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The Effect of Pretreatment Process on Lignocellulosic Materials with a Combination of Microwaves and Alkaline Solvents on Solid Products

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ABSTRACT

The pretreatment process is important in treating lignocellulosic-rich biomass such as sugarcane bagasse. The lignocellulosic structure is strong, and the proportion of crystals is high, complicating the fermentation process. Still, it needs to be converted to a more amorphous structure for easy access to fermenting enzymes. The pretreatment process is carried out with alkaline solvents and microwaves in this study. The process begins by standardizing the size of the bagasse powder used. Sugarcane bagasse powder and NaOH alkaline solvent were mixed in a three-necked round-bottom flask. The reactor used in this study was a modified domestic microwave equipped with a temperature controller and condenser. The results showed that this modification was significant to reduce the weight of the residual solid product compared to the initial weight of the raw material. Process variables such as reaction time and solvent concentration significantly affect the cellulose content of solid products. However, hemicellulose content showed different results. The results of the XRD analysis showed that the crystallization index of the effect decreased with increasing pretreatment time. Pretreatment with microwaves and alkaline solvents was successful with satisfactory structural changes in the cellulosic solid.

Keywords: *lignocellulosic; NaOH base; microwave; pretreatment.*

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ABSTRAK

Proses *pretreatment* menjadi langkah penting dalam pemrosesan biomassa dengan kadar lignoselulosa yang tinggi seperti ampas tebu. Struktur lignoselulosa yang kuat dan memiliki kandungan kristal yang tinggi yang mempersulit proses fermentasi harus diubah menjadi struktur yang lebih amorf sehingga mudah di akses oleh enzim fermentasi. Proses *pretreatment* dengan bantuan pelarut alkali dan gelombang mikro dilakukan dalam penelitian ini. Proses diawali dengan melakukan penyeragaman ukuran serbuk ampas tebu yang digunakan. Setelah itu, serbuk ampas tebu, pelarut basa NaOH bersama-sama dimasukkan ke dalam labu alas bulat leher tiga. Reaktor yang digunakan dalam penelitian ini adalah *microwave* domestik yang telah dimodifikasi dengan dilengkapi pengatur suhu dan kondensor. Hasil penelitian menunjukkan bahwa berat produk solid yang diperoleh menurun signifikan jika dibandingkan dengan berat awal bahan baku. Variabel proses seperti waktu reaksi dan konsentrasi pelarut memberikan efek cukup signifikan terhadap kandungan selulosa dalam produk solid. Namun hasil yang berbeda ditunjukkan untuk kandungan hemiselulosa. Hasil analisis XRD menunjukkan bahwa indeks kristalisasi produk menurun dengan meningkatnya waktu *pretreatmnet. Pretreatment* dengan menggunakan gelombang mikro dan pelarut basa telah berhasil dilakukan dengan hasil yang cukup memuaskan yaitu terjadinya perubahan struktur selulosa produk solid.

Kata kunci: *lignoselulosa;* basa NaOH*; microwave; pretreatment.*

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INTRODUCTION

Bioethanol is equivalent to gasoline, which can be applied as a fuel for transportation. In 2006, global bioethanol production reached 51.3 billion liters, increasing from 45.98 billion liters in

2005. Ethanol from biomass is highly competitive compared to other liquid fuels on a large scale. This is due to improving bioethanol production technology by enzymatic hydrolysis of cellulose [1]. Bioethanol production from biomass is one solution to reduce petroleum and environmental pollution.

As an agricultural country, Indonesia has enormous potential related to the development of bioethanol production from sugarcane bagasse. The availability of sugarcane bagasse is very abundant, about 2,991,114 tons, which is 35-40% of the processed sugarcane. Considering the huge amount of raw materials, bioethanol production can reach 614,827 kl [2][3].

The bioethanol production process converts raw materials in the form of lignocellulose into fermentable sugars such as glucose to be further fermented to produce bioethanol. The high lignocellulose content in bagasse makes bagasse a perfect candidate for the bioethanol raw material. The sustainable production of bioethanol from lignocellulosic has various challenges due to the complex nature of lignocellulosic materials with high crystallization, which requires high cost and complicated pretreatment procedures [4][5][6]. Previous researchers have tried several pretreatment strategies to increase the recovery of sugars from lignocellulose.

