Effect of microwave assisted sodium hydroxide pretreatment on hemicellulose content of oil palm empty fruit bunch for furfural production

I N Sadrina, A F P Harahap, A A Rahman and M Gozan*
Bioprocess Engineering Program, Chemical Engineering Department, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, 16424, Indonesia

*Email: mrgozan@gmail.com

Abstract. Oil Palm Empty Fruit Bunch (OPEFB) is one of the main types of solid waste which is continuously produced from palm oil mills. OPEFB contains lignocellulose to which the hemicellulose can be converted into furfural, an important precursor material used for producing high value chemicals, by means of a hydrolysis reaction. This process must be preceded by pretreatment in order to disrupt compact lignocellulose structure of OPEFB and to expose hemicellulose for further hydrolysis reaction. In this study, the optimum pretreatment conditions of OPEFB for hemicellulose recovery by microwave assisted alkali method with aqueous sodium hydroxide is evaluated by using response surface methodology (RSM) based on three-level three-factorial Box-Behnken design. OPEFB powder with different size ranging from 30-40 mesh was immersed into sodium hydroxide solution at 1:10 solid-liquid ratio. Variations of sodium hydroxide concentrations (1; 2; 3%), microwave power (280; 560; 840 Watt), and radiation time (3; 6; 9 minutes) were examined in this study. The quadratic model showed that pretreatment at 593.43 Watt and 1.15 % sodium hydroxide concentration for 5.99 minutes recovered the highest hemicellulose of OPEFB i.e. 23.22%.

1. Introduction
The increase in palm oil production from year to year has caused an increase in waste from year to year by the palm oil industry. One type of solid waste that is most often produced by palm oil mills is Oil Palm Empty Fruit Bunch (OPEFB). OPEFB is lignocellulosic biomass which contains 39.8% cellulose, 17.3% hemicellulose, and 28.8% lignin [1]. This composition shows that OPEFB has high cellulose and hemicellulose content, so that this waste has great potential to be utilized into several biochemical products. OPEFB has been used as a raw material for the production of levulinic and furfural acids with the highest yield of 52.1 mol% (sugar base C6) and 27.94 mol% (sugar base C5) respectively [2]. In addition, TKS can also be used as raw material in the manufacture of bioethanol through the process of delignification, acid hydrolysis, and fermentation [3].

OPEFB has a very complex lignocellulose structure requires pretreatment to increase the effectiveness of subsequent reactions, namely hydrolysis and fermentation reactions [3]. This pretreatment aims to reduce lignin, and increase the surface area and porosity of the lignocellulose structure so that it makes cellulose and hemicellulose easier to be converted at the next process. After delignification, the structure of lignin and hemicellulose ruptures, the crystalline part of cellulose stretches, and the crystallinity index decreases [4]. Alkali pretreatment has several advantages such as reducing cellulose crystallinity, reducing the degree of polymerization, and requiring low cost and
energy [5]. Delignification with sodium hydroxide can increase the internal surface area of the material with surface enlargement. This surface enlargement causes a decrease in the degree of polymerization, separation of the lignin and carbohydrate structure bonds, and damage the lignin structure [5].

Microwave-assisted alkali pretreatment is generally applied as of its high heating efficiency and easy procedure. Microwave heating helps alkali OPEFB pretreatment using 3% NaOH at 120-Watt microwave power for 12 minutes could remove 74% lignin, while conventional heating at 50°C for 80 minutes only could remove 69% lignin while using the same NaOH concentration [6]. The present study optimizes some conditions of OPEFB microwave assisted alkaline pretreatment such as: microwave power, NaOH concentration, and radiation time.

2. Materials and Methods

2.1 Materials

OPEFB powder was obtained from Center for Starch Technology (BBTP) Research and Assessment of Technology (BPPT) Lampung, Indonesia. First, OPEFB was filtered through a 30 mesh sieve then dried at 125°C for 45 minutes, then placed in sealed plastic bag. Sodium hydroxide pellets for pretreatment was purchased from Merck.

