Article

Kinetic Study on Hydrothermal Decomposition of Glucose in NaOH Solution with ZnO as Catalyst

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Abstract. Hydrothermal liquifaction is a biomass conversion process, where the structure of the biomass is convert into liquid components under super critical conditions with a high temperature. In this study, glucose is used as biomass. The purpose of this study was to study the reaction kinetics and determine the hydrothermal decomposition of glucose in NaOH solution. This experiment used 10 grams of glucose and dissolve it in 80 mL of NaOH solution then put it in an autoclave. Experiments were carried out by varying the heating temperature carried out in an autoclave with a magnetic stirrer. After heating at various temperatures, the autoclave is immediately cooled down. The processed material is filtered to separate insoluble solids from the liquid phase. The solid residue that has been separated from the liquid phase is then dried in an oven at 105°C for 24 hours. The composition of the filtrate was analyzed using the GC-MS method and the glucose concentration was analyzed using the Lane Eynon method. Prior to GC-MS analysis, the filtrate was distilled at atmospheric pressure until a solid residue remained. The sample analyzed is the result of distillation with a temperature above 100°C to ensure that there is no water and residual glucose in the sample. The results of GC-MS analysis of product samples from the hydrothermal decomposition process had 3 peaks. The first peak shows the compound 1,3 Dipalmitin which has an area of 14.74%, the second peak shows the Olealdehyde compound which has an area of 32.35%, and the third peak shows the 1,2-Epoxyhexadecane compound which has an area of 52.91%. The kinetics results in hydrothermal decomposition of glucose in this experiment obtained a reaction order of 2 with an activation energy (Ea) of 15.91 KJ / mol and a pre-exponential factor of 66.12.

Keywords: Hydrothermal liquifaction, glucose, Zno, NaOH, biomass

1. Introduction

The rapid increase in energy demand and the lack in the supply to cater the needs, enables to find the alternatives to meet the current demands of the society which is of primary concern in terms of socio economics of the globe. The rapid growth rate of urbanization in the past decades, water quality degradation became a public health threat. Eutrophication associated with nutrient content of wastewater and treatment plant effluents have become a serious concern to water environment. Combining these two critical environmental and social causes an alternate source for the conventional fossil fuels which has to be sustainable, energy secured, and reduce global warming is highly desirable. This lead several researchers to focus in search of alternate source for commercialization from several decades and came up with one source which is nothing other than the biomass. As of 2010, world biofuel production has been largely focused on first generation bio fuels producing ethanol and biodiesel from starch, sugars, and vegetable oils[4].

The use of non-renewable energy such as fossil fuels in the world has always increased every year. In accordance with data from the Indonesian Downstream Oil and Gas Regulatory Agency, the use of BBM in Indonesia reached 55 million liters in 2017. This figure continues to increase compared to previous years. This means that several threats based on the continuous use of fossil fuels which would pose a serious threat [1].Environmental issues of sustainability, declining fossil fuels, and concerns about energy have made the world look for alternatives in the form of clean, cheap and renewable energy. In this case, biomass is a very appropriate material. Choosing an efficient and appropriate methodology for processing biomass has been a challenge in recent decades. Each technology has its own advantages and disadvantages. In this case the hydrothermal liquefaction process was found to be the right process to convert biomass into renewable energy [4].

Several researchers have conducted experiments related to the manufacture of lactic and acetic acids from carbohydrates under hydrothermal conditions. A two-step hydrothermal process to increase acetic acid production from carbohydrates is proposed. The first step is to accelerate the formation of 5-hydroxymethyl-2-furaldehyde (HMF), 2-furaldehyde (2-FA), and lactic acid the next step is to convert furan (HMF, 2-FA) and lactic acid produced in the first step into acid. acetate by oxidation with oxygen supply. The use of oxygen has its drawbacks due to the hydrothermal oxidation of carbohydrates to acetic acid at a high cost to compress air or oxygen into the reactor. The use of new solids of oxidants to replace air or oxygen is desirable [2]. Therefore, we investigated the possible reduction of ZnO to Zn in the presence of glucose or cellulose under hydrothermal conditions. Jin also performed modeling of the hydrothermal reaction of glucose to lactic acid [10].

