

Pseudo-Homogeneous Kinetic of Dilute-Acid Hydrolysis of Rice Husk for Ethanol Production: Effect of Sugar Degradation

Megawati, Wahyudi B. Sediawan, Hary Sulisty, and Muslikhin Hidayat

Abstract—Rice husk is a lignocellulosic source that can be converted to ethanol. Three hundreds grams of rice husk was mixed with 1 L of 0.18 N sulfuric acid solutions then was heated in an autoclave. The reaction was expected to be at constant temperature (isothermal), but before that temperature was achieved, reaction has occurred. The first liquid sample was taken at temperature of 140 °C and repeated every 5 minute interval. So the data obtained are in the regions of non-isothermal and isothermal. It was observed that the degradation has significant effects on the ethanol production. The kinetic constants can be expressed by Arrhenius equation with the frequency factors for hydrolysis and sugar degradation of 1.58×10^5 1/min and 2.29×10^8 L/mole/min, respectively, while the activation energies are 64,350 J/mole and 76,571 J/mole. The highest ethanol concentration from fermentation is 1.13% v/v, attained at 220 °C.

Keywords—degradation, ethanol, hydrolysis, rice husk

I. INTRODUCTION

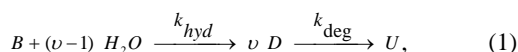
RICE husk is a source of lignocellulosic biomass that may be utilized as raw material for ethanol manufacturing. In Indonesia, there are approximately 60,000 rice mills, with rice husk production of 15 million tons per year. Rice husk predominantly contains hemi-cellulose (approx. 29.3%) and cellulose (approx. 34.4%). Theoretically, rice husk can be hydrolyzed into sugars at about 0.426 g sugar / g of dry rice husk. Then, ethanol can be produced from the sugars, at about 0.21 g ethanol / g of dry rice husk [1]. The three important steps in the production of ethanol from lignocellulosic biomass are hydrolysis to convert hemi-cellulose and cellulose into sugars, fermentation of sugars to produce ethanol, and ethanol purification [2]. According to Badger [3], there are two types of hydrolysis, i.e. enzymatic and chemical

hydrolysis.

Chemical hydrolysis was selected because it is relatively low cost and fast [4, 5]. This research studied dilute-acid hydrolysis and fermentation of sugars to produce ethanol using *Saccharomyces cerevisiae*. The dilute-acid hydrolysis of lignocellulosic biomass was run with operating condition of 0.5% sulfuric acid concentration, 11-12 bar pressure, 45 minutes, at various temperatures. The sugar yield of hemi-cellulose was as much as 80% w/w at temperatures of below 200 °C, but the maximum yield is achieved at temperatures of above 220 °C [6]. Maloney *et al.* [7] studied the kinetics of dilute-acid hydrolysis of hardwood. The kinetic model was derived from the dissociation of xylan group.

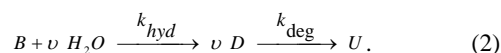
II. FUNDAMENTAL

Hydrolysis of lignocellulosic biomass can be approached as sequential reactions of lignocellulose hydrolysis and sugar degradation. The sugar degradation not only reduces the yield of fermentable sugars, but also forms inhibitors to fermentation, such as hydroxymethyl furfural (HMF), levulinic acid, and formic acid [8]. Schematically, the processes can be represented as

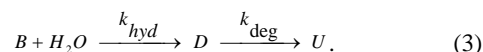


where B = polysaccharide (cellulose and hemi-cellulose), D = monosaccharide (sugars), U = by-products (HMF), and v = coefficient of reaction.

Since v is large, the value of (v - 1) is close to v, so equation (1) can be simplified as



If the value of polysaccharide B is represented as total sugars (with total hydrolysis procedure), equation (2) can be written as



Basically, solid-liquid reactions are usually modeled by heterogeneous or pseudo-homogeneous approach. In this

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paper, a pseudo-homogeneous model was applied. A number of researchers suggest that a pseudo-homogeneous model can be applied for this type of reaction. According to Karimi *et al.* [8], shape and particle size relatively do not give effect to dilute-acid hydrolysis of rice straw. Rice straw was hydrolyzed with dilute acid at 20 bar pressure for 10 minutes. Glucose yield was 43.7% and 44.6% for 2 - 50 mm and 20 - 48 mesh particle size, respectively. This phenomenon showed that the kinetic model can be represented by homogeneous model. Cendrowska [9], Saracoglu *et al.* [10], and Mosier *et al.* [11] also applied homogeneous model for hydrolysis of lignocellulosic materials. The objective of this paper is to study kinetics of dilute-acid hydrolysis of rice husk with applying a homogeneous model. The proposed model includes the effect of chemical degradation of sugars.

