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Article

Kinetic models of candle shell alkaline hydrolysis in obtaining oxalic acid

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Abstract

The kinetic reaction of alkaline hydrolysis of candlenut shells to produce oxalic acid was investigated. It was performed for the non-catalyzed solid-liquid heterogeneous reaction in a range time of 30 to 90 minutes and temperature of 60°C to 90°C. This study showed that the reaction fitted the pseudo-first-order model, confirmed from the determinant coefficient value of 0.9182 to 0.9751, and the kinetic constant, evaluated using Arrhenius' law, was $k= 0.034751\ e^{(-140.23/T)}$. The rate control mechanism based on the shrinking core model was diffusion control, validated from determinant coefficient near one, from 0.9246 to 0.9766.

Keywords: Alkaline hydrolysis, candlenut, kinetic reaction, oxalic acid, shrinking core model.

1. Introduction

Candlenut (*Aleurites moluccana*) is an annual plant that spreads in tropical areas such as Indonesia. This plant has a kernel, used as a flavor of cooks and as a raw material in medicine and vegetable oil production. With its various benefits, the production of candlenut kernel tends to increase every year [1]. However, it has a rigid and thick shell that is commonly underutilized, and dominant becomes an agricultural waste. Of course, the increase in kernels production followed by the increased production in candlenut shells too, which cause environmental problems if not handled properly. Meanwhile, it can be used further due to its high cellulose content.

On the other hand, oxalic acid, a chemical that plays a role in many industries such as the textile, pharmaceutical, marble, metal, and rare-earth industries [2]–[4], has a market demand that increases every year. This compound is the simplest dicarboxylic acid, characterized as a strong acid, soluble in water, odorless and colorless [2]. The anhydrous form of this acid is not available in nature. This acid can be synthesized in several ways, such as through the hydrolysis reaction of cellulose using alkaline [3]. The manufacture of oxalic acid with this method occurs in several stages before finally obtaining the desired acid product, namely the degradation stage of cellulose contained in the raw material, filtering, precipitation, and acidification stages [5], [6]. This method has been applied previously for oxalic acid production from bagasse [7], rice husks [5], and teak wood powder [8], but to the best of our knowledge, it has not been used for candlenut shells.

Therefore, in this study, the manufacture of oxalic acid from candlenut shells was carried out by hydrolysis using alkaline sodium hydroxide. This study aimed to develop the reactions kinetic that occurred during the hydrolysis of candlenut shells. The development of kinetic is vital to know the rate reaction and understand the mechanism.

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In the hydrolysis of candlenut shells, because the reaction involved two phases, solid and liquid, the kinetics development was carried out with the assumption that the reaction was a non-catalyzed solid-liquid heterogeneous reaction where cellulose of candlenut was considered to act as the reactant. The processes in heterogeneous reactions are more complex than homogeneous reactions because many factors need to be considered, including the contact pattern. Many models have been developed to investigate the processes that occur in heterogeneous reactions, one of which is the shrinking core model, which Yagi and Kuni first introduced. This model has been widely used in describing heterogeneous reactions. Levenspiel [9] provided an example of this model describing a gas-solid heterogeneous system. Although the example of shrinking core modeling given was for a gas-solid heterogeneous system, several other studies [10]–[14] have shown that the shrinking core model also could be applied in a solid-liquid heterogeneous system. Therefore, we used the shrinking core model to investigate the reaction mechanism, besides supporting the order model reaction.

2. Materials and Methods

2.1. Materials

The primary material in this study was candlenut shells obtained from Jember, East Java. It was dried in the sunlight then mashed and filtered using a 100-mesh sieve. For initial information, the cellulose content in candlenut shells was investigated through gravimetric analysis in the Energy and Environmental Laboratory of LPPM ITS referred to [15]. The chemicals used were NaOH, H_2SO_4, $CaCl_2$, and $KMnO_4$ obtained from a local chemical store in Surabaya.

2.2. The production of oxalic acid

The first step of the oxalic acid production was dissolving 25 gr of candlenut shell powder into 250 ml of 1.8N NaOH solution in a three-neck flask 500 ml, heated, and stirred using a heating mantle and stirring motor with 300 rpm for 30 minutes at the temperature of 60°C. The process was run out in a system as given in Figure 1. After that, the solution was cooled and filtered, then $CaCl_2$ was added to the filtrate to get the precipitation which was further processed by the acidification through mixing in 100 ml of 4N H_2SO_4. Then, the acidification process mixture was filtered, and the filtrate obtained was stored for analysis. The procedures were replicated for the other time and temperature variation of candlenut shell powder dissolution in NaOH. The time variations were 30, 45, 60, 75, and 90 minutes, and the temperature variations were 60, 70, 80, 90, and 100°C.

