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Pretreatment of Tobacco Stems As Bioethanol Raw Material: The Effect of Temperature and Time Using Chemical Method

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Abstract. One type of alternative energy currently developed in Indonesia is bioethanol. The use of bioethanol as a fuel has several advantages compared to oil fuels such as cleaner burning and environmentally friendly because carbon monoxide gas emissions are lower, so it does not contribute to the accumulation of carbon dioxide in the atmosphere. Bioethanol can be made from biomass raw materials which contain sugar, starch, or cellulose. One of the abundant biomass in Indonesia is tobacco. Jember Regency has 6,078 ha of tobacco plantations. With an estimated number per hectare of 22,000 trees with an estimated stem weight of 0.5 kg, so 66,858 tons of tobacco stem waste will be available in Jember Regency. The availability of abundant tobacco stems is very potential to be used as raw material for making bioethanol. One of the important steps of bioethanol processes is pretreatment. This process aims to separate cellulose, hemicellulose, and lignin. Cellulose produced from the pretreatment process will be hydrolysis in the next stage. The amount of cellulose that can be separated from lignin and hemicellulose will affect the results in bioethanol production. The purpose of this research is to know the effect of temperature and time on the pretreatment process. The pretreatment method used is a chemical method because it has several advantages such as the cost is cheap, the material is easy to get, time is fast, and does not require high energy compared to other methods. The solvents used are H_2SO_4 and HCl. Analysis of lignin, cellulose, and hemicellulose using the Chesson method. Temperature variations in this research were 100ºC, 120ºC, and 140ºC. For H_2SO_4 solvents, the optimum temperature is 100ºC with time 60 minutes obtained the cellulose 23.52%. For HCl solvents, the optimum temperature is 120ºC with time 60 minutes obtained the cellulose 24.43%.

INTRODUCTION

The depletion of fossil energy reserves, encouraging researchers to develop the energy that can replace it in the future. Based on data from the Ministry of Energy and Mineral Resources of the Republic of Indonesia in 2018, proven reserves of petroleum in Indonesia are around 3.3 billion barrels, equivalent to 0.2% of proven reserves of world oil. This encourages the Indonesian government in developing Biofuel to reduce the consumption of fuel oil. This is also in line with the Republic of Indonesia's Presidential Regulation No. 5 of 2006 that targets the use of biofuel by 5% of total primary energy by 2025. This policy is also supported by Minister of Energy and Mineral Resources Regulation No. 12 of 2015, which targets the use of bioethanol to 20% of total needs diesel oil and gasoline in 2025. The use of bioethanol as a fuel has several advantages compared to fuel that is cleaner burning and environmentally friendly because carbon monoxide gas emissions are lower so, it does not contribute to the accumulation of carbon dioxide in the atmosphere [1,2]. Aside from being used as fuel, bioethanol is also used as raw material for alcohol, pharmaceutical, and cosmetic derivatives [3].

Bioethanol can be made from biomass raw materials that contain sugar, starch, or cellulose [4,5]. Biomass is a raw material that is easily available in Indonesia because it is endowed with fertile soil and abundant biological resources. One of the abundant biological resources in Indonesia is tobacco. Based on Indonesian Plantation Statistics data, the area of tobacco plantations of smallholders and state plantations reached a total of 189,657 ha in 2018. East Java Province is a province that has the largest tobacco plant area in Indonesia, namely 94,887 ha. Jember Regency itself has 6,078 ha of tobacco plantations. At present, the use of tobacco is still focused on the leaves, while the stems

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are only left as waste. Even after the harvest season, tobacco stems are only left and stacked on the edge of rice fields. Though this tobacco stem is one of the biomass that can be used as raw material for making bioethanol. With a population range of 22,000 trees per hectare of land and an estimated weight of 0.5 kg of tobacco stems, 66,858 tons of tobacco stem waste will be available in Jember Regency.

Tobacco stems have high cellulose content so that they have the potential to become biofuel raw material for bioethanol. The cellulose content in tobacco stems can reach 35-40% for dry tobacco stems [6]. Tobacco stems contained 56.10% cellulose components, lignin 15.11%, and nicotine 0.26% [7]. The content of lignin, cellulose, and hemicellulose in tobacco stems were 25.2%, 44.6%, and 30.2%, respectively [8]. Lignocellulose in tobacco stems has a density of around 260-350 kg/m^3 with a chemical structure and composition similar to wood from broadleaf wood species [6]. Naturally, cellulose is bound by hemicellulose and protected by lignin [9].

