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Effect of Catalysts H_2SO_4 8% and Baggase Ratio on Yield of Furfural with Hydrolysis Method Using Microwaves

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ABSTRAK
Ampas tebu mengandung pentosan sebesar 12,7%. Kandungan pentosan yang cukup tinggi dalam ampas tebu dapat digunakan sebagai bahan baku pembuatan furfural melalui proses hidrolisis. Penelitian ini bertujuan untuk menentukan pengaruh rasio ampas tebu dan katalis H_2SO_4 terhadap yield furfural yang didapat dari proses hidrolisis menggunakan *microwave*. Ampas tebu ditambahkan dengan H_2SO_4 8% sebagai katalisator dengan variasi rasio ampas tebu dan katalisator H_2SO_4 yaitu 1:20, 1:30, 1:40, 1:50, dan 1:60 pada temperatur *microwave* 100ºC dan waktu reaksi 75 menit. Sampel dianalisa secara kualitatif dengan uji warna menggunakan anilin-asetat sebagai pereaksi. Setelah anilin-asetat ditambahkan ke sampel, warna sampel berubah dari kuning cerah menjadi merah sebagai tanda sampel mengandung furfural. Furfural yang dihasilkan dianalisa untuk mengetahui *yield* dari furfural dengan menggunakan *Gas Chromatography* (GC). Hasil penelitian menunjukkan *yield* furfural terbaik pada rasio ampas tebu dan katalisator H_2SO_4 1:30 yakni sebesar 0,28%.

Kata Kunci : ampas tebu, asam sulfat, furfural, hidrolisis, microwave.

ABSTRACT
The sugar cane bagasse contains 12.7% pentosan. The relatively high pentosan content in the sugar cane bagasse can be used as the raw material of furfural production by utilizing the hydrolysis process. This research aims to determine the effects of ratio variations of bagasse and H_2SO_4 catalyst on the yield of furfural obtained from the hydrolysis process using a microwave. The sugar cane bagasse was added with H_2SO_4 8% as catalyst with a variations ratio of sugar cane bagasse and H_2SO_4 catalyst that is 1:20, 1:30, 1:40, 1:50, and 1:60 in a microwave with the reaction temperature of 100ºC and reaction time of 75 minutes. The sample was analyzed qualitatively with a color test by using aniline-acetic as the reactant. After the aniline-acetic was added to the sample, the color of the sample changed from bright yellow to red as a sign that the sample contains furfural. The obtained furfural was analyzed to find out the yield of furfural by using Gas Chromatography (GC). The research product showed that the best yield of furfural on the ratio of bagasse and H_2SO_4 catalyst of 1:30 is 0.28%.

***Keywords*:** sugar cane bagasse, sulfuric acid, furfural, hydrolysis, microwave.

1. INTRODUCTION
Sugarcane bagasse is often found in Sungai Pinang Dalam Village, Samarinda, through surveys from sugar cane traders or sellers. According to the ice cane traders, the dry bagasse produced per day is 2.51 kg. In a week, sugar cane sellers can yield 17.6 kg of bagasse. So, there is at least 528 kg of bagasse that can be produced in a month by eight ice cane sellers in the village. This amount is quite significant considering that in just a week, more than 60 kg of bagasse has been produced per person. This is also accompanied by the general public's lack of

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understanding about the uses of bagasse, so that a alot of sugarcane bagasse has not been utilized properly. However, bagasse has quite many benefits. Bagasse is the fibrous material that can be used as biofuel, for pulp and building materials, and as a replacement for paper and foam products [1].

Bagasse contains 1.5-3% ash, 0.79% lignin, 12.7% pentosan, 27.9% alcohol extract, 2% benzene extract, 44.7% cellulose, and 3.7% solubility in hot water [2]. Several methods can be used to process bagasse, one of which is the hydrolysis method. Furfural is classified as an aldehyde compound with the structural formula $C_5H_4O_2$ and can be made from food waste or agricultural waste. The content of pentosan in sugar cane bagasse can be hydrolyzed to furfural when contacted with an acid. Furfural can be produced through the hydrolysis reaction of pentosan [3]. Pentosan includes polysaccharides that can be hydrolyzed into monosaccharides called pentoses. If further hydrolysis is carried out by heating in a dilute H_2SO_4 or HCl solution within 2-4 hours, dehydration will occur, and cyclization will produce furfural [4].

