Alkaline Pretreatment Optimization of Tobacco Stalks for Bioethanol Production

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Abstract. The sustainable biomass production of fuels, chemicals, and other commercial products from lignocellulosic materials has received widespread attention. One of the potential biomass resources to be developed into biofuels is tobacco stalks. Production of tobacco plants in East Java Province was 84,100 t, with the highest production from Pamekasan Regency at 13,520 t, followed by Jember Regency at 13,110 t. This shows that Jember Regency has the potential to develop tobacco stalks to produce biofuels because their availability is relatively abundant. One of the biofuels that can be produced from tobacco stalks is bioethanol. Bioethanol production has increased every year along with the increasing demand for bioethanol, so the bioethanol market opportunity is wide open and can strengthen the nation's economy. Besides being used as a source of energy fulfilment, bioethanol is also needed as a raw material for production in the fields of cosmetics and pharmaceuticals. The increasing need for hand sanitizers during the Covid-19 pandemic has caused the need for bioethanol to increase. Pretreatment in this study was carried out using alkaline, namely NaOH, by varying the temperature and concentration. The purpose of this study was to find the optimum conditions for the pretreatment processes during the production of bioethanol. The optimum conditions in this study were a NaOH concentration of 6%, a temperature of 140 °C, and a rotational speed of 150 rpm with the yield of lignin 12.463%, cellulose 31.194%, and hemicellulose 3.172%.

Keywords: Alkaline pretreatment · Bioethanol · Tobacco stalks

1 Introduction

Sustainable biomass production for chemicals, fuels, and other commercial products from lignocellulosic materials gets attention from various parties [1]. One of the potential biological resources to be developed into biofuels is tobacco stalks. Based on Ferdiyansyah and Rachmawati [2], the production of tobacco plants in East Java Province was 84,100 t, with the highest production from Pamekasan Regency at 13,520 t, followed by Jember Regency at 13,110 t. This shows that Jember Regency has the potential to develop tobacco stalks to produce biofuels because their availability is quite abundant. In general, the part of the tobacco plant that is used is the leaf. Tobacco leaves are used

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as raw material for making cigarettes, while the stalks are only discarded or destroyed by burning. At the same time, tobacco stalks contain nicotine, so the smoke from the combustion can pollute the environment [3, 4].

Tobacco stalks contain lignocellulose so that they can be used as raw materials for the manufacture of biofuels, especially bioethanol. Conversion of tobacco stalks into bioethanol is a solution to environmental issues caused by burning tobacco stalks as well as to answer future energy challenges. The use of biomass as fuel is also in line with the government's seriousness in developing new and renewable energy, as stated in Government Regulation no. 22 of 2017 that the utilization of renewable energy is targeted at 23% by 2025. One of the renewable energy that is currently being developed is bioethanol. Bioethanol is an alternative energy option because it can increase combustion efficiency, reduce pollutant emissions, and has a high octane number [5]. Based on the World Bioenergy Association [6], world bioethanol production is 85,100 million liters with a distribution of 60 million liters in Africa, 74,300 million liters in America, 5,770 million liters in Asia, 4,740 million liters in Europe, and 190 million liters in Oceania.

Besides being used as a source of energy fulfillment, bioethanol is also needed as a raw material for production in the pharmaceutical and cosmetic fields [7]. The increasing need for hand sanitizers during the Covid-19 pandemic has caused the need for bioethanol to increase. This is because bioethanol is the raw material for making hand sanitizers. Therefore, the development of bioethanol production has a bright future opportunity.

The development of bioethanol from tobacco stalks requires four steps process, namely pretreatment, hydrolysis, fermentation, and distillation. In a previous study, pretreatment with acids, namely HCl and H_2SO_4, resulted in 6.23% and 6.99% cellulose, respectively [8]. Pretreatment in this study was carried out using an alkaline, namely NaOH, by varying the temperature, stirring speed, and concentration.