The process of making bioethanol from tobacco industry waste goes through several stages of the process. In general, the process of making bioethanol includes pretreatment, hydrolysis, fermentation, and distillation. The biomass pretreatment stage aims to separate lignin, cellulose, and hemicellulose before being processed at a later stage [10,11]. Optimal separation of cellulose and hemicellulose from lignin is expected to produce optimal bioethanol production as well. Based on this, the pretreatment stage of tobacco industry waste is one of the important stages because it will affect the final output of bioethanol production [12,13]. Pretreatment methods are divided into 4, namely physical methods, chemical methods, biological methods, and physicochemical methods. Comparison of each pretreatment method can be seen in Table 1 [1]. Therefore, this research will optimize the chemical method pretreatment to separate lignin, cellulose, and hemicellulose. Pretreatment chemical method was chosen because it has several advantages compared to other methods, namely the cost is cheap, the material is easy to get, the time is fast, and does not require large energy. There are several chemical methods in the pretreatment process, namely using concentrated acids, dilute acids, and bases. The type of base that is often used is NaOH, while the types of acid are HCl and H_2SO_4. Acid pretreatment is done by immersing the material in an acidic solution and heated at a temperature of 100-200°C with a maximum period of 1 h [14]. This method is an option because the price of acid is relatively low and easy to obtain.

TABLE 1. Comparison of Various Pretreatment Methods [1]

No.	Pretreatment Method		Main Effect	Advantages	Deficiency
1	Physical	Mechanical	Reducing the crystallization of cellulose	There is no formation of inhibitors	Consume large energy
2	Chemical	Weak acid	Hemicellulose hydrolysis	- Low corrosion effect - Low inhibitor formation rate	Need to recycle chemicals
		Strong acid	Cellulose and hemicellulose hydrolysis	High glucose yield	High corrosion effect
3	Biological	Microorganisms and fungi	Degrades lignin and hemicellulose	Low energy consumption	The production rate is slow so it requires a long time
4	Physicochemical	Ammonia fiber explosion (AFEX)	Eliminating lignin and hemicellulose	Low inhibitor formation rate	- Expensive costs - Inefficient for biomass that contains a lot of lignin

MATERIALS AND METHODS

Materials

The materials used include tobacco stems (from farmer group of 'Karunia Tembakau' in Tamansari, Jember Regency, Indonesia), aquades, H_2SO_4, HCl, aluminum foil, and filter paper. Lignin, cellulose, and hemicellulose content in raw material can be seen in Table 2.

TABLE 2. Cellulose, Hemicellulose and Lignin Composition in Tobacco Stems

Raw Material	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Tobacco stems	50.320	6.495	32.005

Sampel Preparation

The tobacco stems are dried beforehand in the sun using sunlight. After drying, the tobacco stems are crushed with a chopper machine. Next, the tobacco stems were sieved with 60 mesh sieves so that a uniform size was obtained. The raw material is weighed, then dried in the oven for 1 h at a temperature of 60-70°C.

Pretreatment

One gram of tobacco stem sample was put into a beaker glass and soaked with 10 mL 4% H_2SO_4. Then it is heated in an oven at 100 °C, 120 °C, and 140 °C for 30 minutes. Each variation was repeated three times. Analysis of lignin, cellulose, and hemicellulose content. Then, 1 g sample was prepared again, which was put into a beaker glass and soaked with 10 mL 4% H_2SO_4 with time variations of 45 and 60 minutes using the optimum temperature. Analysis of lignin, cellulose, and hemicellulose content. Repeat the same steps for pretreatment with 4% HCl solution.

Analysis of Lignin, Cellulose, and Hemicellulose

Analysis of lignin, cellulose, and hemicellulose was carried out by the Chesson method. The test methods were:
One gram of dry sample (a) was added with 150 mL of distilled water and heated at 100°C for 2 h. Then filtered with filter paper and the residue is rinsed with distilled water. The residue is then dried in an oven until the weight is constant and then weighed (b). The residue was added with 150 mL of H_2SO_4 1 N, then flushed with water bath for 1 h at 100°C. The results are filtered and washed until neutral. The residue is dried to a constant weight and weighed (c). Dry residue was added to 100 mL 72% H_2SO_4 and soaked at room temperature for 4 h. Then added 150 mL of H_2SO_4 1 N and refluxed at 100°C with a water bath for 2 h. The residue is filtered and washed with distilled water until it is neutral. The residue is then heated in an oven at 105°C until the weight is constant and weighed (d). Then the residue is blushed by heating at 600°C for 4-6 h and weighed (e).

