Production Of 5-Hydroxylimethylfurfural From Starch of Durian Seed (*Durio zibethinus*) Through Dehydration Reaction Using Solvent-Based Choline Chloride: Glycerol

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Abstract. The energy demand is increasing and the production of fossil fuel is decreasing, which is a challenge for humans to produce eco-friendly renewable energy resources. Biomass is the raw materials of renewable energy. One of the plentiful biomass in Indonesia is durian seed (*Durio zibethinus*). Durian production in Indonesia in 2014 reached 859,12 tons, where the weight of durian seeds 20-25% of total fruit weight. Durian seeds have a high content of starch which is 50.40%. 5-HMF (Hydroxymethylfurfural) is one of the most representative monomers of material based on biomass. 5-HMF can be synthesized from carbohydrates, in this case, durian seed is going through two stages of chemical reactions, those are hydrolysis and dehydration reaction. DES (Deep Eutectic Solvents) is a sub-class of IL (Ionic Liquids) that can be used as co-solvents in 5-HMF synthetic from durian seeds. This study applies DES-based Choline Chloride: Glycerol. The variables in this study are sulfuric acid concentration used in hydrolysis reactions and glucose mass ratio: DES, reaction time, glucose concentration in dehydration reactions. The reaction conditions with the highest yield were 61.93% with a glucose mass ratio: DES of 1: 5 and a reaction temperature of 80°C.

1. Introduction
Cellulose Increasing energy needs and the decreasing production of fossil fuel resources is a challenge for humanity to produce environmentally friendly renewable energy sources [1]. Biomass is one of the renewable raw materials on this earth [2]. Conversion of biomass waste into fuel, chemicals and commodity materials has the potential to reduce national dependence on non-renewable raw materials. Utilization of biomass is one of the efforts that have been carried out since a long time ago. One product that can be produced is 5-Hydroxymethylfurfural (5-HMF). 5-HMF is one of the most representative monomers of biomass-based materials. 5-HMF contains the active-aldehyde and hydroxymethyl groups, 5-HMF can be used as an intermediate for many reactions, materials for the synthesis of macrocyclic compounds, polymer synthesis monomers. At present, 5-HMF is produced by dehydration of carbohydrates [3].

Durian (*Durio zibethinus*) is the most popular seasonal fruit in Southeast Asia, especially Malaysia, Indonesia, Thailand, and the Philippines. Durian seeds have a starch content that is high enough so that it has the potential as an alternative substitute for ingredients that require starch properties. In one study, HMF production was studied using ionic liquid / Ionic Liquids (IL) [4]. DES (Deep Eutectic Solvents)

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is a subclass of IL (Ionic Liquids), showing characteristics that are comparable, cheaper and easier to produce because the cost of raw materials is lower, less toxic and often bioavailable, making it a valuable alternative solvent for green analytical chemistry.

Assanosí, et al., 2015 reported the use of DES as a catalyst and solvent consisting of a mixture of N, N-diethylethanolammonium chloride as organic salts and p-Toluenesulfonic Acid Monohydrate (p-TSA) as HBD in fructose dehydration reactions. So that the yield of 5-HMF was 84.8% at 80 °C with a 1 hour reaction time using a molar mixing ratio of DES 1: 0.5, salt: p-TSA and a feed ratio of 5% [1]. Zhang, et al., 2016 reported that DES containing [Emim] Cl and isopropanol was the best in converting fructose to HMF catalyzed by [HNMP] Cl with yields of more than 89% after 3 hours of reaction time at 25°C [5].

Zuo, et al., 2017 reported that DES consisting of MeCN and Choline Chloride with a small concentration of HCl as catalyst produced yield of 90.3% at 100°C operating conditions and a reaction time of 4 hours [6]. In this study, researchers are interested in knowing the effect of DES usage, DES number, and reaction temperature on the 5-HMF yield on processing durian seed waste and are expected to help increase the utilization of durian seed waste in Indonesia.

2. Experimental

2.1 Materials
The materials used in this study are Durian seeds, Choline chloride (ChCl), Glycerol (C₃H₈O₃), Hydrochloric Acid (HCl), Aquadest (H₂O), Sulfuric Acid (H₂SO₄).

2.2 Typical process for the conversion of glucose into 5-HMF
In a typical run, the conversion of glucose into 5-HMF was conducted in a glass flask (100 ml) with a condenser in a hot plate. The DES system was formed with ChCl: glycerol (1:2). 1.2 mol% HCl was added as the catalyst. The flask was then placed in hot plate and heated with vigorous stirring. After the reaction, 5-HMF has analyzed UV-vis spectrophotometer.

