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Microwave-Assisted Hydrotropic Delignification of Rice Straw

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Abstract
Rice straw is the stem and stalk of the rice plant after the rice grains are harvested. Rice straw is the largest agricultural waste that has not been utilized due to technical and economic factors. The high cellulose content in rice straw can be used in various ways, including as a substitute for wood, namely raw materials for making pulp, tissues, handicrafts or very strong ropes. In addition, rice straw waste is environmentally friendly. One of the stages in the biomass fractionation process is the delignification/pulping process. The method used for rice straw delignification is MAE (Microwave Assisted Extraction). MAE has several advantages including shorter extraction time, higher accuracy and precision, higher yield, lower energy, and solvent consumption. This study aims to find the optimum conditions for the delignification process of rice straw waste with microwave-assisted hydrotropic solvents. The process parameters studied include time (30-150 minutes) and differences in solvent addition. The results of the analysis showed that rice straw contains cellulose content of 35.59%, lignin content of 25.39%, and extractive content of 4.53%. The delignification process using microwave heating with a power of 180W, for 150 minutes and the addition of hydrogen peroxide produced a cellulose content of 53.34% and a lignin content of 21.46%.

Keywords: Rice Straw, Delignification, Microwave

INTRODUCTION

Indonesia is an agricultural country that makes agriculture the main commodity in business and profession. Rice straw is the largest agricultural waste that has not been utilized due to technical and economic factors. According to the agricultural data and information system center (2016), national rice production will reach 80.93 million tons per year in 2017-2019. While rice straw production can reach 14.86 tons per hectare per harvest, which varies depending on the location and type of rice plant variety used.

Rice straw is the part of the stem and stalk of the rice plant after the rice grains are harvested (Komar, 1984). Rimandan et al. (2016) stated that rice straw contains 37.71% cellulose, 21.99% hemicellulose, and 16.62% lignin. This fairly high cellulose content can be utilized in various ways, including as an alternative material to replace wood as a raw material for making pulp, for making cloth, making tissues, and for making handicrafts or very strong ropes.

Biomass is a renewable resource that is abundantly available in nature. The main components of biomass are cellulose, hemicellulose, and lignin. Biomass utilization can be done by various methods, one of which is biomass fractionation. Biomass fractionation is the sorting of biomass into its main components without damaging or changing the main components (Lee, dkk. 2014). One of the stages in the biomass fractionation process is the delignification/pulping process. The determining factor in the delignification process is the process of breaking the ether bonds in the lignin structure (Doherty, 2006). The delignification process can be carried out through several pulping methods such as the Kraft process, Soda process, Sulphite process, Organosolv process, hydrothermal, and Hydrotropic process (Devendra, dkk., 2016).

The delignification process has several criteria, including not using compounds containing sulphur, the delignification process uses compounds that can increase the solubility of lignin in water, and the delignification process uses water as a medium to minimize production costs, and does not use acid and base solvents that can cause cellulose degradation and changes in lignin structure. The delignification process that meets the criteria is delignification using hydrotropic compounds (hydrotropic delignification).

The hydrotropic compound used is urea, besides being easy to find, urea is also commonly used. While the organic solvent used is formic acid. The method used for rice straw delignification is MAE (Microwave Assisted Extraction). MAE is a technique for extracting dissolved materials in plant materials with the help of microwave energy. MAE also has several advantages including shorter extraction time, less energy and solvent consumption, higher yield, higher accuracy and precision, the presence of a stirring process that increases the mass transfer phenomenon, and equipment settings that combine soxhlet features and the advantages of microwaves (Purwanto 2010).

RESEARCH METHODS

Research equipment

The tools that will be used in this study include MAE (Microwave Assisted Extraction), round bottom flask, Erlenmeyer, beaker glass, measuring cup, oven, soxhlet, water bath, glass stirrer, spoon, measuring pipette, watch glass, scissors, filter paper, rubber.

Materials

The materials used in this study were rice straw, urea, hydrogen peroxide, formic acid, distilled water, 96% ethanol, alcohol, NaOH, sulfuric acid, and Benzene wash.