Lignin, cellulose, and hemicellulose levels can be calculated using the following formula:

Lignin level = (d-e) / a x 100% (1)

Cellulose content = (c-d) / a x 100% (2)

Hemicellulose level = (b-c) / a x 100% (3)

Data Analysis

To determine the optimum temperature, a graph of pretreatment results (cellulose vs. temperature) was made. The optimum temperature can be seen from the optimum pretreatment results. The optimum time can be determined by graphing the results of pretreatment (cellulose vs. time). The best solvent can be determined by comparing the results of pretreatment, which is the highest cellulose content. Data analysis was also carried out by considering the Arrhenius equation. The Arrhenius equation is as follows:

$$k = A.e^{-\frac{Ea}{RT}} \quad (4)$$

(k is the rate constant, A is the frequency factor, Ea is the activation energy, R is the gas constant, and T is the reaction temperature).

RESULTS AND DISCUSSIONS

Dry tobacco stems that have been crushed with a chopper can be seen in Figure 1. Tobacco stems were obtained from the 'Karunia Tembakau' farmer group in Wuluhan Village, Tamansari District, Jember Regency, East of Java Province, Indonesia.

(a) (b) (c)

FIGURE 1. Sample Preparation: (a) Dry tobacco stems that have been crushed, (b) Sieved tobacco stems with 60 mesh sifter, (c) Oven-dried tobacco stem

Pretreatment

The purpose of the pretreatment process is to break down the structure of lignin and change the crystalline structure of cellulose, so that acids or enzymes can easily hydrolyze cellulose [15]. Comparison of the biomass structure before and after the pretreatment can be seen in Figure 2. From Figure 2 it is clear that lignin, cellulose, and hemicellulose are bound to each other so that pretreatment needs to be done to break the bond

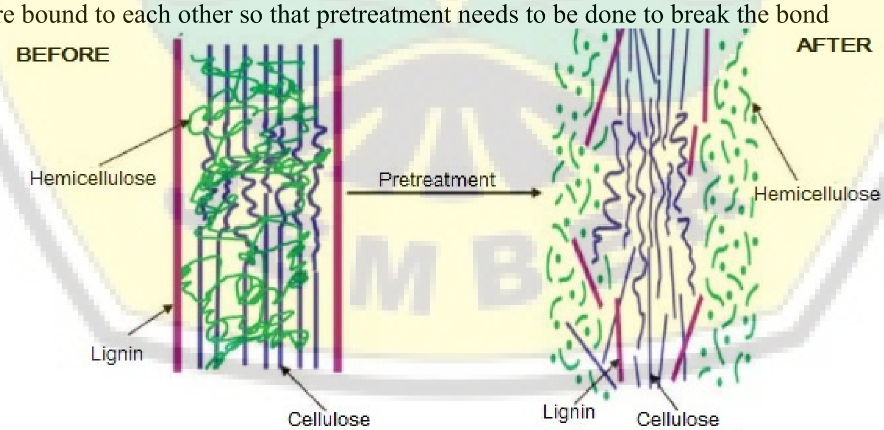

FIGURE 2. Tobacco Stems Before and After Pretreatment [15]

In this study, the tobacco stem pretreatment process was carried out using chemical methods. To get optimal pretreatment results, the sample: acid solution ratio is used 1 g: 10 mL [16]. Acid solutions used are H_2SO_4 and 4% HCl [17]. Samples pretreated with H_2SO_4 and HCl can be seen in Figure 3 and Figure 4.

FIGURE 3. Samples pretreated with H2SO4

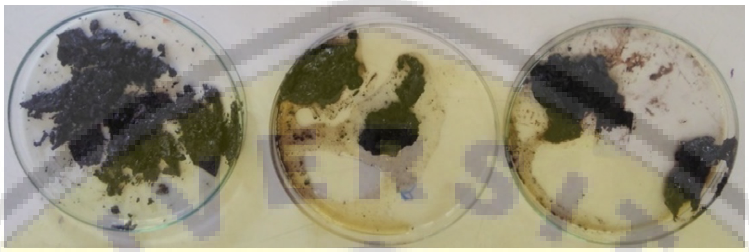

FIGURE 4. Samples pretreated with HCl

The Effect of Temperature

Pretreatment for biomass is generally carried out in a temperature range of 100ºC - 140ºC [18]. Pretreatment with acids can be carried out at high temperatures >160ºC and low temperatures <160ºC [15]. The effect of temperature on cellulose produced with 4% H2SO4 acid solvent can be seen in Figure 5. Based on Figure 5, the highest cellulose content at 100ºC is 6.99%. When the temperature is raised to 120ºC, cellulose levels decrease to 6.60%. Likewise, when the temperature is raised again to 140ºC, the cellulose level decreases to 4.47%. Therefore, the optimum pretreatment temperature with 4% H_2SO_4 in this study was reached at 100ºC.