In hydrothermal process, water is in two conditions, where the proscess at supercritical point condition and the sub-critical point condition. Water in super critical conditions acts as a reactant, used for dissolving cellulose in the biomass. While water is at a sub-critical point around 150°C-230°C acting as an acid or base catalyst from H+ and OH- ions produced by water in a hydrothermal reaction [16]. In order to direct the hydrothermal liquefaction of cellulosic starting materials to certain (main) products e.g. sugars (glucose, fructose), sugar alcohols, 5-HMF or levulinic acid, and to enhance the conversion rate, different types of catalysts have been suggested. These catalysts range from catalysts dissolved in the aqueous phase, as mineral acids or metal salts (AlCl3) to heterogeneous catalysts. It is commonly acknowledged that acidic catalysts are required for the cellulose hydrolytic cleavage. In principle also alkaline catalysis is possible and used for the pre-treatment of lignin/ cellulose mixtures, yet here the glucose monomers are instantaneously degraded. Subcritical water, which supplies an enhanced proton activity due to the increased ionic product of water, provides conditions fostering ionic reaction pathways such as the hydrolytic depolymerisation [10].

However, the use of oxygen has lack due to hydrothermal oxidation of carbohydrates to acetic acid at a high cost for compressing air or oxygen into the reactor. The use of solid oxidants to replace air or oxygen is highly desirable [2]. Alkali as a catalyst for HTL, has been shown to improve the biomass conversion primarily by improved depolymerization . Through the process of deoxygenation, desulfurization, and denitrogenation alkali can reduce the heteroatom content of bio-oil . Besides, the carbon and H_2 content of the bio-oil can

increase due to the application of alkali catalysts . Particularly, it can be seen that alkali is efficient towards the conversion of carbohydrate-rich biomass. The use of alkali as catalysts can decrease the formation of solid residues. Usually, a high amount of solid residues are generated from lignin-rich biomass such as wood during non-catalytic HTL, which is not desirable .However, the use of alkali catalyst could successfully liquefies lignin in woody biomass, and thus reduce solid formation . Apart from that, Alkali is also known to promote the hydrolytic depolymerization of other lignocellulosic polymers, including hemicelluloses and cellulose [11]. Therefore, this study was intended to investigate the possibility of reducing ZnO to Zn in the presence of glucose or cellulose under hydrothermal conditions.

2. Methods

The experiment was carried out following the process shown in the figure above, using a magnetic stirred autoclave with a capacity of 150 mL equipped with a tube furnace. As much as 10 grams of glucose ,3,5 grams of ZnO, and 80 mL of NaOH solution were added to a 150 mL autoclave. Nitrogen gas is exhaled in the autoclave for 5 minutes, then the autoclave is closed and the magnetic stirrer is turned on. After that, the autoclave is heated in a tube furnace until it reaches the desired temperature. The desired temperature variations are 110°C, 210°C, 220°C, 240°C, 260°C, 280°C, and 300°C. When the heating temperature has been reached, the autoclave is immediately removed from the heater and then cooled to ambient temperature. Then the sample is tested for the remaining glucose levels using the Lane-Eynon method, this method is done by making a standard solution of glucose. Then the sample is checked for glucose levels with methyl orange to find out the remaining glucose that is still in the sample.The qualitative test to determine the compounds contained in the sample was carried out by the GC-MS test after the glucose content being removed from the samples.
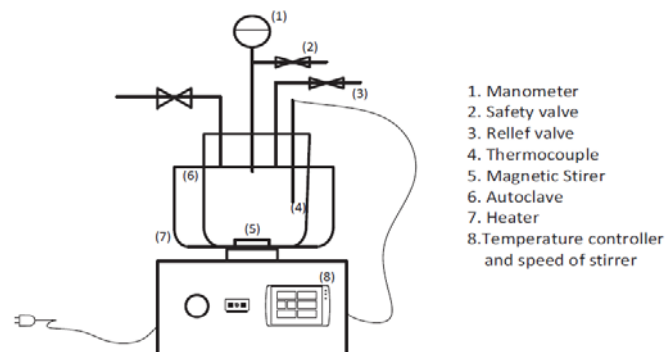

1. Manometer
2. Safety valve
3. Relief valve
4. Thermocouple
5. Magnetic Stirer
6. Autoclave
7. Heater
8. Temperature controller and speed of stirrer

