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# Reaction Kinetics in Conversion Process of Pineapple Leaves into Glucose

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**Abstract**

*This research aimed to determine the reaction kinetics in the process of hydrolysis of pineapple leaves. The experiment was carried out at the temperature (60, 90, and 120°C) and variation of acid catalyst concentration (0.1; 0.5 and 1 M) by observation reaction time every 30 min. The kinetics model of hydrolysis reactions of pineapple leaves has shown first order reaction with activation energy value to find the concentration of sulfuric acid successively: 0.1 M; -15420 KJ/mol; 0,5 M; 3173.8 KJ/mol; 1 M; 100.53 KJ/mol. The reaction rate constant which produced the highest glucose level was on the use of sulfuric acid at a concentration of 0.1 M at a temperature of 120°C with glucose levels produced between 26.366.039 ppm to 155.510.778 ppm with k = 0.0106/min.*

**Keywords:** *glucose; hydrolysis; kinetic model; pineapple leaves*

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## INTRODUCTION

The conversion of cellulose to glucose as a raw material for making bioethanol is an alternative in obtaining raw materials for renewable energy sources. To find out the good conditions in the conversion of raw materials, kinetic data is required. The systematic study of cellulose hydrolysis kinetics against glucose was carried out in 1945 by Saeman. The hydrolysis reaction is modeled using a first-order reaction (Joksimovic and Markovic, 2007). The Kinetics model of reaction for glucose decomposition is influenced by several factors, one of them is temperature. The kinetics model of this reaction can accurately check the rate constants at various acid concentrations including dilute acids (Xiang *et al.*, 2004). The temperature and concentration of the acid greatly influence the rate of cellulose hydrolysis and the conversion of glucose produced. In general, glucose levels will increase with increasing hydrolysis temperature and acid concentration used (Ajani *et al.*, 2011). Dilute acid can be used as a catalyst in the hydrolysis process. The dilute acids commonly used are $H_2SO_4$, HCl, HF, or $CH_3COOH$. These dilute acids can break the heterocyclic ether bond between the sugar monomers in the polymer chain formed by hemicellulose and cellulose. The breakdown of these bonds can release several compounds, especially xylose, glucose and arabinose (Aguilar *et al.*, 2002).

There are several steps in the process of hydrolysis using acid. The reaction begins with a proton that comes from an acid that interacts quickly with glycosidic oxygen that connects two units of glucose, forming a conjugate acid. Then the process is followed by the termination of the C-O bond and the destruction of conjugate acid into carbonium ions. With the presence of excess water, the glucose and proton molecules are released (Xiang *et al.*, 2003).

Dinarsari and Adhitasari (2013) has conducted a study of Sente taro starch hydrolysis into glucose using hydrochloric acid catalyst by determining glucose levels using the DNS method. The results showed that from various pH conditions, the best result is shown at pH 4, while the optimum temperature of the study was 90ºC. Meanwhile the reaction rate constant in the best variable process condition with pH 4 of solution at a temperature of 90ºC, 60 minutes of hydrolysis time and 1:30 (gr starch/mL solution) weight ration of raw material to hydrolysis solution is obtained the rate constant of $9.139 \times 10^{-4}$ $min^{-1}$ and the reaction rate equation is $CA = 0.00112205e^{-0.003747t}$.

The effect of acid concentration and hydrolysis time on bioethanol formation from pineapple leaves by analyzing the glucose levels using Luff Schoorl method showed that to produce bioethanol from pineapple leaves through alkaline pretreatment it is necessary to hydrolyze using sulfuric acid and using *Saccharomyces cerevisiae* for fermentation process. The longer of hydrolysis time formed higher concentration level of glucose and bioethanol in the fermentation product. The best conditions in this study were obtained at 2% sulfuric acid concentration and 120 minutes hydrolysis time which produced 7.3896% glucose and 6.2444% ethanol (Haryani *et al.*, 2015).

The purpose of this study was to determine the effect of $H_2SO_4$ catalyst concentration on glucose levels in product as well as the determination of the effect of time and temperature on product's glucose levels in the hydrolysis process of pineapple leaves.

## MATERIALS AND METHODS

### Research Design

This research was carried out through several stages. First, the pineapple leaves that have been obtained are cut into small pieces then blended until smooth. The reduction of sample size was conducted to make larger surface area and facilitated the hydrolysis process in converting cellulose to glucose. The blended pineapple leaves are then dried under the sun to remove the water content. The hydrolysis process was carried out using $H_2SO_4$ catalyst. The variation of $H_2SO_4$ catalyst concentration was 0.5 M and 1 M. Furthermore, the samples were put into a three neck flask and refluxed for 2 hours. Not only the variation of catalyst as the variable but also the variations of sampling time during the hydrolysis process. The products were sampled at 30, 60, 90, 120, and 150 minutes. The variations hydrolysis temperature were set at 60, 90, and 120ºC. Second stages, the solution of hydrolysis product was taken for glucose analysis. The analysis of glucose content was carried out using the spectrophotometric method. While the characterization of glucose as the product hydrolysis process was performed using FTIR.

