THE EFFECT OF SULFURIC ACID AND *Averrhoa bilimbi* EXTRACT AS CATALYSTS ON FURFURAL YIELD FROM CORN COBS IN THE HYDROLYSIS PROCESS USING MICROWAVE

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Abstract

Furfural is a selective solvent for petroleum that can produce high-quality diesel fuel. Generally, furfural research uses raw materials from corn cobs, but most still use inorganic acid catalysts. Therefore, researchers are trying to find alternative catalysts using environmentally friendly organic acids from *Averrhoa bilimbi* extract. This research aims to determine the effect of the concentration of sulfuric acid catalyst and *Averrhoa bilimbi* extract in the hydrolysis process on the quality and yield of furfural and the impact of using microwave heating on the quality and yield of furfural produced. The method used to make furfural is hydrolyzing corn cobs using a microwave heater (400 Watt power) with various sulfuric acid catalyst concentrations (10%, 15%, and 20%) and *Averrhoa bilimbi*. Observe the number of yields at each time interval of 60, 75, and 90 minutes. The resulting furfural is then analyzed to calculate the yield of each sample and identify furfural compounds using Gas Chromatography-Mass Spectrometry (GCMS). The research results showed that the best furfural yield at a catalyst concentration of 10% H_2SO_4 with a time of 90 minutes was 14.9632%. In GCMS analysis, the compound peaked on gas chromatography at a retention time of 2.208 with a relative molecular mass of 83.

***Keywords**: Averrhoa bilimbi extract, corn cob, furfural, hydrolysis, microwave*

Introduction

Waste generated from corn plants, particularly in the form of corn cobs, is often discarded, contributing to an increase in overall waste. However, these corn cobs can be repurposed for the extraction of furfural, as they contain approximately 35% pentosan (Suprapto and Rasyid, 2002).

Pentosan is a polysaccharide that, upon hydrolysis, breaks down into a five-carbon monosaccharide known as pentose. If hydrolysis continues through heating in a dilute mineral acid for 1 to 3 hours, it leads to dehydration and cyclization, ultimately forming furfural. Additionally, corn cobs consist of complex compounds, including lignin, hemicellulose, and cellulose (Suprapto and Rasyid, 2002).

Furfural serves as a selective solvent for petroleum, capable of extracting aromatic compounds, olefins, and sulfur, enhancing stability, and yielding high-quality fuel. The extraction process using furfural aims to produce diesel fuel with a higher octane number. It is noteworthy that commercially available diesel fuel typically has a low cetane number (Setyadji, 2007).

Recent research on approaches to furfural production has focused on developing different types of catalysts and reaction media. In addition, systems using simultaneous separation, such as N_2 separation or extraction, such as water/organic solvent in a biphasic system for furfural, have also been proposed. Water is a cheap and environmentally friendly solvent for furfural formation. However, using water as a reaction medium provides disadvantages such as low furfural yield. Recent research on furfural production has concentrated on developing various types of catalysts and reaction media. Additionally, systems that utilize simultaneous separation methods, such as nitrogen separation or extraction using a biphasic water system and an organic solvent, have been proposed for furfural production. While water is a cost-effective and environmentally friendly solvent for furfural formation, its use as a reaction medium has some drawbacks, including low furfural yield. (Sievers *et al.*, 2009; Zhang *et al.*, 2013).

Several commercial research and academic projects have proposed lignocellulose to furfural production strategies and compared several benchmark process histories. Zeitsch's book on furfural production describes many furfural technologies and discusses the innovations and weaknesses of these technologies. It will now focus on more recent advances in furfural production integrated with co-production or other biomass products. Integrated technology in making furfural can be seen in the journal written by (Cai *et al.*, 2014) and (Cousin *et al.*, 2022).

Several previous studies regarding furfural were used as references in this research, including research by (Adhiksana *et al.*, 2022). In this research, the researchers used the Microwave method with the best results at a ratio of bagasse and H_2SO_4 catalyst of 1:30, resulting in a furfural yield of 0.28%. The advantage of this research is that the hydrolysis time is faster because it uses a microwave, and the disadvantage of this research is that the furfural yield is still low. The ratio of inorganic acid catalysts is too large. However, the water bath method, as demonstrated by (Hidajati, 2006) used the water bath method with the best results at 3.5 hours, showing great promise with a furfural yield of 13.30%. This method could be a significant player in the future of furfural production. Furthermore, research by (Zulnazri *et al.*, 2021) used the Waterbath method with the best results at a temperature of 110 °C and a time of 100 minutes, resulting in a furfural yield of 7.26%. The advantage of this research is that the furfural yield is high due to constant heating time and temperature, but the disadvantage of this research is that the hydrolysis time is extended.

