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# Synthesis of 5-Hydroxymethylfurfural from Cassava (*Manihot utilissima pohl*) Peels through Dehydration Reaction using Deep Eutectic Solvent Based on Choline Chloride/Citric Acid

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The high cellulose content in cassava peel has an opportunity to produce bio-based chemical products in 5-hydroxymethylfurfural (5-HMF) form. This study aimed to determine the optimum conditions of glucose dehydration reaction as a result of hydrolysis of the best cassava peel cellulose. The variables observed in this study were $H_2SO_4$ catalyst concentrations in the hydrolysis reaction, temperature and amount of deep eutectic solvents based on choline chloride/citric acid. The optimum dehydration reaction conditions in this study was the glucose:deep eutectic solvents mass ratio of 1:6 at the reaction temperature of 80 ºC. The highest yield of 64.50% at an initial glucose concentration of 5.70% using a 1.5% $H_2SO_4$ catalyst during the hydrolysis of cassava peel cellulose. The results obtained in this study indicated that addition of choline chloride/citric acid as deep eutectic solvent can increase the yield of 5-HMF.

**Keywords: Choline choride, Citric acid, Dehydration reaction, 5-Hydroxymethylfurfural.**

## INTRODUCTION

Since the beginning of the 20th century, the use of mineral oil as a source of energy and resources for the production of finished good that has increased rapidly. It has implications for the limited and expensive amount of raw materials. Therefore, finding new forms of resources for the production of finished goods for humanity is an essential task [1]. One of the raw materials for new resources is biomass, which is abundant in Indonesia and acted as one of the renewable raw materials [2,3].

5-Hydroxymethylfurfural (5-HMF) has received a great attention over the past few decades because of its diverse functionality. Due to the presence of one hydroxyl group, one aldehyde group and furan ring, and thus can be used as a versatile precursor for synthesis into various chemicals and value-added fuels [4,5]. 5-HMF can be obtained as a product of $C_6$-based carbohydrate dehydration process, such as fructose, glucose, cellulose and even lignocellulose. Dehydration of carbohydrates (especially fructose) has begun with the use of mineral acid as catalysts [6]. One of the biomass that contains high carbohydrates is cassava peel [7], where most cassava peel processing, several tons of cassava peel are produced as waste products from processing activities. With increase in cassava production, waste empowerment is also expected to continue to increase. Although cassava peel can be used as animal feed, the amount produced and the remoteness of many communities where processing takes place leaves a lot of waste that is left to rot or be burnt with consequences for the environment [8]. The synthesis of 5-HMF through hexose dehydration is the basis of the development and utilization of biomass. Previous studies mostly focused on developing new catalysts and related catalysis mechanisms, and relative, less attention was given to media selection. Actually, the media play an important role in the organic reactions, which can affect the rate of reaction and equilibrium, and even the reaction mechanism. So far, from glucose dehydration to 5-HMF, the most commonly used media are water, organic solvents *e.g.* dimethylsulphoxide or water/organic solvent mixtures *e.g.* water/DMSO [9].

Molecular organic solvents ionic liquid can be considered a green media. Ionic liquid has good thermal stability and low vapour pressure, and its properties can be easily designed [10]. However, the use of ionic liquids as a medium is too expensive, however, these costs can be compensated to some extent by recycling [11]. Deep euthetic solvent (DES) formed by ionic liquid and hydrogen bonding donors (HBD) (*e.g.* carboxylic acids, amides, alcohols, *etc.*) at a stoichiometric ratio has been tried in in recent years as a reaction medium using various hydrogen bond acceptors (HBA) [12]. The use of DES (choline chloride/citric acid) as a medium for dehydration of glucose to 5-HMF reported.

## EXPERIMENTAL

The materials used in this study included cassava peels, choline chloride (ChCl) 99.5%, citric acid > 99.5%, hydrochloric acid 37% and sulfuric acid 99.99% material were purchased from Sigma-Aldrich (St. Louis, USA).

