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Kinetics Study on Hydrothermal Decomposition of Glucose in NaOH Solution with CuO Catalyst

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ABSTRACT. biomass is an abundant resource of renewable energy and can be processed into various chemicals. In its development, hydrothermal decomposition became a method that was considered quite efficient. This study aimed to determine reaction kinetics and product composition of the hydrothermal decomposition process with CuO catalyst. The experiment was conducted by heating glucose in NaOH solution at various temperatures using CuO as the catalyst. The reaction was conducted in an autoclave equipped with a magnetic stirrer. After being heated, the autoclave was cooled to ambient temperature. The treated material is filtered to separate insoluble solid and liquid phases. After being separated, the solid residue was dried in the oven. Filtrate composition was analyzed by GC-MS method and glucose concentration was analyzed by Lane Eynon method. The filtrate was atmospherically distilled before GC-MS analysis to ensure that sample was free of water and glucose residue. According to kinetics calculation, the reaction was 2nd order, activation energy was 28.894 kJ/mol, and pre-exponential factor was 4.17×10^4 min^{-1}. GC-MS analysis showed that there were 20 compounds contained in the product sample with 3 dominant compounds in form of 4,5-Dibromo-hex-2-enoic acid methyl ester, 2-Bromooctadecanal, and 9-Octadecenoic acid, propyl ester.

1. INTRODUCTION

Biomass is considered as one of the most abundant renewable energy resources. In 2019, it is estimated that Indonesia has a biomass potential of 22 million tons [1]. Biomass also has the potential to play a significant role in a more sustainable energy system that will take place in the future. Biomass can also be converted into a variety of chemical compounds [2]. In recent years, there have been many studies conducted into creating conversion technologies and increasing the value of biomass [3].

The methods in biomass conversion are divided into biochemical, biotechnical, and thermochemical methods, such as direct combustion, pyrolysis, gasification, liquefaction, etc [4]. Hydrothermal reactions have proven to be one of the most efficient ways to convert biomass into valuable materials for a variety of purposes [5]. The thermochemical conversion of carbon resources into their derivatives at high temperatures and pressures is known as hydrothermal liquefaction [6].

The hydrothermal process is the process of degradation of macromolecular compounds using water at subcritical conditions. The hydrothermal process is typically carried out at temperatures ranging from 250oC to 500oC and pressures ranging from 5 to 35 MPa. This hydrothermal procedure can be done with or without the use of a catalyst [7]. It was also mentioned that the presence of water in the hydrothermal process can aid the hydrolysis process, allowing the biomass to be converted into biofuel, char, and gas [8].

To improve the efficiency of biomass hydrothermal decomposition processes, several model studies on monosaccharide and disaccharide conversion were recently reported. The use of Lewis-acid catalysts for the hydrothermal process shows promising results [9]. Where the use of sodium and calcium hydroxide for hydrothermal processing of glucose or biomass with lactic acid yields of 20-27% was also reported, with a reaction time of 60 seconds at a temperature of 300oC [10]. Lactic acid molecules were also detected in the hydrothermal process under temperature settings of 340oC, according to another study that used glucose in the form of monosaccharides [11].

Metal catalysts have also been reported to produce satisfactory results. Utilizing the same procedure as the prior studies using Zn or Ni as a catalyst, a yield of 42% was reported [12]. Similar results were recently reported when calcium hydroxide was used for a longer reaction time [13]. In the hydrothermal conversion of glycerol to lactic acid, Cu nanoparticles showed remarkable catalytic activity [14]. The use of a CuO catalyst, on the other hand, can greatly enhance the amount of lactic and acetic acid produced. Due to this, this study focuses on investigating the hydrothermal decomposition process of glucose using NaOH solvents and CuO as catalysts.

2. METHODOLOGY

The experiment was carried out by following the scheme as shown in Figure 1. In general, the research approach was separated into three parts. The steps of research are hydrothermal decomposition process, reaction rate analysis, and product characterization.