2.2 Microwave alkali pretreatment

OPEFB preparation was carried out using a domestic microwave oven (Electrolux EMS3087X). The pretreatment was initiated by mixing 70 g of OPEFB powder and 700 mL of NaOH solution in a 1000 mL volume glass flask, in microwave power, NaOH concentration, and reaction time condition that according to the experimental design. Then, the pre-treated sample were cooled and filtered through a 10 μm BIPMED BI filter paper using vacuum filtration to separate the solid and liquid fractions. After that, the solid fraction was neutralized until it reached pH 7 by using distilled water and then dried using an oven at 80°C for 12 hours. Finally, the solid fraction milled in a blender. The milled OPEFB samples were stored in sealed plastic bottle.

![OPEFB powder used as raw material.](image)
2.3 Design of experiments
Response Surface Methodology (RSM) based on Box-Behnken Design (BBD) is a suitable statistical method for modelling, statistical study, and the optimization. The design was used for a three-level variable on response function. Table 1 explains the experimental design inputs and factors, three independent variables were applied and arranged for low, center, and high levels (-1, 0, +1). The varieties of variables and experimental circumstances are revealed further in Table 1. The experimental design consists of 15 experimental runs by using a software Design Expert v.11 (Stat Ease Inc., Minneapolis, MN, USA) to perform analysis of variance (ANOVA), then it could present response surfaces.

Table 1. Factors, the ranges of variables, and levels in the Box-Behnken Model Design of OPEFB Alkali Pretreatment.

| Factors | Coded Parameters | Uncoded Parameters | Unit | Levels |
|---------|------------------|--------------------|------|--------|
| A       | Microwave power  | Watt               |      | -1, 0, +1 |
| B       | NaOH concentration | % (w/v) |      | -1, 0, +1 |
| C       | Radiation time   | min                |      | -1, 0, +1 |

2.4 Analysis
Before and after pretreatment, chemical component of the sample was analyzed in order to determine the hemicellulose content. Hemicellulose content was determined according to SNI 01-1561-1989. This analysis was carried out at the Chemical Laboratory of the Center for Pulp and Paper (BBPK) Bandung.

3. Results and Discussion
The design of Box-Behnken Design (BBD) model with the percentage of hemicellulose content as a response is shown in Table 2. By default, the high levels of the aspects are implied as +1 then the low levels are implied as -1. From Table 2, it can be seen that the highest percentage of hemicellulose content is 22.61% which achieved at pretreatment conditions: 560-Watt microwave power, 2% NaOH concentration, and 6 minutes radiation time.

Table 2. Box-Behnken Design Model in coded forms of process variables and values of hemicellulose content for OPEFB pretreatment.

| Run | Microwave Power (Watt) | NaOH Concentration (%) | Reaction Time (min) | Hemicellulose (%) |
|-----|------------------------|------------------------|---------------------|------------------|
| 1   | 0                      | -1                     | +1                  | 21.77            |
| 2   | -1                     | 0                      | -1                  | 20.19            |
| 3   | -1                     | +1                     | 0                   | 15.76            |
| 4   | 0                      | +1                     | -1                  | 14.64            |
| 5   | -1                     | -1                     | 0                   | 22.57            |
| 6   | 0                      | -1                     | -1                  | 22.17            |
| 7   | 0                      | 0                      | 0                   | 22.61            |
| 8   | +1                     | -1                     | 0                   | 21.63            |
| 9   | +1                     | 0                      | +1                  | 19.72            |
| 10  | +1                     | 0                      | -1                  | 20.56            |
| 11  | 0                      | 0                      | 0                   | 22.61            |
| 12  | +1                     | +1                     | 0                   | 16.46            |
| 13  | 0                      | 0                      | 0                   | 22.61            |
| 14  | 0                      | +1                     | +1                  | 15.71            |
| 15  | -1                     | 0                      | +1                  | 22.09            |
A regression equation and its coefficients on second-degree polynomial model of coded factors is given by Eqs. (1) where A, B, and C are respectively microwave power [Watt], NaOH concentration [% w / v], and radiation time [minutes]. Regarding to the second-degree polynomial model, the optimal condition for obtaining maximum hemicellulose content of 23.22% is as follows: microwave power of 593.43 Watt, NaOH concentration of 1.15% (w/v), and reaction time of 5.99 minutes.

