



Research Article

# Experimental and Kinetic Modeling of Galactose Valorization to Levulinic Acid

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## Abstract

Levulinic acid, a versatile chemical building block, was derived from C6-sugar galactose using sulfuric acid as the catalyst. Galactose is monosaccharide of polysaccharides constituent that is mostly contained in third generation biomass, macro-microalgae. It currently receives high attention to be a source of renewable feedstock. The effect of temperature, catalyst concentration and initial substrate loadings were studied for 60 min, in the temperature range of 150–190 °C, acid concentration of 0.25–0.75 M and initial substrate loading of 0.05–0.25 M. The highest levulinic acid yield of 40.08 wt% was achieved under the following conditions: 0.05 M galactose, 0.75 M acid concentration, 170 °C temperature, and 40 min reaction time. The kinetic model was developed by first order pseudo-irreversible reaction. The results showed that the proposed model could capture the experimental data well. These results suggested that galactose, derived from macro- and micro-algae, can potentially be converted and applied for platform chemicals.

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**Keywords:** C6-Sugar; Galactose; Levulinic Acid; Kinetics; Valorization

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## 1. Introduction

The conversion of third-generation macro- and micro-algal biomass into bioenergy and biochemicals has been attracting the attention of researchers [1-5] for its superiority to the other generations in terms of ease of cultivation, non-competitive with food ingredients, and convertibility into bio-based products [2,4]. The contents of carbohydrates are the source of sugar-based renewable raw materials and it is a promising

raw material to be converted to an important chemical building block: levulinic acid [3,5–7].

Levulinic acid (LA) or gamma-ketovaleric acid (4-oxopentanoic acid) has two highly reactive functional groups, namely carbonyl ketone (C=O) and carboxyl acid (COOH) [1,3], both of which make LA easy to convert into derivative products. LA can be converted to ethyl levulinate through an esterification reaction [8] and to gamma-valerolactone (GVL) through a hydrodeoxygenation process [9], oxidized to succinic acid [10], hydrogenated to 2-methyl tetrahydrofuran [11], and brominated and further condensed to delta-aminolevulinic acid (DALA)

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[12]. These derivative products are applicable as herbicides, fuel additives, anti-freeze, plasticizers, solvents, food flavoring agents, pharmaceuticals, and resins [1,3].

LA can be synthesized from monosaccharides that are the constituents of complex carbohydrates-polysaccharides [13]. Monosaccharides that have LA route are pentose and hexose. Pentose C5-sugar ( $C_5H_{12}O_6$ : xylose, ribose, arabinose) and hexose C6-sugar ( $C_6H_{12}O_6$ : fructose, glucose, galactose) have different reaction routes in producing LA [13,14]. The C5-sugar route involves furfural and furfuryl alcohol as intermediate products, while the C6-sugar route involves formation of 5-hydroxymethylfurfural (5-HMF). The second route with 5-HMF formation is more favorable for LA production due to its lower production cost [14]. Under acidic conditions, the reaction route of C6-sugar to LA goes through two reaction steps: dehydration of C6-sugar to 5-HMF and rehydration of 5-HMF to LA and formic acid (FA) in equimolar ratio, 1:1, respectively [13–15]. Figure 1 shows the simplified scheme of the C6-sugar-to-LA reaction route. C6-sugar decomposition reaction to LA, besides having the desired reaction (producing LA), also involves the undesired reaction route [16,17], namely producing soluble and insoluble by-products. In this case, the insoluble one produced is called humin [18], from the decomposition of C6-sugar and 5-HMF [19]. Soluble by-products as C6-sugar conversion are levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose), 1,6-anhydro- $\beta$ -D-glucofuranose, isomaltose, gentiobiose, furfural, acetic acid, lactic acid, [16,20].

Galactose is a simple sugar that has 6 carbon chains and is an epimer with glucose, which differs in the configuration of the OH group in the C-4 carbon [21]. It is one constituent of polysaccharides-carbohydrates contained in third-generation biomass that has been shown to produce LA [1]. It is a constituent of polysaccharides in *Gelidium amansii* (red-macroalgae) [22], the first dominant constituent of *Gracilaria verrucosa* (red macroalga) [23,24], and the second dominant constituent after glucose in *Spirulina platensis* (blue-green microalgae) [25,26].