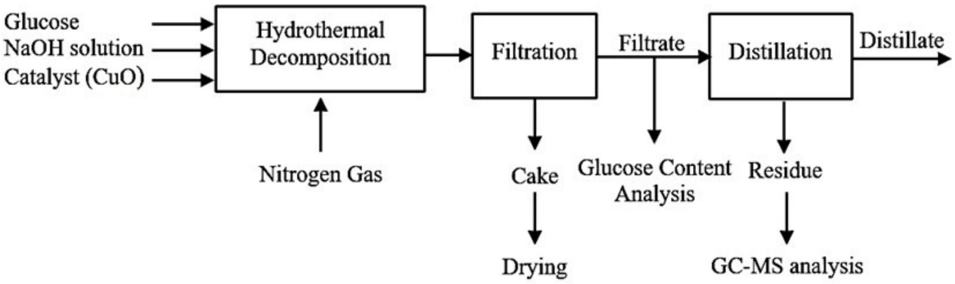
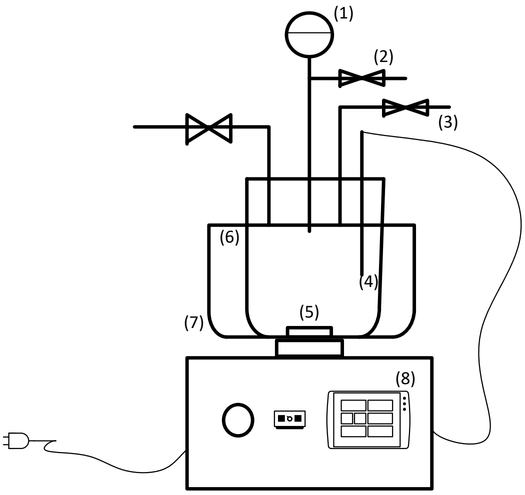


Figure 1. Experimental process flow diagram

2.1 Hydrothermal Decomposition Process

The experiment was carried out with the use of an autoclave with a 150 mL capacity equipped with a magnetic stirrer and a tube furnace. A 150 mL autoclave was filled with 10 grams of glucose and 80 mL of NaOH solution. In the autoclave, nitrogen gas was injected for 5 minutes to remove the presence of oxygen before the autoclave was closed and the magnetic stirrer was turned on. After that, the autoclave is heated in a tube furnace until it reaches the desired temperature, hence the reaction process is non-isothermal. The desired temperature variations were 33, 50, 110, 210, 260, 280, and 288ºC and the desired heating rate was 0.5-1°C/min. The purpose of varying the reaction temperature in this way is to discover the most optimal and efficient hydrothermal conditions. The reactor pressure was not determined in this study because it would follow the temperature. The autoclave is removed from the heater as soon as the heating temperature is reached and cooled to ambient temperature. The set of equipment was shown in Figure 2.



1. Manometer
2. Safety valve
3. Relief valve
4. Thermocouple
5. Magnetic stirrer
6. Autoclave
7. Heater
8. Temperature and stirrer speed controller

Figure 2. The set equipment for the hydrothermal decomposition

2.2 Reaction Rate Analysis

To separate the insoluble solids from the liquid phase, the treated material was removed from the autoclave and filtered using filter paper. After being separated from the liquid phase, the solid residue is dried in an oven at a temperature of 105°C for 24 hours. The Lane Eynon method was used to determine the residual glucose level in the filtrate. The titration process is carried out with 5 mL of sample diluted in 500 mL of distilled water as a blank solution. After heating 5 mL of Fehling A and Fehling B, 2 drops of methyl orange were added. The solution was titrated with the blank solution until it became yellow.

2.3 Product Characterization

The GC-MS test was used to perform a qualitative test to detect the compounds contained in the sample. The GC-MS device used in this test is Shimadzu QP 2010 SE. This device uses FID and MS detectors. Meanwhile, the columns used were Rtx-5MS (5% diphenyl/95% dimethyl polysiloxane) and Carbowax (Polyethylene glycol). The mobile phase used on this device is helium. The filtrate was distilled at atmospheric pressure before GC-MS analysis, leaving only a solid residue. The GC-MS test analyzes samples that have been distilled at 100°C. Distillation aims to remove water and glucose residues in the sample. Water and glucose need to be removed because they can cause damage to the GC-MS test equipment.

3. RESULTS AND DISCUSSION

The hydrothermal decomposition of glucose in NaOH solution using CuO as a catalyst was investigated in this study. The reactor was heated for 395 minutes, reaching a temperature of 288°C with the average value of the heating rate is 0.65°C/min. In this investigation, the temperature rose with time as seen in Figure 3. As the temperature increases, the pressure will also increase as seen in Figure 4. It can be seen that from 0 to 135 minutes the temperature increased significantly. After passing through the heating time of 135 minutes the temperature only slightly increased, as can be seen from the shape of the graph which began to flatten. This indicates that the heating rate has decreased. At the point of 135 minutes and 280°C can be considered as the optimum point of heating rate.