**Cassava peels hydrolysis:** At this stage, using $H_2SO_4$ with various concentration as catalyst, cassava peel was added and stirred using a magnetic stirrer 300 rpm with at 100 ºC for 60 min to generate $H^+$ form.

**Synthesis of deep eutectic solvents:** Choline chloride as hydrogen bond acceptor, citric acid as hydrogen bond donor in a molar ratio 2:1 (M/M). The mixture was heated on a hot plate on 80 ± 5 ºC and homogenized using a magnetic stirrer for 1 h [13]. Then, pH of deep eutectic solvents was measured using a pH meter, density was measured by picnometric method and the viscosity was measured by Ostwald′s viscometer at 30 ºC.

**Glucose dehydration:** Dehydration is the final step in this study and at this stage, 5-hydroxymethylfurfural (5-HMF) was obtained using DES as a solvent.

**Characterization:** The FTIR spectra of 5-hydroxymethylfurfural (5-HMF) using using deep eutectic solvent based choline chloride/citric acid were recorded on Fourier transform infrared spectrometer Shimadzu IR-21 in the wavelength range of 4000-500 $cm^{-1}$.

## RESULTS AND DISCUSSION

Deep eutectic solvent (DES) is a simple mixture of a salt and a hydrogen bond donor (HBD) compound where both connected each other through hydrogen bonds [14,15]. Hayyan *et al*. [16] reported that the physical properties of DES differ depending on the molar ratio of salt and its constituent HBD. In this work, choline chloride and citric acid are used as deep eutectic solvent (DES) and its results are shown in Table-1.

TABLE-1
PHYSICO-CHEMICAL PROPERTIES OF CHOLINE CHLORIDE/CITRIC ACID AS DEEP EUTECTIC SOLVENT

| Parameters | Value |
|---|---|
| Phase (30 °C) | Colourless liquid |
| Density | 1.32 g/mL |
| Viscosity | 120.41 mPa.s |
| pH | 6.0 |

After the complete heating process, DES was obtained in the form of a clear liquid (colorless liquid), then allowed to cool at room temperature (30 ± 2 ºC). It shows that the freezing point of DES is below room temperature as no DES changes occured. According to Zhang *et al*. [15], DES with clear liquid formed is due to the mixing of salt and HBD compound in a similar molar ratio. Moreover, clear liquid or new form of DES indicates a decrease in freezing point which is attributed due to the lower freezing point of the two constituent solids [15]. Secondly, low DES freezing value is also caused by hydrogen bonds and complex interactions of HBD and salt halide anions thereby reducing lattice energy in the mixture which leads to a decrease in freezing value [17].

Density is one of the important physical properties of ionic liquids generally and specifically in DES [18,19]. According to Hayyan *et al*. [20], development of low viscosity DES is highly expected because DES has the potential to be an environmentally friendly media [20]. The lower the viscosity value of DES, the better the DES used as a solvent [21].

**Effect of acid concentration on hydrolysis process:** The hydrolysis process of cellulose from cassava peel was carried out at 100 ºC for 60 min with a stirring speed of 300 rpm using sulfuric acid as a catalyst in different concentrations, *viz.*1.5, 3, 5 and 10% in a cassava peel:acid ratio (1:10 v/v). Fig. 1 shows that glucose yield increases with increasing the concentrations of sulfuric acid. The highest glucose yield of 64.51% was produced at 10% acid concentration.

