



Heterogeneous Reaction Model for Evaluating the Kinetics of Levulinic Acid Synthesis from Pretreated Sugarcane Bagasse

Meutia Ermina Toif^{1,2}, Muslikhin Hidayat², Rochmadi², Arief Budiman^{2,3*}

¹LPP Agro Nusantara, Jalan LPP No. 1 Yogyakarta 55222, Indonesia

²Chemical Engineering Department, Faculty of Engineering, Universitas Gadjah Mada, Jalan Grafika No. 2, Yogyakarta 55166, Indonesia

³Master Program in System Engineering, Universitas Gadjah Mada, Jalan Teknik Utara No. 3, Yogyakarta 55281, Indonesia

Abstract. The abundance of sugarcane bagasse, a by-product of sugarcane juice extraction in sugar factories, serves as an advantage of its potential for producing chemicals such as levulinic acid (LA). Levulinic acid contains carbonyl and carboxyl groups that can be utilized for many applications, such as pharmacies, cosmetics, and solvents. Bagasse hydrolysis into LA was preceded by alkaline-acid pretreatment to separate cellulose from hemicellulose and lignin. This treatment could minimize the disturbance of these unwanted components, so that LA synthesis would be more optimal. Pretreated bagasse contained 82.64% cellulose, about two-fold from the non-pretreated one. It was hydrolyzed with hydrochloric acid (HCl), which acts as a catalyst (a Bronsted acid), at 150-170 °C, 0.1-1 M catalyst concentration, 1-10% solid-to-liquid (cellulose:catalyst-solution) ratio, and 0-200 minutes reaction time. The range of LA yield values obtained in the study were between 15-64.05%. The maximum LA yield was obtained at a temperature of 160 °C, 1 M catalyst concentration, and 1% solid-to-liquid ratio. The high LA yield indicates the importance of pretreatment supported by optimal conditions of synthetic reaction. The reaction route involved in hydrolysis was cellulose-glucose-levoglucosan (LG)-hydroxymethylfurfural (HMF)-LA. The result exhibits that temperature and catalyst concentration do not significantly affect the maximum potential LA yield. However, higher temperatures and catalyst concentration can accelerate the time to achieve the maximum potential LA yield. Meanwhile, the LA yield increases with a lower solid-to-liquid ratio. In contrast to previous studies, this study evaluated the reaction model in a more precise way using combination of models, considering that the reaction occurs between solid and liquid. The heterogeneous reaction model, namely the shrinking core model (SCM) for cellulose conversion to glucose and the first-order homogeneous reaction model for glucose to LA reaction, give good fitting results. The more appropriate reaction model is expected to be the basis of scale-up process carried out for industry one day. The results of this research have the potential to be applied for various other biomass raw materials with some improvements based on their characteristics which can be studied in the future.

Keywords: Heterogeneous reaction model; Hydrolysis; Levulinic acid; Pretreatment; Sugarcane bagasse

*Corresponding author's email: abudiman@ugm.ac.id, Tel.: +62-274-555320; Fax: +62-274-555320
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1. Introduction

Indonesia is ranked among the top ten sugarcane-producing countries. Sugarcane is cultivated to produce sugar through the extraction of sucrose. In Indonesia, 63 existing sugar factories are owned by 18 companies with a total production capacity of 245,000 tons of cane per day (TCD). During the sugarcane milling, the sugar factories also produce a bagasse residue for 140 kg per ton of sugarcane (Sulaiman *et al.*, 2019). Hence, the total amount of bagasse generated is estimated up to 43.3 million tons per day. Due to its abundance, bagasse has an attractive potential to be converted into more precious substances. Bagasse, a lignocellulosic biomass, is now being developed into chemicals such as LA. Levulinic acid (C₅H₈O₃) contains carbonyl and carboxyl functional groups with high reactivity for reactions such as esterification, redox, substitution, and condensation to produce other valuable compounds (Maity, 2015).

