THE EFFECT OF CHEMICAL AND MICROWAVE HEATING TREATMENT FOR REDUCING SUGAR RECOVERY

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Abstract

Microwave heating treatment was the one type of pretreatment process used in the manufacture bioethanol because it can be applied singly or in combination with other chemicals. The purpose of this study was to determine the effect of microwave heating on the pretreatment process using acid and alkaline solvents. The research was carried out in two stages, namely the preparation of raw materials and pretreatment with microwave. At the stage of preparation of raw materials, bagasse was dried for 2 days and then crushed to a size of 50 mesh to uniform the size of the raw materials. The raw materials that have been prepared are then subjected to a pretreatment process. The pretreatment process was carried out using a modified microwave with temperature settings and the addition of a stirrer. 5 grams of bagasse powder and 200 ml of a solution of H_2SO_4 or NaOH (0.2 M, 0.4 M, and 1 M) were put into a round tool flask and then put into the microwave. Pretreatment was carried out at 180°C with time variables of 10, 15, 20, 25, and 30 minutes. Then the solution was separated from the residual solid by filtration and the solution was neutralized with 1 M HCl. The results showed that the use of acidic and alkaline solvents, high concentrations of solvents can lead to smaller the acquisition of reducing sugars in the liquid product phase. The highest percentage of reducing sugar obtained is 0.559% when using an acid solvent with a concentration of 0.1 M for 20 minutes.

Keywords: *microwave, bioethanol, pretreatment*

Introduction

Bagasse is one of the most promising types of raw materials in the manufacture of bioethanol. Bagasse waste generated in sugar production is 35–40% of each processed sugarcane. In addition to the abundant amount, the largest composition contained in bagasse is lignocellulose, making bagasse a very potential raw material for the manufacture of bioethanol. Bagasse is a second-generation raw material for the manufacture of bioethanol. The bioethanol production process can be defined as the process of converting raw materials in the form of lignocellulose into simple sugars such as glucose to be further fermented to produce bioethanol. The production of bioethanol from lignocellulosic through four stages of the process sequentially, namely pretreatment, hydrolysis, fermentation, and separation/purification. The conversion process of lignocellulose to bioethanol is much more difficult than simple sugars due to the nature of the lignocellulosic material which is composed of a very regular and complex structure where the lignin-hemicellulose-cellulose matrix is very dense and protected by lignin (Mikulski and Klosowski, 2020). Various kinds of challenges for sustainable production of bioethanol from lignocellulosic materials, such as the complex nature of lignocellulosic materials with high crystallization areas, required high costs and uncomplicated pretreatment procedures (Pooja et al., 2018).

The pretreatment process is the most important process so that the conversion of lignocellulose into bioethanol is successful. The purpose of pretreatment is to destroy the cellulose structure. The pretreatment process must meet the requirements of an increase in sugar formation or the ability to form further sugars by hydrolysis, avoid degradation and loss of carbohydrates, avoid the manufacture of products that inhibit the hydrolysis process, and subsequent fermentation, and the whole process must be cost-effective (Swiatek and Slawik, 2010). Physical, physicochemical, chemical, and biological processes have been used for the pretreatment of lignocellulosic biomass. Pretreatment either chemical or enzymatic hydrolysis was carried out to remove lignin and hemicellulose from lignocellulosic biomass, reduce cellulose crystallinity, and increase the porosity of the material. Acid chemical hydrolysis is used to break down higher sugar molecules. Chemical pretreatments vary widely from acid to alkaline. Chemical pretreatment methods consist of ozonolysis, acid hydrolysis, alkaline hydrolysis, oxidative delignification, and organosol process. Each method is similar but differs in implementation methodology. Acid hydrolysis targets hemicellulose and lignin, dissolving most of these components from plant cell wall structures and increasing the accessibility of enzymes to cellulose. However, during the process several degradation products are formed such as furfural, 5-hydroxymethylfurfural, phenolic acids and aldehydes, levulinic acid, and other aliphatic acids which can inhibit enzymatic hydrolysis and fermentation (Swiatek and Slawik, 2010). Acid hydrolysis pretreatment was carried out by hydrolyzing the hemicellulose fraction and leaving the cellulose and lignin intact in the residual solid. Concentrated acids such as H_2SO_4 or HCl can be used in this process. Disadvantages of this method are toxicity, corrosivity and dangerous concentrated acids. In addition, concentrated acid must be recovered after hydrolysis to make the process economically feasible.