Furthermore, research by (Listiani *et al.*, 2016), which used the Steam Stripping method with the best results in 3 hours at a temperature of 120 °C and a catalyst concentration of 6%, produced a furfural yield of 6.038 mg/ml. This research has advantages, including the high yield of furfural and the separation occurring in one stage. The possibility of furfural being degraded is tiny because it uses the steam stripping method, and the disadvantage of this research is the longer hydrolysis time.

Research by (Andaka, 2011) used the conventional heating method with the best results at 120 minutes, resulting in a furfural yield of 5.67%. Furthermore, research by (Mirnandaulia, 2017), which used the conventional heating method with the best results on the *Averrhoa bilimbi* catalyst, obtained the highest furfural yield at a temperature of 100 °C and a time of 300 minutes of 7.192%. On the sulfuric acid catalyst, the highest furfural yield was obtained at 120 °C and 150 minutes of 11.13%. The advantage of this research is the high yield of furfural due to the long hydrolysis time, and the disadvantage is that the possibility of the furfural being degraded is enormous because it uses conventional heating methods.

Furfural, a valuable platform chemical, can be synthesized through various methods, including hydrothermal treatment and microwave-assisted synthesis. Below is an overview of these methods, their respective drawbacks, and reasons for preferring microwave-assisted synthesis. Hydrothermal treatment involves heating biomass, such as lignocellulosic materials, in water under high pressure and elevated temperatures to convert hemicellulose into furfural. However, this method has several drawbacks: 1) Extended Reaction Times: Hydrothermal processes often require prolonged heating periods, sometimes lasting several hours, to achieve satisfactory furfural yields. 2) High Energy Consumption: The need for sustained high temperatures and pressures results in significant energy usage. 3) Decomposition Risks: Long exposure to high temperatures can lead to the degradation of furfural, ultimately resulting in lower yields (Antonetti *et al.*, 2015).

In contrast, microwave-assisted synthesis offers distinct advantages that make it a more efficient choice for producing furfural. 1) reduced reaction times: Microwave heating significantly shortens reaction durations, often to just minutes. 2) higher yields: The rapid and uniform heating minimizes side reactions and furfural degradation, enhancing overall yields. 3) lower energy consumption: Shorter reaction times translate to reduced energy requirements. 4) simplified equipment: Microwave reactors typically operate at atmospheric pressure, eliminating the need for high-pressure systems (Möller and Schröder, 2013). Due to its efficiency, shorter reaction times, higher yields, and lower energy consumption, microwave-assisted synthesis is often preferred over hydrothermal methods for furfural production.

Research by (Sánchez *et al.*, 2013) and (Rahim and Nadir, 2015), an attempt was made to conduct hydrolysis using microwave heating. Microwaves play a role in shortening the time of the hydrolysis process and increasing the furfural yield obtained. It is due to the agitation or rotational movement of polar molecules or ions that move due to the presence of a magnetic field. So far, there has been research on furfural from corn cobs. Still, most of them use inorganic acids, so researchers are interested in using organic acids from *Averrhoa bilimbi* extract for comparison to see the yield and quality of furfural from two different types of catalysts. Generally, furfural production still uses inorganic solvents such as sulfuric and hydrochloric acid. The acid contained in *Averrhoa bilimbi* has the potential to be used as an environmentally friendly organic solvent, such as acetic acid, citric acid, formic acid, and lactic acid, where acetic acid is usually used as a catalyst in making furfural.

Based on the background above, research was carried out regarding using organic acid catalysts from *Averrhoa bilimbi* in the hydrolysis process for making furfural using corn cobs as raw material compared to sulfuric acid catalysts. Using organic catalysts in furfural production offers several advantages over inorganic catalysts: 1. environmentally friendly and biodegradable, thus reducing the negative environmental impact. 2. high selectivity organic catalysts can better selectively convert pentosan to furfural. 3. milder operating conditions: using organic catalysts allows the reaction to occur at lower temperatures and pressures, reducing energy consumption and the risk of product degradation. 4. recycling potential some organic catalysts can be recycled and reused without losing their catalytic activity, increasing the overall process efficiency (Hapsari, Yolanda Mardiana, 2022). Considering these advantages, using organic catalysts in furfural production is a more sustainable and efficient choice than inorganic catalysts.

In this study, we utilized sulfuric acid, a catalyst widely available and commonly used in industry for furfural synthesis. Its established role as an effective catalyst for hydrolyzing pentosan-rich biomass into furfural, along with its catalytic power and thermal stability (Adebayo *et al.*, 2023), forms the foundation of our research. We aim to compare its performance with that of *Averrhoa bilimbi* extract, an organic catalyst.

Researchers will use microwaves as a heating agent in hydrolysis to produce furfural quickly by comparing the catalyst capabilities of sulfuric acid and *Averrhoa bilimbi*. It is hoped that the community can develop this technology to produce furfural with better yields and quality than conventional methods.