Bagasse comprises 44% cellulose, 27% hemicellulose, 13% lignin, and 16% others (Behnood *et al.*, 2016). Cellulose is the primary component for LA synthesis, so the bagasse needs to be pretreated to remove undesired components. Furthermore, pretreatment is essential to optimize biomass processing (Hamzah *et al.*, 2019; Hermansyah *et al.*, 2019). Nevertheless, several previous studies have reported the conversion of *Pennisetum alopecuroides* (Yuan *et al.*, 2016), corncobs (Qing *et al.*, 2018), and hazelnut shells (Ozsen, 2020) directly into LA without any pretreatment. Meanwhile, other studies have conducted pretreatment for LA synthesis from biomass. However, Jeong *et al.* (2017) could only dissolve hemicellulose by acid pretreatment, leaving lignin intact in the converted *Quercus mongolica*. On the other hand, Siregar, Saepudin, and Krisnandi (2020) performed dewaxing followed by delignification for sorghum bicolor biomass, but there was still some hemicellulose present. Consequently, the raw materials still contained undesired components that might interfere with the hydrolysis process, making the LA yield not optimal. In this study, the chosen pretreatment method is combined alkaline-acid pretreatment due to its ability to dissolve both lignin and hemicellulose in bagasse for obtaining high-purity cellulose that will be beneficial for further processing. The resulting solid cellulose will be hydrolyzed to LA with a liquid HCl catalyst (a Bronsted acid).

Previous researchers (Qing *et al.*, 2018; Zhi *et al.*, 2015; Dussan *et al.*, 2013) proposed a first-order homogeneous reaction model for the entire sequence of biomass hydrolysis reactions leading to LA (biomass-glucose-LG-HMF-LA). This is despite the fact that the reaction occurs between a solid reactant (biomass) and a liquid catalyst, which is commonly known as a heterogeneous reaction. Therefore, this research will evaluate the reaction kinetics differently by assuming a heterogeneous reaction model. The first part, the conversion of cellulose into glucose (heterogeneous reaction), will be observed by using the shrinking core model (SCM), a type of heterogeneous reaction model. While the second part, the decomposition of glucose into LA (homogeneous reaction), will be studied using a first-order homogeneous reaction model. In addition, the effects of temperature, catalyst concentration, and solid-to-liquid ratio on the LA yield are also observed.

2. Methods

2.1. Materials

The materials used included: (1) sugarcane bagasse from PT. PG. (Pabrik Gula / Sugar Factory) Madubaru Yogyakarta and PG. Pagottan Madiun Indonesia, (2) glucose, sodium hydroxide (NaOH), 50% hydrogen peroxide (H₂O₂), and 37% hydrochloric acid (HCl) obtained from Merck, and (3) LG, HMF, and LA purchased from Sigma Aldrich.

2.2. Sugarcane Bagasse Characterization

Bagasse characterization to determine the composition of cellulose, hemicellulose, and lignin was carried out by using Van Soest Method at the Center Study for Starch Technology, Agency for the Assessment and Application of Technology (BPPT), Lampung Indonesia.

2.3. Levulinic Acid Preparation Method

The levulinic acid preparation method from sugarcane bagasse observed in this research is summarized in Figure 1. The first stage of LA synthesis from bagasse is pretreatment. Initially, bagasse was washed, dried, and crushed using a blender. Next, bagasse was reacted with 5 wt% NaOH solution at 75 °C under constant stirring for 1.5 hours with a NaOH solution and bagasse weight ratio of 10:1. The resulting bagasse pulp was washed with water until a neutral pH was reached. Then, bleaching was carried out by reacting 5 wt% H₂O₂ under alkaline (adding NaOH solution until the pH reached 11) with bagasse pulp by following the same reaction conditions as the previous step. The bleached pulp was filtered using a vacuum filter and then dried. The dry pulp was crushed using a blender to produce cellulose as a raw material for the hydrolysis reaction's second stage.



Figure 1 Levulinic acid preparation method from sugarcane bagasse

The experimental setup scheme of cellulose hydrolysis to LA is illustrated in Figure 2. Cellulose obtained from bagasse pretreatment and an HCl catalyst was added to the reactor consisting of a glass tube containing some small stirring balls enclosed in a stainless steel tube for safety consideration. The reactor was placed in a shaking oil bath and heated to the desired temperature. After reaching a particular time, the reactor was cooled down to room temperature. The reaction products were separated using filter paper to obtain the filtrate containing LA and the remaining solid as residue.

