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OPTIMIZATION OF PRETREATMENT CONDITIONS FOR MICROWAVE-ASSISTED ALKALINE DELIGNIFICATION OF EMPTY FRUIT BUNCH BY RESPONSE SURFACE METHODOLOGY

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ABSTRACT

Oil palm empty fruit bunch (OPEFB) is one of the prominent lignocellulosic wastes from the oil palm industry, and it has the potential for feedstock in biobased products. However, delignification must be applied. This study investigated the effect of microwave-assisted alkaline pretreatment of OPEFB by using response surface methodology with Box-Behnken design (BBD) to find the optimum pretreatment conditions. OPEFB (30-mesh) was treated with various concentrations of aqueous sodium hydroxide. The effect of three variables, microwave power (280–840 W), NaOH concentration (1–3% w/v), and reaction time (3–9 min), was evaluated to improve lignin removal. The quadratic model indicated that microwave power of 832.9 W, NaOH concentration of 2.7% (w/v), and a reaction time of 8.9 min resulted in the highest lignin removal: 88.10%. FTIR and SEM analysis was also conducted on the untreated and treated OPEFB to evaluate the effectiveness of the pretreatment. These results showed that microwave-assisted alkaline pretreatment of OPEFB could effectively remove the lignin under a relatively short time period and low alkaline concentration.

Keywords: Alkaline pretreatment; Lignin; Microwave; Oil palm empty fruit bunch; Response surface methodology

1. INTRODUCTION

The palm oil industry continues to grow in response to increased consumption and demand for palm oil. During the processing of palm oil, OPEFB is produced as solid waste. As lignocellulosic biomass, OPEFB contains 39.8% cellulose, 17.3% hemicellulose, and 28.8% lignin (Kim, 2012). OPEFB has great potential to be utilized for the production of various biochemical products. OPEFB has been specifically used as feedstock for the production of levulinic acid and furfural; the highest yields were 52.1 mol% (C6 sugar basis) and 27.94 mol% (C5 sugar basis), respectively (Gozan, 2018). OPEFB can also be used as a carbon source for the growth medium of microorganisms like *Saccharomyces cerevisiae* to produce bioethanol with the highest yield: 24% (glucose basis) (Hermansyah, 2015).

Due to the complex lignocellulose structure of OPEFB, pretreatment is required to remove the lignin, increase the surface area, and increase the lignocellulose's porosity. This process will make both cellulose and hemicellulose readily available for conversion. Alkaline pretreatment is known to be an efficient method for delignification due to its capability for lignin solubilization and swelling formation of treated biomass. Alkaline pretreatment of OPEFB has

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been performed with either aqueous ammonia or sodium hydroxide for delignification and sugar production by means of conventional heating (Zulkiple, 2016). Microwave-assisted alkaline pretreatment is widely used because of its advantages, including high heating efficiency, rapid heating, and easy operation. Microwave-assisted alkaline pretreatment of OPEFB by using 3% NaOH could remove 74% of the lignin at a microwave power of 120 W in 12 min. This is significantly better than using conventional heating, which only removes 69% of the lignin with the same NaOH concentration at 50°C for 80 min (Nomanbhay, 2015). Although there has been some research regarding microwave-assisted alkaline pretreatment of OPEFB, the application of Response Surface Methodology (RSM) in this study was still less, thus making application more important.

This study focuses on the optimization of important variables of OPEFB microwave-assisted alkaline pretreatment: microwave power, NaOH concentration, and reaction time. The results were statistically processed using Response Surface Methodology (RSM), which had been used previously to study the effect of alkaline treatment on the physical properties of OPEFB (Fatra, 2016). The use of RSM to study the microwave-assisted alkaline pretreatment of OPEFB is appropriate because there are some external parameters affecting this process. By using RSM, effective research can be achieved through the avoidance of higher prices, longer duration, and repetition. The obtained BBD was very effective in determining the amount of research that should be carried out by using a formula that consists of a simple combination. Optimization using response surface design by BBD required random research in terms of dependent variable combinations to systematically diminish the error applied previously when studying the optimization of palm oil mill effluent electrocoagulation (Lubis, 2018).

