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Comparison of Ultrasonic Wave Pretreatment and Microwave-KOH Combination Pretreatment in Producing Bioethanol Using Rice Husk Waste

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Abstract

Rice husk is a type of lignocellulosic biomass that can be chosen as a raw material for bioethanol production because it is abundant, cheap, and renewable. However, when it comes to lignocellulosic biomass, the main obstacle in using rice husks is the pretreatment process to remove the lignin content and prepare the lignocellulose so that it can be easily hydrolyzed. In this study, two combinations of pretreatment were used, namely microwave pretreatment and ultrasonic pretreatment, which used several variables. Microwave pretreatment uses variable time (2.5 minutes, 5 minutes, and 7.5 minutes) and power (100, 180 and 300 watts) as well as ultrasonic pretreatment uses variable time (20 minutes, 25 minutes, and 30 minutes) and power (70, 80 and 90 watts). The pretreatment results were hydrolyzed with sulfuric acid and fermented using saccharomyces cerevisiae yeast at varying times (3, 6, 9, 12, and 15 days). This research shows that microwave pretreatment is the most effective in reducing lignin. The lowest lignin content was 10.58% after 5 minutes and 180 watts of power. Bioethanol levels increased until the 15th day of fermentation, with the highest yield of 16%.

Keywords: bioethanol, microwave, pretreatment, rice husks, ultrasonic

INTRODUCTION

Petroleum fuel continues to experience depletion along with increasing consumption. This is because oil fuel is produced from refining processes that cannot be renewed. The increase in fuel use is also influenced by the rise in the number of motorized vehicles in Indonesia, which reached 2,520,439 or an increase of 1.88% in 2019-2020 and is predicted to continue to increase (Badan Pusat Statistik, 2023). This situation is supported by (Mutezo & Mulopo, 2021). Fossil fuels are insufficient to meet global energy demand due to several challenges (such as greenhouse gas emissions and rapid depletion).

In suppressing this crisis, alternative energy substitution is needed, such as using biomass for bioethanol. Bioethanol is an environmentally friendly biofuel sourced from biomass. The raw material for bioethanol comes from biomass, which has carbohydrates, such as starch and sugar. Bioethanol can be used as a transportation fuel in its pure form, but it is blended to increase the octane of gasoline additives and vehicle emissions (Roy & Abedin, 2022).

Indonesia is an agricultural country that makes rice a commodity whose needs must be met because rice is the staple food of the Indonesian population. According to data from the Badan Pusat Statistik (2023), Central Java Province is one of the rice barns with a productivity of 56.69 qu/ha and a production of 9,578,069 tons in 2022. This high production figure impacts the amount of agricultural waste, such as husks, produced. So far, rice husks have been widely used for fertilizer, and this use is considered less than optimal if we look at the contents contained therein. According to, (Ningrum et al., 2022), rice husks contain high cellulose levels of 59.2%, so they have the potential to be converted into alternative bioethanol fuel.

In the bioethanol processing process made from rice husks, lignin content can be the main obstacle in conversion. Pretreatment must be done because lignin is the primary inhibitor in the cellulose hydrolysis process. Lignin is a phenolic polymer network that glues cellulose fibres together to become very strong (Dinarta Hanum & Suprihana, 2018). Pretreatment or delignification removes the hemicellulose and lignin content by destroying the cellulose crystal structure. Damage to the crystal structure can cause cellulose to degrade into glucose quickly. Next, the sugar compound will be fermented by a microorganism to become ethanol (Tamzil, 2017).

Several delignification methods are commonly applied, including mechanical, chemical, and biological. Examples of mechanical methods are kraft, soda and oxygenation. Meanwhile, chemically, namely pulping, mechanical refining, and biologically, for example, the enzymatic method. However, each of these methods has several disadvantages, including liquid waste from delignification that uses chemicals, which is classified as dangerous waste because it is toxic and pollutes the environment (Dinarta Hanum & Suprihana, 2018).

METHODS

MATERIALS

The rice husks, which were the focus of this research, were obtained from Kedungasem village, Sumber, and Rembang, with the research carried out at the biomass processing technology laboratory, Semarang State University. The main objective of the pretreatment process carried out is to reduce the presence of various compounds, especially lignin, which have the potential to inhibit the rate of hydrolysis to increase the efficiency of converting rice biomass into value-added products. Rice husks, as lignocellulosic biomass residues from rice production, are a readily available agro-industrial waste. Every year, 180 million tones of rice husks are produced worldwide, and approximately 70% are burned for energy production (Fahad *et al.,* 2019).