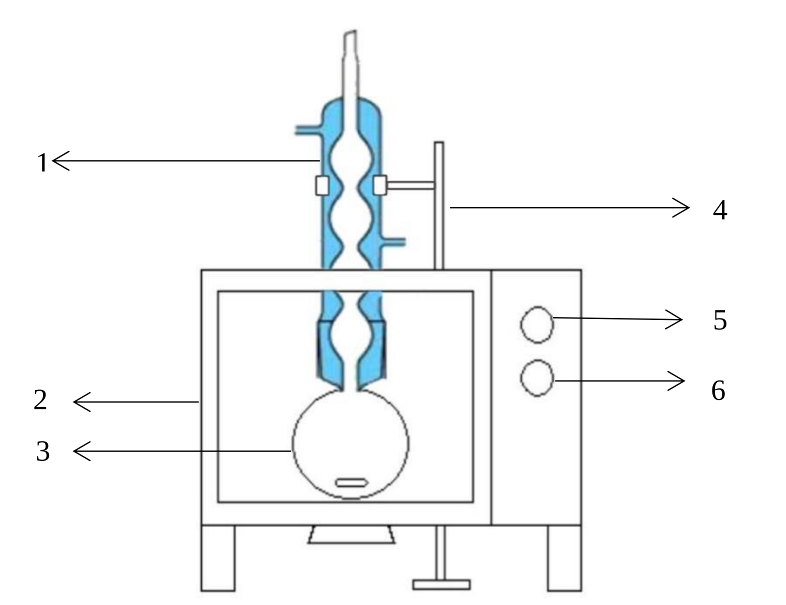
Research Methods

Materials

Materials used in this experiment included corn cobs 10 gr (100 mesh), sulfuric acid (E. Merck, 10%, 15%, and 20% v/v, p.a.), *Averrhoa bilimbi* extract, aniline acetate (5% solution v/v, E. Merck), chloroform (every 1 ml of hydrolyzate, 5 mL of chloroform is used; E. Merck), and demineralization water.

Instrumentation

The heater used is an Electrolux brand microwave, model EMM20K18GW (multimode), with a maximum power of 800 W, Magnetron Frequency 2.45 GHz. Microwave dimensions: p = 45 cm, w = 33 cm, t = 25 cm. Room capacity 20 L. Microwave is equipped with a temperature sensor (Thermocouple), digital temperature control, timer and power. The reactor used was chosen to transmit microwaves, namely a Duran brand round bottom flask with a capacity of 1 liter. This series of microwave equipment is equipped with a temperature sensor, temperature control, timer, and power. So, the temperature and process time can be controlled. The series of microwave equipment for the hydrolysis process can be seen in Figure 1.



1. Bulb Condenser
2. Microwave
3. Distillation Flask
4. Statives & Clamps
5. Power Controller
6. Timer

Figure 1. A series of microwave equipment for the hydrolysis process

Procedure

The research procedure is sequentially presented in the form of a flow diagram in Figure 2. Process operating conditions at atmospheric pressure (1 atm). Fixed variables include a corn cob weight of 10 grams and a particle size of 100 mesh, using 400-watt microwave power, and a corn cob and catalyst ratio of 1:30 (w/v). Variables that changed in the study included operating times of 60, 75, and 90 minutes. The concentration of sulfuric acid catalyst (H_2SO_4) is 10%, 15% and 20%.

1) Sample preparation

Wet corn cobs are dried under the sun, then cut into 2 cm pieces and ground using a grinding machine until they become powder. The corn cob powder is then sieved using a 100 mesh screen. After that, it is dried again using an oven at 105 °C for 30 minutes.

2) *Averrhoa bilimbi* extraction

Averrhoa bilimbi extraction using the procedure reported by (Thamizh Selvam *et al.*, 2015). At this stage, the *Averrhoa bilimbi* was cleaned using demineralization water until the pH was constant (generally within the range of 6.0–7.0**).** The fresh fruits were taken (100 gr) then the *Averrhoa bilimbi* was mashed using a blender to obtain *Averrhoa bilimbi* extract. Then, the *Averrhoa bilimbi* extract was filtered using Whatman paper no. 41. The *Averrhoa bilimbi* extract is stored in the refrigerator (4–8 °C). *Averrhoa bilimbi* extract composition per 100 gram: Moisture content 85–90%, Organic Acids (8–10%), glucose and fructose (low amounts), flavonoid, tannins, calcium, potassium, magnesium, vitamin C. This composition is in accordance with (Alhassan, Alhassan Muhammad, 2016)

3) Hydrolysis

a. Hydrolysis of corn cobs using varying concentrations of sulfuric acid catalyst