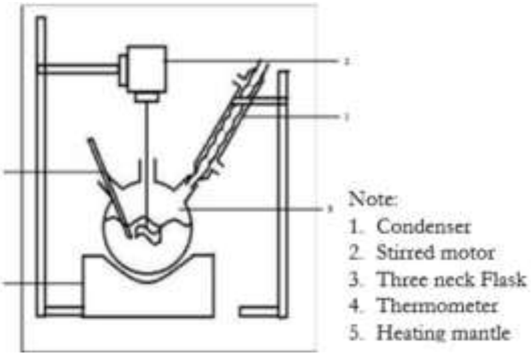

Fig. 1. The set-up of hydrolysis equipment

2.3. Oxalic acid analysis

The level of oxalic acid in the product was analyzed using the permanganate titration method. 10 ml of the product was mixed with 5 ml of concentrated H_2SO_4 solution in an Erlenmeyer. The mixture was heated to a temperature of 75°C. Then, the sample solution was titrated with 0.1N potassium permanganate at this temperature until the solution turned pink.

2.4. Kinetic order models

Kinetic order or reaction power modeling in this study adopted the kinetic modeling described by Levenspiel. In this case, the hydrolysis reaction of cellulose using sodium hydroxide was assumed simply as the following:

$$C + B \rightarrow product$$

with the rate derivation equation

$$-r_C = -\frac{dC_C}{dt} = -\frac{dC_B}{dt} = kC_C C_B$$

$$-r_C = -C_{C0}\frac{dX_C}{dt}$$

$$-r_C = k\left(C_{Co} - C_{Co}X_C\right)\left(C_{Bo} - C_{Co}X_C\right) \quad (1)$$

The first kinetic model tested was assumed that C_{BO} was much larger than C_{CO}, and the changing of C_B was not significant or almost constant over time. Thus, the derivation of the kinetic equation 1 after the arrangement approached model equation 2.

$$-\ln\left(1 - X_C\right) = kt \quad (2)$$

In this case, the equation model was referred to as **pseudo first-order**, a second-order reaction that behaves like a first order.

The next order kinetic model tested was assumed that C_{BO} was the same as C_{CO}. Hence, the reaction kinetics equation could be derived as model equation 3, namely the **second-order kinetic model**.

$$\frac{X_C}{1 - X_C} = C_{CO}kt \quad (3)$$

The adequacy of each model was analyzed from the value of the determinant coefficient (R^2) of the linear regression results.

Because the reaction phenomenon depended on temperature, the rate constant was evaluated using the Arrhenius' equation as defined in equation 4.

$$k = k_O e^{-E/RT} \quad (4)$$

Where k_o is collision frequency constant, E is the activation energy, T is temperature (K), and R is of ideal gas constant (8.314 J/mol.°K). Linearization of these equations can be depicted as in equation 5.

$$\ln k = \ln k_O - \frac{E}{RT} \quad (5)$$

The linear plot of ln k versus 1/T could obtain the value of the activation energy and the collision frequency constant.

2.5. Rate controlling mechanism

The proposed rate control mechanism was the shrinking core model referred to the model offered by Levenspiel [9], with assumptions as the particle was spherical and uniform in size where the size radially changed over time; the core composition was considered constant; the hydrolysis phenomenon took place on the solid surface; the residue obtained from the hydrolysis reaction of cellulose was supposed to be the unreacted core of particles. Besides, the product lost at the separation and precipitation was assumed insignificant. Thus, the models were as in equations 6 and 7, namely the diffusion control rate equation, D(x), and the control reaction, R(x), as a function of cellulose conversion, Xc.

Diffusion control, $D(x) = 1 - \left(1 - X_C\right)^{\frac{2}{3}}$ (6)

Reaction control, $R(x) = 1 - \left(1 - X_C\right)^{\frac{1}{3}}$ (7)

The appropriateness of these models was evaluated from the coefficient determinant.

3. Results and Discussion

3.1. Oxalic acid production from cellulose with alkaline treatment

Oxalic acid production from candlenut shells has been carried out using an alkaline treatment, NaOH. In this case, the candlenut shell component considered as a reactant was cellulose. Its content was about 23.78% based on the analysis result. In an alkaline solution, cellulose can undergo the hydrolysis process, the degradation of cellulose through the scission of glycosidic bonds resulting in the new end groups [16][17]. The method of oxalic acid making through alkaline hydrolysis was followed by several stages of separation viz filtering the results of the hydrolysis reaction followed by the precipitation step by adding $CaCl_2$ into the filtrate to form calcium oxalate deposits. Furthermore, the residue was solved in the H_2SO_4 solution to obtain the oxalic acid solution and deposition of calcium sulfate. Then, the oxalic acid was separated from the precipitated calcium sulfate through a filtration process. The filtrate was later analyzed to determine the oxalic acid product obtained.