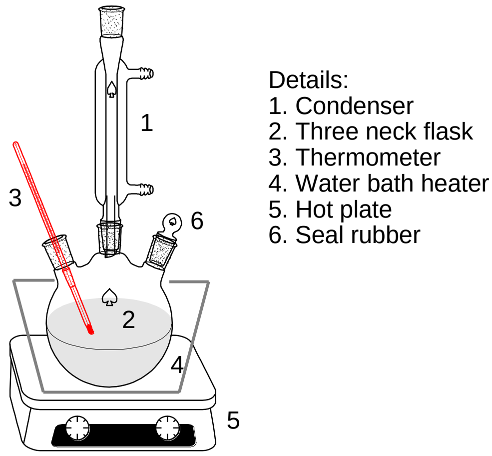



Figure 1. Equipment set in hydrolysis process

### Data Processing of Reaction Kinetics

Every measurement in the physical analysis must have changes in compounds in the form of reactions that can be known the change of reactants or products. This change is sometimes relatively in simple form and shows the changes in term of concentration of both reactants and products. Generally the relationship between physical properties and concentration is a linear function, for example the relationship between concentration and conductance, absorbance, rotation of polarization rays and gas pressure. General equations describe the relationship between physical quantitative measurements and reaction variables and it has been proven that physical quantitative is a linear function with concentration (Triyono, 1999). Determination of glucose levels from hydrolysis using a UV-Vis spectrometer is a relationship between physical properties and concentration. The relationship of physical properties (λ) with concentration is described as :

$$\frac{\lambda_\infty - \lambda_o}{\lambda_\infty - \lambda} = \frac{A_o}{A_t} \quad (1)$$

$$A_t = A_o\left(\frac{\lambda_\infty - \lambda_o}{\lambda_\infty - \lambda}\right) \quad (2)$$

If Equation (2) is sustituted into reaction order equation (1), where:

$$ln[A] = -kt + \ln[A]_o \quad (3)$$

thus,

$$ln\frac{A_t}{A_o} = -kt \quad (4)$$

$$ln\frac{1}{\frac{A_o}{A_t}} = ln\frac{1}{\left(\frac{\lambda_\infty - \lambda_o}{\lambda_\infty - \lambda}\right)} = -kt \quad (5)$$

So that for the first order equation can be written as:

$$ln\frac{\lambda_\infty - \lambda}{\lambda_\infty - \lambda_o} = -kt \quad (6)$$

While for second order equation can be expressed as:

$$\frac{1}{A_t} - \frac{1}{A_o} = kt \quad (7)$$

Equation (7) was multiplied with $A_o$ thus:

$$\frac{A_o}{A_t} - 1 = A_o kt \quad (8)$$

$$\frac{\lambda_\infty - \lambda_o}{\lambda_\infty - \lambda} - 1 = A_o kt \quad (9)$$

Equation (9) was multiplied with $\frac{1}{\lambda_\infty - \lambda_o}$ so that becomes:

$$\frac{1}{\lambda_\infty - \lambda} - \frac{1}{\lambda_\infty - \lambda_o} = \frac{A_o kt}{\lambda_\infty - \lambda_o} \quad (10)$$

Reaction rate constant can be evaluated by ploting the graphical analysis between ln[$\lambda_\infty$-$\lambda_t$] towards time (*t*).

Equation can be solved by using regression approach, y=mx+c, with y is ln[$\lambda_\infty$-$\lambda_t$] and x is t. If the obtained graph is linear equation model then the reaction order is considered as first order reaction and the reaction rate constant k is the slope of the model (Dinarsari and Adhitasari, 2013). However, if the plot doesn't show linear model then other model should be tried for example second order model. The evaluation is performed by plotting the graphical analysis between $\frac{1}{\lambda_\infty - \lambda_o}$ towards time *t* as expressed in equation 10.

## RESULTS AND DISCUSSION

Hydrolysis process breaks down the cellulose in β-1,4-glycoside bonds in cellulose polymer. This process takes place with the help of acid as a catalyst. Acid solutions commonly used in the hydrolysis process are HCl, $H_2SO_4$, HF and organic acids (Huang and Fu, 2013). The addition of acid as a catalyst is to increase the reactivity of water so that the hydrolysis process reaction becomes faster (Sylvia *et al.*, 2015). The acid used in the hydrolysis of pineapple leaves was sulfuric acid at various concentrations. Sulfuric acid is often used in the hydrolysis process because it has high efficiency and able to be regenerated (Emelyanov *et al.*, 2016). Table 1 shows the result data of pineapple leaves hydrolysis using various concentration of sulfuric acid catalyst at temperatures of 60, 90, and 120ºC.

