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The effect of microwave power on lignocellulose content, physical and chemical characteristics of biomass: A review

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Abstract. Bioethanol is alternative energy derived from biomass that can be obtained from the agricultural industry to replace fossil fuels. The issue with biomass to energy conversion is the presence of lignin in lignocellulose biomass which inhibits the hydrolysis process. Microwave-acid pre-treatment is a method that combines microwaves and H_2SO_4 to break down lignin. In other studies, various microwave power is studied. The aim of this review is to provide insight and novelty into the effect of microwave power that is used on the lignocellulose content of rape straw and the physical and chemical characteristics of biomass after pre-treatment. Various microwave powers on delignification processes were presented, while the physical and chemical characteristics of pretreated biomass and also the prospect of future applications of microwave-assisted pretreatment were also discussed.

1. Introduction

Bioethanol is one of the alternative energies that can be used to replace fossil fuels. It has a promising potential in Indonesia since it is derived from biomass that can be obtained easily, especially regarding the fact that Indonesia has one of the largest agricultural industry which could provide a massive quantity of agricultural waste [1]. Since it was considered as a waste, it has a relatively low economic cost, so it has a major benefit economic-wise. One of such biomasses is rape straw, containing cellulose up to 37% and 19.6% hemicellulose [2].

Bioethanol production has 3 different steps: hydrolysis, fermentation, and purification. The major issues that arise from this process are the lignin content. Lignin chemical bond was meant to protect cellulose from external force, so it can naturally resist hydrolysis and hindering the cellulose separation from biomass. To overcome this, pretreatment process is required. Pretreatment (delignification) is used to degrade lignin bonds with cellulose and hemicellulose while increasing the porosity of biomass, therefore maximizing the amount of cellulose yield for bioethanol production.

In this review, the microwave-assisted pretreatment method on rape straw was discussed. This method is combination of physical and chemical pretreatment. The straw was soaked into H_2SO_4 and put into microwave with different microwave power. Microwave heating will loosen the lignin structure within biomass while the chemical solute will accelerate the degradation of lignocellulose. This article review, hopefully, can provide insights and also novelty of the effect of microwave power on lignocelluloses content, and the physical and chemical characteristics of biomass after pretreatment. Microwave power for pre-treatment from several studies were presented, with the physical and chemical characteristics of several biomass after pretreatment and also the prospect of future applications of microwave-assisted pretreatment was also discussed.

2. Rape straw

Rape straw is biomass obtained from rapeseed. Rapeseed is dicot plant that have a large distribution rate worldwide and is largely found in Europe. In China, 45 million tons of rape straw were harvested, while 25 million tons were used in bioethanol production [3]. Rapeseed plant is processed with thermal application for fertilization, leaving a large amount of rape straw (up to 70%) that is barely exploited by a large industry. Rape straw contains a high amount of cellulose (up to 27-37%) and has the potential to be used in bioethanol production [4]. In Indonesia, the cultivation of this species needs further research. The previous study shows that rapeseed has a good adaptability on dry land [5].

3. Pre-treatment process

Pretreatment on bioethanol production is an initial treatment on raw biomass material, and to reduce materials that can prevent the extraction of cellulose in biomass. The main objective of this process is to reduce lignin, a specific compound that can inhibit cellulose hydrolysis. Pretreatment can also be used to reduce cellulose crystallinity and cellulose degradation to obtain high-level carbohydrates [6]. The process to degrade lignin is called the delignification process. Delignification can increase enzymatic digestibility and lignocellulose accessibility.

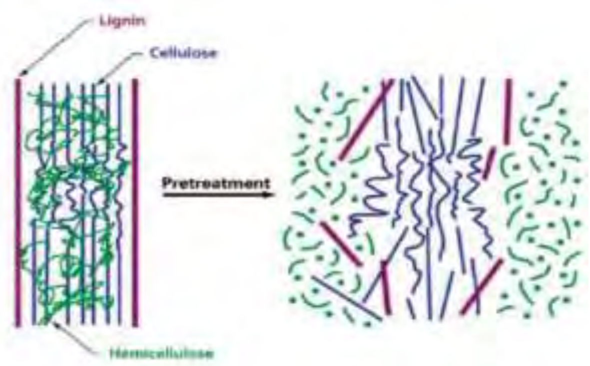

Figure 1 Pretreatment mechanism [6].

