Usage of eutectic solvents throughout the dehydration reaction of durian seeds (*Durio zibethinus*) in producing 5-hydroxymethylfurfural

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Abstract. 5-hydroxymethylfurfural (5-HMF) is an essential compound capable of being synthesized from sustainable biomass. The aim of this study was to characterize DES, and obtain data on the relationship between glucose concentration, the amount of DES, reaction temperature, and yield of 5-HMF. The 5-hydroxymethylfurfural (5-HMF) hexose synthesis has been widely studied in published research. The chemical composition of durian seeds (*Durio zibethinus*) is the water content 10.71%, a fat content 0.38%, protein content 4.76%, and carbohydrate content 83.92%. In recent years, the conversion of carbohydrates has been carried out that is converting biomass to 5-hydroxymethylfurfural. Synthesis of 5-hydroxymethylfurfural from starch by hydrolyzed the starch into glucose under acidic conditions, then it can be used for Dehydration to become 5-hydroxymethylfurfural. This study explores the use of DES-based on Choline Chloride / Ethylene Glycol as a co-solvent in the production of 5-hydroxymethylfurfural. The characteristics of DES-based on Choline Chloride / Ethylene Glycol obtained were viscosity 238.09 mPa.s, the density 1.115 g/cm³, and pH of 6.3. The best condition for dehydration reaction is the mass ratio of glucose: DES of 1: 5, the temperature of reaction was 90°C with the highest yield 70.34%, and at the initial glucose concentration of 10.05%.

1. Introduction

Starch, triglycerides, and lignocellulose are some of the raw materials for making biofuels derived from biomass [1, 2]. Starch is a polymer stored in granules and serves as a food reserve for some plants [3]. 5-hydroxymethylfurfural (HMF) has been described as a potential chemical framework derived from biomass. One investigation researched the synthesis of HMF using ionic liquids (IL)[4]. They still have a significantly lower freezing point than the two other elements [5].

Zhou [6] reported the synthesis of 5-hydroxymethylfurfural (HMF) from glucose was carried out by dehydration method using dimethyl sulfoxide (DMSO) and 1-butyl-3-methylimidazolium chloride ([Bmim] Cl), which was catalyzed by metal (III) chloride (FeCl₃), -6H₂O, CrCl₃-6H₂O, and AlCl₃). The optimum temperature was 393 K or 403 K, and the optimum time was between 30 and 480 minutes. Under optimum reaction conditions, yields of HMF were obtained at 54.43 percent and 52.86 percent respectively.

Based on the result of the above study, it can be seen that the use of DES in the manufacture of 5-HMF by dehydration method can increase of higher yields obtained, but the research of Usage of Eutectic Solvents in the dehydration reaction of durian seeds (*Durio zibethinus*) in producing 5-hydroxymethylfurfural has never been done. The goal of further research on the effect of reaction time and the mass ratio of hydrolysis to DES based on optimum Choline Chloride/Ethylene Glycol is therefore to achieve a maximum yield of 5-HMF in processing and to greatly boost the utilization of durian seed in Indonesia.
2. Materials and Methods

2.1. Materials

The materials needed in this study are Durian Seeds from Ucok Durian Store Medan, Sulfuric Acid, Choline Chloride, and Ethylene Glycol, which each purchased from CV Rudang Jaya, Medan.

2.2. Pretreatment of Durian Seeds

The durian seeds were washed with clean water until the remaining dirt of the durian flesh is no longer stuck to the durian seeds. The durian seeds were peeled with a knife and then cut into small pieces with a knife. Durian seed starch flour was ready to be used as a raw material in the hydrolysis process [7]. The water content of durian seed starch was measured.

2.3. Synthesis of Deep Eutectics Solvent (DES)

The material for HBD is in ethylene glycol and HBA in the form of choline chloride and prepared with a molar ratio of 2:1. Ten grams of Ethylene Glycol and 7.8125 grams of Choline Chloride, which had been prepared was put into 250 ml Erlenmeyer and covered with a cork. The mixture was preheated until the temperature range reached 80℃ and homogenized at a stirring speed of 400 rpm for 2 hours, then DES was cooled to room temperature.