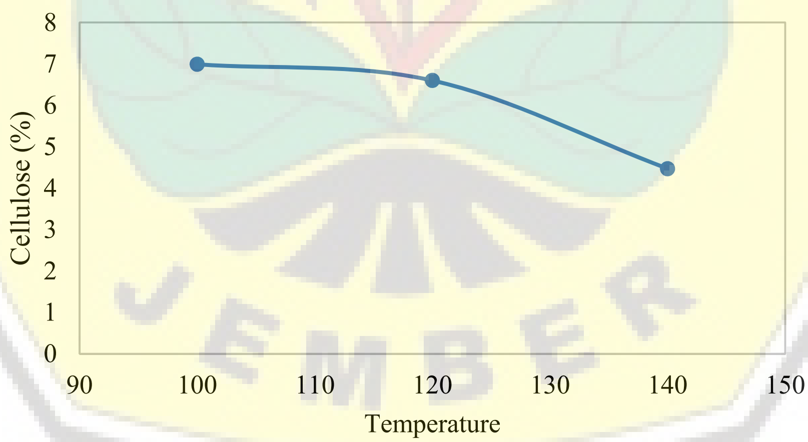

FIGURE 5. Graph of Temperature vs. Cellulose with H_2SO_4 Pretreatment

Based on Figure 5 shows that an increase in temperature indicates a decrease in the amount of cellulose using sulfuric acid pretreatment method This condition was analyzed because the magnitude of the acid strength of sulfuric acid (Ka_1 $1x10^3$ and Ka_2 $1x10^{-2}$) increased temperature instead causing a side reaction namely hydrolysis of cellulose. The magnitude of the temperature will result in greater energy possessed by H_2SO_4 molecules where this condition is by the Arrhenius equation. The amount of energy possessed by H_2SO_4 coupled with high acid strength will initiate the pretreatment process better coupled with the presence of side reactions namely the occurrence of the cellulose hydrolysis reaction itself.

Effect of temperature on cellulose content with 4% HCl acid solvent can be seen in Figure 6. The pretreatment process with 4% HCl at 100°C results in cellulose content of 6.00%. Cellulose levels increased to 6.23% when the temperature was raised to 120°C, but decreased to 5.66% when the temperature was raised to 140°C. Thus, the optimum temperature in the pretreatment process with 4% HCl is 120 °C.

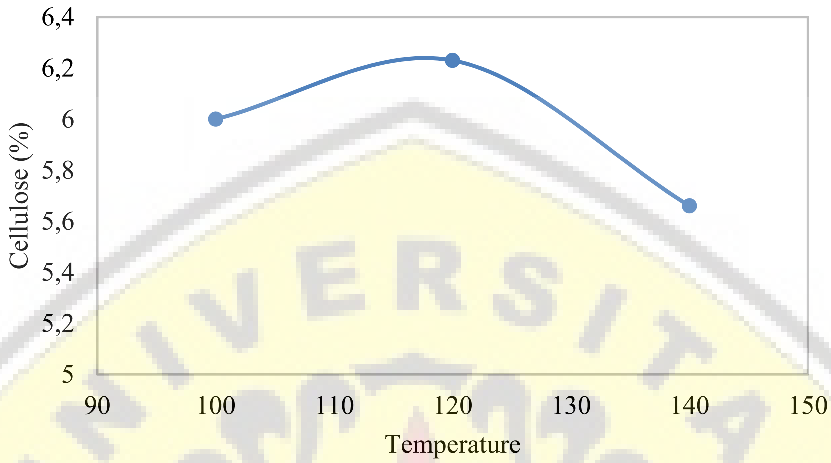

FIGURE 6. Graph of Temperature vs. Cellulose with HCl Pretreatment

Based on Figure 6 shows that at a temperature of 100°C, the pretreatment conditions were not optimal as indicated by the magnitude of lignin levels and small cellulose levels. This is because even though the acid strength of acetic acid is high ($1.3x10^6$), HCl is only able to ionize H+ ions once. So that with the same volume of addition as the pretreatment method using H_2SO_4, higher energy is needed to produce optimum conditions from the pretreatment process. The amount of energy needed in the process will be proportional to the amount of temperature involved during the process. This condition is by the Arrhenius equation where the amount of energy needed during the chemical reaction process is proportional to the temperature involved during the process.