Microwave irradiation has become the focus of recent research as an effective pretreatment method, either applied alone or in combination with other chemicals. Microwave irradiation has high heating efficiency, uniform heating properties, easy operation and short processing time. Microwaves change cellulose structure by removing lignin and hemicellulose to increase the accessibility of cellulose to hydrolytic enzymes. Microwaves allow dipole rotation and ionic conduction in lignocellulosic materials to produce uniform heat in a short time. Microwave heating creates 'hot spots in the lignocellulosic matrix, which results in explosive action on the lignocellulosic crystal structure, which allows disruption of the lignocellulosic structure more rapidly than conventional heating [5].

Some research has been done about the advantages of NaOH base as material pretreatment method lignocellulosic. Sudiyani et al. (2010) [7] reported that pretreatment with alkali (NaOH 1N) on empty oil palm fruit bunches (TKKS) gave a better performance to remove lignin compared to acid with an optimal lignin loss rate of 45.8%. Asgher et al. (2013) [8] also reported that the treatment of 4% NaOH for 30 minutes at 121°C on bagasse resulted in 48.7% delignification. Muslimah (2017) reported the benefits of using NaOH base as a solvent in the pretreatment process using a microwave because it has a high dipole moment value to maximize wave absorption [9]. This research aimed to study the effect of microwave irradiation in combination with alkali solvent for the pretreatment process of sugar bagasse on the obtained solid product.

LITERATURE REVIEW

Lignocellulosic materials such as sugarcane bagasse are promising to be utilized as raw materials for biofuels production. Sugar bagasse is an abundant agricultural waste in Indonesia. It is only used around 60 % for boiler fuel, raw material for paper, mushroom industry, industrial raw materials brake pads and others. Meanwhile, 40% of the sugar bagasse has not been employed. The composition of sugar bagasse is in Table 1.

Tabel 1. Composition of Sugar Bagasse

Component	Percentage (%)
Water	48-52
Sugar	3.3
Fiber	47.7

Bagasse fibre is insoluble in water and consists mostly of cellulose, pentosan and lignin [10]. Lignocellulosic pretreatment is crucial in biomass usage as raw material for bioethanol. It influences the efficiency of the whole process, including saccharification. The primary purpose of pretreatment is to solve the rigid structure of cellulosic biomass [11], an example of the disruption of the higher-order structure of lignocellulosic during pretreatment.

The pretreatment process is intended to elevate the surface area and volume of the pores. It also could curtail the crystallinity of cellulose. The tenacity of the lignocellulosic biomass greatly hinders the production of fermentative sugars. Biomass intolerance is affected by physical properties such as the crystal structure of cellulose and the polysaccharide matrix and lignin layer of cellulose fibres, which hinder the enzymatic penetration in cellulose. Meanwhile, the chemical solvent could increase solubility and depolymerization of lignocellulosic polymer structures and disruption of crosslinks between macromolecules [11].

The pretreatment processes are divided into chemical, physical, biological, or a combination of these processes. Each type has its strengths and weaknesses. A pretreatment method that performs on benign reaction conditions is extremely hunted due to the ability to decrease sugar degradation and inhibitor [2][8]. The pretreatment step is costly, and it spends 18% of the full fermentation alcohol investment cost [11]. Improving the production yields by pretreatment would decrease the production costs.

Alkali catalysts, such as calcium oxide (lime), ammonia, and sodium hydroxide, specifically focus on hemicellulose acetyl groups and lignin-carbohydrate ester bonds are applied in alkaline pretreatment [12][13][14]. Alkaline hydrolysis is the saponification of intermolecular ester bonds crosslinked hemicellulose xylan and other components (lignin) and other hemicelluloses. Along with the loss of crosslinking, it could raise the porosity of lignocellulose [12]. The alkaline pretreatment process produces hemicellulose and whole cellulose [1]. Pretreatment of aqueous NaOH causes swelling, leading to an increase in internal surface area, decrease in the degree of polymerization, decrease in crystallinity, separation of structural relationships between lignin and carbohydrates, and disruption of lignin structure.

Calcium hydroxide has been shown to be an effective and inexpensive pretreatment agent. Amorphous substances such as lignin and hemicellulose are removed by pretreatment with lime. This substance causes an increase in the degree of crystallinity. There is a correlation between lignin content, crystallinity, and acetyl content, such as delignification and deacetylation removing parallel barriers to enzymatic hydrolysis. Crystallinity significantly affects the initial hydrolysis rate but less affects the final sugar yield [15]. The enzymatic hydrolysis of lime treated biomass is affected by the resulting structure of the treatment. The main structure influencing is the degree of acetylation, lignification, and crystallization.