The existence of a covalent bond between lignin and hemicellulose will create a barrier for cellulose extraction and made the hydrolysis process difficult. As shown in Figure 1, another goal of delignification is to unfold lignocellulose structure in order to facilitate decomposing enzyme to access polymer inside. Delignification can improve both accessibility and enzymatic digestibility of cellulose, which later will be hydrolyzed into glucose. The obtained glucose will be fermented into ethanol.

There are many methods of biomass pretreatment and its affectivity on lignin degradation in various biomass materials and also study on the operational cost. A study by [8] shows that the pretreatment method will affect hydrolysis and fermentation. If the method is not optimum, it can produce a poisonous by-product that can prevent the growth of microorganisms used in fermentation. There are three kinds of pretreatments:

- Physical pretreatment, a more environmentally-friendly method that employ physical/mechanical process, usually by applying machine to reduce the size and crystallinity of biomass.
- Biological pretreatment, a method which applying biological agents (such as mold, yeast or fungi) to degrade lignin in biomass. While it is cheap, low energy consumption and barely produced inhibitor substance, it takes a longer time to fully degrade the lignin.

- Chemical pretreatment, a method using chemicals to break chemical bonds in biomass (lignin and hemicellulose). It is also used to lower the crystallinity and polymerization of cellulose. While effective, it has an after-effect on the environment.

3.1. Microwave-assisted pre-treatment
Microwave-assisted pretreatment is a pretreatment method that combines physical force and chemical solvent to combine the strength of each method. The pretreatment is done by soaking biomass on the chemical solvent (either acid or alkali) with a specific concentration, then apply microwave heating on lignocellulose polar structure [8]. Microwave heating will change cellulose structure by removing lignin and hemicellulose while increasing its accessibility. Polar molecules will gather and ionic conduct after electric field change, resulting in instant heating on biomass component that will deconstruct polysaccharide within short amount of time, and the addition of solvent will accelerate delignification process that will increase the amount of obtained cellulose [9].

A combination of physical and alkali chemical pretreatment affects the process. The heating process by microwave (physical) will approximately change lignocellulose structure by increasing its accessibility while at the same time degrade the wall of lignin. The addition of acid on pretreatment process is to dissolve hemicellulose in biomass and also to facilitate enzymes to access cellulose [10].

3.2. The effect of microwave power on lignocellulose content
Microwave power that is used on pretreatment affects the lignocellulose yield, as shown in Table 1. A study by [2] with 3 different microwave powers (550, 750, and 900 Watt) showed that on 900 Watt, the cellulose yield of rape straw increase from 37% to 42.3% during its lignin content decreased from 18% to 15.4% with 1 minute treatment. The increase of microwave power is directly proportional to the decrease of lignin percentage. As studied by [11] on empty oil bunch shows that after pretreatment with microwave, the percentage of lignin went down from 18.8% to 13.5%. Another study by [12] using 3 different range of microwave power (400, 700 and 1000 Watt) also indicate the constant increase of cellulose content for every increase in microwave power from 46.5% to 51%.

Microwave pretreatment on 450 Watt for 4 minutes by Binod [13] exhibits the reduction of lignin content on sugarcane bagasse from 18% to 0.4%, while its cellulose content increase from 34% to 63.5%. A study by Jin [14] with catalpa sawdust by using 3 different solvents (NaOH, $Ca(OH)_2$ and water) and 3 different microwave power (200, 400 and 600 Watt) exhibit an increase in cellulose content from 50.87% to 55.78% on Microwave-NaOH and 56.28% Microwave-$Ca(OH)_2$. Lignin content from the same catalpa sawdust also decreased from 18.95% to 17.09% on Microwave-NaOH treatment.