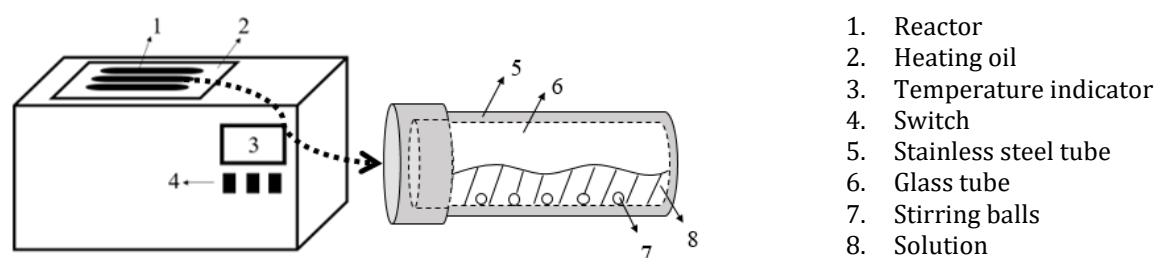


Figure 2 The experimental setup scheme of cellulose hydrolysis to LA (Toif *et al.*, 2021)

2.4. Analysis

The products were analyzed using High-Performance Liquid Chromatography (HPLC) to determine the concentration of glucose, LG, HMF, and LA in the liquid filtrate. Waters Nova-Pak C18 column was used with a refractive index detector. Analysis was performed at 30 °C by using 5 mM sulfuric acid with a flow rate of 0.6 cm³/minute as a mobile phase.

2.5. Modelling

The catalytic degradation of biomass for LA synthesis is challenging to perfectly analyze. Figure 3 shows a simplified scheme of cellulose conversion to LA.

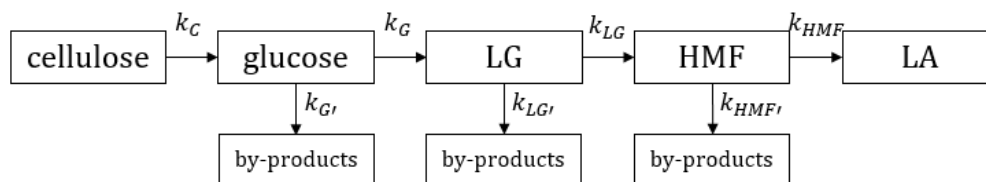


Figure 3 Simplified reaction scheme of cellulose hydrolysis to LA

In the kinetic model evaluation, several assumptions were taken: (1) LA is only formed from cellulose; (2) LA is the final product; (3) by-products have resulted from glucose, LG, and HMF; (4) internal diffusion is negligible; (4) model used is the heterogeneous reaction model, namely SCM for conversion of cellulose to glucose and first-order homogeneous reaction model for glucose to LA reaction. To confirm the negligible impact of internal diffusion, we evaluated the Weisz-Prater parameter following the approach described by Fogler (2006):

$$C_{wp} = \eta\phi^2 \quad (1) \quad \eta = \frac{3}{\phi} \left(\frac{1}{\tanh \phi} - \frac{1}{\phi} \right) \quad (2) \quad \phi = \frac{R}{3} \sqrt{\frac{k_c}{D_e}} \quad (3) \quad D_{eT} = \frac{D_{e298} \mu_{298} T}{289 \mu T} \quad (4)$$

In this expression, C_{wp} corresponds to the Weisz-Prater parameter, η is the effectiveness factor of internal mass transfer, ϕ is the Thiele modulus, R is the cellulose particle radius, k_c is the reaction rate constant of cellulose degradation (1/s), D_e is the effective diffusion coefficient (m^2/s), μ is water viscosity (Pa.s), and T refers to the temperature (K). Internal diffusion is negligible when $C_{wp} \ll 1$. During the SCM evaluation, it was first necessary to determine the rate-controlling stage. The equations used are summarized in Table 1:

Table 1 Controlling regime equations

Film diffusion control	Ash diffusion control	Chemical reaction control
$k_c t = X_c$ (5)	$k_c t = X_c + (1 - X_c) \ln(1 - X_c)$ (6)	$k_c t = 1 - (1 - X_c)^{1/2}$ (7)