Research variables

The research to be conducted includes several processes, namely the delignification process with the help of microwaves which is then continued with the soxhletation process and the maceration process. The variables change the delignification time (30-150 minutes), and the difference in the addition of solvents (hydrogen peroxide and formic acid).

Delignification process

A total of 5 grams of rice straw powder that has been sieved using a 100 mesh sieve is added to 150 ml of Hydrotrope solution (urea). The mixture is put into the microwave and processed for 30 minutes (according to the variable). After the extraction is complete, the extraction results are filtered using a cloth, then washed with 250 ml of hot water and squeezed. The residue is dried in an oven at a temperature of 105℃ for ±6 hours and weighed.

Soxhletation Process

Put 96% alcohol and wash benzene into a round bottom flask. Then put the sample (rice straw that has been MAE in dry condition) of as much as 1.5 grams that has been wrapped in filter paper into the soxhlet and heated with a water bath at a temperature of 70-80°C. Make sure the water in the water bath is filled with about ¾ of the water bath. Soxhlet for 3.5 hours. After finishing, wash the sample with 250 ml of hot distilled water. Dry in the oven at a temperature of 105°C. for 6 hours, then weighed.

Maceration Process

Put the sample (rice straw that has been soxhlet) as much as 1 gram into the flask or Erlenmeyer. Then add 15 ml of sulfuric acid. Shake slowly until perfectly mixed and let stand for 2 hours. After finishing, add 563 ml of distilled water little by little while shaking so that the sample attached to the flask wall dissolves in distilled water. Cover the flask with plastic and rubber. Turn on the water bath at a temperature of 100°C for 4 hours. Make sure the water bath is full of water. After finishing, filter using coarse filter paper. Then wash with 1000 ml of hot distilled water and weigh the cup that was previously put at for 5 minutes at a temperature of 105°C. Record the weight of the hot cup. Scrape the residue using a knife until it is completely clean. After finishing, put the residue into the cup and put it in the oven at a temperature of 105°C for 6 hours and then weighed.

Determination of Yield

The finely ground rice straw powder was weighed as much as 5 grams and then extracted using a hydrotrope solvent, namely urea with the addition of hydrogen peroxide or formic acid. Then the mixture was extracted in a microwave at 180W, with a predetermined time. After completion, the solution was filtered and the residue was put into an oven at a temperature of 105°C for 6 hours. Then weighed and obtained the weight of the rice straw after extraction.

Determination of Lignin Content

Lignin obtained from the delignification of rice straw was taken as much as ±1.0 grams then put into an Erlenmeyer, then added 15 ml of 72% sulfuric acid solution slowly, then added 563 ml of distilled water. After that the mixture was heated to boiling and left for 4 hours. Then the cooking results were filtered using filter paper and washed with hot water until the acid content was gone. After that the solid obtained was put in the oven until a constant weight was obtained.

Determination of Cellulose Content

The initial weight of the remaining sample of the maceration process was put into an Erlenmeyer flask and 10 ml of 17.5% NaOH solution was added. After 5 minutes, 5 ml was added, after 10 minutes, 5 ml was added and after 15 minutes, 5 ml was added. Then the mixture was stirred and left for 45 minutes. After that, 33 ml of distilled water was added and left for 1 hour. After completion, the mixture was filtered using filter paper then washed with 100 ml of 8.3% NaOH and washed again with 250 ml of distilled water. After that, the residue obtained was oven-dried until a constant weight was obtained.

RESULT AND DISCUSSION

Preliminary tests have been conducted on rice straw used as raw material by analyzing its yield, lignin and cellulose content. The aim is to determine the effect of time variables and differences in solvent addition on lignin and cellulose content in rice straw. In the delignification process, the raw material, namely rice straw waste, is dissolved with addition of hydrotrope compounds. Hydrotrope compounds are organic substances that are soluble in water that have hydrophilic and hydrophobic functions in their chemical structure and at high enough concentrations form molecular aggregates, and are able to increase the solubility of organic substances that are not soluble in water. Where the hydrotrope compound used in the study is urea, urea was chosen because it is cheap and also easy to obtain and commonly used.

