Microwave assisted aqueous ammonia pretreatment of oil palm empty fruit bunch: effect on lignin removal and morphological structure

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Abstract. Oil palm empty fruit bunch (OPEFB) is an abundant solid waste produced by oil palm industries to which the cellulose, hemicellulose, and lignin content has potential for conversion into high value biochemical products. However, pretreatment must be applied to remove lignin thus making cellulose and hemicellulose available for further conversion. In this study, effect of three parameters of microwave assisted aqueous ammonia pretreatment such as microwave power (280; 560; 840 Watt), NH₃ concentration (7.5; 10; 12.5 % w/v), and reaction time (3; 6; 9 minutes) on lignin removal (%) were evaluated by using response surface methodology with Box-Behnken design. OPEFB at different size ranging from 30 – 40 mesh was used as the raw material. Moreover, to evaluate the morphological structure, scanning electron microscope (SEM) analysis was employed both on untreated and pretreated OPEFB. The quadratic model showed that microwave power of 837.8 Watt, NH₃ concentration of 12.2% (w/v), and reaction time of 8.9 minutes resulted the highest lignin removal of 81.60%. SEM images showed that pretreated OPEFB encountered a heavy structural destruction. These results show that microwave assisted aqueous ammonia pretreatment can be a promising method to be applied to disrupt the compact lignocellulose structure of OPEFB and to remove its lignin content efficiently under very short period of time.

1. Introduction

Indonesia has great opportunity to utilize many biomasses as alternative fuel. One of Indonesia biomasses that can be used as alternative fuel is palm oil. Indonesia is one of the world’s largest producers of palm oil where its production is expected to increase from 38.5 million tons in 2018 to 40.5 million tons in 2019 [1]. The growth of Indonesia’s palm oil sector is expected to increase by 32% by 2020 to 60 million tons [2]. Due to growing palm oil industry in Indonesia, the availability of palm oil residue will also be created. One of the wastes from oil palm plantation is oil palm empty fruit bunches (OPEFB).

OPEFB is a lignocellulosic biomass which contains 36.67% cellulose, 13.50% hemicellulose, 31.16% lignin, 17.79% extractives, and 0.89% ash [3]. Cellulose and hemicellulose in OPEFB have potential to be converted into valuable biochemical products such as furfural and levulinic acid [4]. Pretreatment are necessary to remove lignin and increase the surface area as well as porosity of lignocellulose structure thus making both cellulose and hemicellulose readily available for further conversions.
Alkaline pretreatment of lignocellulosic biomass belongs to one category of chemical pretreatment processes and is an established process for the separation of the main components: lignin, cellulose, and hemicellulose. The use of alkali such as ammonia causes the cleavage of complex linkages of lignin-carbohydrate between phenolic and hemicellulose side-chains resulting in a structural alteration and removal of lignin which leads to an improved accessibility for further reactions of both cellulose and hemicellulose [5]. Recently, microwave assisted alkaline pretreatment is widely used because of its high heating efficiency and easy operation. Microwave assisted alkaline pretreatment of OPEFB using 3% NaOH solution had been proven to remove 74% lignin at microwave power of 120 Watt for 12 minutes while conventional heating at 50 °C for 80 min only removed 69% lignin with the same NaOH concentration [6].

The present study involves the optimization of some important conditions of OPEFB microwave assisted alkaline pretreatment using aqueous ammonia such as: microwave power, NH₃ concentration, and reaction time. The optimization was done by using statistical analysis method called Response Surface Methodology (RSM) which had been applied to study the effect of alkaline pretreatment on the physical properties of OPEFB [7].

2. Materials and methods

2.1. Materials

OPEFB powder was purchased from Center for Starch Technology (BBTP) Research and Assessment of Technology (BPPT) Lampung, Indonesia. OPEFB was first screened twice through a 30 and 40 mesh sieve then dried at 105°C for 4 h inside an oven. The sample was then put in sealed plastic bag and stored in a closed container at room temperature. Ammonia solution used as solvent was purchased from Merck. (Figure 1)

2.2. Microwave assisted pretreatment

Microwave assisted pretreatment was done using a microwave oven (Electrolux EMS3087X). For the pretreatment, 70 g of OPEFB and 700 mL NH₃ solution were mixed well together in 1000 mL beaker glass. Pretreatment was done under variated microwave power, NH₃ concentration, and reaction time according to design of experiments. After pretreatment, the samples were left to cool and filtered using BIPMED BI filter paper sized 10 µm with vacuum filtration to separate the black liquor and solid fraction. The solid fraction was then neutralized using distilled water at 60 °C. The collected solid fraction was dried inside an oven at 80 °C for 12 h and finally pulverized in a kitchen blender. The pulverized treated OPEFB samples were stored in sealed plastic bottles at room temperature until used for analysis.