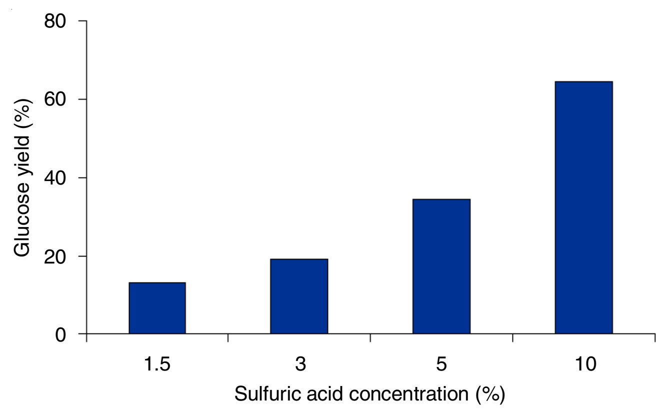
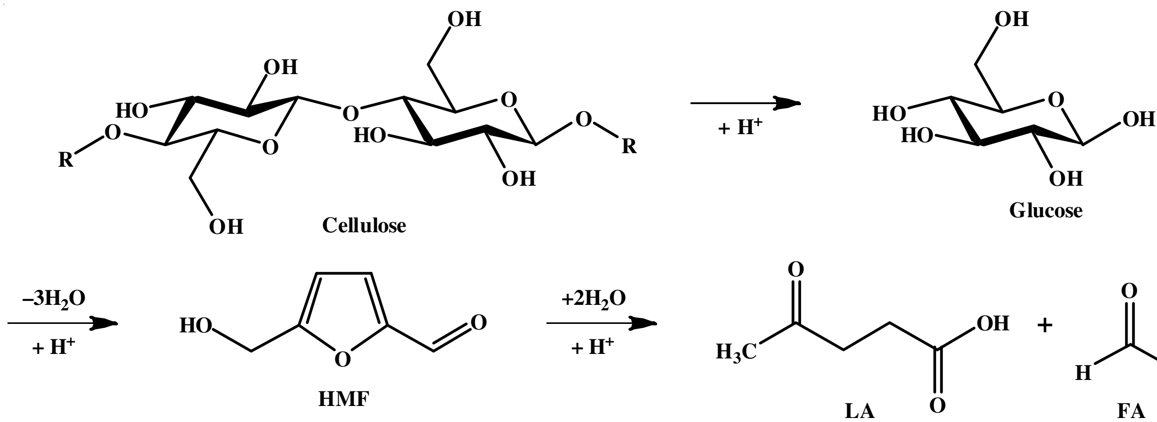



Fig 1. Effect of acid concentration on the hydrolysis of glucose

Sulfuric acid as a catalyst in the cellulose hydrolysis of cassava peel is directly proportional to the glucose yield on the same reaction time because $H^+$ ions in strong acids can help break the glycoside bonds found in cellulose to form the glucose chain [22-24]. At a high acid concentration, it is expected that 5-HMF yield will also be higher. Therefore, 10% sulfuric acid concentration was chosen in this study.

**Synthesis of 5-hydroxymethylfurfural (5-HMF) from glucose:** During the dehydration reaction, glucose molecule releases three water molecules to form 5-HMF (**Scheme-I**), which further yielded levulinic acid and formic acid upon dehydration [25]. Matsumiya & Hara [26] converted glucose molecules into 5-HMF using choline salt and carboxylic acid mixture. The carboxylic acid plays an important role not only to reduce the melting point of the mixture but also as a source of protons.

**FTIR analysis:** FTIR analysis of 5-HMF before and after dehydration was carried out to identify the changes. In Fig. 2b, after the dehydration reaction, appearance of C=C (arom.) and C-H (aldehyde) groups were observed. Moreover, the presence of a C=O group and weak absorption of C-H indicated