Furfural can be produced from biomass that contains many pentosans, hemicellulose, cellulose, and lignin, such as empty fruit bunches, wheat husks, rice husks, wood, bagasse, and others [5]. In agriculture, furfural can be used as a fungicide to kill the Penicillium fungus that grows on wheat, and this is due to the high formaldehyde content in furfural. In the plantation sector, furfural can be used as a nematocide to kill nematodes or roundworms that cause severe disease in plant roots [6].

The essential step in the formation of furfural from pentosan is the acid hydrolysis process in bagasse. There are two stages of furfural formation reaction, 1) the first reaction is the hydrolysis of pentosan or hemicellulose to pentose, followed by 2) the second reaction is dehydration of pentose to furfural. The reaction for furfural formation includes the following sequence reactions [7] :

1. The Hydrolysis of Pentosan

$$(C_5H_{10}O_5)_n + H_2O \xrightarrow{H+} n\, HOCH_2(CHOH)_3CHO$$

2. Dehydration of Pentose

$$\underset{\text{Pentosa}}{HOCH_2(CHOH)_3CHO} \xrightarrow{H-} \underset{\text{furfural}}{(CH)_3COCHO} + \underset{\text{water}}{3H_2O}$$

Acid hydrolysis can be used for the preparation of monosaccharide. Hydrochloric acid, sulfuric acid, and nitric acid are commonly used in the acid hydrolysis. Compared with other methods, acid hydrolysis can produce a higher sugar yield and good reproducibility.

Microwaves play a role in shortening the hydrolysis process time and increasing the yield of obtained furfural. The magnetic field generated by microwaves causes agitation or rotation of polar molecules or ions that move within the material. The motion of the magnetic and electric fields causes the movement of the molecules to be limited by the limiting force, this causes the molecular movement to be restrained and generates random molecular motion, resulting in heat generation [8].

The heat created acts as a heating agent in the microwave. Prolonged heating will place the process at an optimum condition. After optimum condition is reached, the yield of furfural from the hydrolysis process will decrease. In the hydrolysis process, the further reactions occur, resulting in the formation of furfural being decomposed back into other compounds such as furoic acid due to the breakdown of the formed aldehyde group [9].

Sugarcane bagasse can be processed into furfural through a hydrolysis process with catalyst in the form of acids, both strong acids and weak acids. Research on this has been done by Andaka [2] and Atima [10]. In Andaka's research [2], the hydrolysis process was carried out at variations in temperature and time, where the used temperature range was 80^oC to 100 ^oC with a hydrolysis time of 30 minutes to 150 minutes. In this study, the best yield of furfurals were obtained at a temperature of 100^{o}C and 120 minutes, which were 5.07% and 5.67%, respectively. The hydrolysis process carried out by using a catalyst concentration of 12% H_2SO_4 [2]. While in Atima's research [10], the hydrolysis process was carried out at different ratios of bagasse and H_2SO_4 catalyst, namely, 1:20, 1:30, 1:40, 1:50, and 1:60. In this study, the best yield of furfural was 10.67%, at a ratio of 1:40 with a hydrolysis temperature of 100^{o}C, a hydrolysis time of 120 minutes, and a concentration of H_2SO_4 8%.

In the research by Andaka [2] and Atima [10], the hydrolysis of sugarcane bagasse into furfural is still conventional. In Andaka's study [2], to get the best yield of furfural, a relatively high reaction temperature and concentration of H_2SO_4 catalyst is needed, while in Atima's research [10], to get the best yield of furfural, a relatively high ratio of bagasse and H_2SO_4 catalyst volume is required. The hydrolysis of bagasse into furfural was carried out using microwaves to make the process more efficient. Research by Rahim and Nadhir [8] has succeeded in increasing the yield of hydrolysis of oil palm empty fruit bunches into furfural with the help of a microwave compared to the conventional process carried out by Parasta [11]. Therefore, it is necessary to research the effect of the ratio of bagasse to the H_2SO_4 catalyst. In the process of bagasse hydrolysis into furfural assisted by microwaves, the utilization of higher ratio can cause a decrease in the obtained furfural yield because the number of polar H_2O compounds will cause higher interactions of dipole-dipole between polar molecules when irradiated with microwaves. As a result of the molecule's rotation, which will produce higher energy, the furfural formed can decompose into other compounds, such as furoic acid [12].