2.3. Design of experiment

Response surface methodology (RSM) with Box- Behnken design (BBD) was applied to optimize the process variables which influence lignin removal. Three variables were chosen: microwave power A (280, 560, 840 Watt), NH₃ concentration B (7.5, 10, 12.5 % v/v), and reaction time C (3, 6, 9 minutes) to achieve highest lignin removal (%) of OPEFB. From preliminary experiments and literature reviews...
the range for each independent variables was selected. Each parameter was tested at three level coded as (-1) for lower level, (+1) for higher level, and a central coded value considered as zero (0) as it is depicted in Table 1. The experimental design consists of total 15 experimental runs and a software Design Expert v.11 (Stat Ease Inc., Minneapolis, MN, USA) was employed to perform analysis of variance (ANOVA) and to generate response surface curves.

2.4. Analysis methods
Lignin content of the OPEFB fibres was determined according to TAPPI T-222 om-83. Briefly, EFB fibres were hydrolysed and solubilized by H$_2$SO$_4$. The acid-insoluble lignin was filtered off, dried and weighed. In this method, lignin is defined as wood or pulp constituent insoluble in 72% H$_2$SO$_4$ [8]. Lignin content of untreated OPEFB was also determined as negative control for calculation of lignin removal as given in Eqs. (1) below.

$$\text{Lignin removal (\%) = } \left(\text{L}_c - \text{L}_t\right) / \text{L}_c \times 100\%$$

(1)

where $L_c$ = weight of lignin obtained from untreated OPEFB (g) and $L_t$ = weight of lignin obtained from each treated OPEFB (g).

Physical changes and surface characteristics of treated and untreated OPEFB samples were observed by scanning electron microscope (SEM LEO 420i) at Center for Materials Processing and Failure Analysis, Department of Material and Metallurgical Engineering Universitas Indonesia.

3. Results and discussion
The results at each point based on experimental Box-Behnken design template are presented in Table 2. The highest lignin removal of 63.32% was achieved at pretreatment conditions of 840 Watt microwave power, 10% NH$_3$ concentration, and 9 min reaction time. This result is still below the result of previous research by Nomanbhay (2013) whose highest lignin removal was 74% by using microwave assisted sodium hydroxide pretreatment [6]. But this result is higher than the result of previous result by Jung (2011) whose highest lignin removal was 41.1% by using conventional aqueous ammonia pretreatment with 21% ammonia at 60 °C for 12 hours [9].

The second-degree polynomial model for lignin removal in terms of actual factors is given by Eqs. (2)

$$\text{Lignin removal (\%) = } +160.62500 - 0.180451*A - 14.16500*B - 20.27708*C + 0.010821*AB + 0.010848*AC + 0.034000*BC + 0.000029*A^2 + 0.586600*B^2 + 1.51875*C^2$$

(2)

Table 1. Factors and their levels as used in the Box-Behnken model design of OPEFB pretreatment.

| Coded Parameters | Uncoded Parameters | Unit | Levels |
|------------------|--------------------|------|--------|
| A                | Microwave power    | Watt | -1     | 0      | +1     |
| B                | NH$_3$ concentration| % (v/v) | 280    | 560    | 840    |
| C                | Reaction time      | min  | 3      | 6      | 9      |

Table 2. Box-Behnken model in coded forms of process variables and values of experimental data for OPEFB pretreatment.

| Run | Microwave Power (Watt) | NH$_3$ Concentration (% v/v) | Reaction Time (min) | Lignin Removal (%) |
|-----|------------------------|------------------------------|---------------------|--------------------|-------------------|
|     |                        |                              |                     |                    |
Table 3. Statistical analysis for computed OPEFB pretreatment.