The complex mechanisms are generated by microwave heating. It depends on several factors, such as microwave propagation, the interaction between substances and microwaves, the materials dielectric properties, and heat dissipation due to mass transfer and heat. Dielectric properties thus determine a material's ability to change electromagnetic energy into thermal energy in the microwave range, containing its dielectric loss (ε") and dielectric constant (ε`). Dielectric loss refers to the ability of the material to generate heat from electromagnetic radiation. Meanwhile, the dielectric constant is the capability of the material to do polarization due to electric field [11].

A high dissipation coefficient illustrates an increased sensitivity to microwave energy. Microwave heating enhances the collapse of stable structures as it can cause inter-particle explosions. Transformation in the ultra-structure of cellulose after irradiation have been reported. Microwave irradiation and aqueous solution give thermal and non-thermal effects, making microwave irradiation an assuring pretreatment process. Due to the high-temperature hemicellulose degradation, performing a pretreatment process at moderate temperature is desired. Microwave radiation has been well utilized for pretreatment due to its specific thermal and non-thermal effects. These can lead to fragmentation and swelling, which causes the degradation of lignin and hemicellulose [11].

METHOD

This research was carried out in two stages: the preparation of raw materials and the pretreatment stage with the microwave. The raw material used is bagasse which is obtained from the waste of the local sugar industry. The raw material preparation stage begins with drying it under the sun for two days and mashing it using a blender. The bagasse powder is then sieved using a 50-mesh sieve to uniform the size of the raw material. The raw material is ready for the pretreatment process by microwave.

Pretreatment was carried out using a modified domestic microwave with a temperature setting and equipped with a condenser. A total of 5 g of bagasse powder and 200 ml of NaOH solution (technical grade) with various concentrations (0.2, 0.4 and 1 M) were put into a round flask and then put into the microwave. Pretreatment was carried out at 180°C with a reaction time range (5 minutes to 30 minutes). After the pretreatment, the solution was separated from the residual solids by filtration. The solid fraction was rinsed with ethanol (3 × 50 ml) and dried at 50°C overnight. Solid product ready to be analyzed. The XRD method analyzed the solid product's crystal phase and particle size before and after pretreatment. Meanwhile, the cellulose and hemicellulose content analysis were carried out using the Chesson method.

RESULT AND DISCUSSION

Bagasse is a sugarcane processing waste that is not used correctly. With a high lignocellulosic content, bagasse can be used as a promising raw material for bioethanol production. The pretreatment process is important in processing lignocellulosic materials because of their complex structure. The most significant component of bagasse was composed of cellulose by 52.7%, and the remaining lignin by 24.2% and hemicellulose by 20%. The fermentation process can remove high lignin content. The process of removing lignin is known as delignification. The delignification process used varied concentrations of NaOH (0.2, 0.1, and 1 M). The pretreatment process with NaOH can remove the content that binds cellulose in sugarcane bagasse. The purpose of the pretreatment process is to break down the lignin structure, break down crystalline cellulose, increase the material's porosity, break down hemicellulose, and depolymerize hemicellulose [12].

In the pretreatment process was used 5 grams of sugarcane bagasse powder. After the pretreatment process was carried a microwave, the amount of bagasse produced showed a significant decrease. The decrease that occurred ranged between 42-50%. Detailed data on the weight loss of bagasse is shown in Figure 1. The results showed the more intensive delignification activity and degradation of cellulose and hemicellulose with NaOH pretreatment led to a weight loss of sugarcane bagasse.

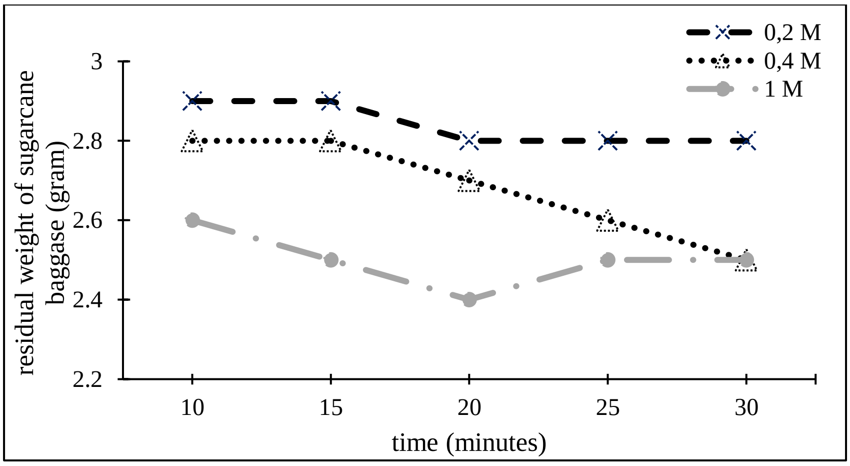


Figure 1. The effect of Reaction Time and Solvent Concentration on the Residual Weight of Sugarcane Bagasse