2. METHODOLOGY

2.1. Materials

OPEFB powder was obtained from the Center for Starch Technology (*Balai Besar Teknologi Pati*) Research and Assessment of Technology (*Badan Pengkajian dan Penerapan Teknologi*) in Lampung, Indonesia. The OPEFB was first screened using a 30-mesh sieve and then dried for 4 h at 105^{o}C. The sample was then sealed in a plastic bag and stored in a closed container at room temperature. Sodium hydroxide pellets for analysis were provided by Merck (Harahap, 2019).

Figure 1 OPEFB used as raw material

2.2. Microwave Alkaline Pretreatment

The microwave used for this pretreatment was a domestic microwave oven (Electrolux EMS3087X). A mixture of 70 g of OPEFB and 700 mL of NaOH solution was prepared and

mixed thoroughly in a 1000 mL glass flask. The pretreatment was done under predetermined microwave power, NaOH concentrations, and reaction times according to the experimental design. After the microwave pretreatment, the samples were cooled and filtered through BIPMED BI filter paper (size: 10 µm) using vacuum filtration to separate solid and liquid fractions. The solid fraction was then washed with distilled water at 60°C until it reached a pH of 7. The solid fraction was dried using an oven at 80°C for 12 h and milled in a domestic blender. The samples were kept sealed in plastic bottles at room temperature until used for analysis (Harahap, 2019).

2.3. Design of Experiments

RSM with BBD was used to optimize the process variables that affect lignin removal (Ferreira et al., 2007). The variables were microwave power (A) (280, 560, and 840 W), NaOH concentration (B) (1, 2, and 3% w/v), and reaction time (C) (3, 6, an 9 min). From preliminary experiments and literature reviews, the range for each independent variable was selected. Each variable was tested at three levels, which were coded as (-1) for the lower level, (+1) for higher level, and a central coded value considered as zero (0). The values for each variable in each level are shown in Table 1. The experimental design consists of 15 total runs, and Design Expert v.11 software (Stat Ease Inc., Minneapolis, MN, USA) was used to perform analysis of variance (ANOVA) and to optimize the three variables from the generated response surface model (Harahap, 2019).

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

Factors		Unit	Levels		
Coded Parameters	Uncoded Parameters		-1	0	+1
A	Microwave Power	Watt	280	560	840
B	NaOH Concentration	% (w/v)	1	2	3
C	Reaction Time	min	3	6	9

2.4. Analysis Methods

The lignin content in the OPEFB fibers was determined according to TAPPI T-222 om-83. EFB fibers were briefly hydrolyzed and solubilized by H_2SO_4. The acid-insoluble lignin was filtered off, dried, and weighed. The lignin is defined as wood or pulp constituent, which is insoluble in 72% H_2SO_4 (Piarpuzán, 2011). Lignin content of untreated OPEFB was also used as a negative control for the calculation of lignin removal, given in Equation 1 (Harahap, 2019),

$$Lignin\ removal\ (\%) = \frac{(L_c - L_t)}{L_c}\ x\ 100\% \quad (1)$$

where L_c is the weight of lignin obtained from untreated OPEFB (g), and L_t is the weight of lignin obtained from each treated OPEFB (g).

The Fourier Transform Infrared (FTIR) spectroscopy was conducted using KBr pellets in the range of 400–4000 cm^{-1} with a Thermo Scientific Nicolet iS5 spectrometer. Changes in surface morphology of treated and untreated OPEFB samples were observed by using a scanning electron microscope (SEM LEO 420i) (Harahap, 2019).

3. RESULTS

The results of each experimental run based on BBD are presented in Table 2. The highest lignin removal from this design was 73.75%, with pretreatment conditions of 840 W of microwave power, a 2% NaOH concentration, and a 9 min reaction time. This result is comparable with previous research done by Nomanbhay et al. (2013), whose highest lignin loss was 74%.