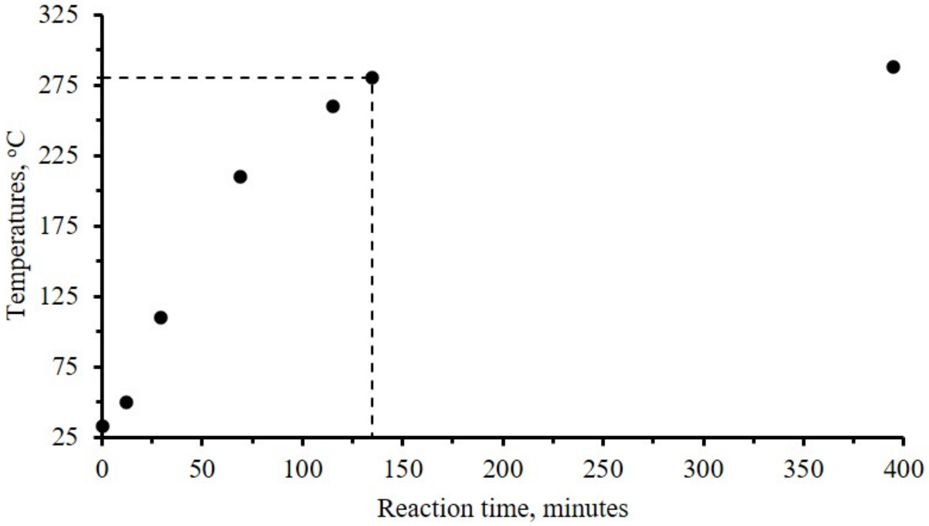


Figure 3. Graph of temperature versus reaction time

The glucose (A) decomposition reaction is assumed as

$$A \rightarrow Products \qquad (1)$$

A had a reaction rate of

$$-\frac{dCa}{dt} = k\,Ca^n \qquad (2)$$

Ca (mol/L) stood for glucose concentration (mol/L), k (min-1) for reaction rate constant, and n for reaction order.

The reaction rate constant k changed with temperature according to Arrhenius law, as shown by the equation.

$$k = A\,exp\left(\frac{-Ea}{RT}\right) \qquad (3)$$

A is the collision/pre-exponential factor (min-1), Ea is the activation energy (kJ/mol), and R is the ideal gas constant. The non-linear regression method was used to calculate parameters A, E, and n. For this investigation, the results are 4.17×104 min-1 for A, 2 for n, and 28.894 kJ/mol for Ea using this approach. Table 1 shows a comparison between the results of the kinetic calculations in this study and various similar studies that have been carried out previously.

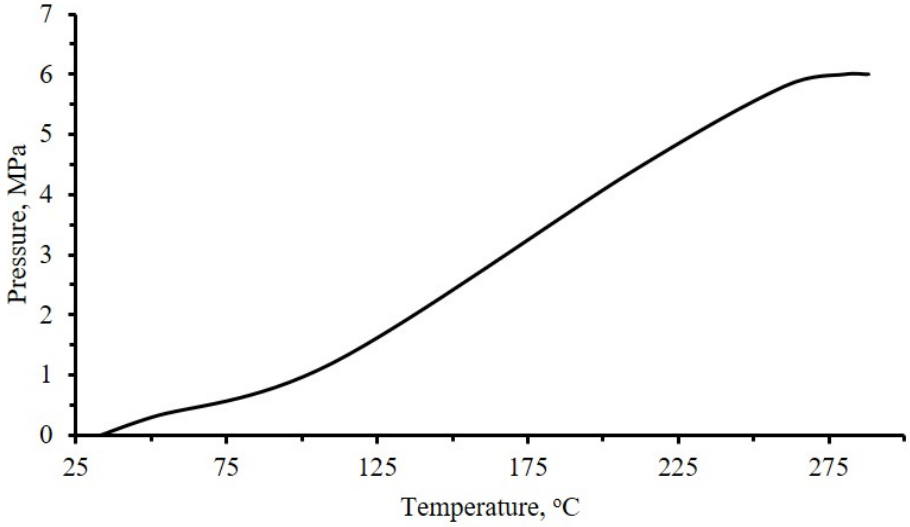


Figure 4. Graph of pressure versus temperature

When comparing the results of this study, references [14] and [15] that employed non-aqueous solvents, it appears that there is a trend for lesser activation energy values and bigger reaction orders when compared to other studies that only use water as a solvent, such as references [16] and [17]. Similar results were also seen with the use of a catalyst which also lowered the activation energy value while increasing the reaction order. This is supported by evidence from reference [17], which while using water as a solvent, has a lower activation energy value due to the employment of a catalyst than reference [16]. It can be concluded that when a non-aqueous solvent and a catalyst were used in the reaction, the activation energy decreased and the reaction order increased.

