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Paper Waste Hydrolysis with Stepwise Sulfuric Acid Catalyst

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ABSTRACT

The need for paper results in a lot of paper waste. Paper waste, which is lignocellulosic, can be hydrolyzed using an acid catalyst to produce various cellulose degradation products. In this study, the effect of the sulfuric acid catalyst addition method on the waste paper hydrolysis process was investigated. The addition of the catalyst was carried out in three types. The Type-1 method was sulfuric acid addition in the 0th minute. The Type-2 method was sulfuric acid addition in the 0th and 30th minutes. The Type-3 method was sulfuric acid addition every 10 minutes. The results showed that the lowest residual mass of waste paper hydrolyzed was produced using the Type-3 method. This showed that the Type-3 method, sulfuric acid addition every 10 minutes, had an effect on the residual mass of the hydrolyzed sample. The Type-3 method was the most effective type of sulfuric acid catalyst addition compared to other types. On the other hand, variations in the concentration of the sulfuric acid catalyst affect the residual mass of the waste paper hydrolyzed sample, where higher sulfuric acid concentration will lower residual mass. The catalyst concentration of 2% sulfuric acid with The Type-3 addition method resulted in the highest conversion which was 38.27%.

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1. INTRODUCTION

Millions of tons of paper waste increase every year, especially in developing areas such as urbanized areas, which have increased literacy and industrial development [1]. Paper waste is a cheap lignocellulosic material consisting of cellulose, hemicellulose, and lignin [2]. Paper waste generally contains chemical compounds such as fillers, retention aids, adhesives, coatings, biocides, and synthetic binders [3].

Several studies have addressed paper waste by recycling it to reduce the environmental impact from a lifecycle perspective [4], [5]. However, the recycling process can only be applied a few times, and after that, the paper still has to be thrown away [6]. In theory, the maximum recycling of waste paper is six to seven times, but in practice, it is only two to four times. After that, it will be thrown away. [7], [8]. Apart from that, recycled paper products generally have low quality because the recycling process makes the paper fibers shorter, so the paper becomes quickly damaged. [8].

Paper waste in the construction sector can be used for plasterboard, cellulose fiber insulation, and bricks mixed with cement [9]. Paper waste can also be used as slow-release fertilizer [10]. Another application of paper waste can be to extract the cellulose and use it to make cellulose-based materials, or it can be hydrolyzed to produce cellulose derivative compounds that have high selling value, such as glucose, ethanol, hydroxymethylfurfural and so on.

Cellulose is a biopolymer that is the main component of plant fiber with glucose monomers linked to β-D-glucose. Cellulose is carbon material produced from the photosynthesis process [11]. The structure of cellulose has amorphous and crystalline phases [12]. Apart from plants, cellulose can also be produced through a fermentation process known as bacterial cellulose. Bacterial cellulose has superior physical and chemical properties compared to cellulose from plants, such as high tensile strength and water-holding capacity [13]. Several cellulose derivative products can be produced by modifying the structure of three hydroxyl groups of cellulose [14].

Acid hydrolysis is commonly used to produce nanocrystalline cellulose. The amorphous part of cellulose is more easily hydrolyzed than the crystalline part. Strong acids such as hydrochloric acid, sulfuric acid, nitric acid, and phosphoric acid can be used as catalysts in hydrolyzing cellulose. [15], [16]. Of the various acids used as catalysts, sulfuric acid is the most commonly used acid [17]. Sulfuric acid resulting from hydrolysis can be recovered using anion exchange resins [18]. Low-concentration acid hydrolysis or dilute acid pretreatment is a promising method for application in industry because it can increase cellulose accessibility [19]. Nearly 100% of hemicellulose can be removed when sulfuric acid is used in a dilute acid pretreatment process [20]. Sugar is the main product of the dilute acid pretreatment process [21], [22].

Various studies have carried out cellulose hydrolysis using a sulfuric acid catalyst, which was added entirely at the beginning of the hydrolysis process [16-22]. However, there has been no research on hydrolysis with a gradual addition of sulfuric acid catalyst.

