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The Effect of Base Catalyst Type and Temperature of Peanut Shell Hydrolysis to Oxalic Acid

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ABSTRACT
The need for oxalic acid increases every year, mainly due to its use in industry. So far, Indonesia continues to import oxalic acid from foreign countries, which requires a high transport cost. To increase the domestic production of oxalic acid, it is necessary to research its production using various raw materials and methods. Oxalic acid can be made from cellulose-containing materials using the alkali hydrolysis method. Cellulose-based materials in Indonesia are abundant, including peanut shells. The purpose of this research is to determine the effect of alkaline catalyst types (NaOH and Ca $(OH)_2$) and temperature variations of (60ºC to 100ºC) on the yield of oxalic acid produced. The product has also been tested in terms of its physical and chemical characteristics. The highest oxalic acid yield of peanut shell waste (12.83%) was achieved by alkaline hydrolysis using a NaOH catalyst at 60°C. Oxalic acid from peanut shell has a melting point of 102.5ºC and has an absorption of a hydroxyl group (O-H) at a wavenumber of 3,408.33 cm^{-1}, a carbonyl group (C=O) at a wavenumber of 1,687.77/1,624.12 cm^{-1}, and the carboxyl group (C-O) at wave number 1,126.47 cm^{-1}. Oxalic acid from peanut shell has a melting point of 102.5ºC and has an absorption of a hydroxyl group (O-H) at a wavenumber of 3,408.33 cm^{-1}, a carbonyl group (C=O) at a wavenumber of 1,687.77/1,624.12 cm^{-1}, and the carboxyl group (C-O) at wave number 1,126.47 cm^{-1}.

Keywords: *oxalic acid, alkaline hydrolysis, alkaline catalysts, yield.*

1. INTRODUCTION

Oxalic acid is usually produced using several methods. The methods used are the oxidation of glucose with strong acids, the smelting of cellulose with a strong-base catalyst, and the decomposition of sodium formate [1]. Among the three existing methods, the most relevant method is the smelting of cellulose with an alkali catalyst. This method is the simplest because the equipment and materials are easy to obtain, and the costs required are quite affordable [2].

The alkali smelting method of cellulose has been carried out using many variations. The hydrolysis of rice husks using a 3.5 N NaOH catalyst with a hydrolysis time of 75 minutes at 98ºC can produce oxalic acid with a concentration of 44.19% [3]. The hydrolysis of used newspapers using a 40% NaOH catalyst with a hydrolysis temperature of 105ºC at 70 minutes produces oxalic acid with a concentration of 3.05% [4]. Rice husks hydrolysis at 60 minutes and a temperature of 60ºC using 3.5 N NaOH catalyst produces oxalic acid with a concentration of 3.42%, while the use of a 3.5 N $Ca(OH)_2$ catalyst produces oxalic acid with a concentration of 2.23% [2].

Several studies have been conducted on the production of oxalic acid using waste cellulose as a raw material. The peanut shell is one of the materials that contain cellulose, and its presence in Indonesia is abundant. Peanut shells can be converted into oxalic acid via the alkali smelting method because they have more than 35% cellulose [5].

Research that specifically studies the effect of alkaline catalyst types and temperature variations on the hydrolysis of peanut shells is not found. The catalyst type and temperature will affect the reaction speed in the alkali smelting process to produce oxalic acid and affect the resulting yield. Therefore, this study will observe the effect of the alkaline catalyst type and the hydrolysis temperature of peanut shells on oxalic acid yield.

2. LITERATURE REVIEW

Peanut shell contains 7.3% protein, 4.5% minerals, 1.2% fat, and 63.5% cellulose [5]. Although cellulose in peanut shells has been widely used as an adsorbent, only a few studies have specifically discussed the cellulose content in peanut shells as a raw material for producing oxalic acid.