The kinetic parameter of the reactions was estimated by using the following equations:

$$r_c = 2k_c C_{c0} (1 - k_c t) \quad (8) \quad k_i = A_i \exp \left[-\frac{E_{ai}}{RT} \right] \quad (15)$$

$$r_G = k_G C_G \quad (9) \quad \frac{dC_c}{dt} = -r_c \quad (16)$$

$$r_{G'} = k_{G'} C_G \quad (10) \quad \frac{dC_G}{dt} = r_c - r_G - r_{G'} \quad (17)$$

$$r_{LG} = k_{LG} C_{LG} \quad (11) \quad \frac{dC_{LG}}{dt} = r_G - r_{LG} - r_{LG'} \quad (18)$$

$$r_{LG'} = k_{LG'} C_{LG} \quad (12) \quad \frac{dC_{HMF}}{dt} = r_{LG} - r_{HMF} - r_{HMF'} \quad (19)$$

$$r_{HMF} = k_{HMF} C_{HMF} \quad (13) \quad \frac{dC_{LA}}{dt} = r_{HMF} \quad (20)$$

$$r_{HMF'} = k_{HMF'} C_{HMF} \quad (14)$$

In these equations, r_i (mol/min) refers to the reaction rate of i , k_i (1/min) is the reaction rate constant of i , C_i is the concentration of i , A (min^{-1}) is the Arrhenius constant, E_{ai} (kJ/mol)

is the activation energy of i , and R (8.314 J/(mol/K)) is the ideal gas constant. Based on the above equations, the reaction rate constant was obtained by minimizing the error between the experimental data and the model's results, sum squared of errors (SSE).

3. Results and Discussion

3.1. Pretreatment

Sugarcane bagasse is majorly composed of cellulose, hemicellulose, and lignin. The desired component for the LA synthesis is cellulose. Therefore, it is necessary to pretreat the sugarcane bagasse. The composition of bagasse analyzed based on the Van Soest method is shown in Table 2.

Table 2 Bagasse composition

Compounds	Percentage, %	
	Before pretreatment	After pretreatment
Cellulose	44.73	82.64
Hemicellulose	19.92	6.14
Lignin	14.17	0.65
Others	21.18	10.57

According to Table 2, bagasse composition before and after pretreatment experienced a significant change. After pretreatment, the cellulose composition in the raw material increased up to 82.64%, about two-fold from the original non-pretreated. It can be said that the pretreatment effectively increases cellulose content in the raw material.

3.2. Controlling Regime Selection

After pretreatment, the pretreated bagasse solids or mentioned as cellulose went through hydrolysis process. The experiment was conducted under various operating conditions, i.e., a temperature of 150-170 °C, an HCl concentration of 0.1-1 M, and a solid-to-liquid ratio of 1-10%. The cellulose hydrolysis reaction to glucose is assumed to be the shrinking core model (SCM). Cellulose is considered a cylindrical non-porous particle. To determine the reaction rate equation, it is necessary to determine the possible controlling regime, as shown in Figure 4.

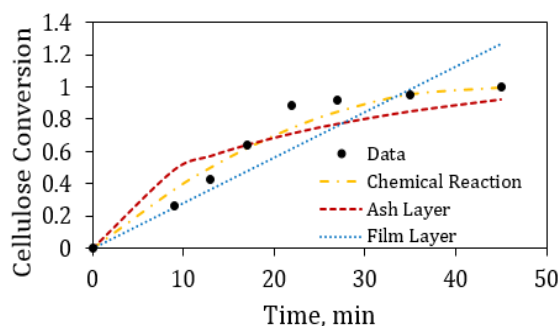


Figure 4 Data fitting for determining controlling regime

Figure 4 exhibits that the cellulose hydrolysis reaction is controlled by a chemical reaction. It is also confirmed that there was no influence of internal diffusion on the reaction with the operating conditions performed since the obtained Weisz-Prater parameter was less than 1.

3.3. Effects of Operating Conditions

The highest LA yield obtained in this experiment was 64.05%, at 160 °C, 1 M HCl, and 1% solid-to-liquid ratio. It is higher than the yield obtained by [Gozan et al. \(2018\)](#), 52.1%,

who performed pretreatment by soaking in aqueous ammonia before the LA production. Meanwhile, [Kang and Yu \(2018\)](#) produced LA from sugar beet molasses through ion exchange pretreatment resulting in 45% LA yield. Figure 5 represents the effect of various operating conditions on the LA yield.