Study on hydrolysis with the stepwise addition of sulfuric acid catalyst will determine how much sulfuric acid is needed to achieve an effective hydrolysis process. The stepwise addition of sulfuric acid catalyst can reduce the amount of catalyst required during hydrolysis and has implications for the economics of the hydrolysis process. In this research, dilute acid pretreatment of waste paper will be investigated using stepwise sulfuric acid addition. This research investigated the effect of the stepwise acid catalyst addition method on the results of the waste paper hydrolysis process.

2. RESEARCH METHODS

2.1 Materials

The equipment used in this research included a hot plate, 500 ml three-neck flask, oven, analytical balance, 1000 ml beaker, filter, stirring rod, thermometer, plastic container, tray, aluminum foil, and tissue. The materials used in this research were A4 size HVS paper waste (70 gsm) from a printing shop in Lampung, NaOH (Merck), H_2SO_4 98% (Merck), and Aquades.

2.2 Waste Paper Preparation

The raw material used in this research was 450 grams of A4 size HVS paper waste (70 gsm). Waste paper will be cut manually using scissors to reduce the size of the paper to 2x2 cm.

2.3 Waste Paper Deinking Using NaOH

The steps for the waste paper deinking process are taken from Kumar et al. (2016) [23] with modification. The crushed paper was weighed 50 grams and put into a beaker. 1% NaOH solution (v/v) was added to the beaker containing paper waste. The mixture of paper and 1% NaOH solution (v/v) was mixed at room temperature for one hour while stirring at 100 rpm. After the paper had been mixed with NaOH, it was then washed using distilled water until the pH was neutral, as measured using pH meter. The washed paper was then dried using an oven until it reached 4.5 – 6% water content, which was then weighed to obtain an initial sample (ma).

2.4 Waste Paper Hydrolysis

The waste paper hydrolysis process was carried out using a series of tools, according to Figure 1. The waste paper hydrolysis process begins by inserting distilled water into a three-neck flask at a predetermined volume, according to the sulfuric acid catalyst concentration to be added. The Hot plate was turned on until the distilled water temperature in the three-neck flask was stable at 90ºC. After that, 7.5 grams of deinking waste paper was put into a three-neck flask. Next, 98% sulfuric acid catalyst was added to the three-neck flask as a catalyst gradually at a predetermined volume until it reached a sulfuric acid concentration of 0.5%, 1%, 1.5%, and 2% (v/v) according to the variable with 300 mL solution volume according to Table 1. The hydrolysis process was also carried out by stepwise sulfuric acid addition at each time, which was duplicated to produce 24 samples, according to Table 2. The heating process was carried out for 1 hour at 90ºC. Once finished, the paper waste deposits in the three-necked flask that had not been hydrolyzed were filtered, washed with distilled water until neutral, and then dried in the oven until it reached 4.5 – 6% water content. The mass of the waste paper sample that had not been hydrolyzed was then weighed to obtain the residual sample mass (mp) and calculated the conversion.