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

Run	Coded Parameter Values			Lignin Removal (%)
	Microwave Power (Watt)	NaOH Concentration (%)	Reaction Time (min)	
	A	B	C	
1	0	-1	+1	43.76
2	-1	0	-1	10.92
3	-1	+1	0	23.11
4	0	+1	-1	38.75
5	-1	-1	0	11.60
6	0	-1	-1	17.71
7	0	0	0	19.11
8	+1	-1	0	42.79
9	+1	0	+1	73.75
10	+1	0	-1	24.40
11	0	0	0	20.84
12	+1	+1	0	63.16
13	0	0	0	21.96
14	0	+1	+1	72.66
15	-1	0	+1	31.49

The mathematical model for lignin removal in terms of coded factors is shown by Equation 2, where A, B, and C are microwave power (W), NaOH concentration (% w/v), and reaction time (min), respectively. According to this second-degree polynomial model, the optimal condition for obtaining the highest lignin removal of 88.10% is at a microwave power of 832.9 W, a NaOH concentration of 2.7% (w/v), and a reaction time of 8.9 min.

$$\textit{Lignin removal (\%)} = 20.63+15.89\times A+10.24\times B+16.25\times C+2.23\times AB+7.20\times AC+1.95\times BC+3.22\times A^2+11.32\times B^2+11.30\times C^2 \quad (2)$$

Table 3 provides evidence that the model is statistically significant, with a high F-value (38.62) and low p-value (0.0004). The p-value was also used to determine the significance of each regression coefficient and the interactions between each process variable.

Table 3 Statistical analysis for computed OPEFB pretreatment

ANOVA for quadratic equation model developed for OPEFB pretreatment						
Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	6099.13	9	677.68	38.62	0.0004	Significant
A-Power	2019.30	1	2019.30	115.09	0.0001	
B-Conc.	838.45	1	838.45	47.79	0.0010	
C-Time	2112.50	1	2112.50	120.40	0.0001	
AB	19.80	1	19.80	1.13	0.3367	
AC	207.36	1	207.36	11.82	0.0185	
BC	15.21	1	15.21	0.8669	0.3946	
A^2	38.30	1	38.30	2.18	0.1996	
B^2	473.21	1	473.21	26.97	0.0035	
C^2	471.12	1	471.12	26.85	0.0035	
Residual	87.73	5	17.55			
Lack of Fit	83.48	3	27.83	13.11	0.0717	Not Significant
Pure Error	4.25	2	2.12			
Cor Total	6186.86	14				
Other statistical parameters						
Std. Dev.	4.19		R^2		0.9858	
Mean	34.41		Adjusted R^2		0.9603	
CV%	12.17		Predicted R^2		0.7826	
PRESS	1345.28		Adeq. Precision		18.7932	

The relationship among these variables was graphically modeled as 3D response surface curves (Figures 2b–2d). Note that a higher lignin removal can be obtained with a higher time and microwave power, a higher NaOH concentration and microwave power, and a highest time and NaOH concentration.