3.3.1. Temperature

Figure 5(a) shows the relation between reaction time on the LA yield at three temperature variations. The longer the reaction time, the higher the LA yield will be. Over the same reaction time, the higher LA yield is consistently obtained at the higher temperature, which aligns with what was reported by [Toif *et al.* \(2020\)](#). The maximum potential LA yield is relatively the same at different temperatures used. However, less time is needed to reach the maximum potential LA yield when the temperature increases. Meanwhile, at the temperature of 140 °C, the LA yield at the end of the reaction is just slightly above 25%, which is possible to rise when the reaction time is extended.

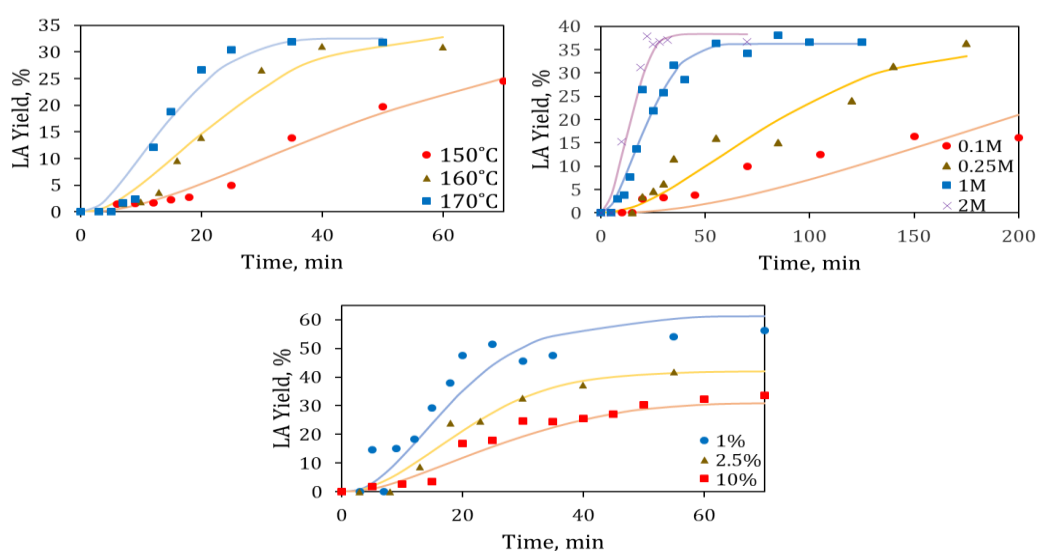


Figure 5 LA yield at various operating conditions (a) temperature; (b) catalyst concentration (CH); and (c) solid-to-liquid ratio (CC)

3.3.2. Catalyst concentration

Figure 5(b) represents the LA yield in relation to the reaction time at different catalyst concentrations. At the same time, higher catalyst concentration promotes higher LA yield, similar to the results from [Jeong *et al.* \(2017\)](#) and [Anggorowati *et al.* \(2018\)](#). The lowest LA yield is 16.35%, obtained by 0.1 M catalyst at 200 minutes, which can increase when the reaction time is prolonged. When the catalyst concentration is increased to 0.25 M, the LA yield increases to 36.31% in 175 minutes. The higher catalyst concentration of 1 and 2 M will produce a similar maximum potential LA yield with 0.25 M catalyst over a faster reaction time (55 minutes for 1 M catalyst and 40 minutes for 2 M catalyst). It implies that catalyst concentration does not significantly affect the maximum potential LA yield. Instead, higher catalyst concentration can accelerate the time to achieve it. The result is also supported by the study regarding glucose hydrolysis, confirming that the maximum LA yield achieved by 1 and 1.5 M catalysts was relatively the same and can be reached at almost the same time ([Toif *et al.*, 2021](#)). For high-concentration catalysts, prolonged reaction time is considered unfavorable and inefficient. Maximum potential LA yield will be achieved in a relatively short time. Thus, when the reaction time is too long, the LA yield will not increase. It can be seen from Figure 5(b) that for the high catalyst concentration of 1 and 2 M, LA yield is stable as it reached maximum potential yield until the end of the reaction.