There are several ways to make oxalic acid commercially, namely the oxidation process with nitric acid, decomposition of sodium formate, and smelting with a strong base catalyst [1]. Catalysts are substances that help a chemical reaction go faster. The catalyst has an active region that donates energy to the reactants, allowing the reactant molecules easier pass the activation energy. In the process of hydrolysis of peanut shells into oxalic acid, the catalyst used is a homogeneous type of alkaline catalyst. The alkaline catalysts used are NaOH and $Ca(OH)_2$ [3]. Several factors that affect the hydrolysis process for the manufacture of oxalic acid are time, temperature, the concentration of the alkaline solution, stirring speed, and particle size.

There are two forms of oxalic acid: anhydrous and dihydrate. The chemical nature of anhydrous oxalic acid is that it has a molecular weight of 90.04 g/mol with a melting point of 187^{o}C. The physical properties of anhydrous oxalic acid are white, odorless, and do not absorb water. Oxalic acid dihydrate has a molecular weight of 126.07 g/mol with a melting point of 101.5^{o}C and contains anhydrous oxalic acid (71.42%) and water (28.58%), has odorless properties, and will lose water molecules when heated at temperatures above 100^{o}C.

The melting point and functional groups of oxalic acid indicate its quality. The melting point can be determined using a Melting Point Tester, while the functional groups can be analyzed using Fourier-transform Infrared Spectroscopy (FTIR).

3. METHODOLOGY

The research was conducted with stages shown in Figure 1. The research began with pre-treatment of raw materials followed by a hydrolysis process with variations in the type of base and the hydrolysis temperature. The reaction products were then precipitated and went through a crystallization process. The product obtained was then analyzed to obtain product characteristics.

Peanut shells were washed with clean water and then dried in the sun for three days. Peanut shell powder was created by grinding dried peanut shells. Peanut shell powder was reacted with various catalysts of NaOH and $Ca(OH)_2$ 4N with stirring at 225 rpm for 70 minutes. The temperature of the reaction was varied between 60 to 100^{o}C.

The reaction products were then filtered and washed with hot water to obtain the mother liquor resulting from the hydrolysis. For the precipitation stage, 10 mL of the mother liquor solution was taken and 12.5 mL of 6% $CaCl_2$ solution was added. The solution was then allowed to stand for 30 minutes to form a calcium oxalate precipitate. The filtrate was then filtered, and 40 mL of 4N H_2SO_4 solution was added to the precipitate for 24 hours, until a calcium sulphate precipitate forms. The precipitate was washed with 15 mL of ethanol then heated at 70^{o}C for 1 hour. The filtrate was allowed to stand for two days until the oxalic acid crystals were formed.

Two types of equipment were used to analyze product characteristics: Fourier-transform Infrared Spectroscopy (FTIR) and a Melting Point Tester. FTIR was used to analyze the functional groups of the resulting oxalic acid compounds. Melting Point Tester is used to determine the physical properties of the resulting oxalic acid crystals.

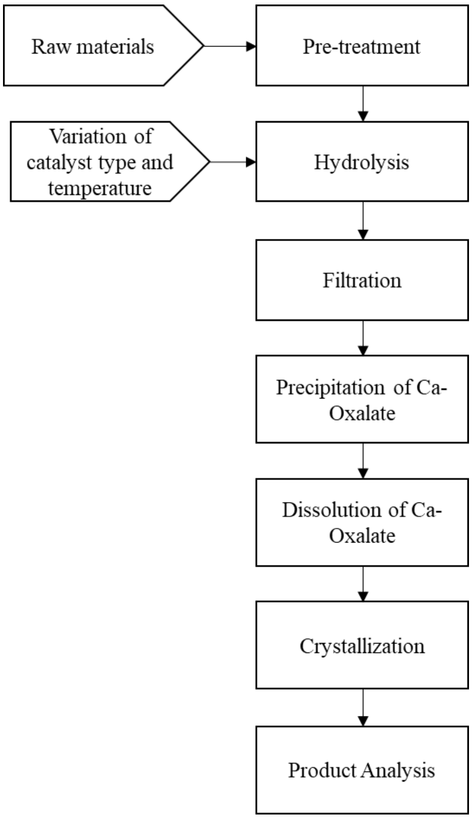

Figure 1 Block Flow Diagram of the peanut shell hydrolysis to oxalic acid process

4. RESULT AND DISCUSSION

4.1. Effect of Base and Temperature Types of Catalysts on Oxalic Acid Yield

Table 1 shows the oxalic acid produced in this study. The yield of oxalic acid catalyzed using a 4N NaOH catalyst decreases when the reaction temperature increases. In a varied temperature range, the optimum temperature for hydrolysis of peanut shells using a 4N NaOH catalyst is 60^{o}C. It is consistent with the findings of research on rice husk material using a NaOH catalyst [2]. When the temperature rises above 60^{o}C, the created product decomposes, lowering the yield.