Microwave irradiation produced higher power density compared to conventional heating, therefore with higher power will increase glucose recovery rate obtained from the pretreatment process [15]. Compared with conventional pretreatment using autoclave, microwave-alkali is way more efficient, as the maximum result is at 900 Watt, 71% of lignin were degraded, compared to conventional that can only reduce 34% lignin [11]. Even though at literature show that higher microwave power means higher obtained cellulose, there are several points that need to be observed. High-level power and exposure will result in a temperature increase in the treatment environment, resulting in a decrease of obtained sugar because of severe heating that will break down sugar compounds. Another study also shows that the usage of 600 W will increase slug temperature by 85°C in 2 minutes, a lot faster compared than conventional heating with 520 Watt that needs 12 minutes to reach the same temperature. High rise on the temperature in such a short time is caused by electromagnetic irradiation that is interacting with the dipolar molecule, such as water, a protein inside biomass that causes molecular rotation, resulting in heating [16] Binod [13] also point out that higher microwave power accompanied by long-duration exposure will cause in charcoal formation, and this is not wanted since in the next step of production biomass is required in good condition.

Table 1. Cellulose content comparison.

No	References	Method	Cellulose content before pretreatment	Cellulose content after pretreatment	Lignin content before pretreatment	Lignin content after pretreatment
1	[2]	Microwave-alkali, 550, 750 dan 900 Watt 1 minute	37%	42.3%	18%	15.4%
2	[12]	Microwave-alkali, 400, 700 and 1000 Watt	46.5%	51%	17.5%	17.4%
3	[13]	Microwave-alkali, 450 Watt 4 Minutes	34.5%	63.5%	18%	0.4%
4	[11]	Microwave-alkali + Dilute Acid 700-1000 Watt, 60-90 minutes	41.8%	85.3%	18.8%	5.3%

3.3. Physical and chemical characteristics after pre-treatment

Physical force and chemical solvent that are used in the pretreatment process, in addition to helping the delignification process, will also cause several changes in the physical and chemical characteristics of biomass, they are stated in Table 2. Park [17] reported that microwave pretreatment on mixed active sludge waste shows some changes in physical and chemical characteristics. Solubility sludge increased from 3.9±1.3 to 10.7 ±2.1 on thermal heating and 12.4±1.2 on microwave pretreatment. Volatile solute also changed from 10,015±642 to 10.007±727 on thermal heating and 10,030±455 on microwave pretreatment. Chemical aspect of biomass that increases after pretreatment, one of it is TCOD from 12.072±1251 to 12.218±1716 and 12.304±1426, sequentially for thermal heating and microwave pretreatment. The chemical aspect that experienced most significant increase is SCOD, from 466±148 to 1283±198 on thermal heating and 1518±197 obtained from microwave pretreatment. This study shows that microwave pretreatment is superior in terms of results compared to thermal heating. The physical aspect of the sludge consisted of turbidity, VSS solubility increase to a certain level during its residence time decrease. Physical change on biomass after pretreatment is also heavily mentioned by Cheng [16], where microwave pretreatment on Tenera palm for a long-time duration will make the palm fruit cracked, dried and turn into brown. Similar color change also happens on wheat straw, and corn stalks by Sapci [18], which after pretreatment took place at 200-300°C, biomass colors change from light brown to dark brown, and its chemical characteristics change by the sign of the decrease in hydrogen content and also its C/N percentage. The chemical compound within biomass also changed, after pretreated, hemicellulose and lignin content decreased for 90% and 10%, respectively. The highest delignification rate can reach up to 71.91%

The pretreatment process will also change biomass morphology; along with the increase of microwave power that is used, biomass structure will decay. It is shown by the existence of cracks and openings within the biomass. The increase of microwave power used in the process will generate heat-producing energy from molecular vibration that will harm biomass's physical structure. This physical change is observed from SEM (Scanning Electron Microscope), wherein some articles such as [19] point out sorghum bagasse degradation after pretreatment, while the delignification can be festered by using certain additives such as lime, that cause biomass cell wall damaged and its fiber eroded.

Table 2. The comparison between physical and chemical characteristics.