**Scheme-I:** Dehydration reaction mechanim of glucose to 5-HMF

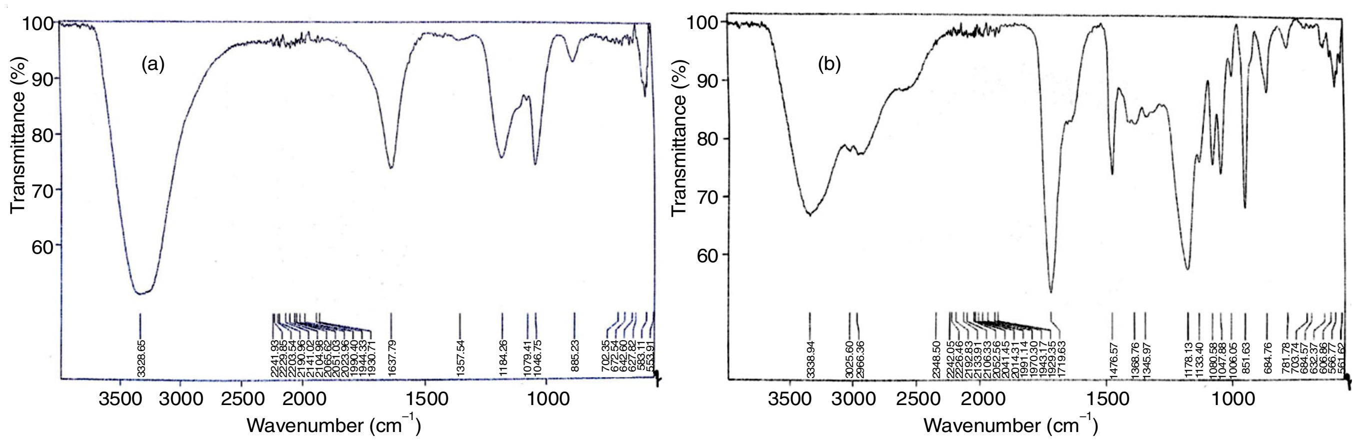



Fig. 2. FTIR before dehydration (a) and after dehydration (b)

an aldehyde group. Similarly, a weak absorption peak of C=C group at 1650 cm$^{-1}$ accompanied by the absorption peak of the C-H group at 3000 cm$^{-1}$ indicated that the aromatic contains ring group [26]. The OH group with H-bound followed by the appearance of the C-O uptake region showed the presence of alcoholic group [27] thus confirmed the formation of 5-HMF [28,29].

**Effect of deep euthetic solvent (DES) in dehydration reaction:** Fig. 3 shows that the 5-HMF yield obtained from the dehydration reaction in the presence of DES was higher than without DES. At 80 ºC, 5-HMF yield was maximum as it increased from 20.71% to 26.60% with increasing hydrolysis mass ratio:DES from 1:0 to 1:4. Li *et al*. [16] also observed the same results and reported that ionic liquids can increase the 5-HMF yield. Moreover, addition of choline/citric acid reduces the viscosity of the mixture as it can facilitate the transfer of mass and heat. Also $Cl^-$ in DES also able to interfere with the hydroxyl bonds in glucose so that three water molecules were released during the dehydration reaction.

Thus, DES is a very potential catalyst in the dehydration reaction because it can overcome the high water content during the reaction. Moreover, ChCl is a better hydrogen bond acceptor (HBA) and due to its polarity it can increase the reaction activity. Fig. 4 shows the dehydration reaction mechanism in the DES system, where glucose was converted to A through a cyclic mechanism facilitated by acid. Acting as a base, chloride

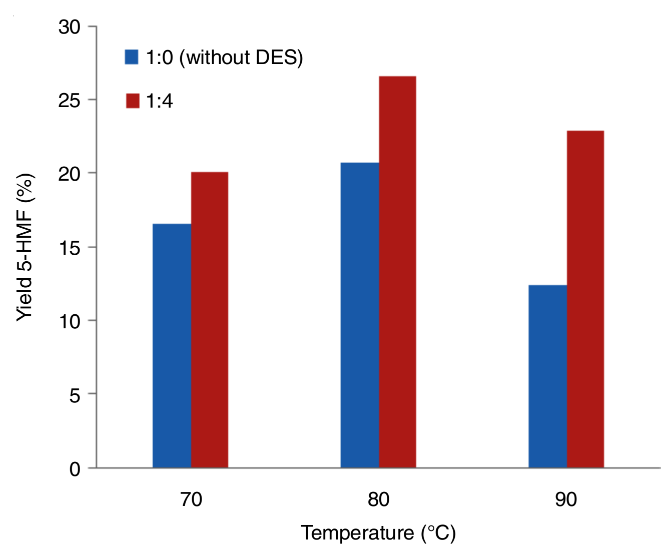



Fig. 3. Effect of deep euthetic solvent (DES) on the yield of 5-HMF

ion ($Cl^-$) converted the oxonium ions to B in path A. But in path B, $Cl^-$ acted both as a base and nucleophile. Finally, intermediate C was converted to 5-HMF with the elimination of water molecule (dehydration reaction) [30].

