Isolation of lignin from rice husk at low temperature

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Abstract. Isolation of lignin commonly was conducted at a high temperature. This paper studies the isolation of lignin from rice husk at low temperature (30 °C) using alkaline hydrogen peroxide (AHP). Optimization of processes variables such as the volume of solvent to the weight of rice husk ratio, H2O2 concentration and pH were done using response surface methodology (RSM) with the central composite design. Characteristic of lignin obtained was analyzed by FT-IR (Fourier Transform Infrared). The results show that the main factor affecting the process isolation is pH both in linear and quadratic. The are several differences characteristics of rice husk lignin isolated at low temperature compared with rice husk lignin isolated at high temperature.

1. Introduction

Lignin isolation from biomass is one of the interesting topics that researchers continue to study. The focus of the research can divide into two types i.e. the sources of biomass and the method for lignin isolation. There are several sources of biomass that have been studied are wheat straw[1], rice straw[2], sugarcane bagasse[3], rice husk [4][5] and etc. Isolation methods can be conducted by several solvents such as acid solvent, alkali solvent, organic solvent (organosolv), ionic solvent, oxidative solvent and hot water. The selection of isolation process and solvent are an important factor in the process of isolation of lignin from biomass. The process and solvent selection will have an impact on the yield of lignin obtained and the costs of the isolation process.

In previous work, isolation of lignin from biomass was done at high temperature (100 °C) using alkaline hydrogen peroxide (AHP)[6]. This paper studies the isolation of lignin from rice husk at low temperature (30 °C) using alkaline hydrogen peroxide (AHP). Optimization of processes variables such as the volume of solvent to the weight of rice husk ratio, H2O2 concentration and pH were done using response surface methodology (RSM) with the central composite design (CCD). The Characteristic of lignin obtained was analyzed using FT-IR (Fourier Transform Infrared). The characteristic of lignin obtained at low temperature (RHL LT) will compare with rice husk lignin isolated at high temperature (RHL HT).

This study aims to examine the most influential variables and process conditions in the lignin isolation process at a low temperature which are characterized by the optimum of lignin yield. The optimum process conditions are expected to reduce the cost of the isolation process.
2. Materials and Methods

2.1. Materials
Rice husk obtained from rice milling in Banyumas district. The husk is blended and filtered until the size of the 60 mesh passes. NaOH and H₂O₂ were obtained from Merck.

2.2. Methods
The lignin isolation process was carried out using an alkaline hydrogen peroxide (AHP). A grain of 8 grams of rice husk is inserted in the erlenmeyer, then add 80 ml demineralized water containing 1% H₂O₂ 0.5% H₂O₂ (volume of solvent/weight of rice husk ratio of 8:1). Add 2N NaOH until pH 10 achieved. The mixture is then extracted at room temperature (29 – 30 °C) for 24 hours. The mixture is stirred by using a magnetic stirrer. After extraction, the mixture was filtered by the paper filter. The concentration of lignin in the filtrate (liquor) was analyzed using UV-Vis at the wavelength of 280 nm.

2.3. Data analysis
The concentration of lignin in the liquor was the yield of the isolation process. The design of the experiment (DOE) and the yield of lignin isolation are shown at Table1. The analysis of RSM was done using STATISTICA 6.0. The quadratic polynomial model was used to determine the response of each variable and the interaction of variables. The equation of quadratic polynomials is shown in Equation:

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i<j}^{k} \beta_{ij} X_i X_j + \varepsilon \]  

Analysis of variance (ANOVA) was used to evaluate the suitability of the model obtained with the experimental data. The F Value was used as a basis for consideration in determining the suitability of the model.

2.4. Characterization of Rice Husk Lignin
Rice husk lignin obtained at low temperature isolation (RHL LT) was then characterized using Fourier Transform Infrared (FT-IR) spectrophotometer (SHIMADZU with DRS-8000). Scans were recorded from 400 to 4000 cm⁻¹ at a resolution of 16 cm⁻¹.

3. Results and Discussion

3.1. RSM Optimization
RSM is a statistical method for experimental design, mathematical modeling, optimization and statistical analysis in research. Table 1 shows the runs of the experiment and the yield of lignin concentration in the liquor. The higher concentration in the liquor during lignin isolation process at a low temperature is 1.5695%. In the previous work, isolation of lignin from rice husk at high temperature, the higher concentration of lignin in the liquor reached 1.885% [4].