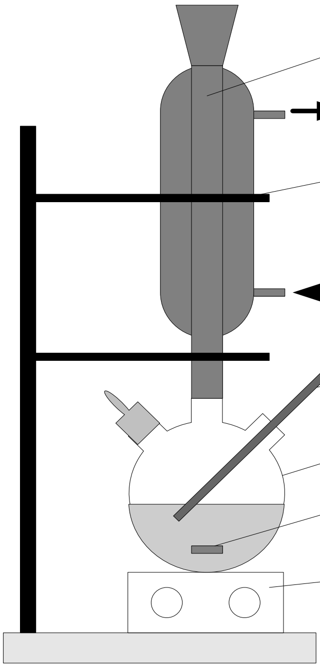


Figure 1. Waste paper hydrolysis equipment

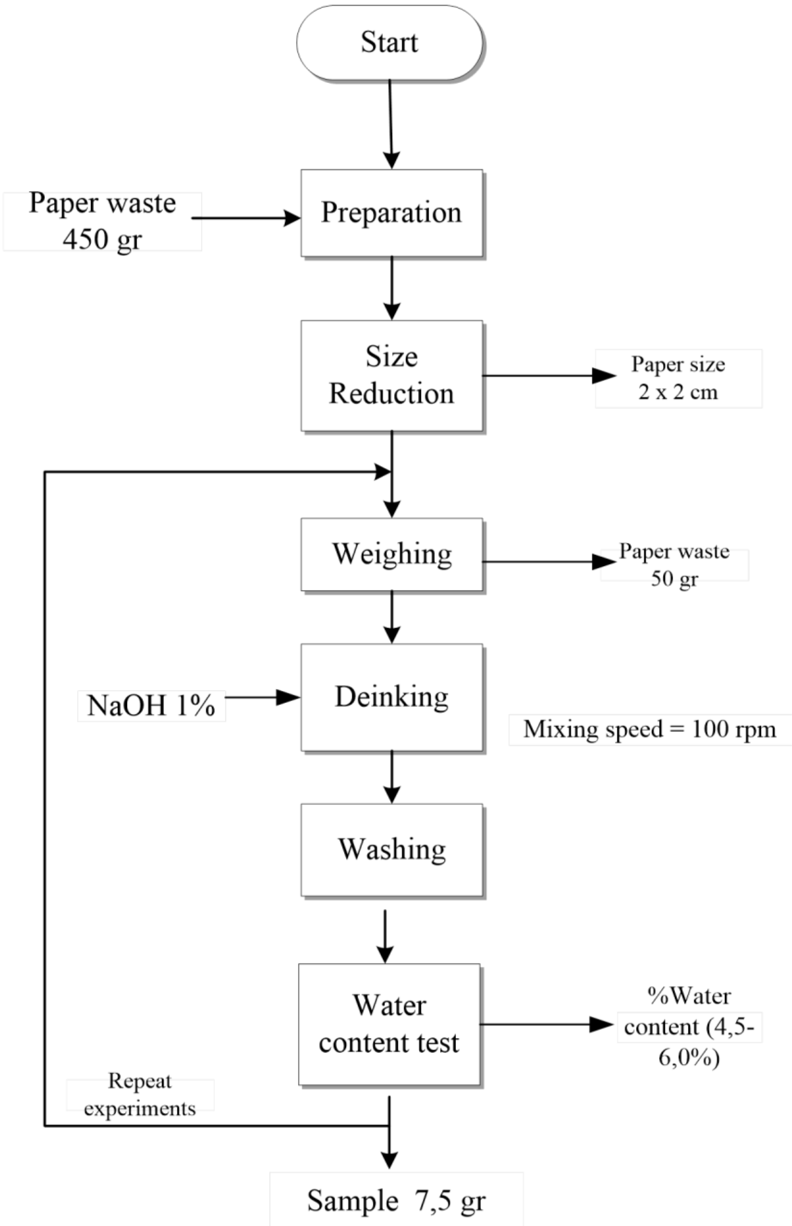
Table 1. Volume of distilled water and acid catalyst at each concentration

Acid catalyst concentration (v/v)	Distilled water volume (mL)	Acid catalyst volume (mL)
0.5	298.469	1.531
1	296.939	3.061
1.5	295.408	4.592
2	293.878	6.122

Table 2. Stepwise acid catalyst hydrolysis experiments

Variables	Catalyst addition time (minutes to)	Sulfuric acid concentration (v/v)			
		0,50%	1%	1,50%	2%
Catalyst addition time minutes to- 0 (Type-1)	0	Sample 1 Sample 2 (catalyst volume=1,5 ml)	Sample 3 Sample 4 (catalyst volume=3 ml)	Sample 5 Sample 6 (catalyst volume=4,5 ml)	Sample 7 Sample 8 (catalyst volume=6 ml)