Alkaline pretreatment is an effective chemical pretreatment method in the delignification process of plants to separate the crystal structure of cellulose and increase the accessibility of decomposing enzymes to cell walls [9, 10]. In addition, alkaline pretreatment can also remove acetyl groups and various uronic acid substitutes, which can reduce the negative effect on ethanol fermentation [11]. During the alkaline pretreatment process, the silica in tobacco stalks can also be removed as dissolved silicate in the pretreatment liquid [1]. This study aims to determine the optimum conditions for the pretreatment of tobacco stalks with the alkaline pretreatment method.

2 Materials and Methods

2.1 Materials

The materials used in this study included tobacco stalks, NaOH, sulfuric acid, sodium chlorate, acetic acid, and distilled water.

2.2 Sample Preparation

Sample preparation begins with refining the raw material in the form of tobacco stalks using a chopping machine. Furthermore, the tobacco stalks are dried in the sun. After the drying process, the raw materials were sieved with a 120 mesh sieve to obtain the same size. Then the raw material is baked for 1 h at a temperature of 60–70 °C.

2.3 Alkaline Pretreatment

Pretreatment was carried out by placing a sample of tobacco stalks into a glass beaker and soaking it with NaOH with a concentration variation of 2–10%. Pretreatment was carried out with a temperature variation of 90–140 °C. The stirring speed was varied in the range of 50–150 rpm. The pretreatment process was carried out for 60 min. The sample was filtered and washed with distilled water. Then dried in the oven for 2–3 h at a temperature of 70 °C. After being baked, the sample was cooled to room temperature.

2.4 Cellulose, Hemicellulose, and Lignin Analysis

This study's analysis of cellulose, hemicellulose, and lignin in this study used the Chesson method. The 2 g of dry sample (mass a) was added to 150 mL of distilled water and heated using a hotplate stirrer at 100 °C for 2 h. The filtered residue is rinsed with distilled water and dried until it has a solid mass (mass b). The residue was added 150 mL of 1N H_2SO_4 and refluxed at 100 °C for 1 h. The result is filtered, and the residue is dried until it has a constant mass (mass c). The residue added H_2SO_4 72% as much as 100 mL and left at room temperature for 4 h. The residue is filtered and dried until it has a constant mass (mass d). Then the residue is heated at a temperature of 600 °C for 4–6 h and weighed the mass (mass e). After testing following the above procedure, the levels of cellulose, hemicellulose, and lignin can be calculated using the Eqs. 1, 2, and 3:

$$\text{Lignin content} = (\text{de})/\text{a} \times 100\% \tag{1}$$

$$\text{Cellulose content} = (\text{cd})/\text{a} \times 100\% \tag{2}$$

$$\text{Hemicellulose content} = (\text{bc})/\text{a} \times 100\% \tag{3}$$

3 Results and Discussion

The raw materials used in this study were tobacco stalks taken from PTPN X, Ajung, Jember. Tobacco stalks are cut into small pieces with a size of 3–4 cm. Then dried in the sun for three days until the color is browned and baked at a temperature of 60–70 °C for 60 min until the water content reaches 15%. The drying process is shown in Fig. 1. After the drying process, the tobacco stalks were sieved in a size of 120 mesh as shown in Fig. 2.

Samples with a size of 120 mesh were pretreated with a temperature of 90–140 with a concentration of 2%-10% NaOH and a stirring speed of 50–150 rpm for 60 min. Running samples with three variables using Design Expert 12 with the Box Behken Design (BBD) method, as shown in Table 1.

The levels of lignin, cellulose, and hemicellulose that were obtained from the test results were then analyzed using ANOVA. ANOVA analysis aims to determine the influential variables in the alkaline pretreatment process. The maximum possible error value of $\alpha = 5\%$ or $\alpha = 0.05$ will be the basic parameter in determining the significance

Fig. 1. The drying process of tobacco stalks

Fig. 2. Sample in a size of 120 mesh

of the variables that can be expressed in the P-value of the lignin content in tobacco stalk powder that has been treated.