LA synthesis has been widely studied using hexose as a raw material with homogeneous acid catalysts, both mineral and organic acids [16,27–30] and heterogeneous acid catalysts [20,31–34]. Fructose and glucose, compared to galactose, are commonly studied because of the molecular structure of fructose and the location of the carbonyl group that make the conversion to 5-HMF more favorable. Besides, the by-products in the form of soluble polymers, are also less [21], making the reaction more effectively to produce more LA as the desired yield. However, the availability of natural fructose is limited which caused higher cost of raw materials. As a result, it makes glucose to be more attractive. Glucose is the second most studied C6-sugar in LA production because it is a constituent of almost all biomass generations [16,20,27,30]. Table 1 shows an overview of LA production from C6-sugar under various operating conditions.

Under acidic conditions and high temperatures, fructose's molecular structure is consid-

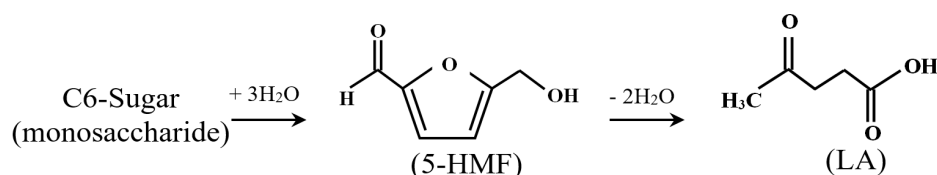


Figure 1. Simplified route of C6-sugar to LA.

Table 1. Overview of C6-sugar conversion to LA.

C6-sugar	Substrate loading	solvent	catalyst	Temperature (°C)	Time (min)	$Y_{LA}$ (mol%)	Ref.
Fructose	9 wt%	H <sub>2</sub> O + GVL	resin Dowex-50	120	1440	72	[31]
	60 g/L	H <sub>2</sub> O	0.4 M MSA	188	36	66	[39]
	0.1 M	H <sub>2</sub> O	1 M H <sub>2</sub> SO <sub>4</sub>	140	15	74	[29]
Glucose	0.1 M	H <sub>2</sub> O	1 M H <sub>2</sub> SO <sub>4</sub>	140	120	60	[16]
	0.1 M	H <sub>2</sub> O	1 M HCl	180	50	48	[30]
	0.1 M	H <sub>2</sub> O	0.75 g Cr/HZSM-5	180	180	64	[20]
Galactose	60 g/L	H <sub>2</sub> O	0.4M MSA	188	27	41	[39]
	0.3 M	H <sub>2</sub> O	2.5 wt% H <sub>2</sub> SO <sub>4</sub>	150	600	34	[40]
	13 wt%	Etanol + H <sub>2</sub> O	15 wt% amberlyst 70	175	140	23	[21]

ered more easily decomposed into 5-HMF than glucose and galactose's [21]. If the catalyst comes from Lewis acids, then the decomposition routes of glucose and galactose go through isomerization to fructose first [31]. Meanwhile, if it comes from Brønsted acids, 5-HMF can be formed without going through isomerization to fructose [19]. Fructose is undetected in the product mixture in the experiment using Brønsted acid, sulfuric acid [16], and solid catalyst CH<sub>3</sub>-SBA-15-SO<sub>3</sub>H [34] because it is converted directly to 5-HMF or is immediately catalyzed to be 5-HMF [34]. This absence because it converted directly to 5-HMF, or that fructose produced immediately catalysed to 5-HMF [34]. Brønsted acids from the mineral acid group commonly used in the decomposition of C6-sugar are H<sub>2</sub>SO<sub>4</sub>, HCl, and H<sub>3</sub>PO<sub>4</sub> [35]. A decomposition route without isomerization can effectively occur with Brønsted acids, which have high acid dissociation constants [19], such as sulfuric acid with pK<sub>a</sub> = -3 [35].

Previous studies that addressed the decomposition of C6-sugar, indeed, reported the effects of temperature, acid concentration, and substrate loading on LA production [16,27–34]. However, only a few of them reported C6-sugar derived from galactose. Whereas, the potential use of galactose to become LA needs to be intensively studied because it is the monosaccharide that builds the third-generation biomass, which has a reaction route to become LA [1,22–24]. Therefore, there is a need to perform a systematic investigation to determine the potential use of galactose to form LA.

Reaction kinetics studies on optimization of LA production from C6-sugar have been done using fructose [28,29,36] and glucose [16,34,36–38] as raw materials. However, there is limited references of kinetics studies on the decomposition of galactose to LA in the present literatures. Previous studies on the production of LA from galactose, based on the references, merely focused on how to yield LA [19,39,40], without addressing the determination of the reaction kinetics parameters. For this reason, our kinetics study on the decomposition of galactose to LA would propose a pseudo-homogeneous first-order irreversible reaction kinetics model, which would consider the formation of by-products as a result of the degradation of galactose and 5-HMF.