2.4. Hydrolysis of Durian Seed Starch

Durian seed flour weighed at 15 grams. Put durian seed flour into a three-neck flask and stirred using a magnetic stirrer for 90 minutes at 100℃. Then the sample was added with a solution of sulfuric acid with the specified concentration volume of 150 ml into a three-neck flask and heated to a boil. After that, the hydrolyzed samples were cooled to room temperature. The hydrolyzed sample was filtered with filter paper, and then the hydrolyzed samples were analyzed using the DNS method using a UV-Vis Spectrophotometer.

2.5. Dehydration from the hydrolysis process

The hydrolyzed sample was put into a three-neck flask. The sample was added with hydrochloric acid (HCl) 1.2 mol% from the hydrolysis. The sample was added with DES with the mass ratio of the sample resulting from hydrolysis of the waste starch from durian seeds to DES = 1: 0, 1: 1, 1: 3, and 1: 5. The sample was stirred with a magnetic stirrer at a speed of 300 rpm with the length of reaction was 1 hour and a reaction temperature of 70℃, 80℃, and 90℃. At the end of the dehydration reaction, it will obtain a brown mixture. The mixture was then cooled. The samples from the dehydration process were analyzed using the SNI 01-3545-2004 method.

2.6. 5-HMF analysis using the SNI 01-3545-2004 method

Distilled water was added with a solution of Carrez I and Carez II, each 0.50 mL, to a volume limit of 50 ml. Sample preparation is carried out to purify the sample by depositing the protein to be analyzed using a UV spectrophotometer. A sample of 5 grams of durian starch was dissolved with distilled water to a volume of 25 ml. The sample solution was added with solution of Carrez I and Carrez II each of 0.50 ml. Then the solution is added with distilled water and homogenized to 50 ml.

3. Results

3.1. Choline chloride / ethylene glycol-based DES characterizations

Important physical properties characterization needs to be studied and analyzed are : density, viscosity, and pH [8]. In this study, DES was synthesized with a mole ratio of Choline Chloride to Ethylene Glycol acid of 1: 2 at a temperature of 70℃ with a stirring speed of 180 rpm for 80 minutes. The DES characteristics test based on ChCl: Ethylene Glycol that was pH, density, and viscosity tests. The DES pH value was 6.3. The density of DES at 30℃ was 1.115 g / cm³, and the viscosity value was 238.090 mPa.s. The results of the characteristic test that have been carried out are in line with the research of Ibrahim, et al., In 2017, which reported that DES based on Choline Chloride / Ethylene
Glycol with a ratio of 1:2 at 30°C has a density whose value is between 1.09 g/cm³ - 1.12 g/cm³ and a viscosity between 180 mPa.s - 250 mPa.s [9, 12]. DES production with low viscosity is ideal because DES is a solvent that is environmentally friendly and thus good for the environment [10]. The lower the DES viscosity value, the better DES is used as a solvent [11].

3.2. Influence of The Concentration of Sulfuric Acid in Glucose Yield

The first stage of this research was the hydrolyzing method of the Durian Seed Starch. This stage was the hydrolysis reaction of starch to glucose with the addition of an acid catalyst in which sulfuric acid (H₂SO₄). Sulfuric acid (H₂SO₄) which was used as a catalyst with various concentrations: 1.5%; 3%; 5%, and 10% (w/v) with the ratio of durian seed starch to acids (1:10 w/v), with operating conditions at 100 °C, time 60 minutes and 300 rpm stirring speed.

Figure 1 indicates that the amount of glucose yield produced is directly proportional to the rise in the sulfuric acid concentration used. At this stage, high glucose yields are predicted. The resulting glucose is used for the next step, i.e. the 5-HMF dehydration step. The highest glucose yield came at an acid concentration of 10%, which was 46.35 percent. The lowest glucose yield came at a sulfuric acid concentration of 1.5 percent, which was 14.91 percent.