Variables	Catalyst addition time (minutes to)	Sulfuric acid concentration (v/v)			
		0,50%	1%	1,50%	2%
Catalyst addition time minutes to- 0 and 30 (Type-2)	0 and 30	Sample 9 Sample 10 (catalyst volume=0,75 ml)	Sample 11 Sample 12 (catalyst volume=1,5 ml)	Sample 13 Sample 14 (catalyst volume=2,25 ml)	Sample 15 Sample 16 (catalyst volume=3 ml)
Catalyst addition every 10 minutes (Type-3)	0, 10, 20, 30, 40, and 50	Sample 17 Sample 18 (catalyst volume=0,25 ml)	Sample 19 Sample 20 (catalyst volume=0,5 ml)	Sample 21 Sample 22 (catalyst volume=0,75 ml)	Sample 23 Sample 24 (catalyst volume=1 ml)



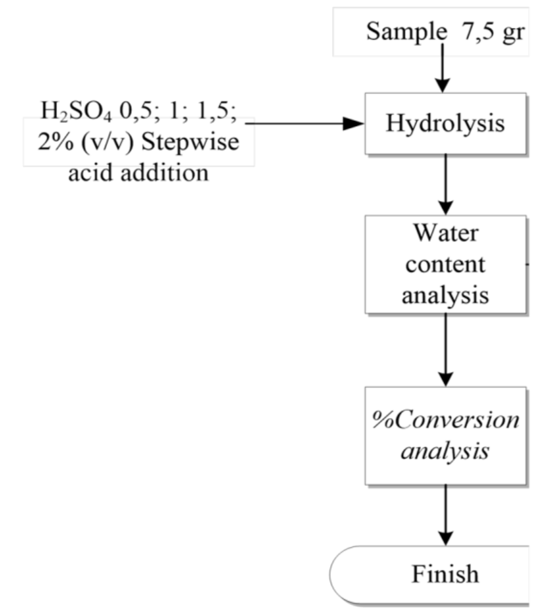


Figure 2. Research flow diagram

2.5 Non-hydrolyzed paper conversion calculation

The conversion of non-hydrolyzed paper can be calculated using the following formula:

$$Conversion = \frac{m_a - m_p}{m_a} \times 100\% \qquad \ldots (1)$$

Where mp was the mass of the remaining sample (gr) and ma was the initial sample mass (gr)