ANOVA analysis was used to determine the effect of variables (concentration, temperature, and stirring speed) on the lignin content of pretreated tobacco stalk powder. The hypotheses to be analyzed in this study are as follows:

H0: there is no variable that affects the response
H1: there is at least one variable that affects the response

The maximum possible error value of $\alpha = 5\%$ or $\alpha = 0.05$ will be the basic parameter in determining the significance of the variables that can be expressed in the P-value of the lignin content in tobacco stalks that have been treated. The temperature variable has a P-value of 0.909. The P-value > 0.05 (α), so the pretreatment temperature variable did not have a significant effect on decreasing the lignin content in tobacco stalks. The concentration variable has a P-value of 0.002. The P-value < 0.05 (α), so the pretreatment NaOH concentration variable had a significant effect on decreasing the lignin content in tobacco stalks. Variable stirring speed (rpm) has a P-value of 0.336. The P-value $<$ 0.05 (α), so the stirring speed variable in the pretreatment had a significant effect on decreasing the lignin content in tobacco stalks.

The effect of independent variables on lignin content in a three-dimensional graph can be seen in Figs. 3, 4, and 5.

Table 1. Content of lignin, cellulose, and hemicellulose

Run Order	Temperature (°C)	Concentration (%)	rpm	Lignin (%)	Cellulose (%)	Hemicellulose (%)
1	90	2	100	28.714	43.146	7.615
2	140	2	100	27.416	44.245	7.591
3	90	10	100	14.015	30.827	6.145
4	140	10	100	13.668	31.409	5.097
5	90	6	50	17.249	31.977	4.568
6	140	6	50	20.624	37.553	4.020
7	90	6	150	13.190	28.953	5.796
8	140	6	150	12.463	31.194	3.172
9	115	2	50	24.819	42.472	8.365
10	115	10	50	15.185	34.366	4.471
11	115	2	150	27.241	44.619	6.742
12	115	10	150	16.151	30.305	3.570
13	115	6	100	17.033	29.021	10.964
14	115	6	100	19.435	35.174	7.145
15	115	6	100	18.012	33.700	6.695

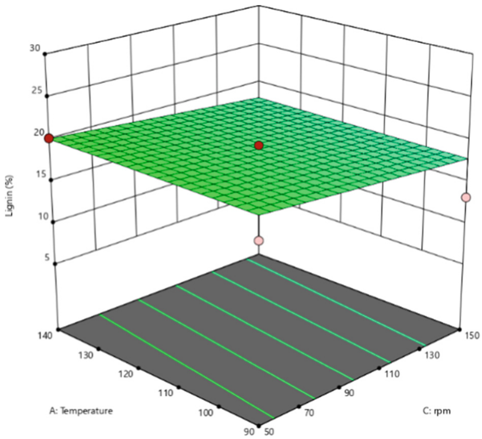

Fig. 3. Effect of temperature and rpm variables on lignin content

The temperature variable has a P-value of 0.250. The P-value > 0.05 (α), so the pretreatment temperature variable did not have a significant effect on the cellulose content in tobacco stalks. The concentration variable has a P-value of 0.001. The P-value < 0.05 (α), so the pretreatment NaOH concentration variable has a significant effect on the