2.3 Product analysis
In this study, the 5-HMF product was degrading due to UV-vis spectrophotometer, at a wavelength of 284 nm and 336 nm. 5-HMF concentrations are calculated as the following:

\[
5\text{-HMF (mg/100mg)} = \frac{(A_{284} - A_{336}) \times 14.97 \times 5}{\text{sample weight (g)}}
\]  

2.4 Synthesis and characterization of DES
DES used in this research was made from a mixture of choline chloride as salt and glycerol as HBD with a molar ratio of 1:2 for 60 minutes at 80°C with a stirring speed of 300 rpm [8]. Density, viscosity, and pH are important characteristics of DES physical properties [9]

2.5 Characterization of product
The FTIR spectra of 5-HMF analysis of compounds before and after dehydration was carried out to identify differences in groups in the compound. recorded on Fourier Transform Infrared Spectrometer Shimadzu IR-21. It was measured in the wavelength range from 4000 cm⁻¹ to 500 cm⁻¹.

3. Results and Discussion
3.1 Characterization of Deep Eutectic Solvent (Des) Based on Chcl: Glycerol
The Characteristic test of ChCl-based DES: glycerol which is carried out is pH test, density, and viscosity. The density value of DES at 30°C was obtained at 1.1892 g / ml, the viscosity was 246.919 mPa.s and the pH was 7.2. This is consistent with the study of Yadav, et al., In 2014 who reported that DES-based ChCl: glycerol with a ratio of 1: 2 at a temperature of 30 °C has a density value of 1.1885 g / ml and viscosity 246.7928 mPa.s [10]
3.2 Effect of Acid Concentration (%) on Glucose Yield (%)
Hydrolysis Process of Durian Seed Starch was carried out using sulfuric acid (H₂SO₄) as a catalyst with various concentrations, namely 1.5%; 3%; 5% and 10% with the ratio of starch of durian seeds: acid (1:10 b/v), temperature of 100°C, time of 90 minutes and stirring speed of 300 rpm.

![Figure 1. Effect of Sulfuric Acid Concentration (%) on Glucose Yield (%)](image)

In the process of hydrolysis of durian seed starch using sulfuric acid, the catalyst is expected to produce high glucose yield to be used as a reactant in the dehydration process to produce 5-HMF. Figure 1 shows that the yield of glucose increases with increasing concentrations of sulfuric acid used. The highest glucose yield was produced at 10% acid concentration, which was 61.98% and the lowest glucose yield was produced at 1.5% sulfuric acid concentration, which was 19.94%. Addition of sulfuric acid as a catalyst in the hydrolysis reaction of starch in durian seeds is directly proportional to the yield of glucose at the same reaction time because H⁺ ions in strong acids can help break the glycoside bonds found in starch to form a glucose chain[11]. The role of H⁺ ions is the main factor causing the increase in glucose.

3.3 FTIR (Fourier Transform Infra-Red) Analysis Results on Compounds and After Dehydration
FT-IR analysis of compounds before and after dehydration was carried out to identify differences in groups in the compound. From the functional group analysis using FT-IR obtained the results of the spectrum in the form of graphs which can be seen in Figure 2.

From Figure 2 it can be seen the difference of the groups in the compound before and after the dehydration reaction, where after the dehydration reaction there is the addition of C = C (Aromatic) and C-H (Aldehyde) groups. According to Pavia, et al., 2001, the presence of C = O groups and weak absorption of C-H showed aldehyde groups. If there is a weak absorption area of the C = C group near 1650 cm⁻¹ which is accompanied by the absorption area of the C-H group at an area of 3000 cm⁻¹, then it shows that there is an aromatic ring group in it. The OH group with H bound followed by the appearance of the C-O absorption area shows an alcohol group [12]. 5-Hydroxymethylfurfural consists of a furan ring, aldehyde group and alcohol [13]. Furan is a class of organic compounds with an aromatic heterocyclic ring consisting of 1 oxygen atom and 4 carbon atoms [14]. Based on this theory, the results of FTIR showed that the samples of the process after dehydration contained aldehyde, alcohol, and furan (aromatic) rings, so that it could be concluded that the dehydration results contained 5-HMF.
3.4 Comparison of Dehydration Reactions without DES and with DES against 5-HMF Yields