Table 1. Effect of Base and Temperature Types of Catalysts on Oxalic Acid Yield

Catalyst Type	Hydrolysis Temperature (°C)	Oxalic Acid Produced (gram)	Yield (%)
NaOH	60	2.565	12.825
	70	2.455	12.275
	80	2.415	12.075
	90	2.305	11.525
	100	2.3425	11.713
$Ca(OH)_2$	60	0.654	3.270
	70	0.448	2.240
	80	0.546	2.730
	90	1.432	7.160
	100	1.319	6.595

Meanwhile, at 60, 70, 80, and 90 degrees Celsius, the yield of oxalic acid rose in a process catalyzed by a $Ca(OH)_2$ 4N. The highest yield (7.16%) is obtained at 90°C. Furthermore, there is a decrease in yield at a temperature of 100°C. This occurs because the reaction kinetics are not yet optimal at temperatures below 90°C, resulting in a low yield. Meanwhile, product degradation occurs at temperatures above 90°C, resulting in a drop in yield.

The weight of oxalic acid catalyzed by the NaOH catalyst is more than the $Ca(OH)_2$. This happens because NaOH's alkaline nature is stronger than $Ca(OH)_2$, allowing the smelting process to run considerably more efficiently.

The optimum temperature required by the two catalysts to produce the highest yield is also different. The composition of the NaOH base catalyst influences the activation energy required in the smelting process, as a stronger base will require less heating than $Ca(OH)_2$, allowing the reaction to occur at a lower temperature. The results of the hydrolysis reaction with a NaOH catalyst at 60°C have a more concentrated color. It indicates the decomposition of the product into CO_2 and H_2O. Table 2 shows a comparison of the findings of several researchers' studies on the synthesis of oxalic acid.

Table 2. Comparison of the findings

Raw Materials	Researcher	Catalyst	Hydrolysis Temperature (°C)	Hydrolysis Time (minutes)	Yield (%)
Rice Husks	[7]	NaOH 3.5N	60	60	3.42
Rice Husks	[7]	$Ca(OH)_2$ 3.5N	60	60	2.232
Peanut Shells	[6]	NaOH 4N	98	70	6.29
Peanut Shells	This Research	NaOH 4N	60	70	12.825
Peanut Shells	This Research	$Ca(OH)_2$ 4N	90	70	7.16

4.2. Oxalic Acid Characteristics

The oxalic acid catalyzed by the NaOH catalyst was then analyzed using the FTIR method and the Melting Point Tester instrument to test its melting point. Table 3 shows the results of FTIR analysis and melting point testing of oxalic acid products.

The FTIR results showed the absorption of the hydroxyl group (3,408.33 cm^{-1}), the carbonyl group (1,687.77 cm^{-1}), and the carboxyl group (1,126.47 cm^{-1}). The results of this study's wave absorption of oxalic acid from peanut shell waste have similar characteristics to standard oxalic acid and oxalic acid synthesized from peanut shells [6].

The result of absorption of standard oxalic acid is the hydroxyl group (3,422.06 cm^{-1}). The carbonyl group (1,685.48 cm^{-1}) and the carboxyl group (1,123.33 cm^{-1}). The difference between the absorption results of synthetic oxalic acid and standard oxalic acid occurs because the oxalic acid obtained is not pure (there are still impurities in the oxalic acid crystals). Figure 2 shows the results of the FTIR analysis.

