Optimization of microwave assisted dilute ammonia pretreatment of oil palm empty fruit bunch using response surface methodology

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Abstract. Indonesia is the largest producer of palm oil in the world. Around one-fifth of the palm oil processing, weight end up as solid waste, named as oil palm empty fruit bunch (OPEFB). OPEFB is lignocellulosic biomass which contains cellulose, hemicellulose, lignin and minerals. The utilization of cellulose and hemicellulose requires pretreatment to open the lignin bond. This study examines the pretreatment of OPEFB using microwave assisted dilute ammonia. The OPEFB (30 - 40 mesh) was pretreated by ammonia solution with solid-liquid ratio of 1:10 under variated parameters such as ammonia concentration (7.5; 10; 12.5 %), microwave power (280; 560; 840 Watt) and reaction time (3; 6; 9 minutes), The hemicellulose content of all samples was characterized according to SNI 01-1561-1989. The results were optimized using response surface methodology with Box-Behnken model. The model showed that the highest hemicellulose content of 27.3% can be reached at pretreatment conditions of 665-Watt microwave power at 7.5% ammonia concentration for 3 minutes.

1. Introduction
The palm oil plantation in Indonesia covers an area of 14.03 million hectares, which make this country the largest producer of palm oil in the world. The good economy of palm oil possesses the consequence of a huge production of palm oil waste, particularly the oil palm empty fruit bunch (OPEFB) [1]. OPEFB comprises 23% by weight of fresh fruit bunches, and is commonly co-combusted for plant utility or used as fertilizers. OPEFB is lignocellulosic biomass which contains cellulose, hemicellulose, and lignin. Those polymers can be used as building blocks to produce more valuable chemicals. Some of those chemicals that are currently on demand in Indonesia are furfural [2] and formic acid [3], which can be obtained through the processing of hemicellulose and cellulose.

To be able to utilize those sugar polymers, pretreatment is needed to remove the lignin coverings, increase the biomass surface area, and reduce the crystallinity of cellulose. One of the most common methods of pretreatment is by using chemical agent, such as ammonia. Ammonia works as a delignifying agent by disrupting the C-O-C bond on lignin and hemicellulose, and also by swelling the biomass up [4]. Due to its volatility, it is fairly recoverable and can be economical compared to other processes. Ammonia also normally used when the recovery of hemicellulose is desired, since it does not hydrolyse hemicellulose. The conventional method of this process is known as Soaking in Aqueous Ammonia (SAA), which involves submerging the biomass in a huge amount of ammonia solution [5]. The drawback of this process is that it requires a long period of time, if not given any additional factor. To speed up the process, the increase of temperature and pressure can be done in a
pressurized chamber [6]. Normally, steam is used as the heating agent. However, the steam usage may cause several issues such as inaccurate temperature control, condensate build up, and uneven heat transfer [7].

Microwave radiation can cause thermal and non-thermal effect which may increase the pretreatment performance [8]. Several studies have used the microwave-assisted alkali method to treat biomass, such as OPEFB [9], Miscanthus sinensis [10], and sugarcane bagasse [11]. So far, the microwave-assisted ammonium hydroxide method has only been used to treat Miscanthus sinensis, and it is still unknown whether this method can be applied on OPEFB, since the two have different structure and composition. This study focuses on the effectiveness of microwave-assisted ammonium hydroxide method to treat OPEFB with regard to its hemicellulose content, along with the conditions to achieve maximum hemicellulose yield.

2. Methodology
2.1. Materials
The OPEFB powder was obtained from Balai Besar Teknologi Pati (Center for Starch Technology), Lampung, Indonesia. The ammonium hydroxide was obtained from Merck. The dilution of the solution used distilled water from PT. Brataco.