**Effect of temperature:** The dehydration process was carried out using 10% $H_2SO_4$ as a catalyst in the presence of choline chloride/citric acid (1:6) at various temperatures (70, 80 and

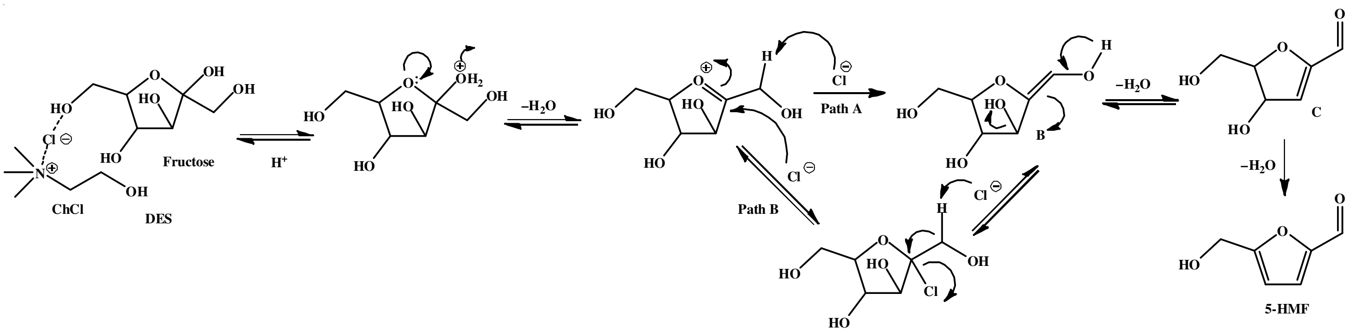



Fig. 4. Dehydration mechanism of glucose to 5-HMF in the presence of DES system (ChCl/citric acid::1:6) [Ref. 30]

90 ºC) with a reaction time of 60 min and stirring 300 rpm. Fig. 5 showed that different temperature affects the 5-HMF yield. In the dehydration process, the choline chloride/citric acid is expected to produce 5-HMF with high yield. The overall 5-HMF yield at 80 ºC, but 5-HMF yield decreases at 90 ºC. The decrease in the 5-HMF yield is due to the polymerization reaction, which results in the formation of humin [32]. The increase in 5-HMF yield is in line with increasing reaction temperature and then decreases when reaction time exceed. This is due to the dehydration reaction because the water produced from the reaction of dehydration as a byproduct [33].

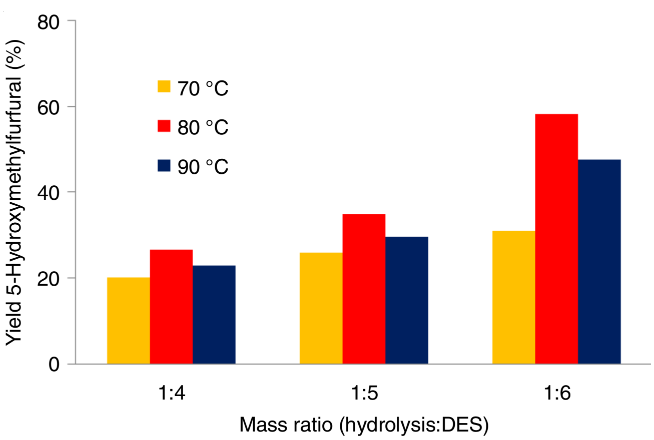



Fig. 5. Effect of DES on the Yield 5-HMF at varoius temperatures

**Synthesis mechanism of 5-HMF:** Jing & Lu [34] have studied the first-order kinetic reaction of 5-HMF formation from glucose at 180-220 ºC with a pressure of 10 MPa (Fig. 6). The activation energy value for each reaction was in the order of $E_3 < E_1 < E_4 < E_2$. It is found that if the activation energy of the desired reaction is smaller than the activation energy of the side reaction at low temperature, then the reaction will proceed smoothly and the reverse is true for the same [35].