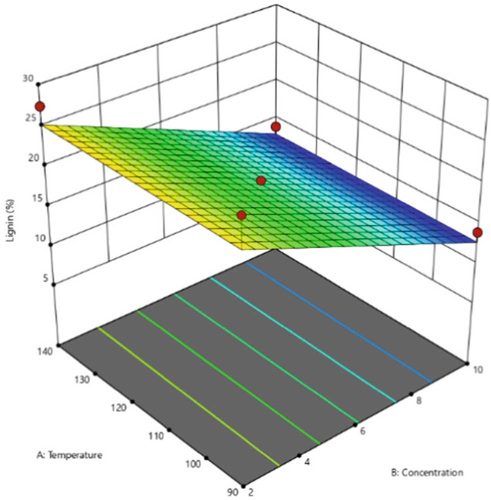

Fig. 4. Effect of temperature and concentration variables on lignin content

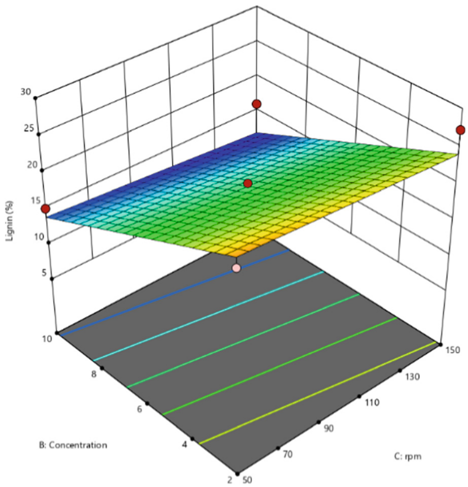

Fig. 5. Effect of concentration and rpm variables on lignin content

cellulose content of tobacco stalks. Variable stirring speed (rpm) has a P-value of 0.182. The P-value > 0.05 (α), so the stirring speed variable in the pretreatment did not have a significant effect on decreasing the cellulose content in tobacco stalks. The effect of independent variables on cellulose content in a three-dimensional graph can be seen in Figs. 6, 7, and 8.

The temperature variable has a P-value of 0.408. The P-value > 0.05 (α), so the pretreatment temperature variable did not have a significant effect on the hemicellulose content in tobacco stalks. The concentration variable has a P-value of 0.066. The P-value > 0.05 (α), so the pretreatment NaOH concentration variable did not have a

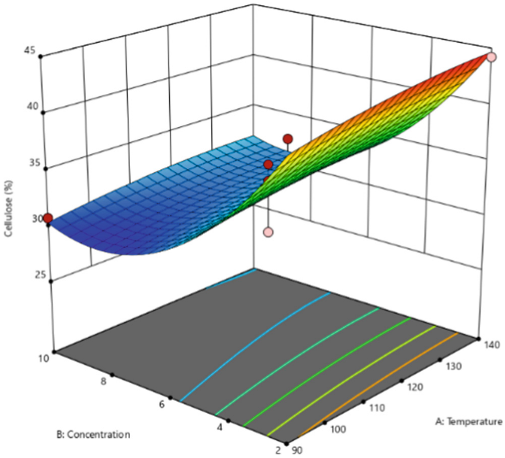

Fig. 6. Effect of temperature and concentration variables on cellulose content

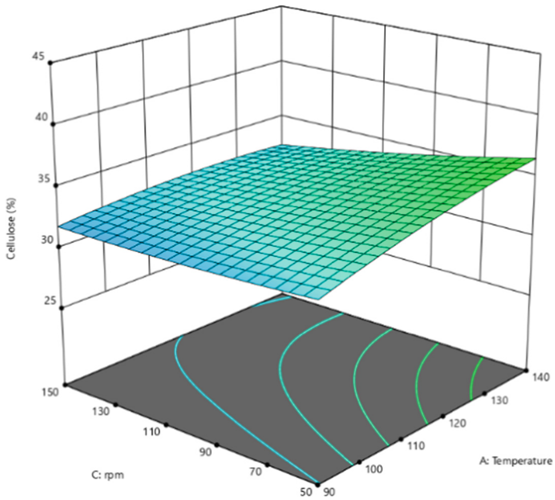

Fig. 7. Effect of temperature and rpm variables on cellulose content

significant effect on the hemicellulose content in tobacco stalks. Variable stirring speed (rpm) has a P-value of 0.667. The P-value > 0.05 (α) so that the stirring speed variable in the pretreatment did not have a significant effect on the hemicellulose content in tobacco stalks. The effect of independent variables on hemicellulose content in a three-dimensional graph can be seen in Figs. 9, 10, and 11.

The mathematical equation presented the relationship between the independent variable and the response. In Eqs. 4, 5, and 6, A is the temperature variable (°C), B is the NaOH concentration variable (%), and C is the stirring speed variable (rpm).