This research data was provided in Figure 2 as a function of the cellulose conversion to oxalic acid at various times and temperatures. Based on the graph, the effect of time (t, minute) and temperature hydrolysis (T, °C) on the oxalic acid product could be analyzed. The increase of

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hydrolysis reaction time from 30 minutes to 90 minutes led to the incline cellulose conversion to oxalic acid. This tendency occurred in all temperature variations used. The phenomenon of increased conversion occurred because the increase in reaction time could cause an increase in the number of collisions between reactant particles.

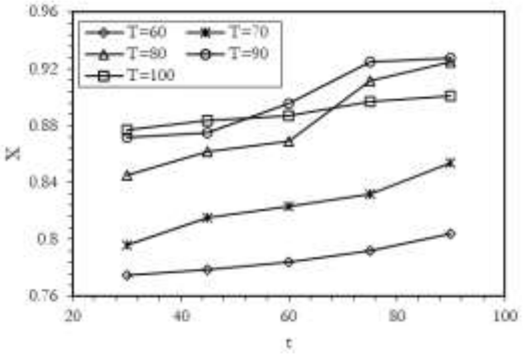

Fig. 2. The graph of cellulose conversion to oxalic acid versus time at various temperature.

Meanwhile, the temperature enhancement from 60°C to 90°C caused an increase in conversion (X, %) in all variation times. However, increasing the hydrolysis temperature from 90°C to 100°C with a reaction time of 60 minutes to 90 minutes resulted in a decreasing graph. The increase in conversion due to the temperature increment was possible because the temperature could accelerate the movement of the particles so that more collisions number between reactant particles might happen. However, an increase in temperature that was too high for a longer time could cause a tendency to increase the rate of evaporation of NaOH solution that was greater than the speed of collision between that solution's particles and cellulose so that the resulting conversion decreased. Besides, this condition could also damage the product and produce unwanted side products.

3.2. Model fitting of reaction kinetic order

Kinetic modeling is a subdivision of chemical engineering essential in investigating reaction phenomena. By modeling the kinetics of a reaction, the kinetic constant of the reaction rate can be obtained. The kinetic models tested in this study were pseudo first-order and second-order models. The former model estimated the NaOH was an excess, so the reaction rate depended only on the cellulose concentration. The latter model assumed the concentration of cellulose and NaOH were equal. The fitting test of the two models was provided in Figures 3 and 4, respectively. The figures pointed that generally, both models adjusted the experimental point on various temperature variables used. However, in the comparative results of linear regression, the determinant coefficient of the pseudo first-order model was higher than the value of the second-order model (Table 1). Thus, the pseudo first-order model was more appropriate in representing the hydrolysis reaction of cellulose in NaOH solution. Loon and Glaus [17] also modeled the hydrolysis of cellulose in alkaline as pseudo first-order. On the other hand, Wen [18] mentioned that the pseudo model fitted with the heterogenous solid-gas system. Still, he added that it lacked accuracy for a solid-liquid system. Nevertheless, the analysis parameter of this study showed that the pseudo first-order model could also represent the heterogenous solid-liquid system.

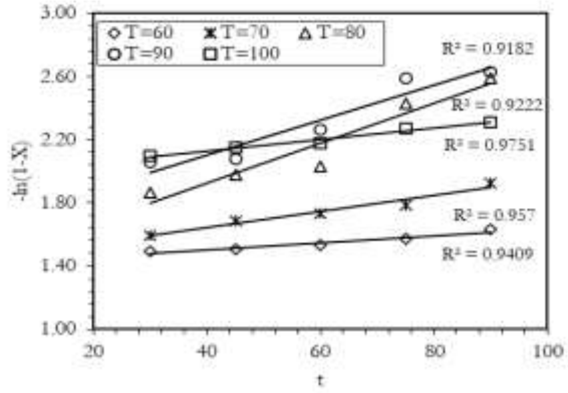

Fig. 3. Fitting for pseudo first-order

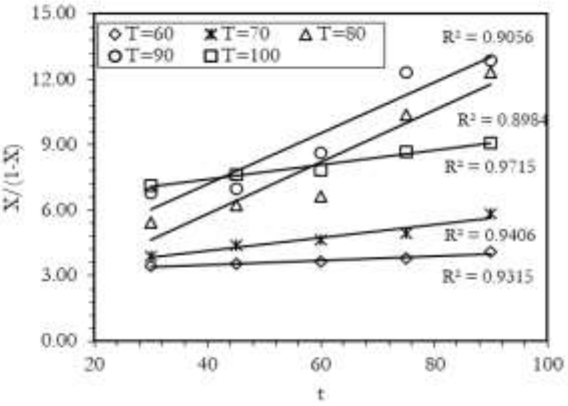

Fig. 4. Fitting for second-order

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Table 1. Determinant coefficient of the kinetic model

T (°C)	R^2 of first-order	R^2 of second-order
60	0.9409	0.9315
70	0.9570	0.9406
80	0.9222	0.8984
90	0.9182	0.9056
100	0.9751	0.9715

The kinetic rate constant obtained from the pseudo first-order model, which was the slope of the graph at each temperature, was applied to the Arrhenius' law. The plot of Arrhenius' equation generated the trend as in Figure 5. Based on the linear equation formed from that graph, the slope (-E/R) value was -140.23, and the intercept (ln ko) was -3.3595. Thus, the collision frequency constant (ko) value was 0.034751. Accordingly, the evaluating result of the kinetic constant, k, as a function of temperature could be written as in equation 8.