This research was intended to increase the use-value of bagasse and obtain maximum yield of furfural. In particular, to study the effect of the ratio of bagasse and H_2SO_4 catalyst on the yield of obtained furfural by using microwave assistance.

2. RESEARCH METHODS

2.1. Materials and Instruments

The raw material used in this research is sugar cane bagasse. The chemicals used were H_2SO_4 8% solution, aquadest, aniline-acetate solution, standard furfural solution, and chloroform.

The microwave used is the Electrolux brand, EMM2007X model with a maximum power specification of 800 W, voltage 220 V, magnetron frequency 2450 MHz (2.45 GHz), dimensions of length 45 cm, width 30 cm, and height 25 cm. The microwave device has a temperature sensor (thermocouple type K), a temperature controller, and a temperature indicator (TIC/temperature indicator controller). Sample was analyzed by GC. The schematic equipment can be seen in Figure 1.

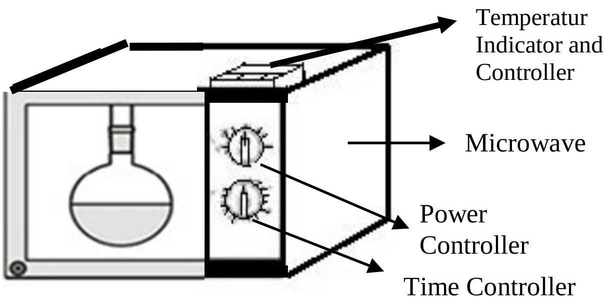


Figure 1. Microwave equipment for the hydrolysis process.

2.2. Research Methods

The research was conducted through the following stages :

a. **Preparation**
   Wet bagasse is dried in the sun, then mashed using a blender until it becomes powder. The bagasse powder was then sieved through a -20+70 mesh sieve. After that, the bagasse powder was dried again using an oven at a temperature of 105^{o}C until a constant weight was reached.

b. Hydrolysis Process

5 g of dry bagasse was put into a 1000 mL two neck flask and mixed with 100 mL H_2SO_4 8% v/v (E Merck). The two-neck flask containing a mixture of bagasse and sulfuric acid was put in a microwave to be heated. The hydrolysis process in the microwave was carried out at a temperature of 100^{o}C, heated by microwave with a power of 400 W for 75 minutes. The procedure was repeated for various ratios of bagasse and H_2SO_4 catalyst 1:30, 1:40, 1:50, and 1:60.

c. Furfural Separation

After the hydrolysis process, the material was cooled at room temperature (30^{o}C), then the liquid (hydrolyzate) was separated from the bagasse solids using Whatman filter paper.

d. Analysis

In the research, two stages of analysis were carried out, namely :

1. Qualitative Analysis

1 mL of obatained hydrolyzate then poured as much as into a test tube. Next, three drops of the aniline-acetate solution were added into the test tube and the color change was observed. If the hydrolyzate solution changes color from bright yellow to red, then the solution is detected to contain furfural.

2. Quantitative Analysis

The hydrolyzate obtained was then extracted before being analyzed using GC (Gas Chromatography) by adding chloroform (E Merck). The amount of chloroform volume used was (1:5) mL compared to the volume of hydrolyzate. The mixed solution of hydrolyzate and chloroform is then stirred vigorously so that the furfural can dissolve in the chloroform. Incubate for the solution to form into two layers. When two layers of liquid have formed, the next step is to take the lower layer using the help of a separating funnel. The formation of these two layers indicates that the top layer is a residual hydrolyzate containing H_2O and H_2SO_4, while the bottom layer is chloroform containing furfural.

3. RESULTS AND DISCUSSION

The Results obtained from this research shown in Table 1 for qualitative analysis. While, the results of quantitative analysis on the effect of the ratio of bagasse and H_2SO_4 catalyst on yield of furfural are presented in Table 2.

Table 1. Results of qualitative analysis (color test).

No	Sugarcane Bagasse Mass (g)	H_2SO_4 Catalyst Volume (ml)	Before Addition of Aniline Acetate	After Addition of Aniline Acetate
1	5	100	Bright Yellow	Red
2		150	Clear Yellow	Red
3		200	Bright Yellow	Red
4		250	Bright Yellow	Red
5		300	Bright Yellow	Red

Table 2. Results of quantitative analysis.