The greater the temperature involved during the pretreatment process, it turns out that the pretreatment condition is not optimal. This is indicated at temperatures of 140°C where the amount of cellulose is significantly reduced. This is because of the magnitude of the temperature results in the high energy possessed by the molecule HCl so that the reaction does not only occur between lignin and HCl but also cellulose with HCl.

The Effect of Time

In the pretreatment process with H_2SO_4 at the temperature of 100°C with time variations of 30, 45, and 60 minutes, the cellulose increased. It can be seen in Figure 7. Consequently for 30, 45, and 60 minutes cellulose produced 6.98%, 18.45%, and 23.52%. So, for the time of 30-60 minutes, the optimum cellulose results were obtained at 60 minutes, with 23.52% cellulose content.

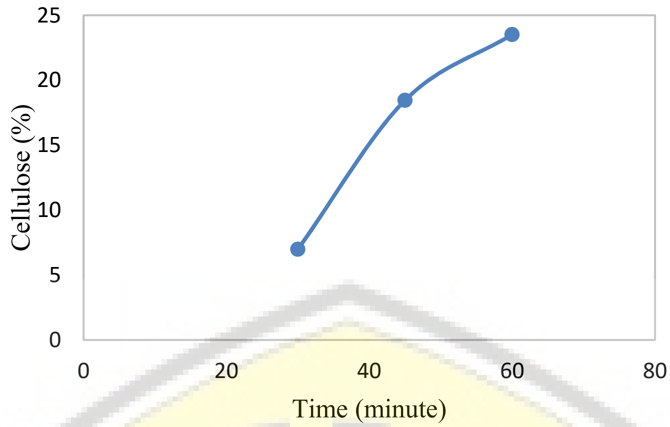

FIGURE 7. Graph of Time vs. Cellulose with H_2SO_4 Pretreatment

Pretreatment with HCl at the temperature of 120ºC with a variation of time 30, 45, and 60 minutes, the cellulose increased, but the change in cellulose levels from 45 minutes to 60 minutes was not significant. It can be seen in Figure 8. Respectively for 30, 45, and 60 minutes cellulose produced 6.23%, 24.12%, and 24.43%. So, for time of 30-60 minutes, the optimum cellulose results were obtained at 60 minutes with 24.43% cellulose content.

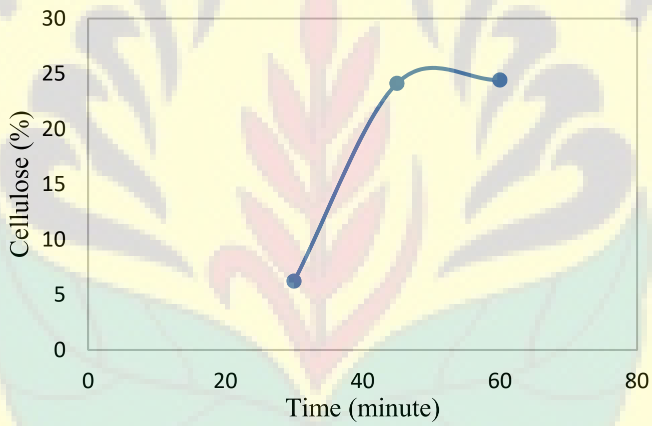

FIGURE 8. Graph of Time vs. Cellulose with HCl Pretreatment

Cellulose in tobacco stems as a raw material before pretreatment is 50.320. After pretreatment with H_2SO_4, cellulose, which can be separated from lignin, was 23.52%, while pretreatment with HCl was produced 24.43%. The result of separation in the pretreatment process is only about 50% of the initial content. This is because the process of separating lignin, cellulose, and hemicellulose is not easy so that separate cellulose cannot be 100%. The results of this research are better than other research that using the same raw material, i.e. tobacco stems. The comparison of research results with other research can be seen in Table 3.

TABLE 3. Comparison of Research Results with Other Research

This Research		**Other Research [17]**	
Solvent	Cellulose (%)	Solvent	Cellulose (%)
H_2SO_4 4%	23.52%	H_2SO_4 4%	16.88
HCl 4%	24.43%	HCl 4%	14.07

CONCLUSION

The optimum time and temperature in the pretreatment process with H_2SO_4 for the temperature range of 100ºC - 140ºC and time span of 30-60 minutes are the temperature of 100ºC and time 60 minutes, with the resulting cellulose content of 23.52%. The optimum time and temperature in the pretreatment process with HCl for a temperature range of 100^{o}C - 140^{o}C and time span of 30-60 minutes are the temperature of 120^{o}C and time 60 minutes, with the resulting cellulose content of 24.43%.

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