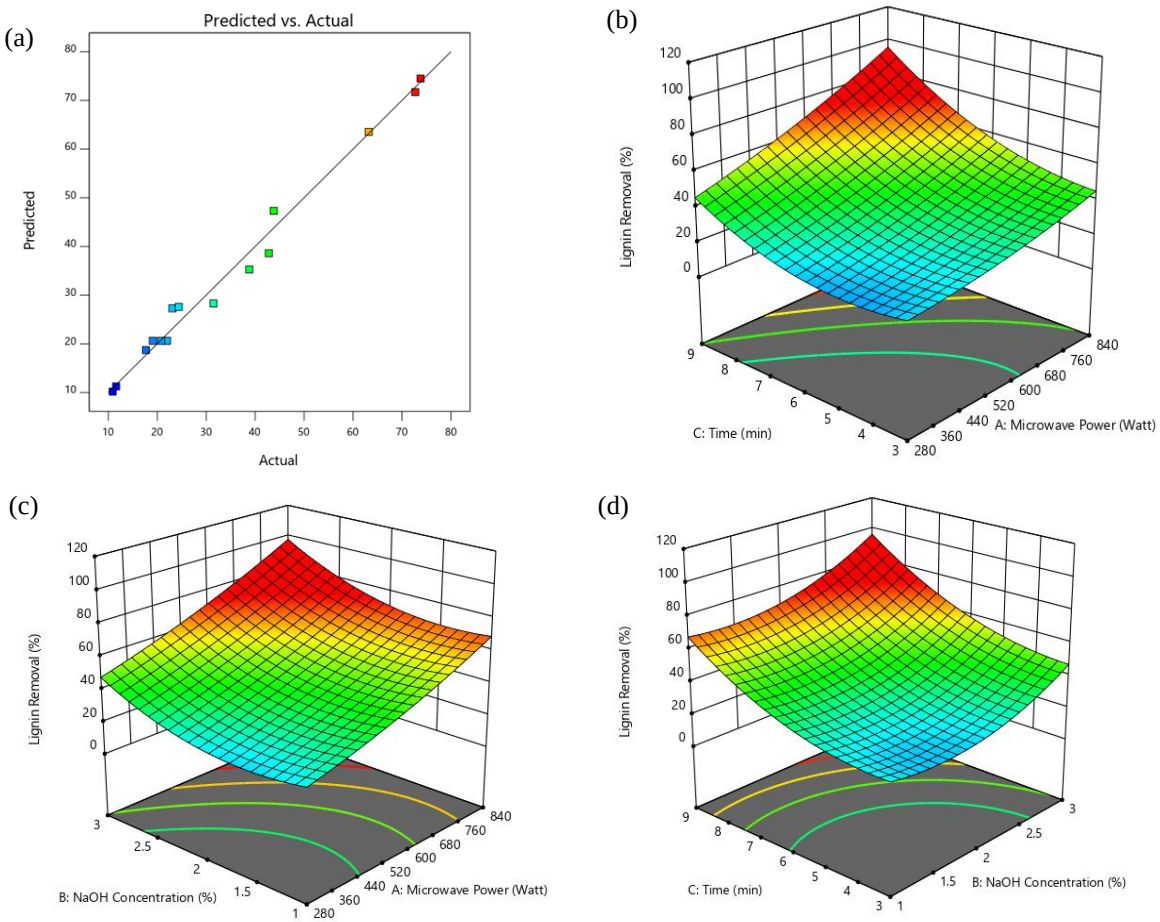

Figure 2 (a) Predicted vs. actual lignin removal of OPEFB; (b–d) Contour plots and response surface for the effect of each variable on OPEFB pretreatment

A SEM micrograph of the OPEFB fibers before and after the pretreatment is shown in Figure 3.

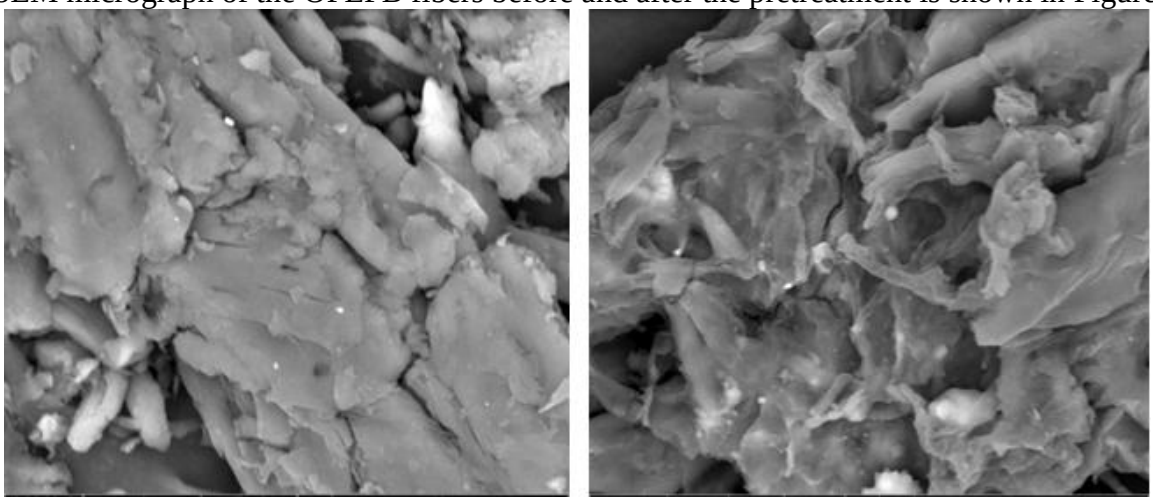

Figure 3 SEM result of treated-run 9 (right) and untreated OPEFB (left) in 5000× magnitude

Prior to the pretreatment, the OPEFB fibers looked solid, hard, and stiff, with a flat, smooth surface structure. However, after the pretreatment, the OPEFB fibers looked damaged and had a perforated structure, which means that the pretreatment had occurred effectively (Harahap, 2019).