3. RESULTS AND DISCUSSION

3.1 Effect of sulfuric acid concentration on the hydrolysis process of waste paper

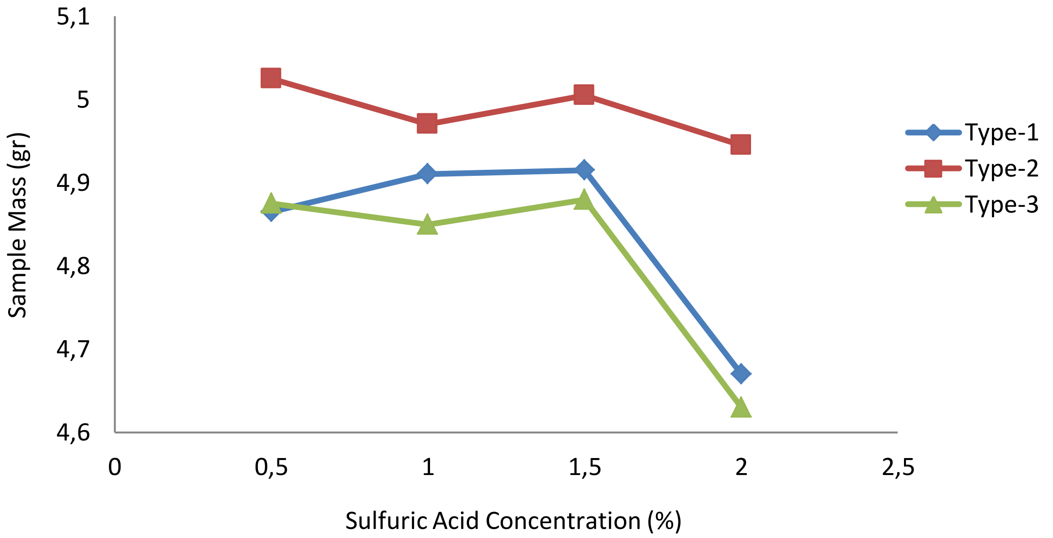


Figure 3. Effect of sulfuric acid concentration on the residual mass of hydrolysis samples

Hydrolysis of waste paper with varying concentrations of sulfuric acid produces the residual mass of paper waste, according to Figure 3. In Figure 3, it can be seen that the addition of Type-1, Type-2, and Type-3 sulfuric acid catalysts results in a decrease in the residual mass of waste paper samples as with increasing acid catalyst concentration. The lower residual mass of the sample produced indicated that a greater amount of paper waste was hydrolyzed. Increasing the concentration of sulfuric acid catalyst had an influence on the residual mass of the sample in each variation. 2% sulfuric acid concentration (v/v) produced the lowest residual mass of the sample for each type of catalyst addition. High acid concentrations can cause cellulose and hemicellulose to be more easily degraded into glucose and other decomposition products. Meanwhile, longer hydrolysis time made the contact between acid and cellulose longer, so a longer hydrolysis reaction was laid [24].

The results of this study can be compared with Safitri et al. (2018)[25]. From the results of research regarding the hydrolysis of dragon fruit peel which had been carried out, it was known that sulfuric acid catalyst concentrations of 0.5, 1, 1.5, and 2 M produced glucose that increased sequentially, namely 0.03, 0.032, 0.041, and 0.05 g/mL. The increasing glucose concentration indicated that there was a decrease in the mass of the sample remaining from the hydrolysis of cellulose from red dragon fruit skin.

3.2 Effect of stepwise addition of sulfuric acid on waste paper hydrolysis

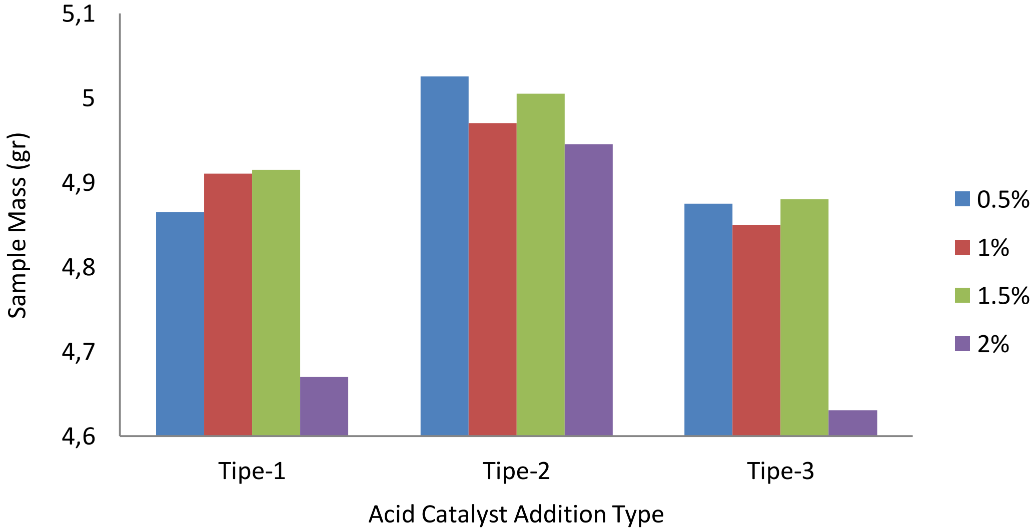


Figure 4. The effect of stepwise addition of sulfuric acid on waste paper hydrolysis