RAW MATERIAL PREPARATION

Rice husks that have been sorted and cleaned from contaminants such as sand using distilled water, then dried in an oven at 100°C for 2 hours and let sit until they reach average temperature. Next, a blending process is carried out to obtain the required size variations and separation using a 35-mesh sieve. This entire process was carried out to prepare 18 samples, consisting of 9 ultrasonic and nine microwave pretreatment samples.

MICROWAVE PRETREATMENT

Several lignocellulose pretreatment methods have undergone development over the years, involving approaches such as the use of microwave waves, treatment with acids, alkalis, and inorganic salts, as well as the ammonia fibre expansion (AFEX) method (Laltha *et al.,* 2021). In this experiment, 20-gram samples from a 35-mesh sieve were prepared together with 200 mL of 0.5M KOH solution, keeping the ratio of rice husk samples and KOH solution constant at 1:10. The mixture was then homogenized in a glass beaker using a glass stirrer. After that, it was transferred to an Erlenmeyer flask, which was tightly secured with cotton wool and aluminium foil to avoid KOH evaporation during pretreatment. The following process involves heating using a microwave at 100 watts for 2.5 minutes, 5 minutes, and 7.5 minutes, 180 watts for 2.5 minutes, 5 minutes, and 7.5 minutes, and 300 watts for 2.5 minutes, 5 minutes, and 7.5 minutes. Neutralization was carried out with distilled water until the pH of the rice husk sample reached 7. The pH was calculated before and after pretreatment using a pH meter. The samples were then dried in an oven until their weight was constant before analyzing the lignin, hemicellulose and cellulose content using the Chesson method.

ULTRASONIC PRETREATMENT

Ultrasonic processes cause the formation, growth, and destruction of bubbles in fluids, resulting in high pressures and intense heating with very short lifetimes (John *et al.,* 2019). In this research, dried rice husk raw materials were prepared and blended to achieve a smaller size. Next, 20 grams of blended rice husks were separated using a 35-mesh sieve. A 0.5 M KOH solution with a volume of 200 mL was prepared, keeping the ratio of the rice husk sample and KOH solution constant at 1:10. The mixture of rice husks and the solution was mixed in a glass beaker until homogeneous with a glass stirrer. The ultrasonic device was prepared with variable power of 70, 80, and 90 watts, with sonication times of 20 minutes, 25 minutes, and 30 minutes, respectively. After sonication, the sample was washed until the pH reached ±7 then filtered using filter paper. The samples were then dried in an oven at a temperature of ±100°C until the sample weight was constant. After the pretreatment process, the sample will be analyzed using the Chesson method.

HYDROLYSIS

The principle of starch hydrolysis involves breaking the starch polymer chains into dextrose or monosaccharide units, especially glucose ($C_6H_{12}O_6$) (Bahri *et al.*, 2019). In this hydrolysis, the pretreatment results are put into a 500 ml Erlenmeyer flask, then 100 ml of distilled water is added, and the pH is adjusted to 4-5 using dilute H_2SO_4 little by little, then heated using an electric stove at 100°C for 120 minutes. The hydrolyzed rice husk slurry is filtered, cooled, and then fermented immediately.

FERMENTATION

One of the microbes generally used in the fermentation process to form ethanol is Saccharomyces cerevisiae because this microbe can reproduce without the need for sunlight and can operate in anaerobic conditions (Maharani *et al.,* 2021). Sterilize the tools that will be used in the fermentation process in an autoclave at 120°C for 20 minutes and cool the tools that have been sterilized. Prepare the saccharomyces cerevisiae microbe, which will be used to convert sugar into bioethanol. This bacterium was chosen because it has good conversion capabilities. Prepare starter bacteria as much as 1.05%w/v part of the substrate volume. This fermentation is anaerobically or without sunlight and maintained at pH 4-5 at a room temperature of 30°C. The fermentation process lasts for 15 days with three-day checking intervals.

CHESSON METHOD

The dried rice husk raw material was analyzed based on the experimental procedures described. Briefly, 1 g of sample (value a) was added with 150 mL of distilled water, then refluxed at 100°C for 1 hour. The residue resulting from filtering and drying (value b) was processed by adding 1N H_2SO_4, then refluxed again at a temperature of 100°C for 1 hour. The reflux results are filtered, neutralized, and dried (c value). Hemicellulose content is calculated from the b value minus the c value, divided by a value, and then multiplied by 100%.