The FTIR spectra of untreated and treated OPEFB is illustrated in Figure 4. The increasing transmittance band at 3332.97 cm^{-1} in the untreated OPEFB suggests that the lignin barrier in the pretreated sample is highly degraded since every lignin infrared spectrum has strong, wide bands between 3500 and 3100 cm^{-1} assigned to –OH stretching vibrations (He et al., 2008).

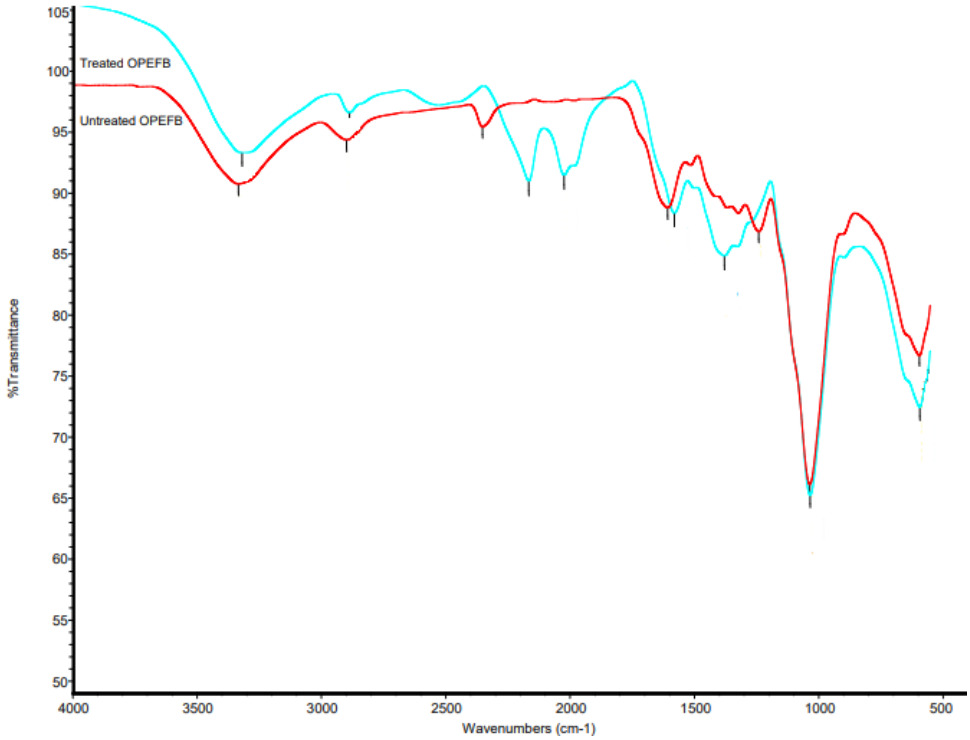

Figure 4 FTIR spectra of treated-run 9 and untreated OPEFB

4. DISCUSSION

From the mathematical model obtained, all of the process variables (A [microwave power], B [NaOH concentration], and C [reaction time]) showed significant effects on lignin removal with a p-value lower than 0.05. The interactive effects between variables A and C and the quadratic effect of variables B^2 and C^2 also exhibit a significant effect on lignin removal. The most significant variable in this experiment seemed to be the reaction time (C) due to its higher F-value (120.40) and lower p-value (0.0001). The coefficient of determination (R^2) and adjusted R^2 was high: 0.9858 and 0.9603, respectively. As shown in Figure 2a, all the data points are arranged very close to the straight line, meaning that there is relatively no variation effect between experimental response and predicted response (Harahap, 2019).

Table 4 compares some studies related to alkaline pretreatment of OPEFB to this experiment. The actual result of this experiment is quite similar to the previous study by Nomanbhay (2013), but the optimum result from the model in this experiment could yield higher lignin removal. It can be seen in Table 4 that, overall, microwave-assisted alkaline pretreatment of OPEFB provided higher lignin removal than conventional pretreatment. Interestingly, microwave-assisted alkaline pretreatment of OPEFB could effectively remove lignin in an extremely shorter period of time than conventional pretreatment.