| Source         | Sum of Squares | df | Mean Square | F-value | p-value | 
|----------------|----------------|----|-------------|---------|---------|
| Model          | 3802.08        | 9  | 422.45      | 111.14  | <0.0001 | significant |
| A-Power        | 416.31         | 1  | 416.31      | 109.52  | <0.0001 |
| B-Conc.        | 733.83         | 1  | 733.83      | 193.06  | <0.0001 |
| C-Time         | 1370.52        | 1  | 1370.52     | 360.57  | <0.0001 |
| AB             | 229.52         | 1  | 229.52      | 60.38   | 0.0006  |
| AC             | 332.15         | 1  | 332.15      | 87.38   | 0.0002  |
| BC             | 0.2601         | 1  | 0.2601      | 0.0684  | 0.8041  |
| A²             | 19.60          | 1  | 19.60       | 5.16    | 0.0724  |
| B²             | 49.63          | 1  | 49.63       | 13.06   | 0.0153  |
| C²             | 689.85         | 1  | 689.85      | 181.49  | <0.0001 |
| Residual       | 19.01          | 5  | 3.80        |         |         |
| Lack of Fit    | 15.93          | 3  | 5.31        | 3.45    | 0.2326  | not significant |
| Pure Error     | 3.07           | 2  | 1.54        |         |         |
| Cor Total      | 3821.08        | 14 |             |         |         |

Other statistical parameter

| Std. Dev.       | 1.95           | R²  | 0.9950 |
| Mean            | 28.37          | Adjusted R² | 0.9861 |
| C.V. %          | 6.87           | Predicted R² | 0.9315 |
| PRESS           | 261.81         | Adeq Precision | 31.7011 |
Figure 2. RSM contour plots for the effect of independent variables on lignin removal of OPEFB. From Table 3, it is showed that the model is statistically significant with p-value at 95% confident level due to higher F-value (111.14) and lower p-value (<0.0001). The significance of each regression coefficient and the interactions between the pretreatment variables was evaluated using p-value. In this model, all the variables A (microwave power), B (NH$_3$ concentration) and C (reaction time) exhibit significant effects on lignin removal since its p-value is <0.05. Moreover, the interactive effects between variables (AB and AC) and quadratic effect of variables (B$^2$ and C$^2$) shows significant effects
on lignin removal. From overall observation, the reaction time (C) is the most significant variable for lignin removal of OPEFB due to its higher F-value (360.57) and lower p-value (<0.0001). The coefficient of determination ($R^2$) and adjusted $R^2$ was found to be 0.9950 and 0.9861, respectively. The relationship between independent and dependent variables was graphically represented by 3D response surface generated by the model (Fig. 2). It is observed that the interaction effect of microwave power (A) and reaction time (C) showed high significant effect on lignin removal than other interactions since it has high F-value of 87.38 and low p-value of 0.0002. This result indicates that increasing the variables (A and C) together will result in increased lignin removal.

**Figure 3.** SEM images of untreated (up) and treated OPEFB (down) in 2500x magnitude. SEM images before and after the microwave assisted aqueous ammonia pretreatment are presented in Figure 3. As shown in Figure 3, prior to the pretreatment, the OPEFB fibres looked hard and stiff, with a flat, smooth surface structure. After the pretreatment, the lignin-carbohydrate bonds in the OPEFB fibres broke down and the surface contained pores indicating that the surface area of the OPEFB had increased [4]. Thus, microwave assisted aqueous ammonia pretreatment appears to be able to break the lignocellulosic structure of OPEFB.

4. Conclusion
The present study showed that microwave assisted alkaline pretreatment using aqueous ammonia can effectively remove lignin from the lignocellulose complex structure of OPEFB within short period of time. The maximum lignin removal of 81.60% from the quadratic model can be achieved under optimal pretreatment conditions: microwave power of 837.8 Watt, NH$_3$ concentration of 12.2% (v/v),
and reaction time of 8.9 minutes. SEM analysis also confirmed that microwave assisted alkaline pretreatment using aqueous ammonia caused morphological changes of OPEFB which can be seen by the disrupted structure.

5. References

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