Figure 3 shows the comparison of dehydration reactions without DES and with DES-based ChCl: glycerol against 5-HMF yield. Figure 3 shows that the highest 5-HMF yield is obtained when adding DES in the reaction. The research conducted provides data that can show that overall the glucose dehydration reaction with the use of DES obtained a higher 5-HMF yield than glucose dehydration reaction without using DES. In this study, the highest 5-HMF yield was obtained when the dehydration reaction using DES with a temperature of 80°C was equal to 22.08%. Meanwhile, the lowest 5-HMF yield was obtained when the dehydration reaction did not use DES with a temperature of 90°C which was 11.65%. According to the previous description, the addition of DES-based ChCl: glycerol into the system can reduce the viscosity of the system so that it can facilitate the transfer of mass and heat in it. Clotting which is contained in DES is also able to interfere with the hydroxyl bond in glucose so that 3 water molecules are released during the dehydration reaction. This result can be attributed to the reaction with the addition of DES.
3.5 Effect of DES Number and Reaction Temperature on 5-HMF Yield

The process of glucose dehydration was carried out using 1.2 mol HCl of glucose as a catalyst and using ChCl-based DES: Glycerol. The effect of glucose mole ratio and reaction temperature on 5-HMF yield was observed in a temperature range of 70°C, 80°C and 90°C and glucose mass ratio versus DES of 1:1, 1:3 and 1:5 with a reaction time of 60 minutes, and stirring 300 rpm. The following is a graph that shows the effect of mass ratio and reaction temperature on the 5-HMF yield.

Figure 4. Effect of DES Number and Reaction Temperature on 5-HMF Yield

Figure 4 shows that the 5-HMF yield increases as the number of DES used increases and the 5-HMF yield increases at a temperature increase of 70-80°C, but the 5-HMF yield decreases at a temperature drop of 80-90°C. The highest 5-HMF yield was obtained at the glucose mole ratio versus DES 1:5 and at 80°C, which was 61.93%. The decrease in 5-HMF yield is caused because the 5-HMF formed undergoes a polymerization reaction and forms humin. This is based on the color of the polymer and humin is dark brown and the color of the sample is getting brown as the reaction temperature increases [15]. The 5-HMF yield increase increases as the reaction temperature increases and then decreases when the reaction time is extended. This is due to a dehydration reaction because the water produced from the dehydration reaction is a by-product [16]. By the previous description that the reaction temperature is very dependent on the activation energy that the reaction has. This can indicate the cause of the high yield of 5-HMF obtained at a reaction temperature of 80°C. While at a temperature of 70, 80 and 90°C it is suspected that an unwanted reaction has occurred to form humin or levulinate acid and formic acid.

3.6 Effect of Initial Glucose Concentration on 5-HMF Yield

The process of glucose dehydration was carried out using 1.2 mol HCl of glucose as a catalyst, glucose mass ratio versus DES of 1:5 with a reaction time of 60 minutes, and stirring 300 rpm. The effect of glucose concentration on 5-HMF yield was observed in variations in glucose concentration of 10.05%; 14.90%; 20.74% and 31.24%. The following is a graph showing the glucose concentration of the 5-HMF yield.

From Figure 5 it can be seen that the 5-HMF yield decreases as the initial glucose concentration increases. The highest 5-HMF yield was 70.75% when the glucose concentration was 10.05% and the lowest 5-HMF yield was 61.93% when glucose concentration was 31.24%. The high initial glucose concentration results in side reactions and produces unwanted products. Research conducted by McKibbins, et al. (1962) stated that the yield of 5-HMF will increase when the initial concentration of glucose is reduced. The reaction mechanism can be seen as shown Figure 6.
Figure 5. Effect of Glucose Concentration on 5-HMF Yield

Through Figure 6 it can be seen that there is I in the reaction, where I am an intermediate; $k_1$, $k_2$, and $k_3$ are reaction speed constants which have first order; and $k_4$ is the reaction speed constant which has an order higher than $k_1$, $k_2$, and $k_3$. [17] For parallel reactions, the concentration of reactants is the key to controlling the product produced in the reaction. A high reaction order requires a high concentration of reactants to increase the reaction product and a low reaction order requires a low concentration of reactants to form the product in the reaction, where the concentration level does not affect the product for reactions with the same order [18]. By this description, it can be indicated that the decrease in 5-HMF yield at high initial glucose concentration is caused by the occurrence of side reactions that form humin and is marked by changes in the color of the sample to dark.

4. Conclusion
In summary, we have shown that 5-HMF can be synthesized from glucose resulting from hydrolysis of durian seed starch. Use of ChCl-based DES: glycerol can increase the 5-HMF yield and reduce side reactions and further reactions in the dehydration process. The maximum yield was obtained in reaction conditions with a glucose mass ratio of DES of 1: 5 and a reaction temperature of 80 °C with a 5-HMF yield of 61.93%. This study provides a promising alternative to the production of 5-HMF from biomass.

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