Table 4 Comparison of OPEFB alkaline pretreatment

Pretreatment Condition	Lignin Removal	Reference
Conventional pretreatment with 10% NaOH at 150°C and 4 kg/cm^2 for 30 minutes	47.31%	(Barlianti et al., 2015)
Conventional pretreatment with 3% NaOH at 50°C for 80 minutes	69%	(Nomanbhay et al., 2013)
Microwave-assisted NaOH pretreatment at 231 W, 3.5% (w/v) NaOH, 5 minutes	54.98%	(Laghari et al., 2016)
Microwave-assisted NaOH pretreatment at 180 W, 3% (w/v) NaOH, 12 minutes	74%	(Nomanbhay et al., 2013)
Microwave-assisted NaOH pretreatment at 840 W, 2% (w/v) NaOH, 9 minutes	73.75%	This study (actual)
Microwave-assisted NaOH pretreatment at 832.9 W, 2.7% (w/v) NaOH, 8.9 minutes	88.10%	This study (model)

The use of microwave radiation on OPEFB pretreatment is a promising process involving thermal and non-thermal effects generated by microwaves in aqueous environments. The superiority of activating polysaccharides by microwave radiation may be due to direct delivery of microwave energy to polysaccharides through molecular interactions with the electromagnetic field. The vibration of polar molecules and the movement of ions results in the generation of heat and extensive collision (Nomanbhay et al., 2013).

SEM was used to observe the structural modification and morphological changes of treated and untreated OPEFB. Generally, the structures of untreated OPEFB are smooth, with waxy surfaces and the presence of silica bodies due to the high degree of crystallinity of the cellulose bundles, which are wrapped in lignin (Figure 3) (Zulkiple et al., 2016). In this study, the structure of the silica body was not observed because the raw OPEFB had been mechanically reduced in size before it was changed into the powder form. The structure of untreated OPEFB, as shown in Figure 3, looked very rigid and solid because the surface of the OPEFB was still covered by a layer of matrix material, like lignin or wax. However, after pretreatment, the SEM image shows the structural damage to the OPEFB. Figure 3 shows that the structure of pretreated OPEFB became more porous, and visible cracks randomly formed. This phenomenon is evidence that microwave-assisted ammonia pretreatment of OPEFB in this study caused disruptions to the OPEFB structure by destroying the cell wall, hydrolyzing lignin or hemicellulose of lignocellulose, and creating a number of large pores (Iberahim et al., 2013). The previous study stated that this phenomenon indicated that some parts of fibers disappeared; the lost parts were predicted to be lignin, hemicellulose, and some amorphous cellulose (Barlianti et al., 2015).

The FTIR spectrum (Figure 4) was used to support the effectiveness of lignin removal from OPEFB by previous SEM image perspective. Principally, FTIR spectra of lignocellulose material, like OPEFB, is divided into two parts, the–OH and –CH stretching vibrations part (4000–2700 cm^{-1}) and the fingerprint part (1800–800 cm^{-1}). In this study, the transmittance bands, which represented the stretching of the –OH group, were at 3332.97 cm^{-1} and 3318.27 cm^{-1} for untreated and treated OPEFB, respectively. After microwave-assisted alkaline pretreatment, the height of the transmittance peak in this area increased, which showed that some hydrogen bond in the lignin structure was ruptured. The transmittance bands related to the C-H stretching in the cellulose molecules of OPEFB were at 2898.86 cm^{-1} and 2856.75 cm^{-1} for untreated and treated OPEFB, respectively. After microwave-assisted alkaline pretreatment, the height of the transmittance peak in this area also increased, indicating that some cellulose molecules were destroyed, mainly in methyl or methylene cellulose, thus reducing the

crystalline structure of the treated OPEFB. These results proved that microwave-assisted alkaline pretreatment in this experiment could effectively remove the lignin content of OPEFB, thus supporting the previous SEM result (Barlianti et al., 2015).

5. CONCLUSION

This study showed that microwave-assisted alkaline pretreatment using sodium hydroxide was effective in removing lignin from the lignocellulose structure of OPEFB within a short period of time. The model obtained from this experiment shows that to achieve the highest lignin removal of 88.10%, the optimal conditions for the pretreatment are a combination of microwave power at 832.9 W, a NaOH concentration at 2.7% (w/v), and a reaction time of 8.9 min. The result was further confirmed by analysis of FTIR and SEM, which showed that microwave-assisted alkaline pretreatment caused chemical and morphological structure changes to OPEFB in terms of lignin removal.