2.2. Pretreatment of OPEFB using microwave-assisted ammonium hydroxide method
The OPEFB powder was sieved to obtain a particle size of 30-40 mesh. The powder was then mixed with ammonium hydroxide solution under varied concentration (7.5; 10; 12.5%). The mixture was covered with aluminium foil and sealed to prevent the ammonia from leaking. The mixture was then put inside a domestic microwave (Electrolux EMS-3087X, Sweden) and was given microwave radiation under varied power (280; 560; 840 Watts) and radiation time (3; 6; 9 minutes). After the radiation has finished, the mixture was filtered using vacuum filtration. The collected solid was then dried and broken down into pretreated powder.

2.3. Characterization of hemicellulose
The characterization of the hemicellulose from the pretreated and non-pretreated samples were done in accordance to SNI 01-1561-1989 [12].

2.4. Optimization using response surface methodology
The optimization of pretreatment conditions with regard to the hemicellulose content was done using response surface methodology. The model used was Box-Behnken (three variables, 15 total experiments). The variables were the microwave power, ammonium hydroxide concentration, and radiation time. The levels of each variables are shown in Table 1.

| Factor                        | Units  | Level -1 | Level 0 | Level +1 |
|-------------------------------|--------|----------|---------|----------|
| A : Microwave power           | Watt   | 280      | 560     | 840      |
| B : Ammonium hydroxide concen| %      | 7.5      | 10      | 12.5     |
| C : Radiation time            | minute | 3        | 6       | 9        |

3. Results and discussion
3.1. Summary on pretreatment conditions
The use of microwave for this pretreatment has several advantages compared to the conventional steam heating. Some of them are faster heat transfer, shorter reaction time, energy efficient, compact equipment, providing a direct heat towards the biomass, and can prevent surface overheating [13]. The three most important factors that may affect the pretreatment process are biomass feedstock, microwave power, and radiation time [14]. The concentration factor was added in this study since the
effect of concentration variation was also observed in other studies [15]. The combination of the three factors follows the Box-Behnken Design of Experiment (DoE). This model has an advantage of having the least number of required experiments, compared to Full Factorial Design or Central Composite Design. The resulting hemicellulose content in each experiment is shown in Table 2.

Table 2. Resulting hemicellulose content in each experiment.

| Run | Decoded Variable | Hemicellulose (%) |
|-----|------------------|------------------|
|     | Power (Watt)     | Concentration (%)| Time (minute) |
| Control | -               | -                | -             | 23.63 |
| 1    | 280              | 7.5              | 6             | 25.13 |
| 2    | 840              | 7.5              | 6             | 25.93 |
| 3    | 280              | 12.5             | 6             | 25.73 |
| 4    | 840              | 12.5             | 6             | 25.21 |
| 5    | 280              | 10               | 3             | 24.66 |
| 6    | 840              | 10               | 3             | 25.34 |
| 7    | 280              | 10               | 9             | 24.99 |
| 8    | 840              | 10               | 9             | 24.31 |
| 9    | 560              | 7.5              | 3             | 27.26 |
| 10   | 560              | 12.5             | 3             | 25.39 |
| 11   | 560              | 7.5              | 9             | 25.02 |
| 12   | 560              | 12.5             | 9             | 26.38 |
| 13   | 560              | 10               | 6             | 26.25 |
| 14   | 560              | 10               | 6             | 26.18 |
| 15   | 560              | 10               | 6             | 26.32 |

3.2. Statistical analysis

Statistical analysis was done to determine the model that will be used in the analysis of variances (ANOVA). The test includes sum of squares, lack of fit, and R-Squared. All the test result shows that the quadratic source is the suggested model, and therefore was used in the statistical analysis. The ANOVA shows a significant model with not significant lack of fit, meaning that the model does show the effect of each factor, in terms on individual, interaction, and quadratic effect. However, the concentration-time interaction as well as power squared does not show a significant effect.