The increasing heating time and NaOH concentration increased weight loss in bagasse. Using 1 M NaOH and a reaction time of 10 minutes, the weight of bagasse obtained at the end of the reaction was 2.6 grams and decreased slightly to 2.5 grams with an extension of the reaction time by 30 minutes. The same results are shown for the other concentration of NaOH used. The increasing reaction time gave the higher weight loss in sugarcane bagasse. The effect of NaOH concentration on bagasse weight loss can be seen in the same picture (Figure 1). Increasing the concentration of NaOH gives more weight loss of bagasse. At the reaction time of 10 minutes, the most significant loss of bagasse was obtained when using NaOH with a concentration of 1 M, which was 48% and decreased to 42% when using 0.2 M. This delignification resulted in a reduction in the original weight associated with the loss of lignin levels of the sugarcane bagasse. The same result with Fajriutami (2016) reported increasing heating time and NaOH concentration tend to increase the loss in bagasse [17].

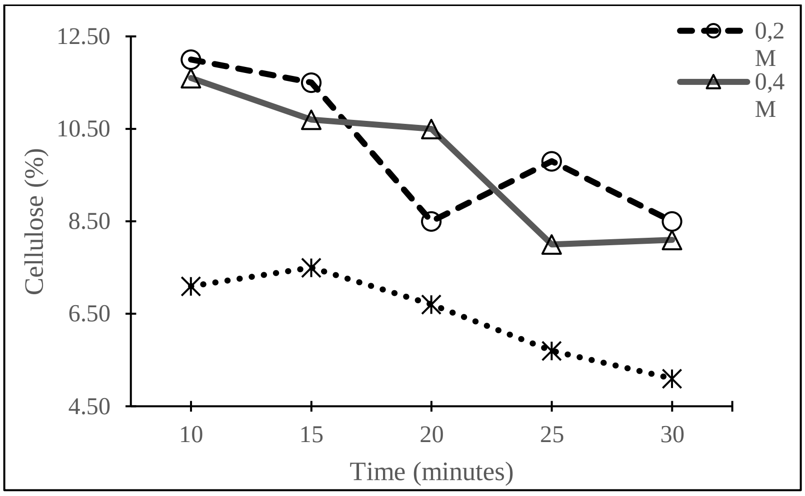


Figure 2. The effect of Reaction Time and Solvent Concentration on the Percentage of Cellulose

The effect of reaction time and alkali solvent concentration on cellulose content can be seen in Figure 2. Cellulose content decreased with increasing pretreatment time when 1M NaOH was used. The cellulose content after 10 minutes was 7.10% and dropped to 5.10% as the reaction time increased to 30 minutes. The same trend is observed when using alkaline solvents with 0.1M and 0.4M. The longer the reaction time, the longer the breakdown of the cellulose into fermented sugars, the more sugar is released as a liquid product. After the pretreatment process, the cellulose will be in the solid-state, and some will be in the liquid state.

Figure 2 also shows the effect of the concentration of the alkaline solvent used in the cellulose composition. The higher the concentration used, the lower the cellulose content obtained. Figure 2 shows that the higher the concentration used, the more efficient the hydrolysis of lignocellulose and the breakdown of long cellulose chains into reducing sugars. The results showed that the most significant cellulose degradation occurred in 1 M NaOH for almost all reaction time variables.