**Effect of initial glucose concentration:** The hydrolysis results of cassava peel were carried out using by varying the

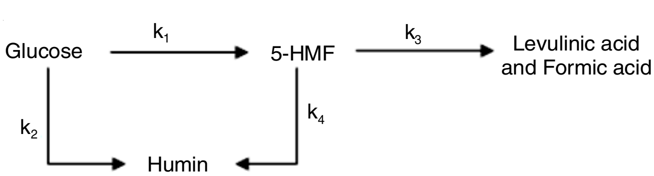



Fig. 6. Kinetic reaction mechanism of 5-HMF [Ref. 34]

catalyst concentrations. It was observed that with increasing glucose concentration, the yield of 5-hydroxymethylfurfural obtained decreases (Fig. 7). The highest yield of 5-HMF was obtained at 64.50%, when a low glucose concentration used (At 5.70%). Thus, an increase in glucose concentration will result the decrease in the yield of 5-HMF. Similar effects have been reported by Assanosi *et al.* [36].

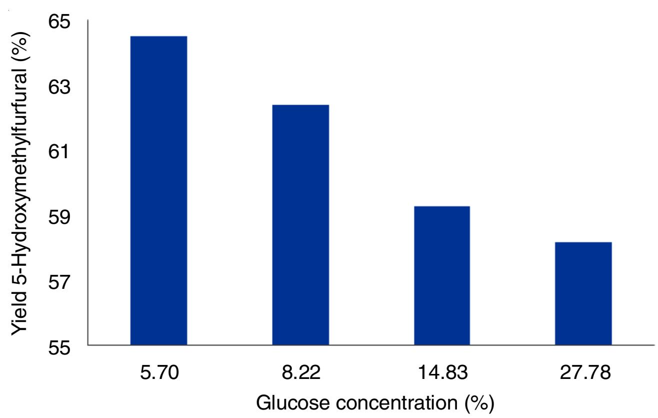



Fig. 7. Effect of glucose concentration on the yield of 5-HMF

McKibbins & Samuel [37] proposed the mechanism (Fig. 8), which explained the stated that the due to the formation of intermediate (I) in the reaction, where $k_1$, $k_2$ and $k_3$ are first order reaction velocity constants, while $k_4$ is the reaction speed constant which has a higher order of $k_1$, $k_2$ and $k_3$, indicated that at high glucose concentration, the conversion rate of 5-HMF to humin is higher than the conversion reaction. The results obtained are in accordance with the existing theories where at low glucose concentrations will produce higher yield of 5-hydroxymethylfurfural.

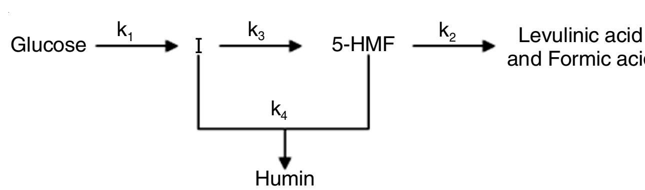



Fig. 8. Kinetic Reaction mechanism of 5-HMF [Ref. 37]

## Conclusion

Deep eutectic solvent (DES) was prepared from choline chloride and citric acid (HBD) with a molar ratio of 2:1 at 80 ºC with stirring for 2 h, suitable for isolating 5-hydroxymethylfurfural. The concentration of sulfuric acid as a catalyst in the hydrolysis process greatly affects the hydrolysis of cassava peel. The highest yield obtained was 64.51% using a 10% sulfuric acid. Eutectic mixture in the form of DES can prevent dehydration reaction. The best dehydration reaction conditions were optimized at the ratio of glucose mass:DES 1:6 at 80 ºC obtaining highest yield 64.50% at an initial glucose concentration of 5.70%. The initial glucose concentration is inversely proportional to 5-HMF obtained due to the occurrence of side reactions due to the formation of humin and the dehydration reaction.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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