This research aimed to study the decomposition of galactose through consecutive dehydration and rehydration reactions to LA with sulfuric acid as the catalyst by extensively observing the effects of temperature, acid catalyst concentration, and initial substrate loading on

the conversion of galactose and LA products. A kinetics model derived from a reaction mechanism involving the formation of by-products was developed. An irreversible pseudo-order reaction kinetics model approach was proposed to determine the reaction kinetics parameters.

## 2. Materials and Methods

### 2.1 Materials

The chemicals used in this study had analytical grade and were used without purification. Sulfuric acid and D-galactose were obtained from Merck, 5-HMF was from Sigma Aldrich, while LA was obtained from Tokyo Chemical Industry (TCI).

### 2.2 Experimental Procedures

The experimental setup that we used in the present study is similar to our previous work in [5]. Briefly explained here, the reaction was let run in eight sealed glass ampoules, each of which had an inner diameter of 15 mm and a length of 10 cm. Each ampule, containing a solution of galactose and sulfuric acid, was inserted into a reactor in the form of a stainless-steel tube placed in an oil bath shaker at a set temperature. The reaction started when the temperature in the oil bath shaker reached the desired operating temperature. In each reaction process, eight reactors used were taken from the oil bath shaker and opened after a specified time ranging from 3 min to 60 min. After the reaction was complete, the reactors were immediately cooled by immersing them in an ice bath (4 °C) to stop the reaction. The solutions produced were obtained by centrifuging at 5000 rpm for 10 min to separate the solids and the supernatants (liquid phase). Then, the supernatants were filtered using a 0.2 μm syringe filter for further analysis by high-performance liquid chromatography (HPLC). The operating conditions set were 0.05–0.25 M for initial galactose concentrations and 0.25–0.75 M for catalyst concentrations at temperatures ranging from 150 to 190 °C.

### 2.3 Analytical Methods

The samples resulting from the hydrolysis reaction in the form of galactose, 5-HMF, and LA compounds were detected and quantified by the HPLC unit, which was equipped with a Waters Nova-pak C18 Refractive Index column as the detector. The HPLC unit was operated at 30 °C using a solution of 0.005 M H<sub>2</sub>SO<sub>4</sub> as the mobile phase, with a flow rate of 0.6 mL/min and an injection volume of 20 μL [7].

The concentrations of the compounds produced were obtained based on standard curves made from several concentrations for each standard compound whose concentration was known. The conversion of galactose ( $X_{gal}$ ) and the yielded LA ( $Y_{LA}$ ) were calculated by the following equations:

$$X_{gal}(\%) = \frac{\left[ \begin{matrix} \text{Initial} \\ \text{galactose (gr / L)} \end{matrix} \right] - \left[ \begin{matrix} \text{galactose} \\ \text{remain (gr / L)} \end{matrix} \right]}{\left[ \begin{matrix} \text{Initial} \\ \text{galactose (gr / L)} \end{matrix} \right]} \times 100\% \quad (1)$$

$$Y_{LA}(\%wt) = \frac{LA \text{ product (gr/L)}}{\text{initial galactose (gr/L)}} \times 100\% \quad (2)$$

$$Y_{5-HMF}(\%wt) = \frac{5-HMF \text{ product (gr / L)}}{\text{initial galactose (gr / L)}} \times 100\% \quad (3)$$

### 2.4 Kinetic Modelling

A kinetic model was proposed to determine and understand the effects of temperature, acid catalyst concentration, substrate loading intake concentration, and reaction time on the products of galactose decomposition. The reaction model scheme of galactose decomposition refers to the model proposed by Girisuta [16] in converting glucose to LA and Fachri [29] who decomposed fructose into LA. Figure 2 shows the schematic model of the reaction mechanism of galactose decomposition by acid treatment using sulfuric acid as the catalyst in this experiment. There were 4 reactions: (1)  $r_1$ : dehydration reaction of galactose into 5-HMF, (2)  $r_2$ : degradation reaction of galactose into by-products, (3)  $r_3$ : rehydration reaction of 5-HMF into LA, and (4)  $r_4$ : degradation reaction of 5-HMF into by-products. Some of the assumptions applied to the proposed galactose decomposition mechanism model include: (a) all reactions involved are irreversible reactions, (b) by-products are derived from the degradation of galactose and 5-HMF, and (c) the reaction rate equation follows a first-order reaction.