Next, the residue was added with 72% H_2SO_4 and soaked at room temperature for 4 hours. After that, 150 mL of 1N H_2SO_4 was added and refluxed at 100°C for 1.5 hours. The samples were filtered, dried, and weighed as weight (d value). The total cellulose content can be calculated from the weight c minus the weight d, divided by the value a, then multiplied by 100%.

Finally, the residue, which has a known weight d, is ashed using a furnace at a temperature of 700°C for 40 minutes and weighed according to value (e). Total lignin can be calculated by subtracting the weight d from e, dividing the value a, and multiplying by 100%. This procedure provides important information regarding the composition of hemicellulose, total cellulose, and lignin in raw rice husk materials processed in the laboratory.

RESULTS AND DISCUSSION

Characteristics of rice husks

Rice husk, as a lignocellulosic material, presents cellulose, hemicellulose, and lignin composition, making it a potential source as a raw material in the bioethanol production process. The natural structure of cellulose is bound by hemicellulose, which protects lignin. As stated, the presence of lignin compounds is the main factor that makes hydrolysis of lignocellulosic materials difficult (handayani, 2018).

Through analysis, it was found that rice husks have a high cellulose content, allowing efficient conversion into bioethanol. However, it should be noted that bioethanol production from lignocellulosic biomass is more complex compared to sugar or starch because lignocellulose is challenging to hydrolyze directly. Therefore, in this research, the approach to reducing lignin content in biomass was carried out through a pretreatment method using a combination of microwave and ultrasonics. The aim is to overcome the obstacles to lignocellulose hydrolysis and increase the efficiency of the conversion process to bioethanol.

Table 1. Rice Husk Content Before Pretreatment Process

Parameter	Composition (%)
Cellulose	16.00
Hemicellulose	19.00
Lignin	33.00

Table 2. Rice Husk Content After Pretreatment Process

Sample	*Power (watt)*	Time (minute)	Cellulose (%)	Lignin (%)	Hemicellulose (%)
Ultrasonic	70	20	24,52	14,5	15,09
	80	20	18,63	25,49	11,76
	90	20	19,61	20,59	9,80
	70	25	20,00	20,00	9,00
	80	25	20,00	17,00	20,00
	90	25	24,47	16,04	7,55
	70	30	24,27	20,39	15,53
	80	30	19,80	19,80	19,80
	90	30	17,92	13,21	16,98
Microwave	100	2,5	25,00	20,00	23,00
	180	2,5	28,30	15,09	10,38
	300	2,5	20,37	22,22	17,59
	100	5	18,63	23,53	14,71
	180	5	26,92	10,58	15,38
	300	5	29,13	13,59	18,45
	100	7,5	22,77	15,84	14,85
	180	7,5	19,80	16,83	20,79
	300	7,5	19,23	17,31	22,12

PRETREATMENT TO INCREASE CELLULOSE LEVELS

In this research, temperature and power from ultrasonic and microwave treatment were measured as determining variables for the increase in cellulose content. This measurement aims to determine the optimal temperature and energy for the pretreatment of rice husks. The observation results can be seen in Figure 1 and Figure 2.

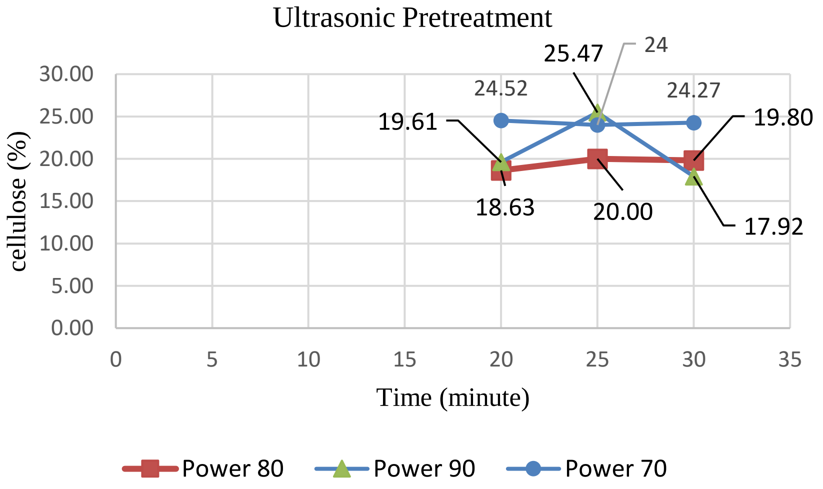

Figure 1. Effect of Ultrasonic Pretreatment on Increase in Cellulose Content (%)