For a pseudo-homogeneous model, the mass balance of B in a batch reactor can be written as

$$\frac{dC_B}{dt} = -k_{hyd} C_{H_2O}^l C_B^m, \quad (4)$$

while the mass balance of D can be written as

$$\frac{dC_D}{dt} = k_{hyd} C_{H_2O}^l C_B^m - k_{deg} C_D^n. \quad (5)$$

During the reaction, the amount of H_2O is assumed to be constant, so equation (4) can be simplified as

$$\frac{dC_B}{dt} = -k_{hyd} C_B^m, \quad (6)$$

while equation (5) can be simplified as

$$\frac{dC_D}{dt} = k_{hyd} C_B^m - k_{deg} C_D^n, \quad (7)$$

where,

$$k_{hyd} = k_{hyd} C_{H_2O}^l. \quad (8)$$

The reaction rate constants, k_{hyd} and k_{deg} , are influenced by the temperatures. Those constants are then be correlated by the Arrhenius's equations [12], as follows

$$k_{hyd} = A_{hyd} \exp\left(\frac{-E_{hyd}}{RT}\right), \quad (9)$$

and

$$k_{deg} = A_{deg} \exp\left(\frac{-E_{deg}}{RT}\right). \quad (10)$$

For non-isothermal condition, the correlation between temperature and time is needed. The correlation are modeled by the equation of

$$T = T_o + at^b, \quad (11)$$

where a and b are constant.

III. EXPERIMENT

The hydrolysis of rice husk was conducted in an autoclave with the volume of approximately 2 L, equipped with an electric heater and a temperature controller, and continuously shaken during the operation.

Initially, 1 L of 0.18 N sulfuric acid solution and 300 g of 20 mesh rice husk were put in the autoclave, and then the autoclave was perfectly closed. The heater was turned on as well as the temperature controller. As a result, the temperature increased and when it reached 140 °C, the time was taken as zero, and sample (7 cm³) was taken through sample outlet pipe. As temperature reached a certain value, the temperature was then kept constant as the final temperature. The reaction was expected to be at constant temperature (isothermal), but before that temperature was achieved, reaction has occurred. During the process, every 5 minute interval, the temperature was recorded and sample was taken. The sugars concentrations in the samples were then analyzed by Fehling method. The experiment was conducted with various final temperatures, i.e. 160 °C, 180 °C, 200 °C, and 220 °C. The experiment resulted in the data of temperatures and sugar concentrations at various times. Prior to fermentation, the hydrolyzate was detoxified to eliminate inhibitor compounds and neutralized (pH of 7). Those processes were carried out by addition of $Ca(OH)_2$, alum, and activated carbon, followed by filtration. The filtrate was then fermented using *Saccharomyces cerevisiae* for 5 x 24 hours. The ethanol concentration was analyzed by GC (gas chromatography) method.

IV. RESULT AND DISCUSSION

The experiment provided data of temperatures (T) and total sugars concentrations (C_D) at various times (t) for four runs (final temperatures of 160 °C, 180 °C, 200 °C, and 220 °C). The experimental data are shown in Table II, III, IV, and V, as well as in Fig. 1, 2, 3, and 4. Empirical equations were then set up to correlate the temperature and time for each run. The results are as follows:

Run 1: Before reaching 160 °C:

$$T = 140 + 8.395 t^{0.6781} \quad (12a)$$

and then be constant at 160 °C.

Run 2: Before reaching 180 °C:

$$T = 140 + 8.395 t^{0.6781} \quad (12b)$$

and then be constant at 180 °C.

Run 3: Before reaching 200 °C:

$$T = 140 + 6.928 t^{0.8091} \quad (12c)$$

and then be constant at 200 °C.

Run 4: Before reaching 220 °C:

$$T = 413 + 7.101 t^{0.8174} \quad (12d)$$

and then be constant at 220 °C.

The data and empirical equation (12) were then applied to verify the kinetics model as well as to evaluate the values of A_{hyd} , E_{hyd} , A_{deg} , and E_{deg} by using curve-fitting method. For a set of values of m , n , A_{hyd} , E_{hyd} , A_{deg} , and E_{deg} , the values of C_D can be calculated based on equations of (6), (7), (9), (10), and (12). Since (6) and (7) are differential equations, those equations need to be solved. The Runge-Kutta method was applied. The chosen values were the ones giving the minimum values of the Sum of Squares of Error (SSE) for run data. The SSE was defined as

$$SSE = \sum (C_{D\text{ calc}} - C_{D\text{ data}})^2 \quad (13)$$

It was then obtained the value of A_{hyd} , E_{hyd} , A_{deg} , and E_{deg} for each run data. The values were listed in Table I.