Ten grams of dried corn cobs were put into a two-neck flask (1000 mL) and dissolved in 300 mL of sulfuric acid (10%, 15%, and 20% v/v). Then, the reactor (two-neck flask) was heated in a microwave. The hydrolysis process in the microwave takes place at 100 °C, heated by microwaves with a power of 400 W for 60, 75, and 90 minutes.

b. Hydrolysis of corn cobs using *Averrhoa bilimbi* extract as a catalyst

Ten grams of dried corn cobs were put into a two-neck flask (1000 mL) and mixed with 300 mL of *Averrhoa bilimbi* extract. Then, the reactor (two-neck flask) was heated in a microwave. The hydrolysis process in the microwave took place at a temperature of 100, heated by microwaves with a power of 400 W for 60, 75, and 90 minutes.

4) Furfural separation

After hydrolysis, the material is left at room temperature (30 °C) for [specific duration]. Then, the liquid (hydrolyzate) is separated from the corn cob solids using vacuum filtration with a Whatman filter.

5) Analysis srocedure

a. Qualitative analysis

The hydrolyzate was obtained and then poured 1 ml into a test tube. Then, three drops of aniline-acetate solution were in the test tube, and the color change occurred. If the color of the hydrolyzate solution changed from bright yellow to brick red, then the solution was detected to contain furfural.

b. Quantitative analysis

The hydrolyzate obtained was extracted before being analyzed using a Gas Chromatography-Mass Spectrometer by adding chloroform (E Merck). The amount of chloroform used is (1:5) mL of chloroform volume versus hydrolyzate volume. The mixed hydrolyzate and chloroform are then stirred vigorously so that the furfural can dissolve in the chloroform. Wait a few moments until the solution forms into two layers. If two layers of liquid have formed, the next step is to take the bottom layer using a separating funnel. The formation of these two layers indicates that the top layer is the remaining hydrolyzate containing H_2O and H_2SO_4, while the bottom layer is chloroform, which contains furfural.

