanillin concentration) shown in Fig. 1 was applied to determine the adequacy of the regression model obtained. The actual

Table 1 Box-Benhken design of vanillin concentration from lignin conversion using a hydrothermal method and the results of the experiments

Order	Temperature X_1	NaOH concentration X_2	Reaction time X_3	Vanillin concentration yield (experimental data) (mg/L)
1	-1	-1	0	18.0
2	1	-1	0	9.3
3	-1	1	0	15.1
4	1	1	0	13.9
5	-1	0	-1	15.0
6	1	0	-1	12.1
7	-1	0	1	17.1
8	1	0	1	10.6
9	0	-1	-1	14.1
10	0	1	-1	15.1
11	0	-1	1	12.1
12	0	1	1	16.8
13	0	0	0	16.9
14	0	0	0	17.4
15	0	0	0	17.2

Fig. 1 The experimental vanillin yields and predicted values (mg/L)

vanillin concentration was the measured value for a run, and the predicted value was calculated from Eq.(2). As shown in Fig 1, a good agreement was obtained between the predicted vanillin concentration and the experimental values with R^2 of 0.9724.

As illustrated in Fig. 2, the residual plots were used to test whether the model satisfied the assumption made for analysis of variance (ANOVA). The response model was checked against four analyses, as shown in Fig. 2. The normal probability plot (Fig. 2 (a)) shows that the experimental data were scattered on the straight line, indicating that the normality assumption was satisfied. In Fig. 2 (b), the residual versus fits plot scattered randomly.

It can be seen that the data seemed to exhibit a relatively persistent variance across the predicted values. The histogram chart was presented in Fig. 2 (c), and it showed that the histogram had a form of an overturn bell. It implied that there was no abnormality in the data used. Fig. 2 (d) illustrated the residual versus order plot to indicate the random scatter around the centerline (in the range of ± 2)¹⁰. All the experimental data well distributed. Based on this discussion, it leads to the conclusion that the model was accurate and reliable.

Fig. 3 presents the contour plot representing the interactive effects of temperature, NaOH concentration, and reaction time on vanillin concentration yield by the hydrothermal reaction. Fig. 3 (a) demonstrates how the interactive relationship between temperature and NaOH concentration affects vanillin concentration. As can be seen, the system worked well under lower temperatures and lowered NaOH concentration. Fig. 3 (b) illustrates when the system works with a low temperature in the range of 140-150 °C, and the vanillin concentration increases with reaction time in the range of 30-35 min.

Fig. 3 (c) explains the interaction between NaOH concentration and reaction time. It has also demonstrated, when the system begins with higher NaOH concentration, the vanillin concentration increased with extended reaction time in the range of 20-40 min. As a summary in Fig. 3, we can conclude that when the system initiates with lower

Fig. 2 Internal standardized residual plots versus (a) normal probability, (b) fits, (c) histogram and (d) observation order for vanillin concentration

Fig. 3 Interaction effects of (a) NaOH concentration (mg/l) and temperature (°C), (b) reaction time (min) and temperature (°C), and (c) NaOH concentration (mg/l) and reaction time (min)

temperature, the vanillin concentration will increase along with that of NaOH concentration and reaction time. The results indicated that vanillin concentrations decreased with an increase in the reaction temperature due to the faster degradation of vanillin to other products at high temperatures¹¹⁾. Thus, the shorter reaction time yielded a higher vanillin concentration at high temperatures, as reported in the oxidation of kraft lignin to vanillin under alkaline conditions¹²⁾.

The performance of hydrothermal reaction can be evaluated in term of vanillin concentration, which largely varies with the change and the interactions in variables. Thus, Eq.(2) was used to generate the necessary data for the Response Surface Method for determining the optimal condition; It was found that the optimum conditions of reaction were given by the reaction temperature of 142 °C, 9.20 g/L of NaOH concentration, and 32 min of reaction

time. At this optimum condition, lignin could be converted to 18.1 mg/L of vanillin. The prediction of the regression model was verified by an additional three runs under the optimal conditions, resulting in a vanillin concentration of 18.1 ± 2 mg/L. This experimental value closely agreed with the theoretical value of 18.1 mg/L predicted by RSM, indicating that the RSM was an effective and reliable method for determining the optimum condition for the vanillin production from lignin conversion.

4. Conclusion

In lignin conversion to vanillin by the hydrothermal method, it was discovered that NaOH concentration, temperature, and reaction time were the influential operational parameters for the reaction. The optimum condition was determined to be given by the reaction temperature of 142 °C, NaOH concentration of 9.2 g/L,

and reaction time of 32 min. For the 18.1 mg/L of vanillin, concentration predicted, optimum conditions tested confirmed the vanillin concentration at 18.1 ± 2 mg/L. Finally, lignin can be converted to a higher value-added product such as vanillin by the hydrothermal conversion.

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