TABLE I
VALUES OF KINETIC PARAMETER

T (°C)	Hydrolysis		Sugar Degradation	
	A_{hyd} (1/min)	E_{hyd} (J/mole)	A_{deg} (L/mole/min)	E_{deg} (J/mole)
160	169,860	64,350	22,853,198	76,571
180	146,970	64,350	22,853,198	76,571
200	158,370	64,350	22,853,198	76,571
220	158,370	64,350	22,853,198	76,571

In this case, the value of m (order of reaction for hydrolysis) was chosen to be 1 and the value of n (order of reaction for sugars degradation) was 2. Activation energy to sugar degradation is relatively higher than to hydrolysis. This is an indication that sugar degradation is more sensitive to temperature than to hydrolysis.

The values of kinetic parameter that were listed in Table I just can be applied for the arbitrary range of temperatures. From Table I, the values of E_{hyd} , A_{deg} , and E_{deg} were constant. However, the values of A_{hyd} were not constant. Therefore, the values of kinetic parameter were recalculated in order to obtain the single values of A_{hyd} , E_{hyd} , A_{deg} , and E_{deg} for all runs data. The chosen values of A_{hyd} , E_{hyd} , A_{deg} , and E_{deg} were the ones giving the minimum values of the Sum of Squares of Error (SSE) for all runs data. From the result of recalculation, it was found that the value of $A_{hyd} = 1.58 \times 10^5$ 1/min, $E_{hyd} =$

64,350 J/mole, $A_{deg} = 2.29 \times 10^8$ mole/L/min, and $E_{deg} = 76,571$ J/mole. These kinetic parameters can be applied for all temperatures. The values of calculated C_D were shown in Table II, III, IV, and V as well as in Fig. 1, 2, 3, and 4.

TABLE II
SUGAR CONCENTRATION AND TEMPERATURE
AT VARIOUS TIMES
(RUN 1: FINAL TEMPERATURE = 160 °C)

Time (min)	Temperature (°C)		Total Sugar Concentration (mole/L)	
	Data	Calc.	Data	Calc.
0	140	140	0.115	0.115
5	160	160	0.120	0.121
10	160	160	0.130	0.128
15	160	160	0.137	0.135
20	160	160	0.145	0.141
25	160	160	0.150	0.147
30	160	160	0.156	0.154
35	160	160	0.160	0.159

TABLE III
SUGAR CONCENTRATION AND TEMPERATURE
AT VARIOUS TIMES
(RUN 2: FINAL TEMPERATURE = 180 °C)

Time (min)	Temperature (°C)		Total Sugar Concentration (mole/L)	
	Data	Calc.	Data	Calc.
0	140	140	0.114	0.114
5	165	165	0.120	0.121
10	180	180	0.133	0.134
15	180	180	0.145	0.148
20	180	180	0.156	0.160
25	180	180	0.167	0.172
30	180	180	0.175	0.182
35	180	180	0.186	0.191

TABLE IV
SUGAR CONCENTRATION AND TEMPERATURE
AT VARIOUS TIMES
(RUN 3: FINAL TEMPERATURE = 200 °C)

Time (min)	Temperature (°C)		Total Sugar Concentration (mole/L)	
	Data	Calc.	Data	Calc.
0	140	140	0.115	0.115
5	165	166	0.121	0.122
10	187	185	0.136	0.136
15	200	200	0.155	0.160
20	200	200	0.175	0.181
25	200	200	0.195	0.197
30	200	200	0.200	0.209
35	200	200	0.215	0.218

TABLE V
SUGAR CONCENTRATION AND TEMPERATURE
AT VARIOUS TIMES
(RUN 4: FINAL TEMPERATURE = 220 °C)

Time (min)	Temperature (°C)		Total Sugar Concentration (mole/L)	
	Data	Calc.	Data	Calc.
0	140	140	0.115	0.115
5	166	166	0.121	0.122
10	188	187	0.141	0.136
15	206	205	0.159	0.161
20	220	220	0.183	0.191
25	220	220	0.212	0.210
30	220	220	0.218	0.218
35	220	220	0.221	0.219

At run 1 (Fig. 1) and run 2 (Fig. 2), the curve shows that until 35 minutes of reaction the total sugars concentration (C_D) tends to increase. These data show that the degradation of sugars has not existed. However, at run 3 (Fig. 3) and run 4 (Fig. 4), it can be seen that after 30 minutes of reaction, the concentration of total sugars decreases. This phenomenon implies that sugar degradation was encountered. Those figures also show that the highest sugar concentrations achieved for each run were 0.165 mole/L, 0.186 mole/L, 0.215 mole/L, and 0.221 mole/L, respectively.