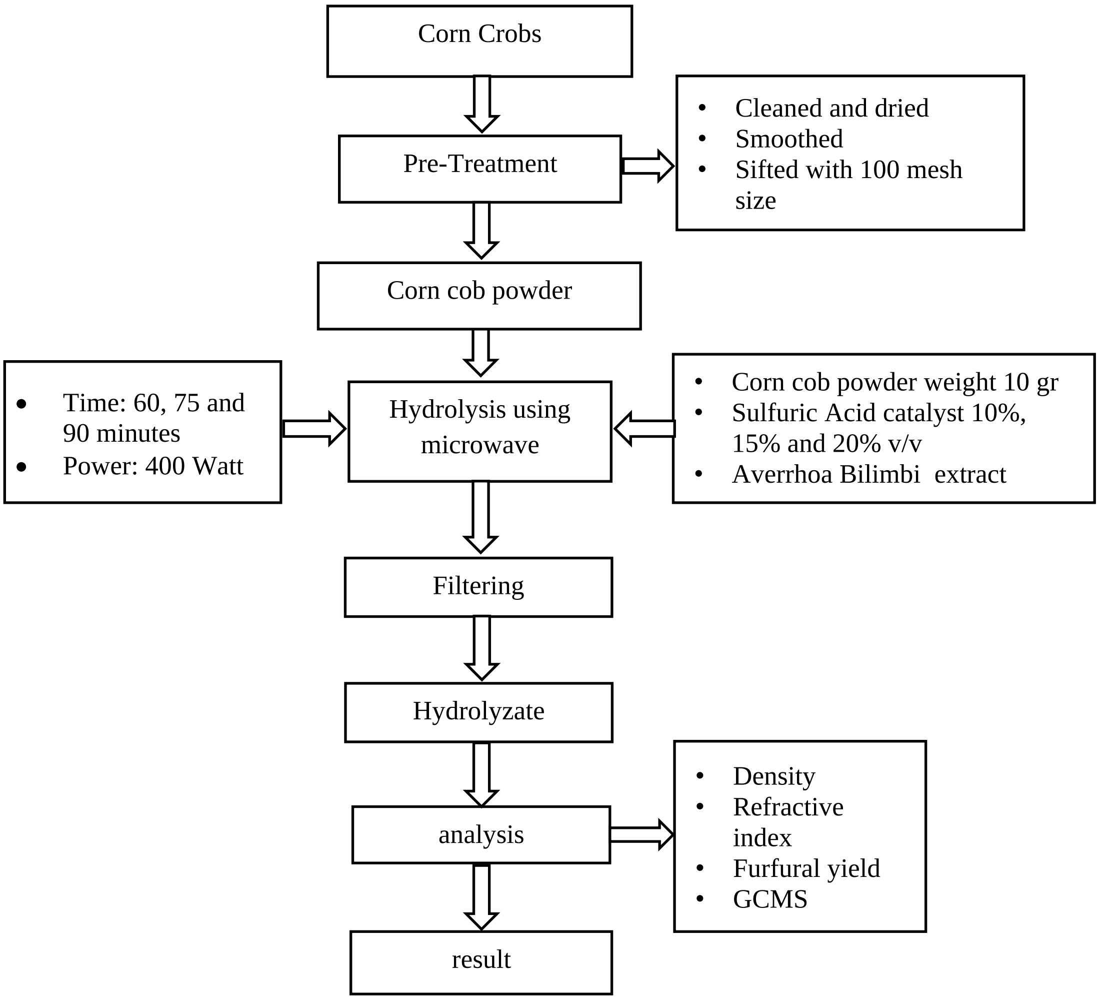


Figure 2. Research flow diagram using the sulfuric acid catalyst and *Averrhoa bilimbi* extract

Results and Discussion

Qualitative analysis (color test results)

This qualitative analysis was carried out by testing the color change in the hydrolyzate solution. 1 ml of hydrolyzate solution in a test tube was dripped with three drops of aniline-acetate solution. It is done on all samples/experimental variables. If the color of the hydrolyzate solution changes from bright yellow to brick red, then the solution was detected to contain furfural. The results from all samples showed a color change from bright yellow to brick red. It is in accordance with the theory which states that there is furfural content in the sample if the color changes from yellow to brick red. Following the statement (Mitarlis *et al.*, 2011)The hydrolyzate solution turns brick red when aniline-acetate is added to furfural; it was initially clear yellow. This suggests that the tested yield is furfural. Condensation between furfural and aniline produces dianyl hydroxy glutaric dialdehyde molecules, which causes this hue shift.

Quantitative analysis

1) Density analysis

In the results of the research that has been carried out, a high density is obtained, which is greatly influenced by the reaction time, where the longer the time is used, the denser it is, indicating that there are more furfural molecular particles. It can be seen from Figure 3 that the highest density was found in sample 9, with an H_2SO_4 catalyst concentration of 20% and a hydrolysis time of 90 minutes. For samples, the lowest density was found in sample 12 with a catalyst from *Averrhoa bilimbi* extract with a hydrolysis time of 90 minutes. The furfural quality standard has a density value of 1.16 gr/cm^3 (Eller and Cassinelli, 1994). Therefore, it can be concluded that the density results for each sample are pretty good because they are almost close to the quality standard of furfural density value.

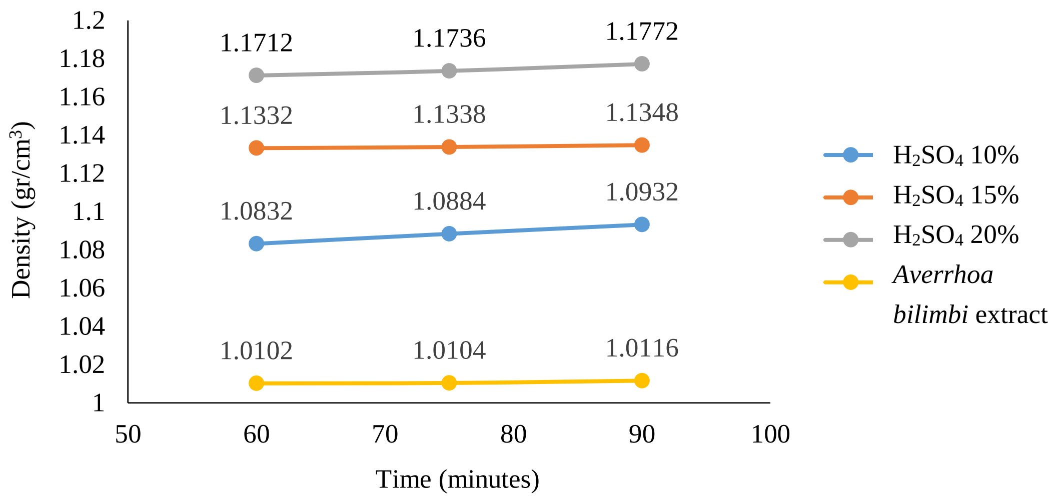


Figure 3. The effect of reaction time and catalyst concentration on density

2) Refractive index

Based on Figure 4, the refractive index value has increased, so we can conclude that the greater the concentration of a substance, the greater the refractive index value. Another factor that influences the refractive index is density. The greater the specific gravity of a substance, the denser the molecules in the substance/sample are, so the refractive index of the substance/sample is greater. It is based on theory because the resulting density of each sample is also greater. The furfural quality standard has a refractive index value of 1.524 at a temperature of 200C (Eller and Cassinelli, 1994). Therefore, the refractive index results for each sample are pretty good because they are close to a quality standard refractive index value of furfural.