3.3. Effect of Using DES as a Solvent in Dehydration Process

3.3.1. Analysis of FTIR (Fourier Transform Infra-Red), before and after dehydration

Analysis of FTIR on durian seed starch samples before and after dehydration was conducted to classify group discrepancies in differences in glucose compounds (before dehydration) to 5-hydroxymethylfurfural compounds (after dehydration). The findings of the spectrum seen in Figure 2 from functional group analysis using FTIR.
Figure 2. FT-IR analysis on durian seed starch samples (a). before Dehydration (b). after Dehydration

Figure 2 (a) shows the results of the analysis using FTIR before the dehydration process. The peaks that appear are in the area of 3335.60 cm\(^{-1}\), 1637.55 cm\(^{-1}\), and 1182.24 cm\(^{-1}\). Figure 2 (b) shows the results of the analysis using FTIR after the dehydration process. The peaks that appear are in the area of 3289.61 cm\(^{-1}\), 2951.87 cm\(^{-1}\), 1638.75 cm\(^{-1}\), 1458.95 cm\(^{-1}\) and 1038.44 cm\(^{-1}\). According to Pavia, et al., 2001, the area 3200-3400 cm\(^{-1}\) shows the OH absorption with H bound, in the 1630-1680 cm\(^{-1}\) area shows the C = O group absorption area, in the 1475 and 1600 cm\(^{-1}\) regions shows the C = C group absorption area (Aromatic), 1000-1300 cm\(^{-1}\) shows the absorption area of the C-O group, 2850-3000 cm\(^{-1}\) shows the absorption area of the C-H group (Aldehyde)[13].

From Figure 2, there are variations before and after the dehydration reaction, there is an inclusion of C = C (Aromatic) and C-H (Aldehyde) groups after the dehydration reaction. According to Pavia, et al., 2001, an aldehyde group suggests the presence of C=O groups and low C-H absorption. If there is a weak absorption area about 1650 cm\(^{-1}\) for the C=C group followed by the absorption area for the
C-H group in the 3000 cm$^{-1}$ regions. This means that it contains an aromatic ring group. An alcohol group is seen in the OH group with H bound, followed by the presence of the C-O absorption region [13]. 5-Hydroxymethylfurfural consists of a ring of furan, aldehyde and alcohol [14]. Furan is an organic compound with an aromatic heterocyclic ring composed of 1 oxygen atom and 4 carbon atoms. [15].

3.3.2 Correlation of Dehydration Reaction without DES and with DES for Yield 5-HMF

Figure 3 demonstrates a comparison of the dehydration reaction lacking DES and the choline chloride/ethylene Glycol-based DES to the 5-HMF yield. From this graph, it can be shown that the maximum yield of 5-HMF was obtained while using DES as a co-solvent.

![Figure 3. Effect of dehydration reaction without DES and with DES on Yield 5-HMF](image)

Analysis conducted reveals that the maximum yield of 5-HMF was achieved when the dehydration process using DES at a temperature of 90$^\circ$C was 34.35%. Besides that, the lowest yield of 5-HMF was reached when the dehydration process not using DES at a temperature of 80 $^\circ$C, which was 16.56%. Research conducted by Zuo, et al. (2017) showed the effect of DES on the dehydration reaction of 5-HMF formation. ChCl is a better HBA in DES systems because of its polarity and can increase reaction activity. Figure 4. shows the mechanism of the dehydration reaction in the DES system. Fructose is converted to A through a cyclic mechanism assisted by acids. Cl- acts as a base in converting oxonium ions to B in path A. Cl- acts as a base and nucleophilic in path B. C is converted to 5-HMF by a dehydration reaction [16].