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7. REFERENCES

Barlianti, V.B., Dahnum, D., Hendarsyah, H., Abimanyu, H., 2015. Effect of Alkaline Pretreatment on Properties of Lignocellulosic Oil Palm Waste. *Procedia Chemistry*, Volume 16, pp. 195–201

Fatra, W., Rouhillahi, H., Helwani, Z., Zulfansyah, Z., Asmura, J., 2016. Effect of Alkaline Treatment on the Properties of Oil Palm Empty Fruit Bunch Fiber-reinforced Polypropylene Composite. *International Journal of Technology*, Volume 7(6), pp. 1026–1034

Ferreira, S.L., Bruns, R.E., Ferreira, H.S., Matos, G.D., David, J.M., Brandão, G.C., da Silva, E.G., Portugal, L.A., dos Reis, P.S., Souza, A.S., dos Santos, W.N., 2007. Box-Behnken Design: An Alternative for the Optimization of Analytical Methods. *Analytica Chimica Acta*, Volume 597(2), pp. 179–186

Gozan, M., Panjaitan, J.R.H., Tristantini, D., Alamsyah, R., Yoo, Y.J., 2018. Evaluation of Separate and Simultaneous Kinetic Parameters for Levulinic Acid and Furfural Production from Pretreated Palm Oil Empty Fruit Bunches. *International Journal of Chemical Engineering*, Volume 2018, pp. 1–12

Harahap, A.F.P., Rahman, A.A., Gozan, M., 2019. Microwave Assisted Aqueous Ammonia Pretreatment of Oil Palm Empty Fruit Bunch: Effect on Lignin Removal and Morphological Structure. *In:* Journal of Physics: Conference Series, 1311 012027

Hermansyah, H., Wisman, A.P., Firdaus, D., Arbianti, R., Utami, T.S., Kurnia, A., 2015. Effect of Aeration and Nutrients on *Saccharomyces Cerevisiae* Cultivation using Lignocellulosic Hydrolysate from Empty Fruit Bunch. *International Journal of Technology*, Volume 6(7), pp. 1110–1118

He, Y., Pang, Y., Liu, Y., Li, X., Wang, K., 2008. Physicochemical Characterization of Rice Straw Pretreated with Sodium Hydroxide in the Solid State for Enhancing Biogas Production. *Energy & Fuels*, Volume 22(4), pp. 2775–2781

Iberahim, N.I., Jahim, J.M., Harun, S., Nor, M.T.M., Hassan, O., 2013. Sodium Hydroxide Pretreatment and Enzymatic Hydrolysis of Oil Palm Mesocarp Fiber. *International Journal of Chemical Engineering and Applications*, Volume 4(3), pp. 101–105

Kim, S., Park, J.M., Seo, J.W., Kim, C.H., 2012. Sequential Acid-/Alkali-Pretreatment of Empty Palm Fruit Bunch Fiber. *Bioresource Technology*, Volume 109, pp. 229–233

Laghari, S.M., Isa, M.H., Laghari, A.J., 2016. Delignification of Palm Fiber by Microwave Assisted Chemical Pretreatment for Improving Energy Efficiency. *Malaysian Journal of Science*, Volume 35(1), pp. 8–14

Lubis, M.R., Fujianti, D.S., Zahara, R., Darmadi, D., 2018. The Optimization of the Electrocoagulation of Palm Oil Mill Effluent with a Box-Behnken Design. *International Journal of Technology*, Volume 10(1), pp. 137–146

Nomanbhay, S.M., Hussain, R., Palanisamy, K., 2013. Microwave-assisted Alkaline Pretreatment and Microwave Assisted Enzymatic Saccharification of Oil Palm Empty Fruit Bunch Fiber for Enhanced Fermentable Sugar Yield. *Journal of Sustainable Bioenergy Systems*, Volume 3(1), pp. 7–17

Piarpuzán, D., Quintero, J.A., Cardona, C.A., 2011. Empty Fruit Bunches from Oil Palm as a Potential Raw Material for Fuel Ethanol Production. *Biomass and Bioenergy*, Volume 35(3), pp. 1130–1137

Zulkiple, N., Maskat, M.Y., Hassan, O., 2016. Pretreatment of Oil Palm Empty Fruit Fiber (OPEFB) with Aquaeous Ammonia for High Production of Sugar. *Procedia Chemistry*, Volume 18, pp. 155–161