Dilute acid hydrolysis has also been successfully developed for the pretreatment of lignocellulosic materials. There are two types of dilute acid pretreatment process: 1) high temperature (more than 433 K), continuous flow process for low raw material loading; 2) low temperature (less than 433 K), batch process for high raw material loading (Cheng, 2002). The use of dilute sulfuric acid is to hydrolyze hemicellulose and to make cellulose more available for enzymatic hydrolysis. The reduction of sugar degradation is carried out through a two-step process. The first stage was carried out under mild processing conditions for pentose recovery. The second stage was carried out under higher conditions for hexose recovery. One of the disadvantages of dilute acid hydrolysis is the higher cost of dilute acid pretreatment than physicochemical methods. In addition, pH neutralization is required for downstream enzymatic hydrolysis or fermentation processes. In the alkaline hydrolysis pretreatment, alkaline catalysts such as calcium oxide (lime), ammonia, and sodium hydroxide, which specifically target the hemicellulose acetyl groups and lignin-carbohydrate ester bonds are used in this pretreatment. Alkaline hydrolysis is the saponification of intermolecular ester bonds crosslinked hemicellulose xylan and other components (for example: lignin) and other hemicelluloses. Along with the loss of crosslinking can increase the porosity of lignocellulose. The alkaline pretreatment process produces hemicellulose and whole cellulose. Pretreatment of aqueous NaOH causes swelling and it leads to: increase in internal surface area, decrease in degree.

In the pretreatment process for lignocellulosic materials, the use of microwaves has advantages such as more effective heating, faster heating, reducing equipment size and process steps and increasing production. Microwave as an energy source generates heat from the interaction between materials at the molecular level without changing the molecular structure. Microwave heating has several advantages over conventional heating, such as indirect heating (non-contact heating) which reduces excess heating of the surface of the material, transfers energy instead of heat transfer (penetrative radiation), and reduces thermal gradients.

The purpose of this study was to determine the effect of microwave heating on the pretreatment process using acid and alkaline solvents. In this research, the effect of using chemicals, both acids and bases, in the pretreatment process will be studied. This research was conducted because there have not been many studies on the pretreatment of raw materials using microwave heating

Research Methods

The materials used in this study were bagasse, H_2SO_4 (0.2 M, 0.4 M and 1 M), NaOH (0.2 M, 0.4 M and 1 M), and HCl (1M).

This research was conducted in two stages, namely the preparation of raw materials and pretreatment with a microwave. At the stage of preparation of raw materials, the bagasse is dried which is obtained from the waste of the local sugar industry. Dried using sunlight for 2 days (T = ±30˚C) and then mashed using a blender. The refined bagasse (bagasse powder) was sieved with a size of 50 mesh to uniform the size of the raw material.

The raw materials that have been prepared are then continued for the next stage, namely the pretreatment process. The pretreatment process was carried out using a modified microwave with temperature settings and the addition of a stirrer. 5 grams of bagasse powder and 200 ml of H_2SO4 or NaOH solution (0.2 M, 0.4 M, and 1 M) were put into a round flask and then put into the microwave. Pretreatment was carried out at 180 °C with time variables of 10, 15, 20, 25, and 30 minutes. After the pretreatment, the solution was separated from the residual solids by filtration. Then the sample solution was neutralized with 1 M HCl. The characterization method used was the reducing sugar test.

Results and Discussion

The pretreatment process becomes an important stage when using lignocellulose-based materials into bioethanol raw materials. The purpose of the pretreatment process is to break down the complexity structure of the lignocellulose so that enzymes can access the fermentation process. Various kinds of pretreatment processes have been developed by previous researchers such as chemical processes using acid and base solvents, physical processes, biological processes and physical chemical processes. In this study, a combination of the pretreatment process will be carried out, namely pretreatment using chemicals with *microwave* heating. The variables of the processes studied are the concentration of solvents, the length of the pretreatment process and the type of solvent used. The reactor used in the study was a modified conventional microwave equipped with a condenser, thermocouple and stirrer.

The pretreatment process with acidic solvents is carried out at a temperature of 120 °C for 10–30 minutes. Temperature pretreatment was chosen below 150 °C to avoid the process of forming inhibitors due to the continued reaction of lignocellulose hydrolysis (Rasmussen et al, 2014). Rahman et al., (2020) stated that two operating conditions can be chosen to avoid inhibitors forming, as followed 1) pretreatment using a low concentration of acid solvents below 2 % (v/v) with a reaction temperature above 150 C and a reaction time of more than one hour or 2 hours pretreatment using a high acid concentration above 2% (v/v) with a low reaction temperature for one hour.