Table 1 shows that the highest glucose content is at a temperature of 120ºC with the concentration of sulfuric acid used is 0.1 M. The glucose content at this condition was 155,510.778 ppm when the hydrolysis process at 150$^{th}$ minute. While the lowest concentration was 304.089 ppm at 60ºC when the hydrolysis process at 30 minutes with the concentration of sulfuric acid used was 0.1 M.

### The Effect of Sulfuric Acid Acid Concentration, Time, and Temperature on Glucose Content

Figure 2 showed that the longer hydrolysis time produced higher glucose content in hydrolysis products. The use of sulfuric acid concentrations at various concentrations in the hydrolysis process also affects the glucose levels produced. Based on Table 1 and Figure 2, they exhibited that the use of sulfuric acid with a concentration of 0.1 M produces higher glucose levels compared to the use of sulfuric acid with concentrations of 0.5 M and 1 M. This shows that the use of concentrated sulfuric acid is ineffective in glucose production in the hydrolysis process. Dussán *et al.* (2014) in their research on the use of dilute sulfuric acid in determining glucose levels in bagasse showed that the glucose levels obtained were very high.

### Reaction Rate Constant of Pineapple Leaves Hydrolysis

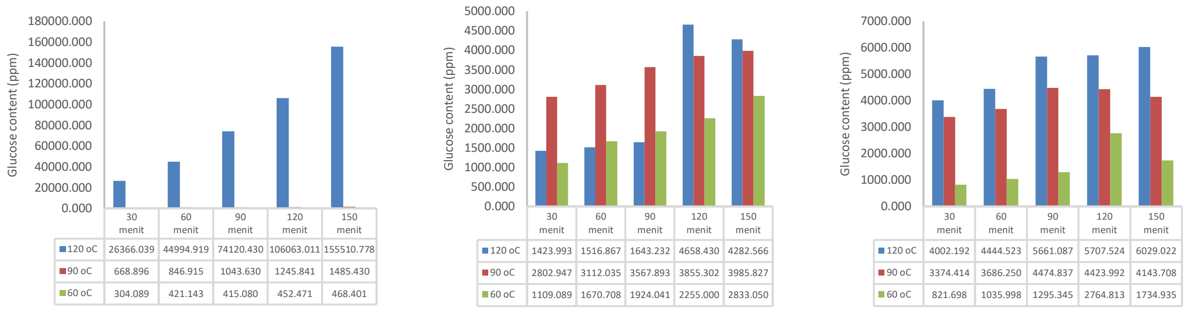
A chemical reaction has its own chemical rate. Some of them have fast reaction rate and the other have slow reaction rate. Slow chemical reaction rate can be accelerated by adding a catalyst (Achmad, 1992). In determining the rate of hydrolysis of pineapple leaves, sulfuric acid is used to accelerate the reaction rate. Based on Figure 3, it shows the relationship between the hydrolysis time of pineapple leaves towards ln ($\lambda_\infty - \lambda$) which has a linear regression value ($R^2$) which varies according to the concentration of sulfuric acid and the hydrolysis temperature condition. The regression values approached 1 except for the use of sulfuric acid at a concentration of 1 M at temperatures of 60ºC and 90ºC. This shows that the use of sulfuric acid which is too concentrated with hydrolysis temperatures below 90ºC is less effective in converting pineapple leaves cellulose into glucose. The reaction rate constants for pineapple leaves are presented in Table 2.

Table 2. reaction rate constant of pineapple leaves hydrolysis process

| Temperature (ºC) | 0.1 M | 0.5 M | 1 M |
|---|---|---|---|
| 60 | $8x10^{-6}$ | 0.0061 | 0.0027 |
| 90 | $4x10^{-5}$ | 0.0141 | 0.0035 |
| 120 | 0.0106 | 0.0013 | 0.0233 |