Fig. 1.   Schematic diagram of autoclave of 150 mL

3. Results and Discussion

The experiment of glucose hydrothermal process in NaOH solution with ZnO as catalyst. The reactor heating caused the reaction temperature to change from ambient temperature to 300°C, then the reaction temperature was maintained for an hour with heating control at the reactor. It took 333 minutes to reach a temperature of 300°C. Temperature increase tends to be slow when the temperature is above 250°C. this happens because the performance of the reactor to increase the pressure tends to be slow.Thus, this process initially took place non-isothermal up to a temperature of 300°C, and then maintained isothermal at a temperature of 300°C. The temperature raised versus time in this study showed in the figure 2 below
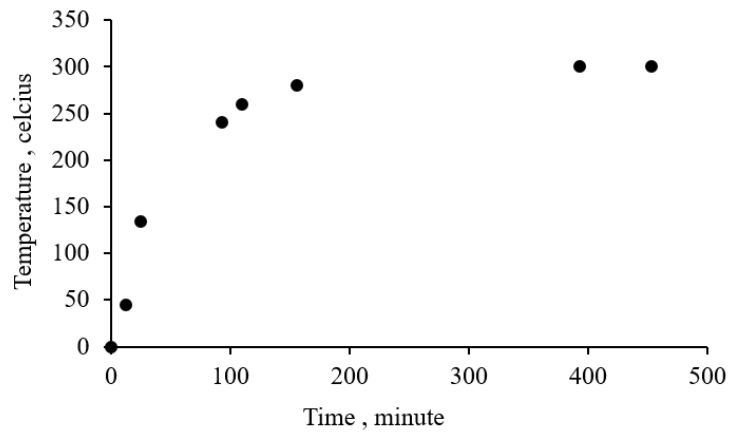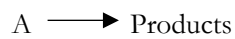
Fig. 2.   Temperature versus time of reaction

The glucose (A) decomposition reaction was assumed as

$$A \longrightarrow Products$$

The reaction rate of A was

$$-\frac{dCa}{dt} = k\ Ca^n \tag{1}$$

where CA was glucose concentration (mol/L), k was the reaction rate constant and n was reaction orde.

According to Arrhenius law, k changed with temperature following the equation

$$k = A\exp\left(\frac{-Ea}{RT}\right) \tag{2}$$

A is the collision factor (min-1), Ea is the activation energy (joule/mole) and R is the ideal gas constant. Parameter A, E and n were calculated by non-linier regresion method. With this method, for this study the result is 66,12 min-1 for A, and 15,91 kJ/mol for Ea.
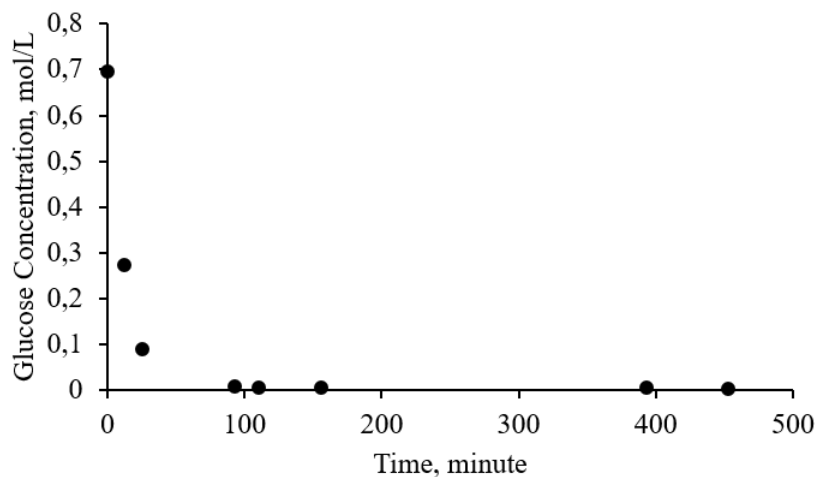

Fig. 3.   Glucose concentration versus time of reaction

As shown in figure 3, changes in glucose concentration versus reaction time in the hydrothermal reaction process shown in Figure 1. The glucose concentration dropped drastically at 110°C reaching 86.93% conversion. After a temperature of 110°C the glucose concentration decreased slowly. This can also be caused by a slowly temperature rise, otherwise that will not happen. But this can also happen because there is no glucose left to react at the reactor.
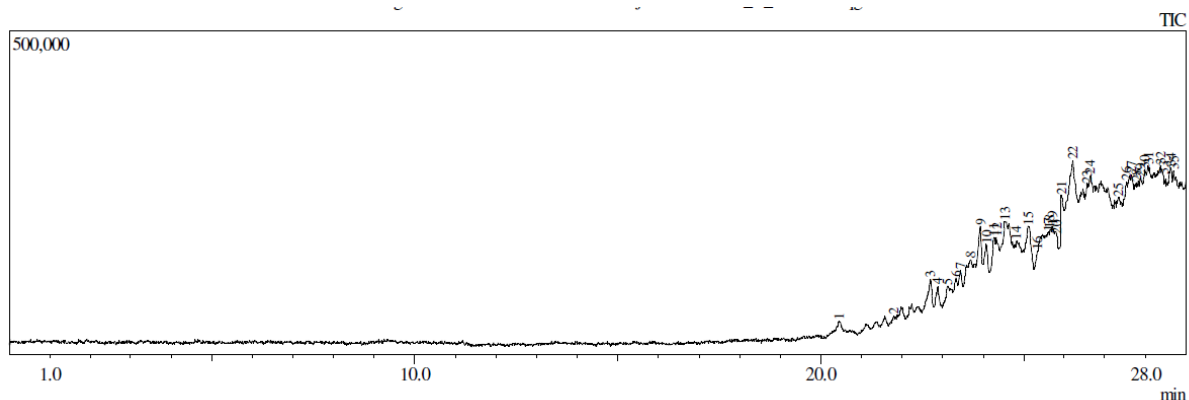