$$\text{Lignin} = 1.1 + 0.473A - 4.54B + 0.178C - 0.00174A^2 + 0.2425B^2$$

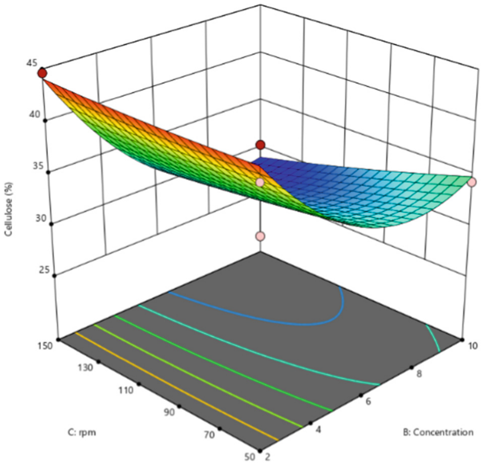

Fig. 8. Effect of concentration and rpm variables on cellulose content

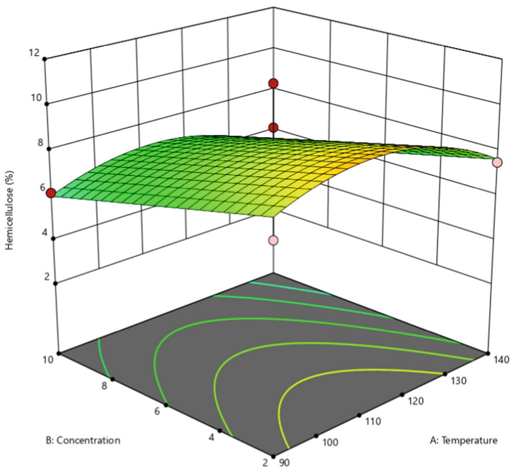

Fig. 9. Effect of concentration and temperature variables on hemicellulose content

$$- 0.000477C^2 + 0.0024AB - 0.00082AC - 0.00182BC \quad (4)$$

$$\text{Cellulose} = 30 + 0.259A - 4.42B + 0.082C - 0.00060A^2 + 0.3218B^2 - 0.000064C^2 - 0.0013AB - 0.00067AC - 0.00776BC \quad (5)$$

$$\text{Hemicellulose} = - 34.7 + 0.598A - 0.04B + 0.225C - 0.00244A^2 - 0.0081B^2 - 0.000941C^2 - 0.00256AB - 0.000415AC - 0.00090BC \quad (6)$$

Before pretreatment, the cellulose content in tobacco stalks was 41.714%. After alkaline pretreatment, the most optimal content was 31.194%, followed by a decrease

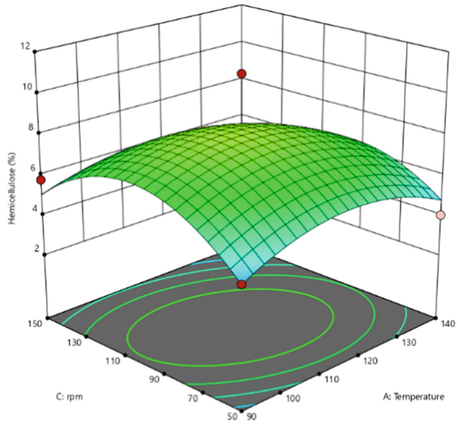

Fig. 10. Effect of rpm and temperature variables on hemicellulose content

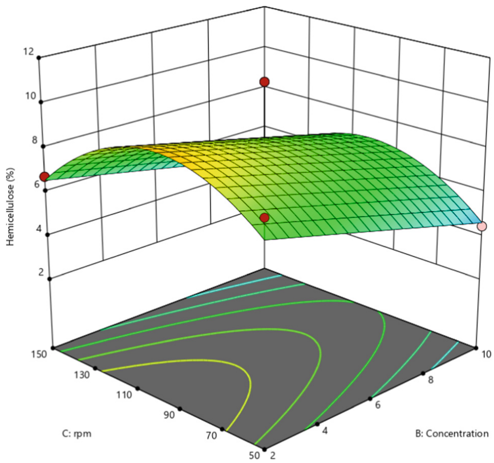

Fig. 11. Effect of rpm and concentration variables on hemicellulose content

in the amount of hemicellulose and lignin. The decrease in cellulose in the pretreatment process was 25.219%. This is because, in the lignin degradation process, there is cellulose which is also degraded and dissolved with lignin. According to Ingrid et al. [12], the increase and decrease in cellulose content can be caused by several things. First, the cellulose content in each run sample is different, while the cellulose content calculation uses the same initial content for each run.