In this study, the hydrotropy process was modified by the addition of hydrogen peroxide and formic acid. The addition of hydrogen peroxide can reduce the levels of lignin in rice straw, where hydrogen peroxide breaks the lignin chains into short ones, so that lignin can be dissolved during washing. While in the delignification stage, the addition of formic acid can dissolve lignin that has been separated from lignin macromolecular compounds such as lignocellulose.

Table 1. Cellulose, lignin, and extractive of rice straw

	Cellulose content (%)	Lignin content (%)	Extractive (%)
This work	35,59	25,39	4,53
Yulianingsih (2010)	29,7	25,58	7,83
Pratiwi (2016)	37,71	21,99	16,62
Zulmawardi (2019)	28,74	16,69	18,5

Effect of Delignification Time on Lignin Content

Figure 1 shows that the lignin content in rice straw when formic acid is added decreases, which means that more lignin is dissolved. The research that has been done obtained the smallest lignin content of 20.22% at a reaction time of 150 minutes. Although from the results of the research that has been done, there were several times when the dissolved lignin had increased. The longer the reaction time, the longer the formic acid solvent in degrading lignocellulose takes. Zulfansyah et al. (2011) stated that the longer the cooking time, the more lignin is dissolved.

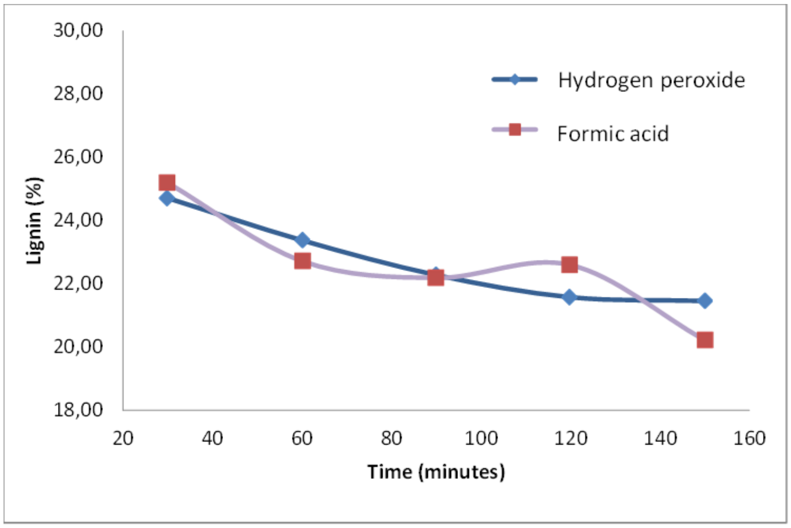

Figure 1. Lignin content of rice straw was obtained through the delignification process using urea solvent with a power of 180 watts.

With the addition of hydrogen peroxide, the lignin content in rice straw decreased and obtained a lignin content of 21.46% at 150 minutes. This can be caused by the unstable nature of hydrogen peroxide. The results of the study from (Postlewait, 2015) showed that the activity of hydrogen peroxide decreased with increasing time.