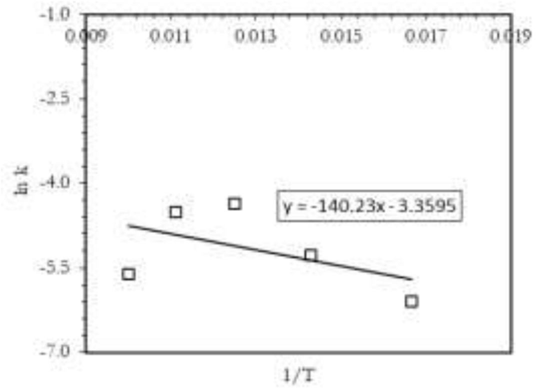

Fig. 5. Graph of Arrhenius' law

$$k = 0.034751\, e^{-140.23/T} \tag{8}$$

3.3. Fitting of rate-controlling mechanism

The slowest step plays a role as the rate-controlling mechanism. Here the shrinking core model for solid-liquid particles changing in sizes has been created to determine the rate-controlling mechanism of the process in this study. The model was displayed in Figures 6 and 7, called diffusion control and reaction control. The graph in those figures showed that the linearization of the model generally passed through the experimental data points. It meant that the shrinking core model could represent the phenomenon. The further analysis showed that the diffusion control had a higher value of the coefficient of determination than reaction control (Table 2), which meant the rate-controlling mechanism of the hydrolysis reaction of cellulose using sodium hydroxide, in this case, was diffusion control. Levenspiel [9] stated that many parameters affected the resistance for diffusion control, such as particle dimension and fluid properties. Besides, Yasar [9] mentioned that a diffusion-controlled reaction was affected by the complex morphology of the surface structure that restricts the process of transport phenomena. It was acceptable for this study as the candlenut shell has a rigid structure that became resistant to the reaction.

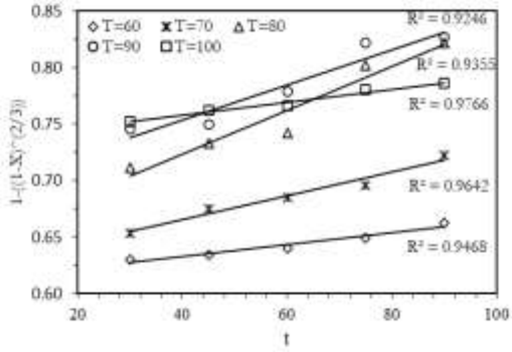

Fig. 6. Diffusion control approaching

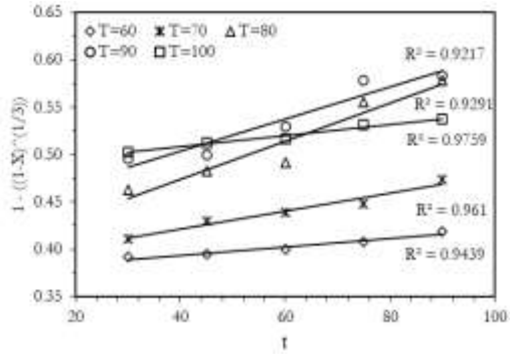

Fig. 7. Reaction control approaching

Table 2. Determinant coefficient of rate controlling mechanism

T (°C)	R^2 Diffusion control	R^2 Reaction control
60	0.9468	0.9439
70	0.9642	0.9610
80	0.9355	0.9291
90	0.9246	0.9217
100	0.9766	0.9759

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4. Conclusions

In order to solve the environmental issue due to the existence of candlenut shells, alkaline hydrolysis was carried out to produce oxalic acid. The kinetic investigation was performed for the non-catalyzed solid-liquid heterogeneous reaction in a range time of 30 to 90 minutes and temperature of 60 °C to 90 °C. The results showed that the reaction followed the pseudo-first-order model, confirmed from the determinant coefficient value of 0.9182 to 0.9751, where the kinetic constant evaluated based on Arrhenius' law was k= 0.034751 e^(-140.23/T). The rate control mechanism based on the shrinking core model was diffusion control, validated from determinant coefficient near one, from 0.9246 to 0.9766.

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