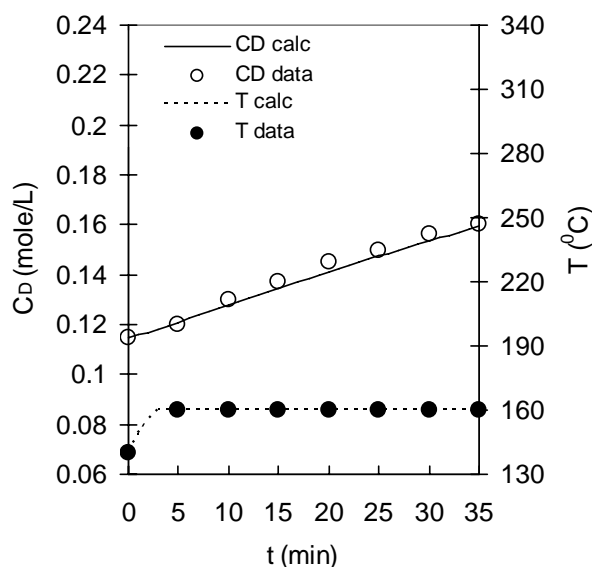


Fig. 1 Plot of C_D and T vs time at final temperature 160 °C

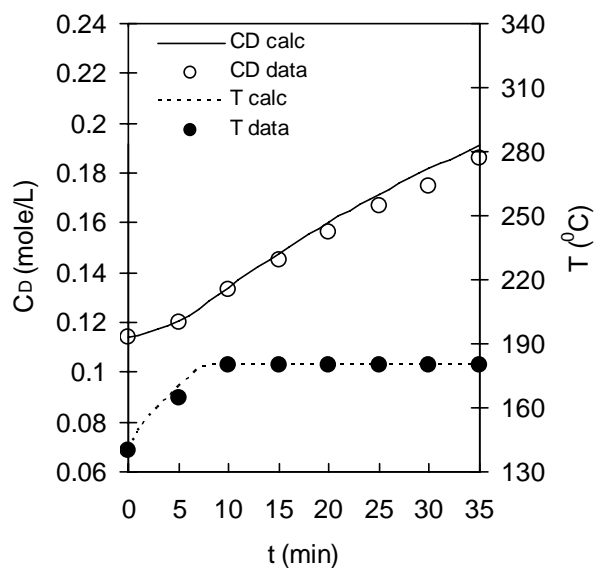


Fig. 2 Plot of C_D and T vs time at final temperature 180 °C

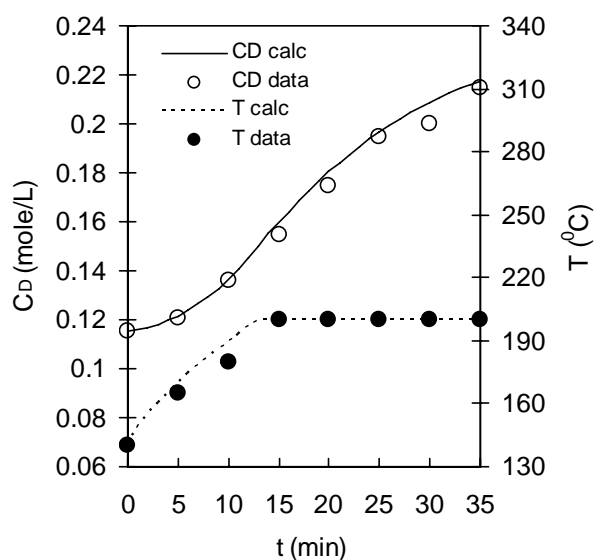


Fig. 3 Plot of C_D and T vs time at final temperature 200 °C

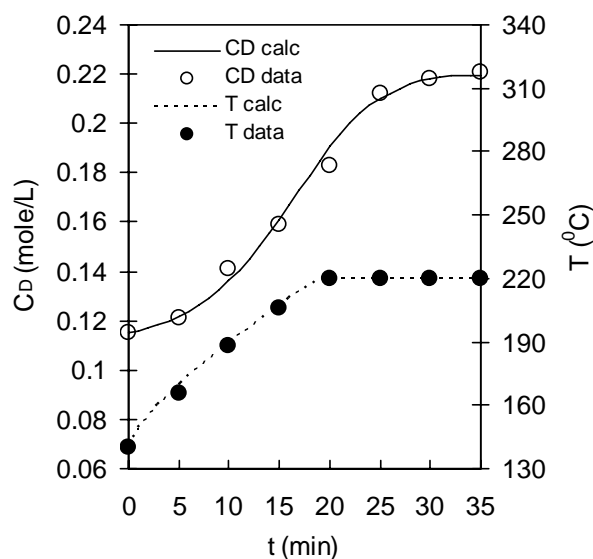


Fig. 4 Plot of C_D and T vs time at final temperature 220°C

The values of kinetic parameters obtained were in good agreement with the ones from other investigators. Cendrowska [9] reported that hydrolysis of lignocellulosic materials of forest and agricultural biomass follows a pseudo first order homogeneous reaction with activation energy of 76.6 kJ/mole and 68.9 kJ/mole, respectively. Hydrolysis of lignocellulosic materials of corn cob and sunflower seed hull were investigated by Saracoglu *et al.* [10], and it turned out that the values of activation energy were 80.34 kJ/mole and 78.35 kJ/mole, respectively. Study on hydrolysis of corn fiber (a co-product of corn wet-milling) by Mosier *et al.* [11] results in E_a of 72.6 ± 22.5 kJ/mole.

Sugar yield resulted from this research was around 38.16 g / 300 g raw materials (12.72% of raw materials). It was achieved at final temperature of 220°C , catalyst concentration of 0.18 N (0.5%). The acid hydrolysis of oil palm empty fruit bunch with acid concentration of 2 – 6% yields sugars of 31.74% [13]. A study on concentrated acid conversion of pine sawdust to sugars was conducted by Miller and Hester [14] and results in optimum condition at acid concentration of 30% and temperature of 130°C , with the sugars yield was about 50%. This comparison suggests that higher yield of sugar can be obtained by higher concentration of acid. Further studies on hydrolysis at higher acid concentration are in progress.