The following are the reaction equations used to determine the kinetic parameters:

$$r_1 = k_1 \cdot C_{gal} \quad (4)$$

$$r_2 = k_2 \cdot C_{gal} \quad (5)$$

$$r_3 = k_3 \cdot C_{5-HMF} \quad (6)$$

$$r_4 = k_4 \cdot C_{5-HMF} \quad (7)$$

$$\frac{dC_{gal}}{dt} = -r_1 - r_2 \quad (8)$$

$$\frac{dC_{5-HMF}}{dt} = r_1 - r_3 - r_4 \quad (9)$$

$$\frac{dC_{LA}}{dt} = r_3 \quad (10)$$

Equations (4)–(10) were used to estimate the values of the reaction kinetics parameters using MATLAB software. The reaction rate coefficients were estimated by minimizing the errors between the experimental data and the kinetic model (Sum of Squared Error, SSE). Here,  $C_{gal}$ ,  $C_{5-HMF}$  and  $C_{LA}$  represent the concentration of galactose, 5-HMF and LA at time  $t$  (min), in gmol/L. Whereas,  $k_1$ ,  $k_2$ ,  $k_3$ ,  $k_4$  are reaction rate coefficients ( $\text{min}^{-1}$ ).

The reaction rate kinetic coefficient ( $k$ ) obtained for each reaction ( $i = 1, 2, 3$ , and 4) were then correlated with temperature ( $T$ , Kelvin) by applying the Arrhenius equation (Equation (11)) to get the kinetics parameters,  $A$  and  $E$  values. Meanwhile, the effects of catalyst concentration on the reaction rate coefficients were followed Equation (12) to get  $k_{i0}$  values.

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad (11)$$

$$k_i = k_{i0} (C_H)^m \quad (12)$$

Here,  $A$ ,  $E$ ,  $C_H$  and  $m$  are the frequency factor ( $\text{min}^{-1}$ ), the activation energy ( $\text{kJ}\cdot\text{mol}^{-1}$ ), acid concentration (M) and the reaction order for catalyst concentration. Value of  $k_0$  independence to acid concentration,  $m = 1$ . Symbol  $R$  is the ideal gas constant,  $8.314 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

### 3. Results and Discussion

In this study, the decomposition of C6-sugar galactose into LA with sulfuric acid as the catalyst was investigated. Variations of reaction process parameters were applied to study the effects of temperature, catalyst concentration, and initial substrate loading on galactose conversion, the LA and 5-HMF yielded, and reaction kinetics parameters (reaction rate coefficient, activation energy, and frequency factor). The experiment ran for 60 min at temperatures ranging from 150 to 190 °C, with acid

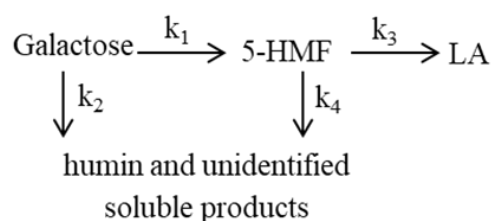


Figure 2. Simplified model of galactose decomposition scheme to LA.

concentrations ranging from 0.25 to 0.75 M and galactose feed concentrations ranging from 0.05 to 0.25 M.

The conversion of galactose, the yield of LA and 5-HMF were largely affected by the reaction temperature than that of the acid catalyst concentration and galactose feed concentration.

The conversion of galactose, the amount of the LA and 5-HMF yielded by various operating conditions are shown in Figures 3, 4 and 5.

In all experiments under the operating conditions, galactose was almost completely converted to 100%. Meanwhile, 5-HMF was observed as intermediate product. It was detected