Table 3 shows the ANOVA result of this experiment. For a factor to be considered as significant, its p-Value must be lower than 0.05. The ANOVA shows that the model is significant with a not-significant lack of fit. With exception of linear effect on power (A) and concentration (B), all the factors affect the model. The resulting equation obtained from the ANOVA above is represented in the following equation:

\[
\text{Hemicellulose content} = 27.2425 + 0.0211A - 1.1135B - 0.3229C - 0.0005AB - 0.0004AC + 0.1076 BC - 0.0001A^2 + 0.0350B^2 - 0.0506C^2
\]

(1)

Where:

A : Microwave power (Watt)
B : Ammonium hydroxide concentration (%)
C : Radiation time (minute)
Table 3. Analysis of variances from the experimental result.

| Source    | Sum of Squares | df  | Mean Square | F Value | p-Value |  
|-----------|----------------|-----|-------------|---------|---------|
| Model     | 8.43           | 9   | 0.9368      | 61.29   | 0.0001  | significant |
| A-Power   | 0.0098         | 1   | 0.0098      | 0.6412  | 0.4596  |         |
| B-Concentration | 0.0496     | 1   | 0.0496      | 3.25    | 0.1315  |         |
| C-Time    | 0.4753         | 1   | 0.4753      | 31.10   | 0.0026  |         |
| AB        | 0.4356         | 1   | 0.4356      | 28.50   | 0.0031  |         |
| AC        | 0.4624         | 1   | 0.4624      | 30.25   | 0.0027  |         |
| BC        | 2.61           | 1   | 2.61        | 170.64  | < 0.0001|         |
| A²        | 3.47           | 1   | 3.47        | 226.70  | < 0.0001|         |
| B²        | 0.1767         | 1   | 0.1767      | 11.56   | 0.0193  |         |
| C²        | 0.7686         | 1   | 0.7686      | 50.28   | 0.0009  |         |
| Residual  | 0.0764         | 5   | 0.0153      |         |         |         |
| Lack of Fit | 0.0666     | 3   | 0.0222      | 4.53    | 0.1860  | not-significant |
| Pure Error | 0.0098     | 2   | 0.0049      |         |         |         |
| Cor Total | 8.51           | 14  |             |         |         |         |

3.3. Optimization of the pretreatment conditions
Optimization of the pretreatment conditions is done to see how each factor interacts and affect the hemicellulose content under different condition combination. To better visualize the results, three dimensional response surface plots as well as contour maps on experiment with highest hemicellulose result are modelled. Figure 1. shows those plots and maps.

![Figure 1](image.png)

**Figure 1.** Response surface plot and contour maps from interaction of two factors: (a) Microwave power and ammonium hydroxide concentration; (b) Microwave power and radiation time; and (c) Ammonium hydroxide concentration and radiation time.
Figure 1 shows that in general, high microwave power combined with low ammonia concentration and short radiation time will result in the highest hemicellulose content. Since the hemicellulose could not have been formed during the pretreatment process, its rise is most likely due to the lignin removal from the biomass complex, increasing the biomass’ accessibility. However, if the hemicellulose is decreasing, it may be caused by the decomposition of the polymer due to prolonged exposure to the microwave. The optimum hemicellulose content that was obtained from this study is shown in Table 4.

**Table 4.** Pretreatment condition to achieve optimum hemicellulose content.

| Microwave Power (Watt) | NH4OH Concentration (%) | Radiation Time (minute) | Hemicellulose Content (%) |
|------------------------|-------------------------|-------------------------|---------------------------|
| 665.04                 | 7.50                    | 3.01                    | 27.3                      |

4. Conclusions

The pretreatment of OPEFB using microwave-assisted ammonium hydroxide method was investigated. It was found that to obtain maximum amount of hemicellulose, the pretreatment condition should consist of medium-to-high microwave power, low amount of ammonium hydroxide, under short radiation. By doing an analysis using RSM, the optimum pretreatment conditions can be identified: microwave power of 665 Watts, ammonium hydroxide concentration of 7.5%, and radiation time of 3 minutes, with hemicellulose yield of 27.3%.

Acknowledgements

Authors gratefully thank the financial support by Badan Pengelola Dana Perkebunan Kelapa Sawit (BPDPKS) Indonesia (Contract Nr: PRJ-20/DPKS/2018).

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