Ethanol yields from sugar at fermentation are listed in Table VI. It can be observed that as the catalyst concentration increases, the ethanol concentration also increases. The maximum ethanol concentration was 1.13 % v/v indicating 89.9% yield. The result of ethanol yield of this research is promising. Latif and Rajoka [15] conducted the simultaneous and saccharification and fermentation (SSF) of corn cobs using *Saccharomyces cerevisiae* and *Candida tropicalis*, with 50 g/L substrate, produced ethanol with yield 0.42 g/g (2.1 %

v/v and 82.2% yield) and 0.363 g/g (1.8 % v/v and 71.0% yield) for fermentation using *Saccharomyces cerevisiae* and *Candida tropicalis*, respectively. Fermentation of glucose-xylose mixtures of lignocellulosic biomass using *Saccharomyces cerevisiae* also had been researched by Govindaswamy and Vane [16], with 50.1 g/L initial glucose, result in yield of 0.49 g/g (2.5% v/v and 95.9% yield).

TABLE VI
ETHANOL CONCENTRATION

Final Temperature ($^\circ\text{C}$)	Ethanol Concentration (% v/v)	
160	Sample 1	0.2766
	Sample 2	0.3259
180	Sample 1	0.6204
	Sample 2	0.8798
200	Sample 1	0.6688
	Sample 2	0.8902
220	Sample 1	1.1832
	Sample 2	1.1319

V.CONCLUSION

The kinetic of dilute acid hydrolysis of rice husk can be quantitatively described the kinetic by pseudo first order homogeneous reaction. Sugar degradation is encountered, and it can be modeled by pseudo second order homogeneous reaction. Kinetics constants can be expressed by Arrhenius equation, with the frequency factors of 1.58×10^5 1/min and 2.29×10^8 mole/L/min, for hydrolysis and sugar degradation, respectively. The energy activations for hydrolysis and sugar degradation are 64,350 J/mole and 76,571 J/mole, respectively. The temperature strongly influences total sugars concentration. However, sugar degradation will start to exist at temperature of above 200°C and reaction time of above 30 minutes. The highest ethanol concentration in fermentation product using *Sachharomyces cerevisiae* is 1.13%, attained at final temperature of 220°C .

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