The effect of reaction time and solvent concentration on the percentage of sugar reduction with acid solvents can be seen in Figure 1. From Figure 1, it can be seen that the use of high concentrations of acid solvents, 0.4 M and 1 M, resulted in a lower percent of reducing sugar when compared to the use of acid concentrations of 0.1 M. The higher the concentration of acids used, the lower the result of reducing sugar. The tendency shown for the use of concentrations 0, 4 and 1 M is almost the same, performing a slight increase with an increase in reaction time, although the increase is not significant enough. For the use of a concentration of 0.1 M, the prolongation of reaction time from 10 minutes to 25 minutes caused the obtained reducing sugar increased from 0.168% to 0.18% and went down to 0.161% when the reaction was extended to 30 minutes. Meanwhile different results were shown for the use of solvent concentrations of 0.2 M where the extended of reaction time from 10 minutes to 20 minutes led to enhancement in reducing sugar from 0.05% to 0.559% and decreased to 0.227% when the reaction time was extended to 30 minutes.

The reduction in the amount of reducing sugar released may be due to the phenomenon of further degradation of sugar into other components such as acetic acid, furfural and 5-HMF (Rahman et al., 2020). The compound furfural resulted from the further degradation of xylose and arabinose. Meanwhile acetate acid is formed from the process of further hydrolysis of the acetyl group in the hemicellulose. The same trend was also reported by previous studies such as Rahman et al., (2020) and Rajan and Carrier (2014). At the use of longer pretreatment times and higher concentrations of acid solvents, furfurals compounds will undergo a further degradation reaction to formic acid and levulinic acid (Rahman et al., 2020).

Hydrogen ions released from the breakdown of cellulose and hemicellulose will become sugar monomers that are soluble in hydrolysate. However, at the same time, hydrogen ions are also bound to the hydroxyl sugar group resulting in a dehydration reaction. This could lead the furfural concentrations increased (Islam et al., 2017).

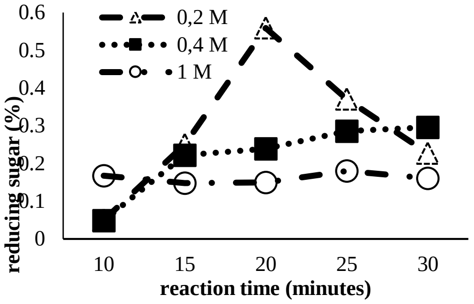

Figure 1. The effect of reaction time and concentration of acid solvents on the percentage of reduced sugars

The process of pretreatment using alkaline solvents is the most effective method by which this process affects the biomass lignin content. The main effect of alkaline solvents is delignification by the breakdown of lignin and xylene cross-bond esters, thereby increasing biomass porosity (Sudiyani et al., 2015) . During the NaOH pretreatment reaction, NaOH is dissociated into hydroxide ions (OH^-) and sodium ions (Na^+), the elevation of hydroxide ion concentrations increase the rate of hydrolysis reactions (Portero-Barahona et al., 2019) . The effect of the concentration of alkaline solvents and the reaction time of pretreatment can be seen in Figure 2. The Figure showed that for the use of base concentrations 0.2 M and 0.4 M have a tendency to the same result, but different tendencies are shown in the use of 0.1 M. At the usage of a lower concentration of alkaline solvents of 0.1 M, the extended in reaction time from 10 minutes to 25 minutes leads to degradation in the reducing sugar obtained from 0.067% to 0.021% and again rose up on the increase in the 30-minute reaction time to 0.076%. This decrease may be due to the destruction of the internal structure of biomass caused by the long pretreatment time (Chatkaew et al., 2021) .

The same trend is shown by the results of research conducted by Mandra Harahap et al (2020). In the use of alkaline solvents, the phenomenon of an increase in the yield of reducing sugar within 30 minutes, after which the reducing sugar decreases from a reaction time of 10 to 25 minutes, may be due to the instability of the process. In addition, this may be due to the fact that the rate of decomposition of reducing sugars into furan is lower than the rate of reducing sugars extrication from the lignocellulosic structure.

Meanwhile, for the use of alkaline concentration 1 M, the increase in reaction time from 10 minutes to 15 minutes caused a slight increase in reducing sugar from 0.006% to 0.009% and return went down to 0.005% when the reaction is extended to 30 minutes.