No	Sugarcane Bagasse Ratio and H_2SO_4 Catalyst	Hydrolyzate Volume (ml)	Chlorofom Volume (ml)	Extract Volume (ml)	Furfural Concentration (% v/v)
1	1 : 20	30	6	35	0.0776
2	1 : 30	78	16	28	0.0725
3	1 : 40	136	27	21	0.0223
4	1 : 50	167	33	12	0.0179
5	1 : 60	215	43	3	0.0125

Table 3. The effect of ratio sugarcane bagasse and h_2so_4 catalyst to yield of furfural.

No	Ratio of Sugarcane Bagasse and H_2SO_4 Catalyst (g/ml)	Yield of Furfural (% w/w)
1	1 : 20	0.07
2	1 : 30	0.28
3	1 : 40	0.15
4	1 : 50	0.16
5	1 : 60	0.14

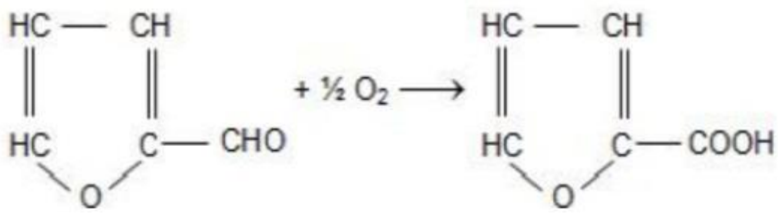
In Table 1, it can be seen that the average hydrolyzate solution is bright yellow. Then, after the addition of aniline-acetate to the sample, the color changed to red. This change indicates that the sample contains furfural. Following the statement by Mitarlis et al. [13], the addition of aniline-acetate to furfural causes the hydrolyzate solution, which was originally clear yellow to become red. It indicates that the yield tested is furfural. This color change was caused by condensation between furfural and aniline to form dianyl hydroxyglutaric dialdehyde compounds.

Table 3 shows a profile of the relationship between the ratio of bagasse and H_2SO_4 catalyst to yield of furfural obtained from this research. Based on Table 3, the results of quantitative analysis shows that the yield of furfural has decreased from ratio of 1:30 and 1:40. However, the highest yield of furfural from the study was obtained from the variation of 5 g bagasse mass compared to 150 ml H_2SO_4 catalyst volume or a ratio of (1:30) which was 0.28%.

In this study, the catalyst for reaction using H_2SO_4 8%, it means contain 92% water. The H_2O molecule is a polar molecule with two poles, each with a positive and negative charge. If one pole or both poles are in a similar electric field originating from the microwave, it can causes a repulsive force so that the water molecules will rotate. This rotational movement causes the increasing of friction between the H_2O and pentosan molecules so that heat energy will arise. This heat acts as a heating agent for the material and the hydrolysis reaction can take place more quickly to produce furfural. It follows the statement from Adhiksana et al. [14] and Rahim et al. [15], microwaves can shorten reaction time and maximize yield gains because radiant heating penetrates directly into the material. For obtained furfural from rice husk using microwave, the processing time need 90 minutes. It is faster than using conventional methods, about 30-60 minutes depends on extraction conditions.

The increase in the catalyst ratio from a ratio of 1:20 to 1:30 indicates that the number of H_2O compounds as polar compounds is sufficient to carry out the hydrolysis reaction. There is an increase in the yield of furfural in this ratio range. At a ratio greater than 1:30, there is a decrease in the yield of furfural produced so that the optimum condition is achieved at a catalyst ratio of

1:30, which is 0.28%. Increasing the ratio above 1:30 will further increase the amount of H_2O in the hydrolysis process. The number of polar compounds that will cause friction between the H_2O molecules and the formed furfural molecules. The furfural undergoes decomposition back into other compounds such as furoic acid, resulting in the breakdown of the aldehyde group [9]. The decomposition reaction of furfural into furoic acid can be seen in Figure 2.



furfural Asam Furoat

Figure 2. Mechanism of Furfural Reaction being Furoic Acid.

4. CONCLUSION

Microwaves can shorten the processing time of bagasse hydrolysis into furfural. The more ratio of bagasse and H_2SO_4 8% catalyst used in the hydrolysis process, the yield of furfural obtained tends to decrease. The best yield from the research is the ratio of bagasse and H_2SO_4 8% catalyst, 1:30 were from 5 g of bagasse with 150 mL H_2SO_4 8%, yield of furfural is 0.28%.

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