Table 3. Product Characteristics

Raw Materials of Oxalic Acid	Absorption Result			Melting point (^{o}C)
	O-H Group	C=O Group	C-O Group	
Standard [8]	3,422.06	1,685.48	1,123.33	101.5
Peanut shells [6]	3,404.36	1,683.86/1,622.13	1,116.78	102.2
Peanut shells (This research)	3,408.33	1,687.77	1,126.47	102.5

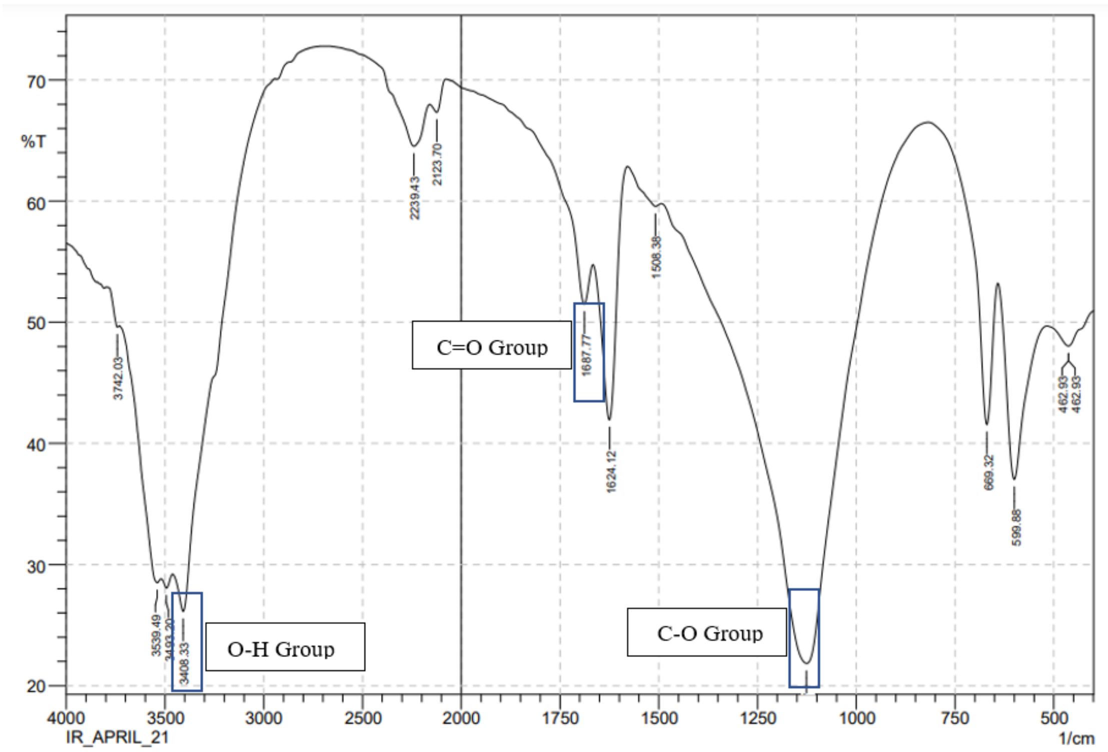

Figure 2 FTIR Analysis of Oxalic Acid Product

Melting point analysis is used to identify a solid (crystal) and to determine its purity. The obtained oxalic acid crystals have a melting point of 102.5ºC. The melting point of oxalic acid made from peanut shells [6] is 102.2ºC, and the melting point of standard oxalic acid is 101.5ºC. According to the analysis, the oxalic acid produced has nearly the same properties as oxalic acid dihydrate ($C_2H_2O_4.2H_2O$). The difference in melting point occurs because the resulting oxalic acid crystals contain impurities.

5. CONCLUSIONS

Based on the research, the following conclusions can be drawn:

1. The NaOH-catalyzed process yields 12.83 percent oxalic acid, which is higher than the $Ca(OH)_2$ yields.
2. The optimum temperature for producing the highest yield of oxalic acid when using the 4N NaOH catalyst is 60ºC, while the optimum temperature for using the 4N $Ca(OH)_2$ catalyst is 90ºC.
3. The melting point of oxalic acid produced by the base smelting of peanut shell waste is 102.5ºC, and its wavelength absorption meets the standard.

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