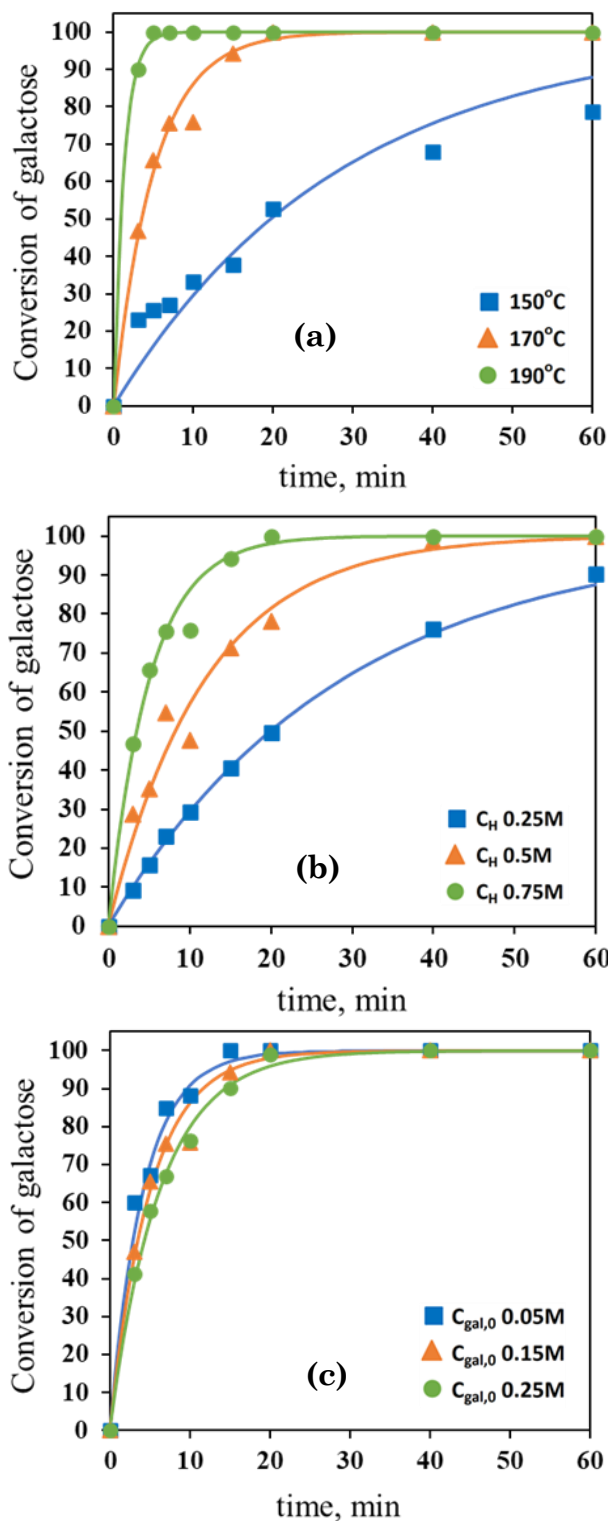


Figure 3. Conversion of galactose in several reaction parameter; (a) Reaction temperature, (b) Acid concentration, and (c) Loading intake galactose.

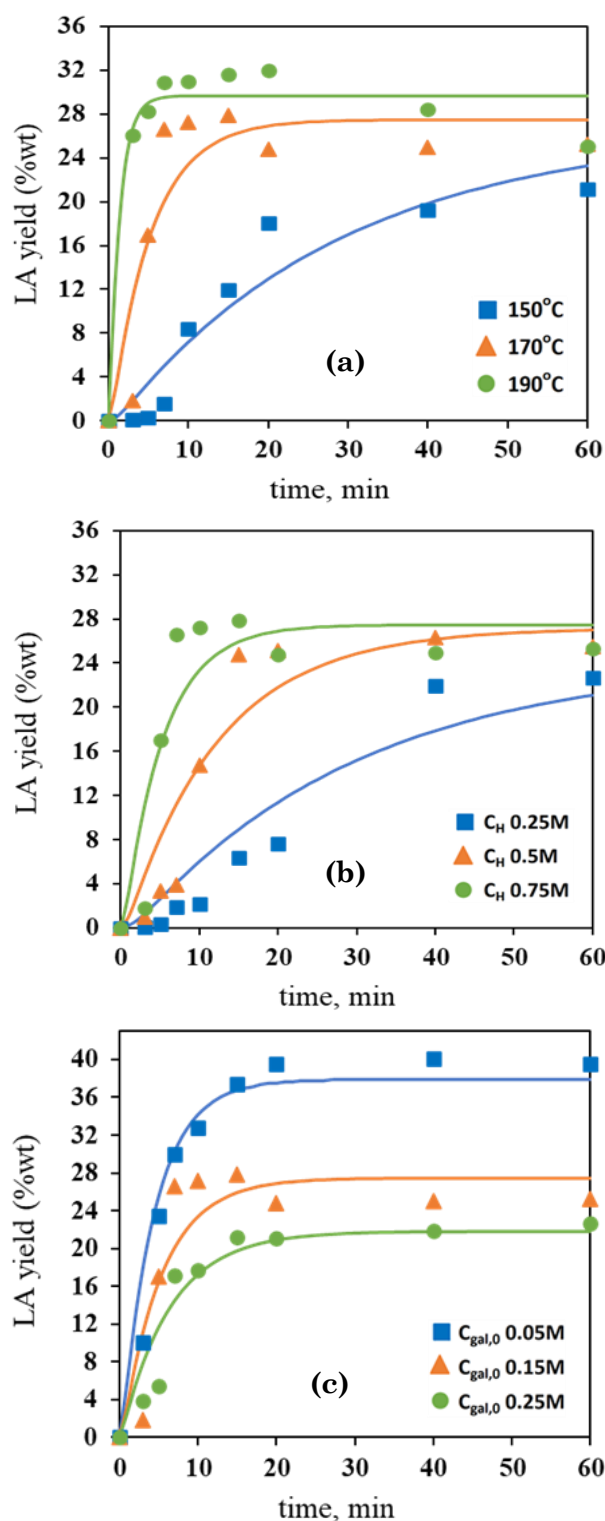


Figure 4. LA yield and model in several reaction parameter; (a) Reaction temperature, (b) Acid concentration, and (c) Loading intake galactose.