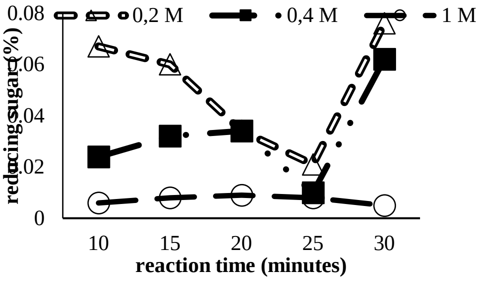

Figure 2. Graph of the effect of reaction time and concentration of base solvents on the percentage of reduced sugars

From Figure 2, it can be seen that the use of alkaline solvents with high concentrations leads to much lower the reducing sugar when compared to the application of low alkaline concentrations. The higher the concentration of the base solvent used, the lower the reducing sugar released in the liquid product. The effectiveness heating of microwaves may lead milder operation conditions (lower concentrations of NaOH and shorter reaction time) gave better results when compared to high operation conditions. The high concentrations of solvent can cause take place hydrolysis quickly so that further degradation reactions can occur. This is what causes the percentage of reducing sugar to decrease.

The interaction between solvents, water and microwaves exerts a complex effect on the biomass pretreatment process. The process of pretreatment with microwave heating provides more effective heating when compared to conventional heating. The interaction between heat and biomass occurs directly and heat in generation from within biomass. The direct interaction of microwaves causes the molecules to collide, and eventually organic reactions in biomass are accelerated. This results in heating biomass becoming more effective. The process of pretreatment using a microwave could cause the hard structure of lignocellulose could be damaged and cellulose crystallization could be reduced.

Table 1. The effect of pretreatment process on the degree of acidity

Solvent	Pretreatment time (minutes)	pH initial	pH result
Base	10	13,301	13,010
	15	13,301	13,199
	20	13,301	13,161
	25	13,301	13,153
	30	13,301	12,801
Acid	10	0,398	0,275
	15	0,398	0,331
	20	0,398	0,067
	25	0,398	0,234
	30	0,398	0,258

The phenomenon that occurs during the pretreatment process using microwaves is the silicified waxy surface destroyed that could cause ester and ether bonds between lignin to break down (Mandra Harahap et al., 2020). The usage of a microwave as a heating source depends on the polar properties present in the system. Polar properties are defined by system dipole moments. Sodium hydroxide has a dipole moment of 6.89 Debye, higher than sulfuric acid of 3.09 Debye (Keshwani et al., 2009). The higher the moment dipole, the more heat is generated in the sample and the easier the process of destroying biomass cell (Jönsson, 2016).

The degree of acidity (pH) is one of the parameters of the occurrence of the sugar degradation process in a pretreatment process. The selection of the type of pretreatment solvent has a significant effect on the final pH of the product. The alteration in pH after the application of sulfuric acid vary between 0.05-0.33 and 0.02-0.46 for the use of sodium hydroxide solvents. The alteration in pH that occur may be caused by changes in the structure of lignocellulose during the pretreatment process. In general, whether the use of acidic or alkaline solvents, the pH of the product is lower when compared to the initial pH. This decrease in pH may be due to the formation of organic acids, such as acetic acid and lactic acid as a result of the process of degradation of sugar monomers (Ethaib et al., 2016). The same result was also shown by (Dwi Argo et al., 2016). Ph changes may be caused by ionization of H^+ from water compounds due to compression.

The pretreatment process using microwaves can accelerate the release of reducing sugars from the lignocellulosic complex structure. This is because microwaves can produce effective heating where heat is generated from the internal biomass. Besides, the interaction between biomass, solvent and microwaves complexly results in a strong breakdown of the lignocellulosic structure. This mechanism will reduce heat losses due to the radiation process (Keshwani et al., 2009).

Conclusion

The pretreatment process using chemical methods combined with microwave heating has been successfully carried out. The results showed that both the use of acidic and alkaline solvents, high concentrations of solvents can lead to smaller the acquisition of reducing sugars in the liquid product phase. This may be due to the further degradation of sugar monomers formed after the pretreatment process becomes another component. The interaction between solvents, water and microwaves results a complex effect on the biomass pretreatment process which causes the reaction could be run done under milder conditions. The highest percentage of reducing sugar obtained is 0.559% when using an acid solvent with a concentration of 0.1 M for 20 minutes.

Process optimization should be studied further considering the pretreatment process using microwave produces complex interactions. Determination of optimal operating conditions is influenced by biomass loading, solvent concentration and reaction time.

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