Table 1. Comparison of the kinetic results of several previous studies

Activation energy, Ea (kJ/mol)	Pre-exponential factor, A (min^{-1})	Reaction order, n	Main reactant	Solvent	Catalyst	Temperature (°C)	References
28.894	4.17×10^4	2	Glucose	NaOH	CuO	288	This study
-	2.46×10^{11}	2	Glycerol	NaOH	Cu/ZrO^2	230	[14]
6.65576	-	1.54	Glucose	Ethanol	-	200	[15]
121	6.9×10^7	1.13	Glucose	Water	-	460	[16]
76.48	2.34×10^7	-	Glucose	Water	$H_2O/LiCl$	140	[17]
1426.68	-	1	Glucose	H_2SO_4	-	180	[18]

By using the Lane Eynon method, the results of the glucose concentration in the sample are obtained. With an R-value of 0.9998 and calculation error of 4%, the calculation findings appear to be very close and have a strong relationship to the experimental data values. Changes in glucose concentration with time are shown in Figure 5. The glucose concentration decreased drastically after 12 minutes from the initial concentration of 0.59 mol/L to 0.12 mol/L. Figure 6 shows that in 12 minutes, the conversion of the reaction that occurred reached 79.96%. After 29 minutes, the remaining glucose concentration was 0.01 mol/L or reached a reaction conversion of 97.73%. Based on this, it can be concluded that the higher the reaction temperature, the lower the glucose concentration and the greater the reaction conversion. The same can be said for the reaction time. The longer the reaction time, the lower the glucose concentration and the greater the reaction conversion. The drastic decrease in glucose concentration and the increase of conversion on this reaction is caused by the help of the catalyst which sped up the reaction, hence within 29 minutes, a high reaction conversion rate has been obtained with the value nearing 100%.