Based on Figure 1, you can see the relationship between cellulose conversion and time and ultrasonic power. The maximum cellulose conversion results were obtained at 90 watts of power and

25 minutes of ultrasonic time with a conversion of 25.47%. In contrast to samples not subjected to ultrasonic pretreatment, the cellulose conversion rate was only 16%. After a sonication time of 25 minutes, there was a decrease in cellulose conversion to 17.95%. This also happened to other samples that underwent ultrasonic pretreatment because there were too many cavitation bubbles at high ultrasonic power, which produced a decoupling effect (Sui et al., 2023).

Apart from the influence of sonication time, variable ultrasonic power does not significantly impact the pretreatment of rice husks. As a comparison, samples of 70 watts show this for 25 minutes, 80 watts for 25 minutes, and 90 watts for 25 minutes, respectively, showing cellulose conversion results of 24%, 20%, and 25.47%. The use of ultrasonic waves in the pretreatment process is not aimed at hydrolyzing biomass into simple sugars but rather to facilitate the yield for hydrolysis using acid (Hapsari et al., 2015).

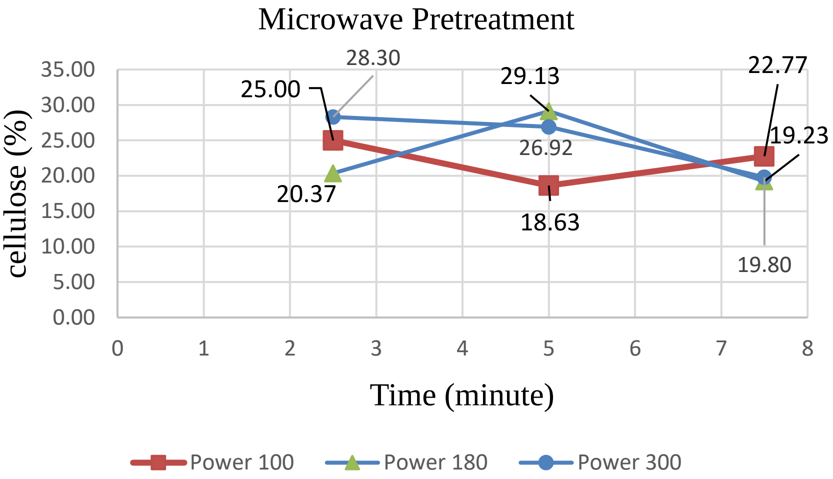

Figure 2 Effect of Microwave Pretreatment on Increase in Cellulose Content (%)

This research pretreated rice husk samples using a microwave and KOH solution. To determine the increase of cellulose and the decrease of lignin and hemicellulose, the lignocellulose content of the samples was measured before and after the processing process. This emphasizes that alkali affects the recovery of fermentable sugars and can be used efficiently for bioethanol production (Kamalini et al., 2018).

The highest cellulose conversion result of 29.13% was obtained from a sample with 180 watts of power for 5 minutes, followed by a 300-watt sample for 2.5 minutes with a cellulose conversion of 28.30%. At 7.5 minutes, there was a decrease in cellulose conversion with microwave-KOH pretreatment with 180-watt power by 9.9% and 300% power by 7.12%. According to (Ocreto et al., 2021), this is most likely caused by excessive exposure to high microwave power, which has a negative impact on sugar production. In general, increasing the power and contact time will increase the evaporation of water in the structure, damage the dielectric properties of raw materials, and generate toxic substances. This was also conveyed by (Kumar et al., 2019), who observed that increasing pretreatment time negatively influenced sugar yield.