![Figure 4. Dehydration reaction mechanism in the DES System [16]](image)
3.3.3 Effect of Amount of DES and Reaction Temperature on Yield 5-HMF

Glucose dehydration reactions were conducted using HCl 1.2 mol percent of glucose as a catalyst, and DES-based on Choline Chloride/Ethylene Glycol. The influence of the sum of DES and the reaction temperature on the yield of 5-HMF was observed in the glucose mass ratios to DES of 1:1, 1:3 and 1:5 with a temperature range of 70°C, 80°C, and 90°C. Figure 5 reveals that the yield of 5-HMF improved with an improvement of 90°C in the amount of DES with the strongest dehydration reaction temperature in this sample.

![Figure 5](image_url)

**Figure 5.** Effect of amount of DES and dehydration reaction temperature on 5-HMF Yield

Analysis performed by Zuo, et al. (2017) recorded that during the dehydration of glucose in a mixture of DES based on ChCl and Fructose (1:1), an improvement in 5-HMF yield was observed from 30% to 89% at a reaction temperature of 32°C to 110°C and length of reaction of 0.5 hours to 8 hours [17]. It can be said that the 5-HMF yield will increase with increasing temperature if the reaction has not reached its degradation point[18]. The drop in yield of 5-HMF was due to the formation of 5-HMF following a polymerization process which forming the humin. This is dependent on the colour of the polymer, the humin becoming dark brown, and the colour of the sample being browner with a rising reaction temperature. [19]. Humin is a black solid resulting from a side reaction of Dehydration, which can reduce the yield of 5-HMF [20].

![Figure 6](image_url)

**Figure 6.** Comparison of product colour resulting from dehydration at 90°C with the mass ratio of glucose to DES (a) 1:0 (b) 1:1 (c) 1:3 (d) 1:5
From Figure 6, it can be seen that a decrease in mass glucose ratio to DES causes discoloration darkening dehydration results.

![Figure 6](image)

**Figure 6.** From Figure 6, it can be seen that a decrease in mass glucose ratio to DES causes discoloration darkening dehydration results.

From Figure 7, it can be seen that an increase in the temperature of the dehydration results in a darker color.

![Figure 7](image)

**Figure 7.** Comparison of the colour of dehydration products at the mass ratio of glucose to DES (1:3) with temperature (a) 70°C (b) 80°C (c) 90°C

3.3.4. Impact of Glucose Concentration on the 5-HMF yield

The glucose dehydration method was conducted using HCl 1.2 mol percent of glucose as a catalyst, the glucose to DES mass ratio was 1:5 with a response period of 60 minutes and a stirring time of 300 rpm. The impact of glucose concentration on 5-HMF yield was obtained at glucose concentration variations of 10.05 percent; 14.90 percent; 20.74 percent; and 31.24 percent.

![Figure 9](image)

**Figure 9.** Effect of Glucose Concentration on 5-HMF Yield

Figure 10 indicates that the yield of 5-HMF decreases with the rise in the initial glucose concentration used. The maximum yield of 5-HMF was 70.34% while the glucose concentration was 10.05%, although the lowest yield of 5-HMF was 61.93% which the glucose concentration was 31.24 percent. Teng, et al. (2016) conducted a study to see the effect of the initial glucose concentration on the 5-HMF yield. The highest yield was achieved at 56.4% at an initial glucose concentration of 22.5
wt% and the lowest yield at 40.4% at an initial glucose concentration of 90.0 wt%. greater initial glucose concentrations lead in side reactions which create undesirable products [21, 22].

4. Conclusions
The glucose yield obtained improved along with the concentration of sulfuric acid used within the hydrolysis process of starch derived from durian seeds. The optimal condition for the dehydration reaction is the ratio of glucose to DES of 1:5 and the reaction temperature of 90°C with the maximum yield of 70.34% at the initial glucose concentration of 10.05%. The initial glucose concentration is inversely proportional to the 5-HMF yield, which caused due to side reactions of humin formation and rehydration reactions due to the presence of water.

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