in very small value. This indicated that 5-HMF can be easily rehydrated and converted to LA and other byproduct. The highest LA yield was achieved at 40.08 wt% at initial concentrations of galactose and  $H_2SO_4$  of 0.05 M and 0.75 M, respectively, at a temperature of 170 °C. Based on the observations in the experimental window, insoluble black solids similar to humins and unidentified soluble products were formed as a by-product of the conversion of galactose. A solid part of humin was found and stuck tightly to the inner walls of the reactor. Thus, it was impossible to properly collect all the solids of humin. Meanwhile, unidentified soluble products appeared as HPLC peaks, but could not be identified due to facility limitations.

### 3.1 Effects of Operating Conditions in LA Production

#### 3.1.1 Reaction Temperature

The effects of reaction temperature on galactose conversion, LA and 5-HMF are shown in Figures 3(a), 4(a) and 5(a). The effect of reac-

tion temperature was studied on acid concentration  $C_H = 0.75$  M and initial substrate loading  $C_{gal,0} = 0.15$  M. Figure 3(a) shows that the higher the temperature, the higher and faster the galactose conversion. The higher the reaction temperature, the faster the rate of the galactose decomposition reaction. At 190 °C, galactose was completely converted at the first 5 min and at the 20<sup>th</sup> min at 170 °C. Meanwhile, at a lower reaction temperature (150 °C), the conversion achieved at the end of the reaction time under consideration (60 min) was not completely converted (70%). This data showed that temperature is a reaction parameter that has a major influence on galactose conversion because it affects the decomposition reaction rate, as shown by the conversion value, which increased significantly with the increasing the reaction temperature from 150 °C to 170 °C and 190 °C.

The amounts of the LA yielded by the decomposition of galactose at three different reaction temperature variations are shown in Figure 4(a). With increasing reaction temperature, the yield generally increased with a longer reaction time. However, after a certain time, it tended to be constant although the reaction time increased. At 150 °C, the yield achieved only about 21.14% at 60 min. However, at higher reaction temperatures, a higher amount was achieved in a shorter time. At a temperature of 170 °C, at a reaction time of 15 min, the yield reached 27.86% and reached 30.97% at 190 °C for 10 min. This data showed that at a higher reaction temperature, the equilibrium of LA formation becomes faster.

The amounts of the 5-HMF yielded by the decomposition of galactose at three different reaction temperature variations are shown in