Table 1. Glucose content in pineapple leaves hydrolysis products with various concentrations of catalysts used

| Time (minute) | 0.1 M | | | 0.5 M | | | 1 M | | |
|---|---|---|---|---|---|---|---|---|---|
| | 120 ºC | 90 ºC | 60 ºC | 120 ºC | 90 ºC | 60 ºC | 120 ºC | 90 ºC | 60 ºC |
| | Glucose content (ppm) | | | | | | | | |
| 30 | 26,366.039 | 668.896 | 304.089 | 1,423.993 | 2,802.947 | 1,109.089 | 4,002.192 | 3374.414 | 821.698 |
| 60 | 44,994.919 | 846.915 | 421.143 | 1,516.867 | 3,112.035 | 1,670.708 | 4,444.523 | 3,686.250 | 1,035.998 |
| 90 | 74,120.430 | 1,043.630 | 415.080 | 1,643.232 | 3,567.893 | 1,924.041 | 5,661.087 | 4,474.837 | 1,295.345 |
| 120 | 106,063.011 | 1,245.841 | 452.471 | 4,658.430 | 3,855.302 | 2,255.000 | 5,707.524 | 4,423.992 | 2,764.813 |
| 150 | 155,510.778 | 1,485.430 | 468.401 | 4,282.566 | 3,985.827 | 2,833.050 | 6,029.022 | 4,143.708 | 1,734.935 |




(a) (b) (c)

Figure 2. effect of sulfuric acid concentration, time, and temperature on glucose content of pineapple leaves hydrolysis products: (a) 0.1 M; (b) 0.5 M; (c) 1.0 M

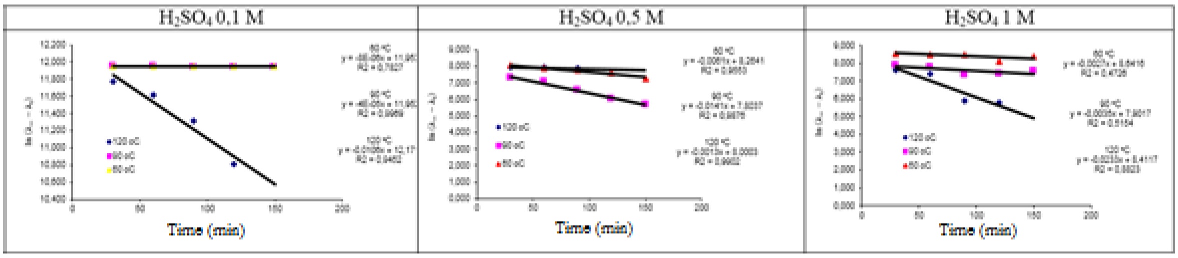
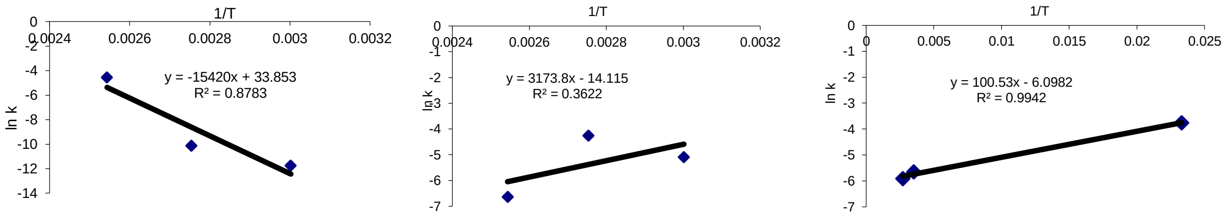



Figure 3. Graphical plot of rate constant in pineapple leaves hydrolysis process




(a) (b) (c)

Figure 4. Graphical plot of activation energy for each catalyst concentration of pineapple leaves hyrolysis (a) 0,1 M; (b) 0,5 M; (c) 1 M

**Activation Energy of Pineapple Leaves Hydrolysis**

Figure 4 shows the activation energy values of each concentration of sulfuric acid used in the hydrolysis process of pineapple leaves. The slope value linear model of 1/T towards ln(k) is considered as the value of activation energy obtained from the anti-tangent graph in Figure 4. The activation energy values of 0.1, 0.5, and 1.0 M catalyst concentration based on Figure 4 are -15,420 KJ/mol, 3173.8 KJ/mol, and 100.53 KJ/mol, respectively.

## CONCLUSION

The reaction kinetics of the pineapples leaves hydrolysis followed the first order reaction with the highest glucose level at a temperature of 120°C with a glucose level of 155,510.778 ppm. Whereas for the rate constant of hydrolysis of pineapple leaves which produces the highest glucose level was 0.0106 min$^{-1}$ with an activation energy value of 15,420 KJ/mol.

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## LIST OF NOTATION

$\lambda_\infty$ = Physical properties at $t$ = infinite
$\lambda_o$ = Physical properties at $t$ = 0
$\lambda_t$ = Physical properties at $t$ = $t$
$A_o$ = Initial concentration
$A_t$ = Concentration at $t$ = $t$
$k$ = Chemical reaction rate constant
$E_a$ = Activation energy

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