3.3.3. Solid-to-liquid ratio

In this study, the LA synthesis involved cellulose in the solid state and the HCl catalyst in the liquid form. The solid-to-liquid ratio (ratio of the mass of cellulose to the volume of liquid catalyst) also influences the hydrolysis reaction of cellulose to LA. Figure 5(c) denotes the relation between reaction time on the LA yield at different solid-to-liquid ratios. The lowest LA yield is obtained at a ratio of 10%. Too high a cellulose ratio will cause a lack of water in the reactor. The LA yield only rises slightly when the ratio is lowered to 2.5%. Yield increases significantly when the solid-to-liquid ratio is kept minimal at 1%. Levulinic acid yield with a solid-to-liquid ratio of 1% can reach 64.05%. The lower solid-to-liquid ratio is required to obtain a higher LA yield, which aligns with the report by [Yang et al. \(2013\)](#).

3.4. Reaction Kinetics

The result of experimental data fitting under different operating conditions is shown in Figure 6. The selected model provides an accurate approximation of the reaction and shows a consistent trend. During cellulose degradation, glucose is the first compound formed in the liquid phase, which then converts to LG. In contrast to the obtained results, other researchers stated that fructose is an intermediate of glucose isomerization ([Feng et al., 2020](#)). We did not detect any fructose in this study. When using Bronsted acids such as HCl, the pathway for LA synthesis is via the LG pathway ([Herbst and Janiak, 2016](#)). [Takahashi et al. \(2009\)](#) stated that glucose is decomposed into LG. It is double dehydrated into HMF ([Weingarten et al., 2014](#)). Finally, HMF undergoes rehydration to LA. The kinetic parameters involving the entire sequence of reactions under different operating conditions are summarized in Table 3.

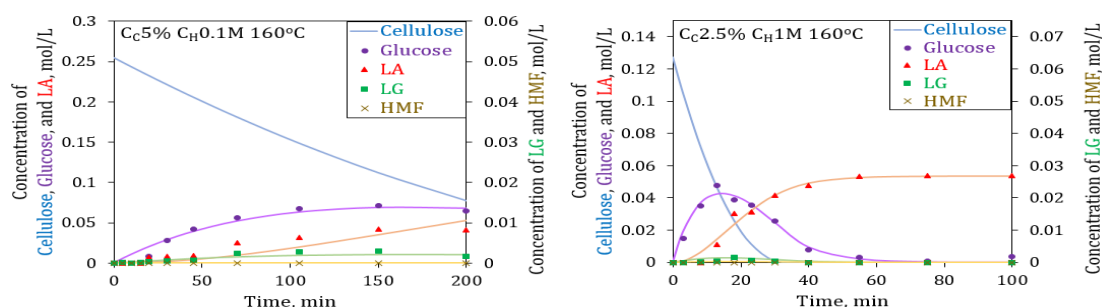


Figure 6 Data fitting at different operating conditions

Table 3 Kinetic parameters at various operating conditions

T, °C	C _c , %	C _H , M	k _c , min ⁻¹	k _G , min ⁻¹	k _{G'} , min ⁻¹	k _{LG} , min ⁻¹	k _{LG'} , min ⁻¹	k _{HMF} , min ⁻¹	k _{HMF'} , min ⁻¹
150			0.0116	0.0198	0.0461	1.5537	0.1808	3.8606	0.1331
160	10	1	0.0212	0.0444	0.0897	2.0001	0.3012	5.6794	0.2133
170			0.0326	0.0755	0.1564	2.5001	0.4856	8.323	0.3054
		0.1	0.0022	0.0052	0.0051	0.174	0.5994	4.7579	0.1977
	5	0.25	0.0066	0.0118	0.022	0.6513	0.7000	6.0000	0.3889
		1	0.0225	0.0511	0.0897	2.2601	0.851	8.2328	0.5952
160	1		0.0423	0.0534	0.0334	1.2540	0.5558	4.031	0.4096
	2.5	1	0.0304	0.0427	0.0587	1.2597	0.4818	7.5819	0.1344
	10		0.0189	0.0377	0.0835	1.5004	0.8373	8.0041	1.0066
	E _a , kJ/mol		80.58	104.41	95.21	37.07	76.97	59.83	64.75

According to Table 3, the controlling step is the cellulose decomposition into glucose, as the value of K_c is the smallest among all k in the range of operating conditions. Figure 6 demonstrates that LG concentration is always small, implying that LG decomposition occurs faster than its formation. It can also be observed from the value of k_{LG} in Table 3, where its

value is higher than k_g . Hydroxymethylfurfural is very unstable under reaction conditions and decomposes rapidly into the final LA product. Therefore, the concentration of HMF in the system is very small during the whole process. As mentioned in the study regarding glucose hydrolysis to LA (Toif *et al.*, 2021), the concentration of HMF will be extremely low or even undetectable when the glucose concentration is extremely small. The low concentration of HMF can also be observed from the value of k in Table 3, where k_{HMF} is always more significant than the k value for other reactions. It implies that the rate of HMF rehydration to LA is significantly faster than the other reaction steps.