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\text{Hemicellulose (%) } = + 20.61 - 0.28A - 3.20B + 0.22C + 0.41AB - 0.69AC + 0.37BC -0.72A^2 - 2.79B^2 - 1.25C^2
\]

As shown in Table 3, Analysis of Variance (ANOVA) could determine the significance of the model for the hemicellulose content in each condition of OPEFB pretreatment.

| Source                | Sum of Squares | df | Mean Square | F-value | p-value |
|-----------------------|----------------|----|-------------|---------|---------|
| Model                 | 119.17         | 9  | 13.24       | 90.66   | < 0.0001 significant |
| A-Microwave Power     | 0.6272         | 1  | 0.6272      | 4.29    | 0.0930 |
| B-NaOH Concentration  | 81.73          | 1  | 81.73       | 559.61  | < 0.0001 |
| C-Time                | 0.3741         | 1  | 0.3741      | 2.56    | 0.1704 |
| AB                    | 0.6724         | 1  | 0.6724      | 4.60    | 0.0847 |
| AC                    | 1.88           | 1  | 1.88        | 12.85   | 0.0158 |
| BC                    | 0.5402         | 1  | 0.5402      | 3.70    | 0.1125 |
| A²                    | 1.91           | 1  | 1.91        | 13.06   | 0.0153 |
| B²                    | 28.66          | 1  | 28.66       | 196.27  | < 0.0001 |
| C²                    | 5.78           | 1  | 5.78        | 39.58   | 0.0015 |
| Residual              | 0.7302         | 5  | 0.1460      |         |         |
| Lack of Fit           | 0.7302         | 3  | 0.2434      |         |         |
| Pure Error            | 0.0000         | 2  | 0.0000      |         |         |
| Cor Total             | 119.90         | 14 |             |         |         |

Other statistical parameter

| Std. Dev. | R²         | Adjusted R² | Predicted R² | Adeq Precision |
|-----------|------------|-------------|--------------|----------------|
| 0.3822    | 0.9939     | 0.9829      | 0.9026       | 26.2754        |

Table 3 shows that the model F-value of 90.66 implies the experimental model is significant. The value of Adjusted R² shows that 98.29% of the total variation in the experiment can be explained by the model. The significance of each regression coefficient and the relations between the pretreatment variables was assessed by means of p-value. p-value less than 0.0500 specify model terms are significant. In this instance, NaOH concentration (B), interactive effects between microwave power and time (AC), and quadratic effect of variables (A², B², & C²) are significant model relations. By default, value more than 0.1000 indicate the model terms are not significant. From overall observation, the NaOH concentration (B) is the most significant variable for increasing hemicellulose content of OPEFB due to its highest F-value (559.61) and the lowest p-value (<0.0001).

The normal plot of residual graph that indicates the relationship between the actual value and the predicted value (Figure. 2), where residual point is near the specified straight line (normal line). This shows that the data for hemicellulose content has spread normally so that the actual results approach the predicted results by Design Expert Program 11.
Figure 2. Predicted vs actual hemicellulose content of OPEFB.

Interactions between variables in OPEFB pretreatment can be presented in a three-dimensional (3D) response surface plot. Through the 3D response surface plot, the optimum hemicellulose content of each variable interactions can be observed. The 3D response surface plot is presented in Figure 3 a-c. Figure 3 can be observed that the effect of interaction between microwave power (A) and radiation time (C) shows a highly significant effect on increasing hemicellulose content compared to other interactions. This caused by the AC interaction has the highest F-value of 12.85 and the lowest p-value of 0.0158. These results indicate that increasing variables (A and C) could increase the hemicellulose content.

Figure 3. (a-b) Contour plots and 3D response surface for the effect of independent variables on OPEFB pretreatment.
4. Conclusion
The present study showed that microwave assisted sodium hydroxide OPEFB pretreatment was effective for furfural production by increasing hemicellulose content. Regarding the second-degree polynomial model, the optimal condition for obtaining maximum hemicellulose content of 23.22% is as follows: microwave power of 593.43 Watt, NaOH concentration of 1.15% (w/v), and reaction time of 5.99 minutes. Optimization with RSM showed that the most significant interaction effect with hemicellulose content was the interaction between microwave power and radiation time.

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