3) Furfural yield

Based on Figure 5, the % yield of furfural increased from 13.11 to 14.69 in the 10% concentration H_2SO_4 catalyst sample with 60, 75, and 90 minutes reaction times. It is by the theory, which states that the higher the catalyst concentration and the longer the reaction time, the higher the furfural content in the sample. However, H_2SO_4 catalyst samples with concentrations of 15% and 20% with reaction times of 60, 75, and 90 minutes experienced a decrease in the % furfural yield, which means that the acid concentration has reached the optimum point so that the furfural yield will decrease. It is due to the decomposition of furfural into furoic acid due to the breakdown of the aldehyde group and is also not directly proportional to the increase in processing time because too long a reaction time will produce a type of black resin (Dunlop, 1948).

It can also be seen that the % yield of furfural in the *Averrhoa bilimbi* catalyst sample is lower compared to the H_2SO_4 catalyst; this shows that the H^+ ions in sulfuric acid are higher compared to the H^+ ions in *Averrhoa bilimbi* , and the *Averrhoa bilimbi* catalyst requires longer time to hydrolyze pentosan because *Averrhoa bilimbi* contains much water, so with the evaporation of water, the concentration of *Averrhoa bilimbi* acid becomes more concentrated so that the pH drops further and H^+ ions hydrolyze pentosan more quickly to form furfural (Mirnandaulia, 2017).

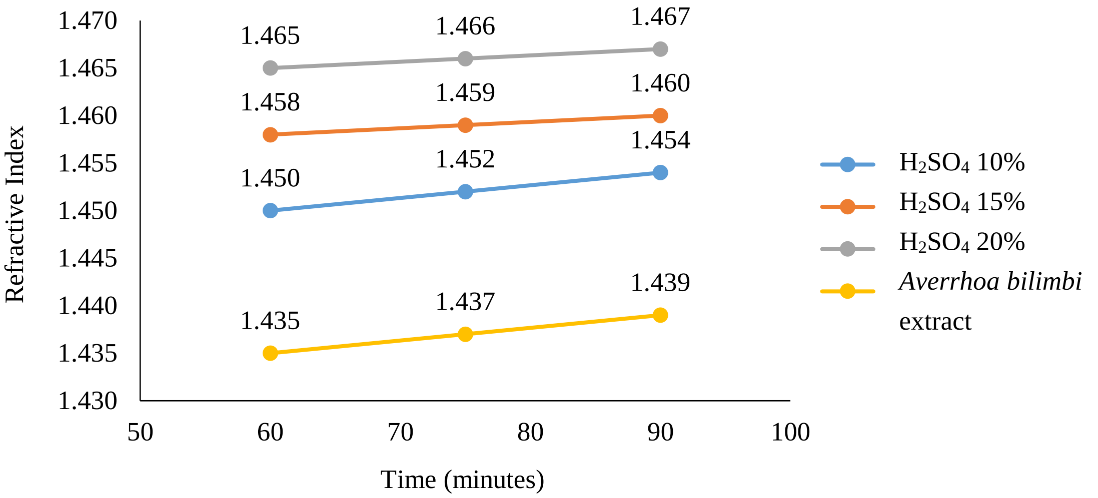


Figure 4. The influence of reaction time and catalyst concentration on the refractive index of furfural

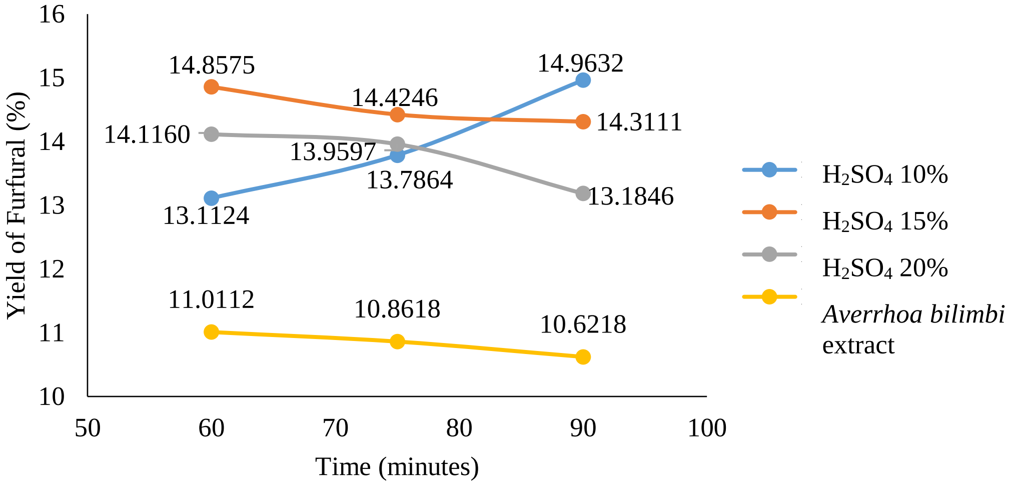
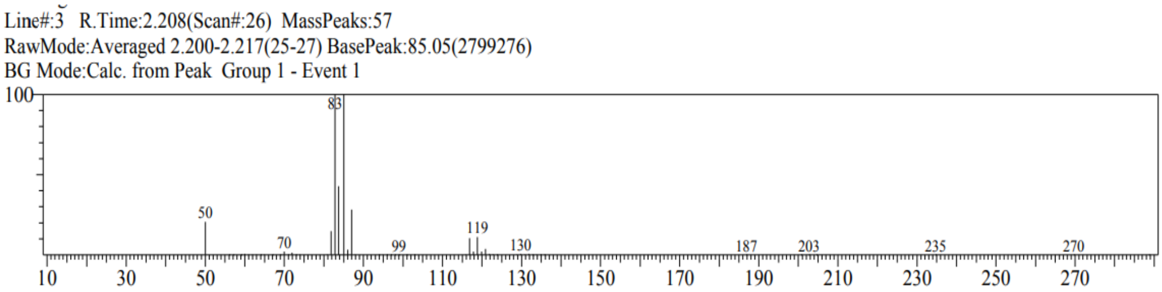