As shown in Table 3, all k values increase with the increasing temperature. It is similar to the results obtained by Zhi *et al.* (2015), Zheng *et al.* (2017), and Qing *et al.* (2018). Higher temperature is suitable for promoting biomass hydrolysis. However, it should also be noticed that the reaction rate constant to the decomposition products also increases. Increasing the temperature will also trigger the formation of decomposition products that competes with the LA formation. As a result, by-products and LA concentration increase simultaneously (Shen and Wyman, 2011).

The effect of temperature can also be observed from the value of activation energy. The highest activation energy is for glucose decomposition, indicating that the glucose decomposition step is the most sensitive to the temperature. The activation energy of glucose formation is lower than its decomposition. Therefore, high temperature conditions will drive glucose decomposition faster than its formation, as in the study by Gozan *et al.* (2018). The formation of by-products from LG and HMF has higher activation energy than the formation of the desired product. It represents that more by-products will be formed when the reaction is carried out at higher temperatures. The formation of HMF has the lowest activation energy, suggesting that the conversion from LG to LA does not require a high temperature.

Another observed variable in the estimation of kinetic parameters is the catalyst concentration. The higher the catalyst concentration, the greater the value of k at all stages, leading to the product and the side compounds. According to the results obtained by Zhi *et al.* (2015), Zheng *et al.* (2017), and Gozan *et al.* (2018), increasing the catalyst concentration not only helps to enhance the primary reaction but also promotes the formation of by-products. If the concentration of the used acid catalyst is too high, LA decomposes, and the decomposition rate is higher than the formation rate (Yuan *et al.*, 2016).

This experiment also studied the solid-to-liquid ratio, but it has no clear significant relation with the rate constant value. Shen and Wyman (2011) also obtained similar results. The value of k obtained changes irregularly with increasing the solid-to-liquid ratio, so it is concluded that the reaction rate is independent of the solid-to-liquid ratio.

4. Conclusions

Sugarcane bagasse hydrolysis into LA, which was preceded by pretreatment, gave satisfactory results. The alkaline-acid pretreatment successfully increased the cellulose content to 82.64% from the initial 44.37%. The pretreatment was able to break down hemicellulose and lignin in the bagasse. Therefore, components other than cellulose were not involved and do not interfere LA synthetic reaction. The elimination of these components is not only beneficial for LA synthesis, but the separated hemicellulose and lignin can also be utilized in other purposes. Hopefully, integrated LA industry with hemicellulose and lignin derivative products can be developed in the future. The cellulose resulting from the pretreatment process was hydrolyzed with HCl, a Bronsted acid that acts as a catalyst. The reaction routes with this catalyst included cellulose-glucose-LG-HMF-LA. The highest LA yield achieved from this experiment was 64.05% at a temperature of 160

°C, a catalyst concentration of 1 M, and a solid-to-liquid ratio of 1%. The high LA yield value was the result of raw material pretreatment combined with optimal conditions of synthetic reaction. Higher temperature and catalyst concentration can accelerate the rate to obtain the maximum potential LA yield, which is relatively the same under various temperatures and catalyst concentrations. Meanwhile, a lower solid-to-liquid ratio leads to a higher LA yield. The kinetics of cellulose hydrolysis reaction to LA was evaluated with the heterogeneous reaction model, namely the shrinking core model for the conversion of cellulose to glucose and the first-order homogeneous reaction model for the series of reactions starting from glucose to LA. The selected model was proven to provide a good-fitting result. The more appropriate reaction model is expected to offer more precise calculations when a scale-up process carried out for industry in the future. Subsequently, after successfully synthesizing LA from bagasse with a relatively high yield, further studies regarding purification are needed to investigate the separation of LA from other compounds in the filtrate. Therefore, the LA purity can be improved. The outcome of this study has potential to be applied for other biomass raw materials with several modifications according to their characteristics which can be studied further.

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