Effect of Delignification Time on Cellulose Content

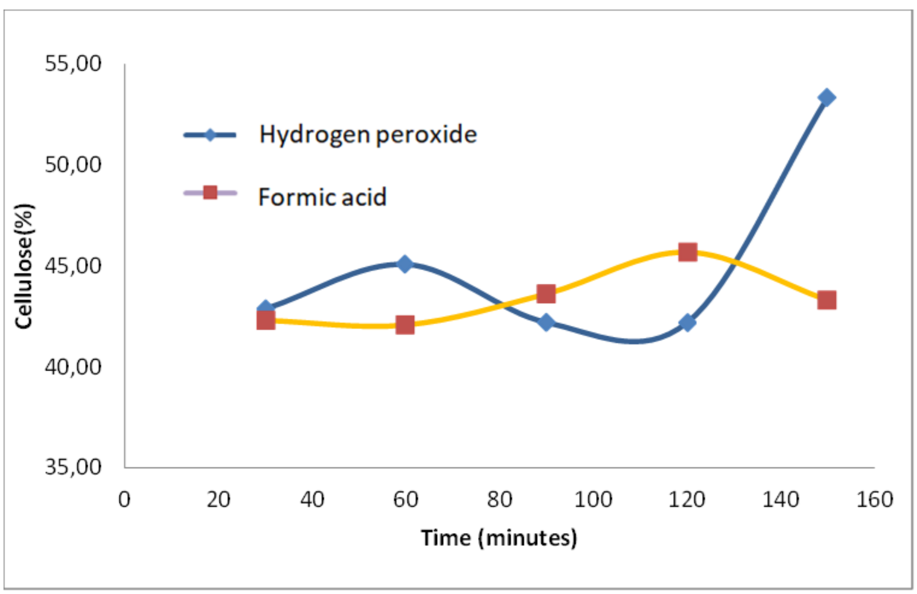

Figure 2. Cellulose content of rice straw was obtained through the delignification process using urea solvent with a power of 180 watts

Figure 2 shows that the cellulose content increased with the addition of hydrogen peroxide. Meanwhile, the delignification process increased with the addition of formic acid, although it decreased at certain times. According to Hidayat (2013), the increase in cellulose content occurs because the longer the solvent is in contact with the lignocellulosic structure in the material, the greater the cellulose's accessibility.

Effect of Delignification Time on Yield

As can be seen from Figure 3, the results of the study on the addition of hydrogen peroxide experienced a decrease of 63.02% at 150 minutes, although there were some times when the yield increased. Meanwhile, the addition of formic acid obtained the smallest yield at 90 minutes at 66.48%. The longer the cooking time, the lower the straw yield obtained because the longer the contact between the solvent and the raw material (biomass) so that the resulting yield is lower. According to (Zulfansyah et al., 2011), increasing the cooking time causes the amount of lignin dissolved in the cooking liquid to be greater, so that the straw yield will decrease.

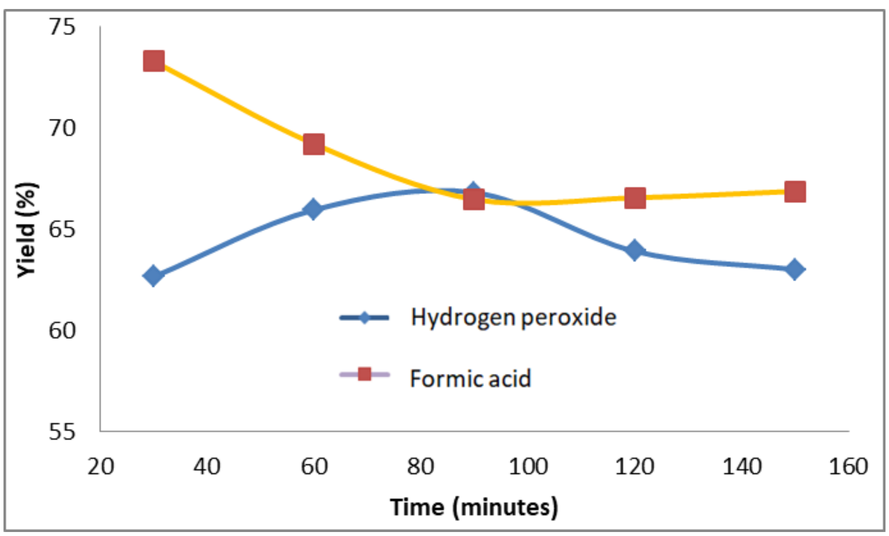

Figure 3. Yield of rice straw was obtained through the delignification process using urea solvent with a power of 180 watts

CONCLUSION

The analysis showed that rice straw contained 35.59% cellulose, 25.39% lignin, and 4.53% extractives. The delignification process, using microwave heating at 180W for 150 minutes and the addition of hydrogen peroxide, resulted in a cellulose content of 53.34% and a lignin content of 21.46%.

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