The stepwise addition method of acid catalysts in waste paper hydrolysis has three types, according to Table 1. In Figure 4, it can be seen that the effect of stepwise addition in sulfuric acid catalysts of various concentrations was quite significant on the mass of paper that was not hydrolyzed. The stepwise addition of catalyst aimed to increase the reaction rate and reduce the activation energy while the hydrolysis process was taking place [26]. The stepwise addition of catalyst in the hydrolysis process had different catalyst concentrations, where the concentrations used were 0.5%, 1%, 1.5%, and 2%. The difference in concentration affects the residual mass of sample. High catalyst concentration can affect the reactivity of cellulose and reduce the lignin in the paper so that high glucose concentration was produced in the hydrolysis process.

In this study, waste paper hydrolysis with stepwise addition of Type-3 at 2% sulfuric acid concentration produced the lowest residual mass of the sample. This was because, during the hydrolysis, the catalyst was introduced gradually every 10 minutes for 1 hour. The stepwise addition of Type-3 was an effective addition of sulfuric acid catalyst because the reactivity of sulfuric acid was maintained by adding new sulfuric acid every 10 minutes so that the lowest residual mass of paper waste was produced compared to other types.

The stepwise addition of Type-1 produced a residual mass of paper waste that was not much different from Type-3. The stepwise addition of a Type-1 catalyst, namely the addition of a sulfuric acid catalyst at minute 0, caused the hydrolysis process to take place optimally at the start of the hydrolysis reaction, although the reactivity of sulfuric acid catalyst will decrease with longer hydrolysis time. On the other hand, in contrast with the stepwise addition of Type-1 and Type-3 sulfuric acid catalysts, the stepwise addition of Type-2 sulfuric acid catalyst produced the highest residual mass of hydrolysis samples. The high residual mass of the hydrolysis sample in Type-2, namely at 0 and 30 minutes, showed that the treatment with Type-2 was not effective enough for paper waste hydrolysis.

3.3 Conversion of waste paper hydrolysis with stepwise addition of sulfuric acid catalyst

Table 3. Hydrolysis conversion of waste paper by stepwise addition of sulfuric acid catalyst

Concentration (v/v)	Acid-catalyzed addition type (minutes)	Conversion (%)
	Tipe-1	35.13
0.5	Tipe-2	33.00
	Tipe-3	35.00
	Tipe-1	34.53
1.0	Tipe-2	33.73
	Tipe-3	35.33
	Tipe-1	34.47
1.5	Tipe-2	33.27
	Tipe-3	34.93
	Tipe-1	37.73
2.0	Tipe-2	34.07
	Tipe-3	38.27

The hydrolysis conversion of waste paper by stepwise addition of sulfuric acid can be seen in Table 3. Based on Table 3, the stepwise addition method of sulfuric acid catalyst in waste paper hydrolysis produced low conversion. This could have happened because the operating temperature used in hydrolysis was too low, about 90ºC. One of the disadvantages of the acid hydrolysis process was that it required a large amount of energy to carry out the reaction [27]. The highest conversion of waste paper hydrolysis with the stepwise addition method of sulfuric acid catalyst was obtained 38.27% from Type-3 stepwise addition of sulfuric acid catalyst with 2% sulfuric acid concentration.

4. CONCLUSION

The effect of the stepwise addition of sulfuric acid catalyst on waste paper hydrolysis resulted in the lowest residual mass of the sample when the Type-3 stepwise addition method was used. This proved that the stepwise addition of sulfuric acid catalyst every 10 minutes had an effect on the residual mass of the sample. Type-3 stepwise addition method produced the lowest residual mass of samples compared to other types, which indicated that Type-3 was the most effective type of sulfuric acid catalyst addition. Variations in sulfuric acid concentration affect the residual mass of the sample. Higher sulfuric acid concentration resulted in less residual mass of the sample. 2% sulfuric acid catalyst concentration with Type-3 stepwise addition method produced the highest waste paper hydrolysis conversion which was 38.27%.

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