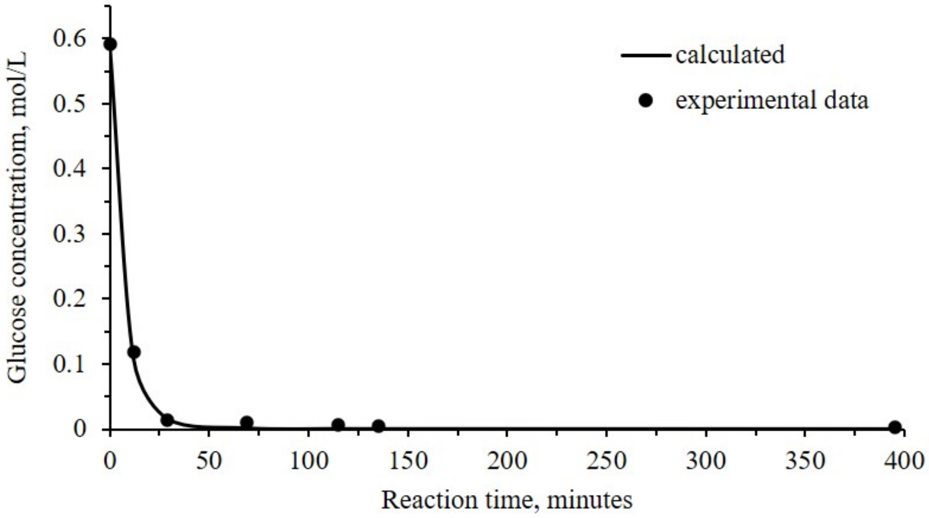


Figure 5. Graph of glucose concentration versus reaction time

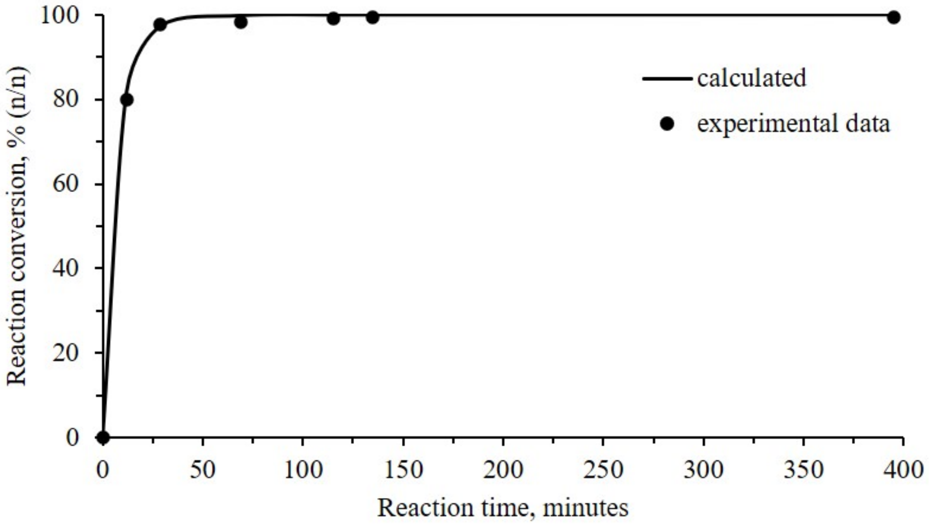


Figure 6. Graph of reaction conversion versus reaction time

The results of the GC-MS analysis showed that there were 20 compounds contained in the sample. Table 2 shows the compounds contained in the product sample of glucose hydrothermal decomposition. Of the 20 compounds contained, 3 compounds were more dominant than other compounds. The first peak has a height of 19548 with an area of 187230 (6.75%) indicating the type of compound 4,5-Dibromo-hex-2-enoic acid methyl ester, the second peak has a height of 35543 with an area of 254834 (9.19%) indicating the type of 2-Bromooctadecanal compound, the third peak has a height of 86454 with an area of 485345 (17.51%) indicating the type of compound is 9-Octadecenoic acid, propyl este. The 3 dominant compounds in the sample are commonly used in the pesticide industry as substances to prevent, destroy or mitigate pests

Table 2. GC-MS analysis result of glucose hydrothermal decomposition samples

No.	**Compound**	**Area (%)**
1.	9-Octadecenoic acid, propyl ester	17.51
2.	2-Bromooctadecanal	9.19
3.	4,5-Dibromo-hex-2-enoic acid methyl ester	6.75
4.	9-Octadecenoic acid (9Z)-, tetradecyl ester	6.67
5.	2-Tridecenal	5.87
6.	9-Octadecenoic acid, butyl ester	5.62
7.	9-Octadecen-1-ol, (Z)-	5.59
8.	Glycerine-1-oleate-3-palmitate	4.97
9.	[1,1'-Bicyclopropyl]-2-octanoic acid, 2'-hexyl-methyl ester	4.49
10.	9-octadecenoic acid	3.86
11.	Eicosanoic acid	3.79
12.	Undecansaure, 11-bromo-, undecyl ester	3.64
13.	D-Fenchyl alcohol	3.32
14.	3-Octadecenoic acid, methyl ester	3.22
15.	1,12-Dibromododecane	2.96
16.	1,2-Dipalmitoylphosphatidylcholine	2.91
17.	(3aS,9aS,9bR)-6,6,9aa- trimethyl-trans- perhydronaphtho[2,1-b]furan	2.76
18.	9-Octadecenoic acid (Z)-, 2-hydroxy-1-(hydroxymethyl) ethyl ester	2.42
19.	1,4-Azaphosphiran, 1-(3-hydroxypropyl)-2,6-dimethyl-4-oxo-4-phenyl-	2.25
20.	18,19-Secoyohimban-19-oic acid, 16,17,20,21-tetradehydro-16-(hydroxymethyl)-, methyl ester, (15.beta.,16E)-	2.22
	Total	100

4. CONCLUSIONS

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

1. According to the kinetics calculations, the reaction was 2nd order, the activation energy was 28.894 kJ/mol, and the pre-exponential factor was 4.17×104 min-1.
2. The GC-MS analysis shows there are 20 compounds contained in the product sample with 3 dominant compounds in the form of 4,5-Dibromo-hex-2-enoic acid methyl ester, 2-Bromooctadecanal, and 9-Octadecenoic acid, propyl ester.

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