No	References	Physical	Chemical
1.	[17]		Solubility of sludge and its VS increased, TCOD increased from 12,072±1251 to 12,304±1426 after microwave pretreatment
2	[18]	Turn darker compared to the untreated sample,	
3	[20]	The physical structure of water hyacinth that's a complete block	
4	[13]	Went from soft and continuous to broken at its external biomass layer by SEM	

Any other proof of the change in biomass physical structure is shown on the pretreatment process of water hyacinth. Before pretreatment, water hyacinth structure looks like a layered membrane structure with soft surface and even block arrangement. On 126 Watt, surface structure slowly forming a rift and cracked surface showed up at 329 Watt. The membrane structure experienced its total breakdown at 567 Watt [20]. A similar result was also indicated by Diaz [21], where the research on corn wheat and rice husk soaked into three different solvents (water, glycerol-water, glycerol-alkali) shows that biomass soaked in glycerol and alkali has a different structure compared to its initial characteristics before irradiation. A modification on hemicellulose structure and change on lignocellulose bound during pretreatment process when observed by using FTIR. Observation by using SEM indicates the morphological change on both biomass after getting treated, microwave-water shows a small amount of change, while microwave-glycerol shows a structural change and the existence of trachoma that can be inferred. The most significant change happens on microwave-alkali, where the individual cell of corn wheat can be seen clearly, and the discord on rice husk after microwave pretreatment.

Other research by Binod [13] shows that sugarcane bagasse's initial structure was soft and continuous when observed with SEM, and then after pretreatment, its external layer starts to degrade, and it increases the surface area of biomass, making it easier for the enzyme to hydrolyze it. Observation using FTIR also shows that hydrogen bond on biomass increased so it can be concluded that pretreatment directly changes the characteristic of biomass.

3.4. Microwave- alkali prospect based on bioprocess and energy viewpoint

Biomass usage, especially from agriculture waste, is one of a way to apply second generation biofuel. One of such method to facilitate its processing is by using microwave pretreatment, as this method is also an application of sustainable-green pretreatment to minimize the usage of conventional heating that requires a large amount of energy and also producing a secondary product (aliphatic acid, phenol) that is an inhibitor on hydrolysis process. Such a method can be considered as the main option because it is environmentally friendly and easy to apply. Besides the usage of this method can be used to replace conventional heating in the industry since microwave application has a higher yield and shorter processing time. Another factor to consider is that applying this method can also improve enzymatic hydrolysis ratio at higher number compared to conventional heating and better scarification number compared to steam explosion method on a lower temperature. The effects of microwave pretreatment have been stated in Table 3.

Table 3. The effect of microwave pretreatment.

Treatment	The increase of cellulose (%)	Lignin Degradation (%)	References
Microwave-NaOH 0,5 M (5 minutes) Corn cob	25.09	-11.06	[23]
Microwave-NaOH 1 M (4 minutes) Cocoa skin	39.72	-8.1	[24]
Microwave-NaOH 100 Mesh (40 minute) P = 950 W 89°C	42.32	4.27	[25]
Ultrasonic-Pretreatment NaOH 2 M, 50 kHz	26.9	0.15	[26]
Pretreatment Organosolv Formiat acid (120 minute)	19.48	11.23	[27]

Another advantage of this method is smaller amounts of secondary products produced after the process. From an economic viewpoint, this method is way better compared to conventional heating since it has a lower capital cost. Microwave irradiation itself has been applied on sludge waste treatment, and it’s still in developing state, so a proper and up-to-date design is needed. Treatments on sludge also can produce extra biogas that can be converted into electric and heat power, adding a reason to considering to development of this method. The only problem is the small amounts of industries that utilizing it [22]. The lack of application is because of many obstacles, specifically on its operation unit, since it needs a large-scale facility accompanied by high energy consumption to support the operation unit that causes the disinterest of industry to use it in the production process.

4. Conclusions

Microwave power in the pretreatment process has a significant effect on the lignocellulose content of biomass. Both the main article and the comparative articles show that the increase of microwave power will also increase the amount of cellulose obtained and the total amount of degraded lignin. The proper method to obtain the maximum amount of cellulose is by using high microwave power with a short duration process. The physical and chemical characteristics of biomass after pretreated also change in significant ways. Several articles show the amount of chemical content change (such as COD), while the others mention the change in physical characteristics (change in colors, microstructures). Comparative articles gave a better insight into this aspect since the main article didn’t mention any physical nor chemical characteristics change on rape straw. In the aspect Bioprocess and energy point of view, Microwave-alkali pretreatment is a way to apply sustainable-green pretreatment, as it has lower energy consumption and has a higher yield, shorter duration, and is environmentally friendly compared to conventional heating. But it still needs further research for it to be applied in the larger scale industry.

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