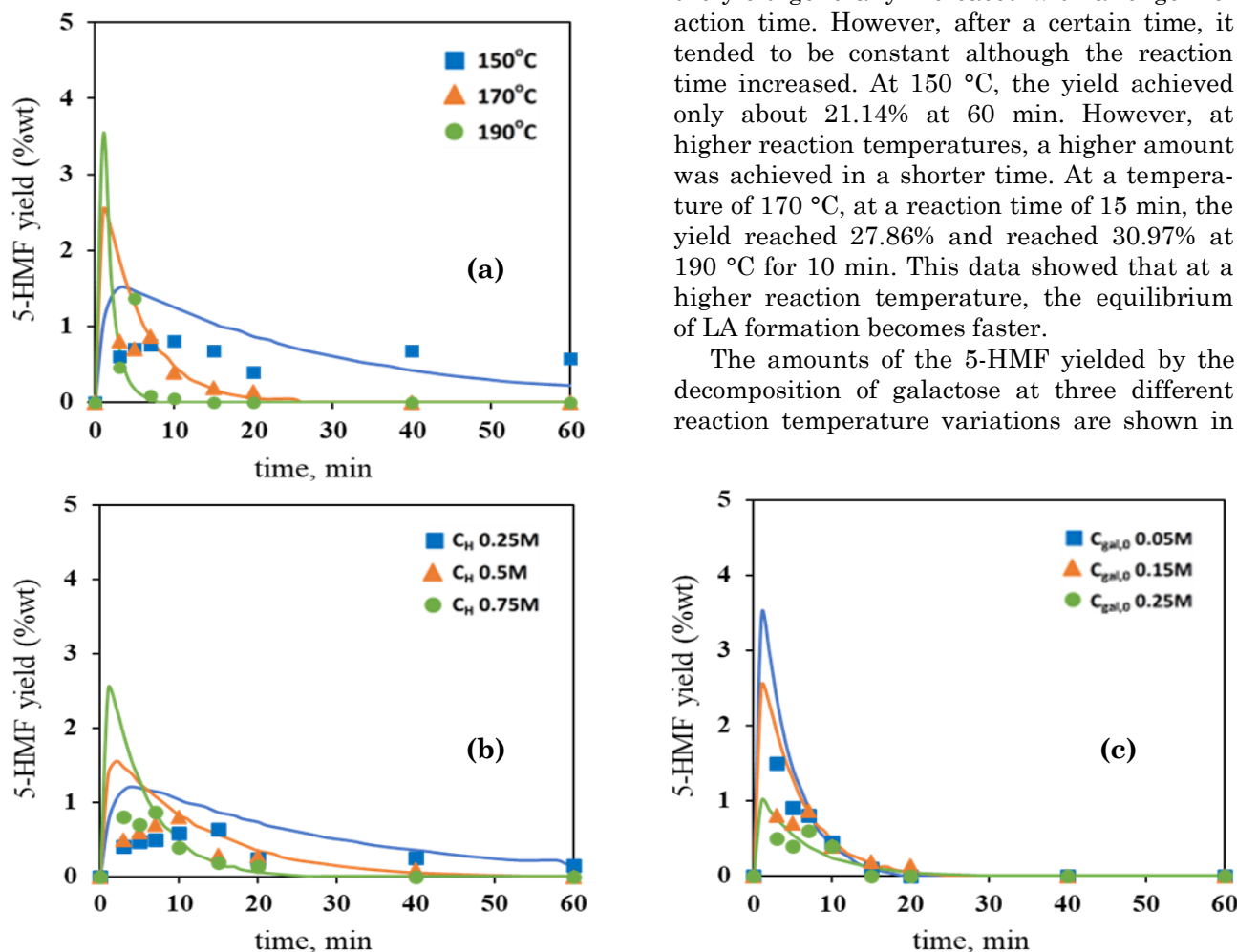


Figure 5. 5-HMF yield and model in several reaction parameter; (a) Reaction temperature, (b) Acid concentration, and (c) Loading intake galactose.

Figure 5(a). In the reaction time period, 5-HMF had similar profile. Increases in the initial reaction until it reaches maximum formation, then decreases for a longer time. At a higher reaction temperature, maximum 5-HMF was achieved higher and faster. In addition, after reaching the highest yield, the decrease in HMF formation at higher reaction temperature occurred at a faster time. The temperature of 190 °C reached its maximum yield in 5 min of 1.37 %wt, which then completely rehydrated and degraded at 7 min. While the lower reaction temperature reached 150 °C, the maximum yield at a reaction time of 10 min with a yield of 0.8% and till end of time reaction period 5-HMF is still detected. This phenomenon was in line with previous study on decomposition C6-sugar glucose. Using Brønsted acid of HCl in the range of reaction temperature 140–180 °C, reached maximum yield of 0.0325 M at 180 °C in the time of less than 5 min [27], whereas in the reaction temperature range of 160–200 °C, solid acid catalyst Cr/HZSM-5 reached maximum yield 6.5 %mol at 200 °C and taken 120 min to completely degraded. At 160 °C, the yield was still detectable even after 210 minutes [20].

The increase in reaction temperature gave a higher reaction rate coefficient (Table 2), bringing the reaction rate to increase because, on a molecular scale, the higher the reaction temperature, the higher the motion rate of each molecule, making the frequency of collisions between molecules to increase and the reaction to be more quickly. The motion rate is a function of temperature: the higher the reaction temperature, the higher the motion rate, causing the kinetic energy to increase, thus bringing the energy for the collision to exceed the activation

energy. This finding, namely the effect of reaction temperature on galactose conversion and LA formation, was in line with the experiment by Kim & Jeong [39] who studied galactose with methyl sulfonic acid (MSA) as the catalyst. They found that galactose was converted almost completely in the first 5 min at a temperature of 188 °C, while the optimum yield of 40.7 mol% was achieved at 20 min. The same effect was found by Toif [30] who studied the synthesis of LA from glucose with HCl as the catalyst and by Fachri [29] who studied the synthesis of LA from fructose with H<sub>2</sub>SO<sub>4</sub> as the catalyst.