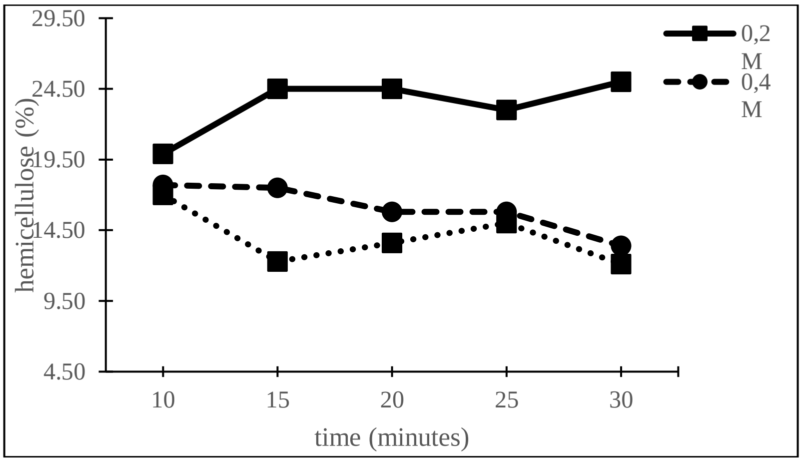
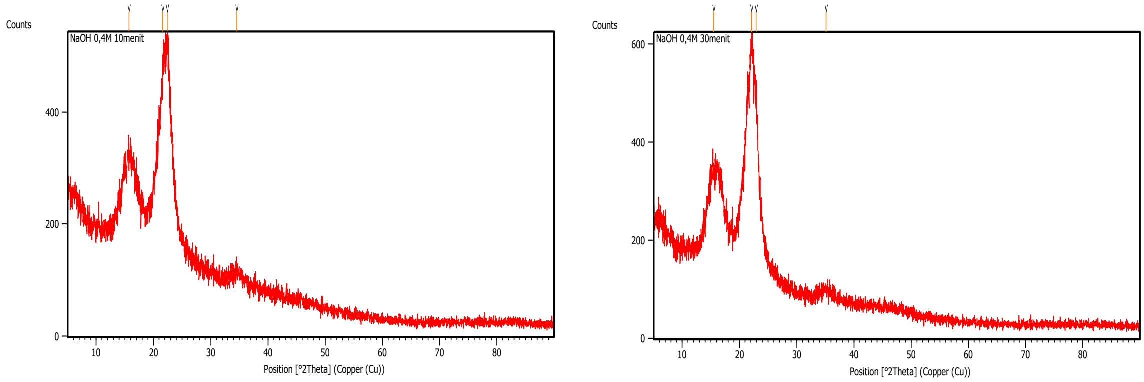


Figure 3. The Effect of Reaction Time and solvent Concentration on the Percentage of Hemicellulose

Figure 3 depicts the effect of pretreatment time and NaOH concentration on hemicellulose composition. The hemicellulose hydrolysis process will produce simple sugar compounds such as xylose, mannose, glucose and galactose that are ready to be fermented to produce bioethanol. As a result, when using 1 M and 0.4 M concentrations, the hemicellulose content in the solid material decreased as the pretreatment time increased. The reduction was not significant enough. On the other hand, we obtained different results for a variable concentration of 0.1 M. It was found that the hemicellulose content of the solids increased when the pretreatment time was increased from 10 minutes to 30 minutes**.** These results indicate that with a reaction time ranging from 10-30 minutes with a concentration of 0.1 and 1 M, NaOH is not effective enough to pretreat the hemicellulose components. The results show not enough significant changes that happened with changes in process variables**.** NaOH provides better performance in the hydrolysis of cellulose compared to hemicellulose.



(a) (b)

Figure 4. XRD Pattern of Sugarcane Bagasse for (a) 10 minutes and (b) 30 minutes

The pretreatment process is used to reduce the crystallinity of the cellulosic structure and accelerate the fermentation process. Figures 4 (a) and (b) show the XRD analysis results related to the crystallinity of the product. The analysis results showed that the longer the reaction time, the lower the crystallinity of the product. XRD analysis presented that the peaks 2θ around 23° and 15° indicates cellulose peaks. The height illustrates the crystallinity level of cellulose is rigid [15]. The peak in the crystallinity index decreased in prolongation time reaction. This may be because NaOH treatment can change the structure of cellulose. Base solvent diffuses into the matrix of cellulose, and it causes the long chain of cellulose to expand and rearrange during processing. It led to destroy the structure of crystalline cellulose. The crystal structure change causes the increase of the amorphous cellulose, leading to a decrease in the crystallinity index. In this diffractogram, the cellulose crystallinity was calculated by Eq. 1 [16].

$$I_c = \left(\frac{I_{200} - I_{am}}{I_{200}}\right) x\ 100 \quad \text{..........} (1)$$

I_c represents index of crystallinity of substance, meanwhile represent peak at 2θ around 23° and peak at 2θ between 23° and 15° respectively. The calculation showed that the crystallinity index of the product was 71.7% in the reaction time of 10 minutes and decreased to 67.5% when the reaction time was extended to 30 minutes. These results indicate that the longer the pretreatment time, the lower the crystallization index of the cellulose compound and the more sugar is released into the liquid phase.

CONCLUSION

The bagasse pretreatment process with the assistant of alkaline solvents and microwaves was successfully carried out. The results showed that this method was sufficiently effective to deal with the cellulose component. The changes in process variables lead to transform in the cellulose structure of the product. Increasing the reaction time could lower the crystallization index of the product. This means that more amorphous phases are formed, and more sugar is released.

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