The mathematical model of a second-order polynomial equation for the three factors of yield in this experiment was obtained through regression analysis as shown in Equation (2):

\[ Y = 1.532935 - 0.042895 X_1 + 0.053956 X_2 + 0.624128 X_3 - 0.124287 X_1^2 - 0.131686 X_2^2 - 0.499332 X_3^2 - 0.033980 X_1 X_2 - 0.005410 X_1 X_3 - 0.004699 X_2 X_3 \]
Table 1. The design of $2^3$ full factorial CCD and yield

| Run | Volume to weight ratio ($X_1$) | $H_2O_2$ concentration ($X_2$) | pH ($X_3$) | Yield, % |
|-----|--------------------------------|-------------------------------|------------|----------|
| 1   | 8 (-1)                         | 0.5 (-1)                      | 10 (-1)    | 0.599326 |
| 2   | 8 (-1)                         | 0.5 (-1)                      | 12 (+1)    | 1.433495 |
| 3   | 8 (-1)                         | 1.5 (-1)                      | 10 (-1)    | 0.683271 |
| 4   | 8 (-1)                         | 1.5 (+1)                      | 12 (+1)    | 1.504832 |
| 5   | 10 (+1)                        | 0.5 (-1)                      | 10 (-1)    | 0.606744 |
| 6   | 10 (+1)                        | 0.5 (-1)                      | 12 (+1)    | 1.426882 |
| 7   | 10 (+1)                        | 1.5 (+1)                      | 10 (-1)    | 0.619518 |
| 8   | 10 (+1)                        | 1.5 (+1)                      | 12 (+1)    | 1.433471 |
| 9   | 7.318321 (-α)                  | 1 (0)                         | 11 (0)     | 1.569556 |
| 10  | 10.68179 (+α)                  | 1 (0)                         | 11 (0)     | 1.475254 |
| 11  | 9 (0)                          | 0.159104 (-α)                 | 11 (0)     | 1.454327 |
| 12  | 9 (0)                          | 1.840896 (+α)                 | 11 (0)     | 1.569556 |
| 13  | 9 (0)                          | 1 (0)                         | 9.31821 (-α) | 0.703037 |
| 14  | 9 (0)                          | 1 (0)                         | 12.6818 (+α) | 1.280985 |
| 15  | 9 (0)                          | 1 (0)                         | 11 (0)     | 1.57003 |
| 16  | 9 (0)                          | 1 (0)                         | 11 (0)     | 1.486037 |
| 17  | 9 (0)                          | 1 (0)                         | 11 (0)     | 1.486037 |

The accuracy of the model can be known by the coefficient of determination, $R^2$ which reaches 0.81385. It can be concluded that the estimated value with the model approaches the value obtained from the experimental results. The result of ANOVA using STATISTICA indicate that the calculated F-value of the lignin concentration of liquor at 31,9501 is much greater than that of F distribution table ($F_{table(0.95;7,16)} = 3.4944$) at 5% level of significance (Table 2). Figure 1 shows the comparison between the observed value and the projected lignin concentration value in the liquor.

Table 2. ANOVA results for the lignin concentration of liquor model

| Source   | Sum of square | Degree of freedom | Mean Square | F-value |
|----------|---------------|-------------------|-------------|---------|
| SS regresi | 2.143707     | 9                  | 2.143707    | 31.9501 |
| SS error  | 0.469667     | 7                  | 0.067095    |         |
| SS total  | 2.522991     | 16                 |             |         |
| $R^2$     | 0.81385       |                    |             |         |
Figure 1. Observed value versus the projected value of lignin concentration in liquor

Table 3 shows that the pH ($X_3$) has the greatest effect on rice husk isolation process with 95% confidence level indicated by the smallest p-value ($0.002964 < 0.05$). The quadratic pH ($X_3^2$) also has an effect on the isolation of rice husk with a 95% confidence level indicated by p-value ($0.0143 < 0.05$). These results show that the isolation of lignin from rice husk at low temperature has the same condition with one at high temperature [4].