PRETREATMENT TO REDUCE LIGNIN LEVELS

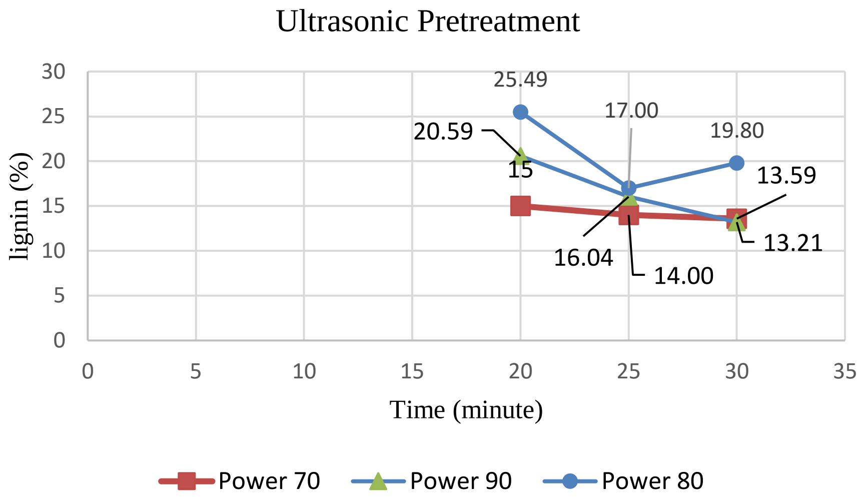

Figure 3. Effect of Ultrasonic Pretreatment on Reducing Lignin Levels (%)

From Figure 3, the lignin levels in all samples decreased at the 25th minute. Through Chesson-Datta calculations, the most optimal sample was identified at 90 watts of power with a lignin content of 20.59% at the 20th minute, which decreased by 4.55% at the 25th minute and reached 13.21% at the 20th minute. In accordance with (Saputra et al., 2018), high ultrasonic amplitude results in many bubbles forming and breaking, so the more significant the ultrasonic amplitude, the lower the lignin content.

Apart from the 90-watt power sample, the 70-watt power sample also experienced a decrease in lignin levels at 20, 25 and 30 minutes. However, in contrast to the 90-watt and 70-watt power samples, the 80-watt sample experienced a decline at 25 minutes and 30 minutes. Increase at 30 minutes. This is caused by the negative impact of high ultrasonic power on the cavitation effect (Sui et al., 2023).

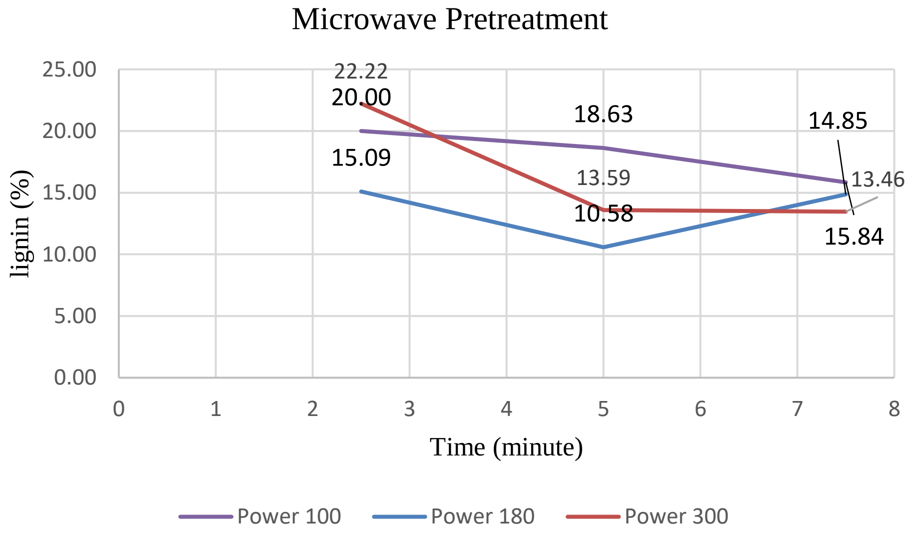

Figure 4. Effect of Microwave Pretreatment on Reducing Lignin Levels (%)

Pretreatment using alkaline solutions can increase efficiency by heating using microwave radiation as a heating system. Alkaline pretreatment using various solutions such as NaOH, NH_4OH, KOH, $NaCO_3$, and $Ca(OH)_2$ is often used in the decomposition of lignin as well as cellulose and hemicellulose simultaneously. The microwave-KOH method showed the most optimal results at 180 watts of power for 5 minutes with a lignin content of 10.58%. (Abeln et al., 2019) emphasized that short contact times ranging from 12 seconds to 8 minutes can produce higher sugar.