Figure 5. The influence of reaction time and catalyst concentration on the yield of furfural

4) GCMS Identification

Analysis using GCMS confirmed that the compound resulting from the hydrolysis of corn cobs was furfural. The sample we analyzed for GCMS was sample 3, a sample with an H_2SO_4 catalyst concentration of 10% and a hydrolysis time of 90 minutes. The compound shows a peak in gas chromatography with a retention time of RT 2.208, as shown in Figure 6.

Based on the results of GCMS, the mass of the furfural compound resulting from hydrolysis of corn cobs has a relative molecular mass of 83, shown in peak 3 with the compound identified, namely tetrahydrofuran, which indicates the furfural group. The fragmentation pattern of this compound has slightly similar results to furfural in the GCMS library data, namely 95 because the difference in results is not too big for the fragmentation pattern, as shown in Figure 7.



Peak	R. Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H
1	2.017	2.008	2.033	12155981	29.13	24155074	29.68	0.50
2	2.192	2.183	2.200	386873	0.93	727189	0.89	0.51
3	2.208	2.200	2.217	14654328	35.12	29212676	35.90	0.50
4	2.384	2.375	2.392	390172	0.94	739979	0.91	0.51
5	2.400	2.392	2.425	14138669	33.88	26543698	32.62	0.53
				41726023	100.00	81378616	100.00	

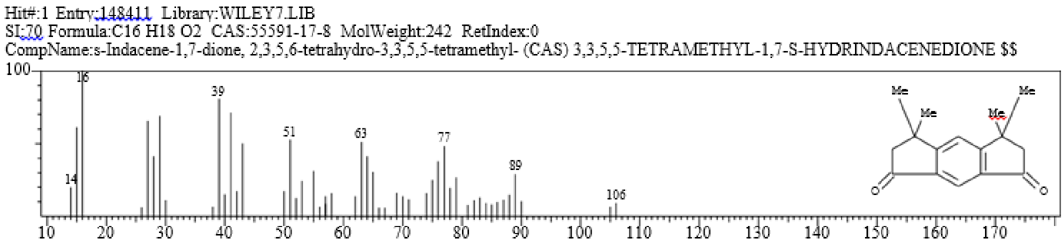


Figure 6. GCMS results at RT 2,208

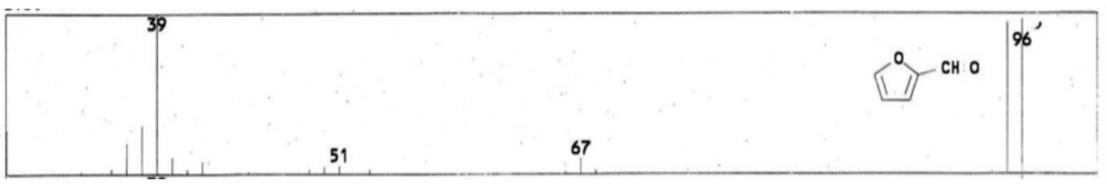


Figure 7. GCMS Library Data Furfural Fragmentation Pattern

Based on the results, it can be concluded that the compound produced from the hydrolysis of corn cobs is furfural, which shows a spectrum identical to the comparison furfural. In this research, the highest maximum yield of furfural was in 90 minutes with a sulfuric acid catalyst concentration of 10% at 14.96% and *Averrhoa bilimbi* catalyst concentration in 60 minutes at

11.01%. The results showed that large furfural yields were obtained with a shorter hydrolysis time than previous research. Radiation is transferring heat from one object to another without any physical contact. Microwave radiation even heats the mixture of ingredients. The heat produced by microwaves comes from microwaves in a microwave oven, which spins water molecules. Water molecules are polar molecules, meaning they have a negative charge on one side and a positive charge on the other. As a result, with a changing electric field induced via microwaves on each side, they will rotate to align themselves with each other (Adhiksana *et al.*, 2022).