| Factor | Coefficient | p-Value |
|--------|-------------|---------|
| Intercept | 1.532935 | 0.000018 |
| $X_1$ | -0.042895 | 0.768513 |
| $X_1^2$ | -0.124287 | 0.447014 |
| $X_2$ | 0.053956 | 0.711743 |
| $X_2^2$ | -0.131686 | 0.421638 |
| $X_3$ | 0.624128 | 0.002964 |
| $X_3^2$ | -0.499332 | 0.014327 |
| $X_1.X_2$ | -0.033980 | 0.858082 |
| $X_1.X_3$ | -0.005410 | 0.977263 |
| $X_2.X_3$ | -0.004699 | 0.980250 |

Table 4 shows that the optimum conditions for lignin extraction from rice husk at low temperature are at the volume to weight ratio of 8.78, the $\text{H}_2\text{O}_2$ concentration of 111 % and pH of 11.62. In optimum condition, the amount of lignin extraction is 1.5357%. Figure 2 shows the lignin concentration in the liquor at various pH and $\text{H}_2\text{O}_2$ concentration.
Table 4. The critical condition of lignin isolation at low temperature

| Factors                      | Observed minimum | Critical value | Observed maximum |
|------------------------------|------------------|----------------|------------------|
| volume to weight ratio       | 7.318207         | 8.78353        | 10.68179         |
| \( \text{H}_2\text{O}_2 \) concentration | 0.159104         | 1.11082        | 1.84090          |
| pH                           | 9.318207         | 11.62509       | 12.68179         |

Figure 2. The surface response of lignin isolation at various \( \text{H}_2\text{O}_2 \) concentration and pH

3.2. FT-IR Analysis

Figure 3 shows the FT-IR spectra of rice husk lignin isolated at low temperature and high temperature. There are several differences based on the peaks. The peaks of 1670–1640 (C=O stretching in conjugated p-substituted aryl ketones) and 1035–1030 (Aromatic C-H in plane deformation (\( G > S \)) plus C-O deformation in primary alcohols plus C=O stretching (unconjugated) are not found in the FT-IR spectra of lignin isolated at low temperature. Detail of FT-IR analysis of rice husk lignin can be seen at Table 5.

Figure 3. FT-IR spectra of rice husk lignin: (a) low temperature; (b) high temperature
Table 5. FT-IR spectroscopy of rice husk lignin

| Wavelength (cm\(^{-1}\)) | Assignment                                                      | RHL LT      | RHL HT      | Organosolv RHL [5] |
|--------------------------|-----------------------------------------------------------------|-------------|-------------|--------------------|
| 1740–1680                | C=O stretching in unconjugated ketone, carbonyl and ester groups | 1712.79     | 1720.50     | 1700               |
| 1670–1640                | C=O stretching in conjugated p-substituted aryl ketones         | n.d         | 1635.64     | 1650               |
| 1515–1505                | Aromatic skeleton vibrations                                    | 1535.34     | 1512.19     | 1510               |
| 1470–1450                | C-H deformation (asymmetric in -CH\(_3\) and -CH\(_2\)-)        | 1458.18     | 1458.18     | 1455               |
| 1440–1420                | Aromatic skeleton vibrations combined with C-H in plane deformations | 1396.48     | 1419.61     | 1420               |
| 1370–1350                | Aliphatic C-H stretching in CH\(_3\) (not -OCH3) and phenolic –O-H | 1365.60     | 1365.60     | 1355               |
| 1170–1160                | Typical for H, G, S units of lignin                             | 1203.58     | 1180.43     | 1165               |
| 1120–1115                | Aromatic C-H in plane deformation                               | 1126.43     | 1141.36     | 1120               |
| 1035–1030                | Aromatic C-H in plane deformation (G > S) plus C-O deformation in primary alcohols plus C=O stretching (unconjugated) | n.d         | 1095.53     | 1035               |
| 845–830                  | p-Substituted phenolic                                         | 941.26      | 964.41      | 835                |

4. Conclusion

That the main factor affecting the process isolation is pH both in linear and quadratic. The optimum conditions for lignin extraction from rice husk at low temperature are at the volume to weight ratio of 8.78, the H\(_2\)O\(_2\) concentration of 1.11 % and pH of 11.62. In optimum condition, the amount of lignin extraction is 1.5357%. The rice husk lignin isolated at low temperature has specific characteristic and different with the rice husk lignin isolated at high temperature.

Acknowledgments

The authors are grateful to Dissertation Program of LPDP ministry of finance in providing a grant to conduct this research.

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