However, extending the pretreatment contact time using microwave-KOH reduces sugar yield and may increase the opportunity to produce inhibitors (Kumar et al., 2019). In addition, samples with

180 watts of power experienced an increase in lignin levels of 4.27% at 7.5 minutes. Most likely, this is caused by a lack of efficiency in the manual sediment transfer process, causing very fine residue and preventing maximum filtering and drying results.

EFFECTIVENESS ON FERMENTATION RESULTS

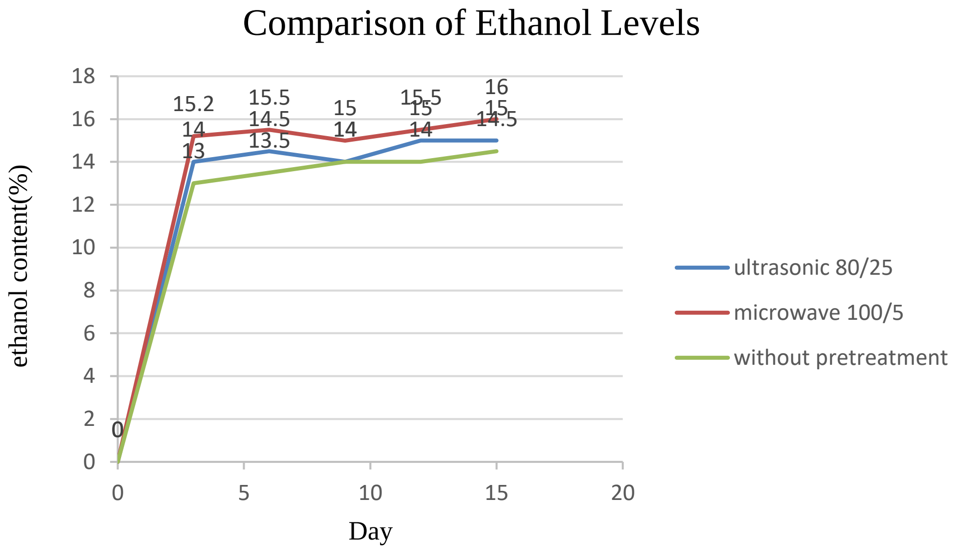

Figure 5. Comparison of microwave pretreatment and ultrasonic pretreatment to increase ethanol content.

In this research, two types of pretreatments were carried out: microwave-KOH pretreatment and ultrasonic pretreatment. The highest ethanol content results from microwave pretreatment were seen in the 100-watt sample for 5 minutes, reaching 16% on the 15th day. Meanwhile, in ultrasonic pretreatment, the highest results were found in samples at 80 watts for 25 minutes, with ethanol levels reaching 15% on the 15th day. Research without pretreatment produced the highest ethanol content of only 14.5%.

The fermentation process is influenced by glucose levels resulting from the hydrolysis of lignocellulosic biomass polysaccharides, such as cellulose and hemicellulose, into their constituent sugar monomers, namely glucose and xylose (Malau & Nugraha, 2022). In general, hydrolysis techniques are divided into two types: enzymatic hydrolysis and chemical hydrolysis using strong acid catalysts such as HCl, HNO_3 Monsieur, and H_2SO_4.

From the research results, it can be concluded that microwave-KOH pretreatment can produce the highest levels of ethanol. This is caused by the influence of microwave waves, which positively affect increasing cellulose and ethanol levels during the pretreatment process. This finding aligns with the explanation (Ocreto et al., 2021), which states that the microwave method is easier to manage, saves energy and time, and produces less pretreatment waste. In addition, microwave-assisted hydrolysis (MAH) has a hydrolysis concentration above 20% (w/v) and produces less pretreatment waste. The interaction between microwaves and materials during pretreatment produces a heating effect, damages the lignin structure more effectively, and increases ethanol content significantly compared to other pretreatment methods (Rosyidin *et al.*, 2015).

CONCLUSION

At the pretreatment stage, using both microwave and ultrasonic methods, it was observed that the samples experienced a significant increase in cellulose content compared to samples that did not undergo pretreatment. The results show that microwave pretreatment, especially at 180 watts with a contact time of 5 minutes, is optimal for effectively reducing lignin levels. The research also noted that microwave pretreatment positively impacted increasing ethanol levels because microwave waves succeeded in destroying the lignin structure more efficiently and growing cellulose levels in the pretreatment process.

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