The most effective pretreatment treatment with cellulose content was found in the experimental NaOH concentration of 6%, the temperature of 140 °C, and the stirring speed of 150 rpm for 1 h. From Fig. 6, it is known that the smaller the NaOH concentration and the rotating speed, the higher the cellulose content will be. However, the high content of cellulose was not followed by a decrease in lignin content according to the purpose of delignification, namely the removal of lignin content. This is presumably because OH- is not selective in attacking lignocellulose. OH- can break the bonds of lignin to cellulose because, in the process of severing lignin, the cellulose bonds can swell and enlarge. If OH- continues to attack, it will reduce the level of cellulose that dissolves with NaOH [13].

4 Conclusion

The conclusion of this research is the optimum conditions in this study were a NaOH concentration of 6%, a temperature of 140 °C, and a rotational speed of 150 rpm with the yield of lignin 12.463%, cellulose 31.194%, and hemicellulose 3.172%.

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References

1. Yuan, Z., Wei, W., Wen, Y., Wang, R. 2019. Comparison of alkaline and acid-catalyzed steam pretreatments for ethanol production from tobacco stalk. Industrial Crops & Products. 142 (111864): 1-8.
2. Ferdiyansyah, A.R. dan Rachmawati, R. 2019. Analisis Data Tembakau Provinsi Jawa Timur. Surabaya: Badan Pusat Statistik Jawa Timur.
3. Cai, J., Li, B., Chen, C., Wang, J., Zhao, M., Zhang, K. 2016. Hydrothermal carbonization of tobacco stalk for fuel application. Bioresource Technology. 220: 305–311.
4. Sun, D., Wang, B., Wang, H.M., Li, M.F., Shi, Q., Zheng, L., Wang, S.F., Liu, S.J., Sun, R.C. 2019. Structural elucidation of tobacco stalk lignin isolated by different integrated processes. Industrial Crops & Products. 140 (111631): 1-9.
5. Sudiyani, Y., Aiman, S., Mansur, D. 2019. Perkembangan Bioetanol G2: Teknologi dan Perspektif. Jakarta: LIPI Press.
6. World Bioenergy Association. 2019. Global Bioenergy Statistics 2019. Stockholm: World Bioenergy Association.
7. Hendrawati, T.Y., Ramadhan, A.I., Siswahyu, A. 2018. Pemetaan Bahan Baku dan Analisis Bioetanol dari Singkong (Manihot Utilissima) di Indonesia. Jurnal Teknologi. 11 (1): 37-46.
8. Palupi, B. Fachri, B.A., Rahmawati, I., Susanti, A., Setiawan, F.A., Adinurani, P.G., Mel, M. 2020. Bioethanol used as topical antiseptics: Pretreatment optimization of bioethanol production from tobacco industrial waste. Annals of Tropical Medicine & Public Health. 23 (8): 1-7.
9. Kim, J.S., Lee, Y.Y., Kim, T.H. 2016. A review on alkaline pretreatment technology for bioconversion of lignocellulosic biomass. Bioresource Technology. 199: 42–48.
10. Wang, Y., Guo, X., Li, K., Nan, Y., Wang, J., Zhang, J., Dou, S., Li, L., Liu, G., Yang, M. 2019. Comparison of a solvent mixture assisted dilute acid and alkali pretreatment in sugar production from hybrid Pennisetum. Industrial Crops & Products. 141 (111806): 1-8.
11. de Carvalho, D.M., de Queiroz, J.H., Colodette, J.L. 2016. Assessment of alkaline pretreatment for the production of bioethanol from eucalyptus, sugarcane bagasse and sugarcane straw. Industial Crops and Products. 94: 932–941.

12. Inggrid, M., Yonathan, C., & Djojosubroto, H. 2011. Pretreatment Sekam Padi dengan Alkali Peroksida dalam Pembuatan Bioetanol.
13. Lestari, M.D., J., Sudarmin, Harjono. 2018. Ekstraksi Selulosa dari Limbah Pengolahan Agar Menggunakan Larutan NaOH sebagai Prekursor Bioetanol. Indonesian Journal of Chemical Science, 7(3): 237–241.