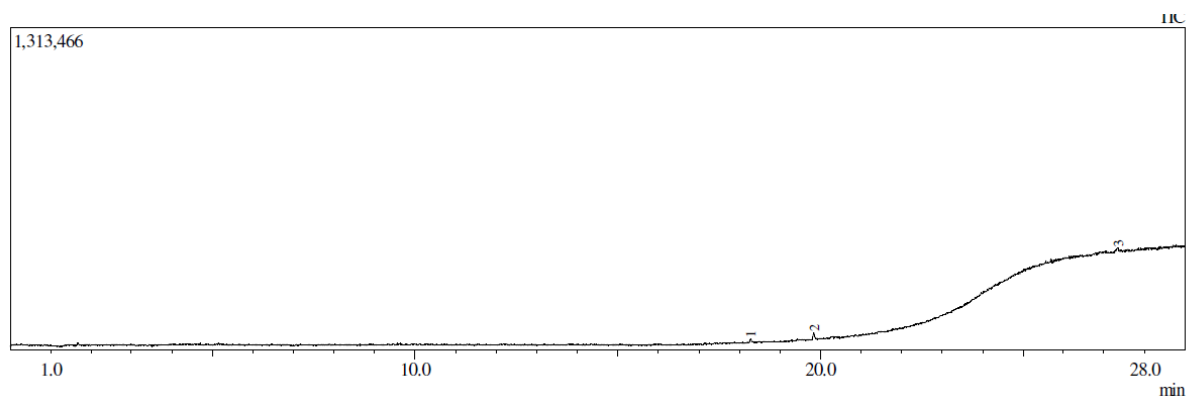Fig. 4. GC-MS analysis for 210°C temperature sample

Fig. 5. GC-MS analysis for 300°C temperature sample

After the experiment, the samples were then analyzed using GCMS. In this study two samples were analyzed. For temperature of 300 °C and 210 °C. As shown in figure 1, for 210°C some components have not been formed completely. For example, 1,2 epoxyhexadecane at a temperature of 210°C, the content in the sample is still 1.2%, while for a temperature of 300°C the content increase to 52.91%. It also applies to other content such as 1,3 dipalmitin the temperature of 210°C the content in the sample is 2.38% while for the temperature of 300°C it is increasing to 14.74% and for oleadehyde at a temperature of 210°C the content in the sample is 3.87% while for a temperature of 300°C it is also increasing to 32.35% . This indicates that the components are formed optimally at a temperature of 300°C.

The results of the GC-MS analysis of the product from the hydrothermal decomposition at 300 °C process shown in Table 1 that had 3 peaks. The first peak has a height of 11.239 and an area of 25.070 (14.74%) which indicates a compound of 1,3 Dipalmitin, the second peak has a height of 25.799 and an area of 55.009 (32.35%) which indicates Olealdehyde compound, and the third peak has a height of 20.550 and area amounted to 89.964 (52.91%) which indicates a 1,2-Epoxyhexadecane compound, this compound is the most dominant compound in the product sample.

1,2-Epoxyhexadecane is a chemical that can be used for lubricant industry (lubricants for engine, brake fluids, oils, etc.) from other sources it can be used for cosmetic industry as well. For Olealdehyde can be used for the food industry as an additive for flavoring agent. Then for 1,3 Dipalmitin this substance functions as an emulsifier and surfactant that can improve product quality.

Table 1. The results of GC-MS analysis of hydrothermal decomposition of glucose with ZnO

No.	Compound	Area % (210°C)	Area % (300°C)
1.	1,3 Dipalmitin	3,87	14,74
2.	Olealdehyde	2,38	32,35
3.	1,2-Epoxyhexadecane	1,2	52,91
4.	Other Component	92,55	0
	Total	100	100

4. Conclusion

The study of hydrothermal decomposition of glucose with ZnO as catalyst has been performed. The glucose decomposition reaction order in this study was 2 and the activation energy was 15,91 kJ/mol . The results of the GS-MS analysis showed that the reaction products of the glucose decomposition contained three compounds, i.e. 1,3 Dipalmitin, Olealdehyde, and 1,2-Epoxyhexadecane.

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