The movement of these molecules will create heat as friction arises between one molecule and another. Heating using a microwave is even more effective because it directly interacts with the material and microwaves. Heating is even more effective because it does not transfer heat from outside but generates heat from within the material. This results in energy transfer taking place more quickly than conventional heating because, in conventional heating, the walls of the container are heated first, followed by the solvent. As a result, there is a temperature difference between the wall and the solvent (Fernández Sainz *et al.*, 2005). So, it can be concluded that this microwave method is more efficient because it can shorten hydrolysis time and produce relatively high yield values in furfural production.

The amount of furfural yield obtained is influenced by the presence of by-products that can be formed from the manufacture of furfural from corn cobs. The formation of these by-products reduces the efficiency of the conversion of pentose to furfural, thereby reducing the yield of furfural, including organic acids (acetic acid, formic acid, and levulinic acid), Hydroxymethylfurfural (HMF), gas (CO_2 and CO) (Mitarlis *et al.*, 2011; Zulnazri *et al.*, 2021). Efforts to reduce by-products by controlling reaction conditions include optimizing temperature, reaction time, and catalyst concentration to minimize the formation of by-products and purifying the product to separate furfural from by-products. The comparison results of previous research with the results of this research are shown in the following Table 1.

Table 1. Comparison of previous research results with the results of this research

No	Research	Operating Conditions			Method	Furfural Yield
		Raw Materials	Hydrolysis Time	Catalyst		
1	(Mirnandaulia, 2017)	Sembang Rambat	150 minutes	*Averrhoa bilimbi* extract	Heater	7.19%
2	(Zulnazri *et al.*, 2021)	Corn Cobs	100 minutes	Acetic Acid 6%	Waterbath	7.26%
3	(Adhiksana *et al.*, 2022).	Sugar cane bagasse	75 minutes	H_2SO_4 8%	Microwave	0.28%
4	Results of this research	Corn Cobs	90 minutes	H_2SO_4 10%	Microwave	14.96%
5	Results of this research	Corn Cobs	60 minutes	*Averrhoa bilimbi* Extract	Microwave	11.01%

Scaling up furfural production using *Averrhoa bilimbi* extract as a natural catalyst presents a promising avenue for sustainable industrial processes. However, several factors must be considered to ensure feasibility and efficiency. 1). availability of raw materials, 2). catalytic activity: studies have demonstrated that *Averrhoa bilimbi* extract effectively catalyzes the conversion of biomass to furfural, offering yields comparable to inorganic acid catalysts. (Patil *et al.*, 2020), incorporating microwave technology can enhance reaction rates and improve energy efficiency, making the process more viable for industrial applications.(Patil *et al.*, 2021). 3). economic considerations: cost of catalyst production and energy consumption: Microwave-assisted processes can reduce energy requirements, potentially lowering operational costs. 4). Environmental Impact: minimizing environmental pollution and waste management: byproducts from the process are biodegradable, simplifying disposal and reducing environmental impact.

Leveraging *Averrhoa bilimbi* extract as a natural catalyst for furfural production offers a sustainable and efficient alternative to conventional methods. While challenges exist, particularly in standardizing catalyst preparation, reactor technology, market adoption, and scaling the process is essential. Furthermore, the environmental and economic benefits make it a compelling option for future industrial applications. With further optimization and pilot-scale trials, this approach could revolutionize furfural production and set a benchmark for green industrial practices.

Conclusions

Averrhoa bilimbi, a potential alternative natural catalyst, has shown promising yields that are comparable to those achieved with a sulfuric acid catalyst. The use of microwaves, a novel approach, has the potential to significantly reduce the hydrolysis process time and produce high furfural yield values. The furfural yield with the *Averrhoa bilimbi* catalyst reached an impressive 11.01%. The best furfural yield results were obtained with a 10% sulfuric acid catalyst in 90 minutes, with a yield value of 14.9632%, a density of 1.0932 gr/cm3, and identification of GCMS as having a relative molecular mass of 83 at peak 3.
The integration of *Averrhoa bilimbi* as a natural catalyst and microwave technology in furfural production represents a promising step toward sustainable industrial practices. Future research should focus on optimizing and scaling up this method to fully realize its potential in both economic and environmental terms. This approach not only addresses the demand for green alternatives in chemical processes but also leverages innovative technologies to enhance efficiency and applicability.

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