### 3.1.2 Acid concentration

Figures 3(b), 4(b) and 5(b) show the conversion of galactose, LA yield and 5-HMF yield at various acid concentrations. The effect of acid concentration was studied at 170 °C with an initial substrate loading ( $C_{gal,0}$ ) of 0.15 M. Figure 3(b) shows that at the same reaction time, the higher the acid concentration level, the higher and faster the galactose conversion. In the first 5 min, the galactose conversion increased from 15.65%, 35.15%, to 65.70% by acid concentrations of 0.25, 0.5, and 0.75 M, respectively. For the acid concentration of 0.75 M, galactose was completely converted at the 20<sup>th</sup> min, followed by the acid concentration of 0.5 M, which could convert galactose completely at 60 min. Meanwhile, for the acid concentration of 0.25 M, the maximum galactose conversion of 90.17% was achieved at the end of the reaction time under observation. This data indicates that lower acid concentrations take longer to achieve completed conversion. Proton H<sup>+</sup> originating from the acid catalyst is related to the galactose decomposition reaction rate.

Table 2. Reaction rate coefficient of galactose hydrolysis.

Reaction Temperature (°C)	$C_{gal}$ (M)	$C_H$ (M)	Reaction rate coefficient (min <sup>-1</sup> )				SSE	R <sup>2</sup>
			$k_1$	$k_2$	$k_3$	$k_4$		
150			0.0257	0.0094	0.5490	0.4264	0.0014	0.9748
170	0.15	0.75	0.1253	0.0724	1.7089	0.8362	0.0012	0.9671
190			0.5543	0.2304	2.9866	1.5940	0.0002	0.9947
		0.25	0.0165	0.0182	0.5888	0.1702	0.0005	0.9931
170	0.15	0.5	0.0473	0.0366	1.2563	0.4303	0.0014	0.9693
		0.75	0.1253	0.0724	1.7089	0.8362	0.0012	0.9671
	0.05		0.2103	0.0278	2.0696	1.0390	0.0001	0.9847
170	0.15	0.75	0.1253	0.0724	1.7089	0.8362	0.0012	0.9671
	0.25		0.0179	0.0882	3.0129	0.9891	0.0012	0.9865

As shown in Figure 4(b), increasing the level of acid concentration gave higher amounts of the LA produced. Equilibrium conditions at maximum yields were achieved at different times for each variation in acid concentration. For the acid concentration of 0.75 M, at the beginning of the reaction (5 min), the amount of the LA yielded increased sharply (17%), and it only took a short time to reach equilibrium, namely 10 min, producing 27%. As for the acid concentrations of 0.5 M and 0.25 M, in 5 min, the first reaction only reached 3.33% and 0.35%, respectively. At the acid concentration of 0.5 M, an almost equilibrium yield was reached at a reaction time of 60 min, while for the lower catalyst (0.25 M), equilibrium had not been reached.

As shown in Figure 5(b), three concentrations of acid catalyst gave 5-HMF yielded. The profile of 5-HMF yield was similar to reaction temperature variation. The 5-HMF formation occurred in the initial reaction, then decreased in longer time of reaction. This decreasing value of 5-HMF in longer time of reaction, because it rehydrated to LA and degraded to by-product. Higher acid concentrations produced higher and faster 5-HMF. 5-HMF yield at higher acid concentration was not detected in more less time. In acid concentration of 0.75 M, it needed 20 min for 5-HMF almost undetectable. Meanwhile, at lower acid concentration (0.25 M), it still detected until the end of the reaction time observed. It was indicated that higher acid concentration, 5-HMF more easily rehydrated and degraded. It was in line with Kumar [38] reported that the formation of 5-HMF during the catalytic reaction is not highly stable and easily rehydrated. Three levels of acid concentration achieved maximum 5-HMF yield in different yield value. Acid concentration of 0.25 M, at a reaction time of 15 min, reached the maximum yield of 0.63%. Whereas higher acid concentration (0.5M) reached 0.81% for 10 min.

From the start of the reaction, the increase in acid concentration increased the conversion of galactose and LA. The increase in acid concentration increased the frequency of contact with galactose, thus increasing the decomposition reaction rate of galactose. Along with the increasing conversion of galactose, LA ap-

peared as the final product of the decomposition. Table 2 also shows that the reaction rate constant increased along with the increase in acid concentration, indicating that the reaction rate was directly proportional to the acid concentration. Table 3 shows values of coefficient of acid concentration ( $k_0$ ). Determining value of  $k_0$  to describe correlation  $k$  and acid concentration. For third of acid concentrations of catalyst on each reaction involved ( $r_1$ ,  $r_2$ ,  $r_3$ , and  $r_s$ ), the value of  $k_0$  is relatively same. However, it shown in Table 3, that the value of  $k_{30}$  gave a slightly fluctuating trend, but it was actually relatively constant. It indicates that acid concentration ( $H^+$ ) give effect proportionally to  $k$  value.

Although the increase in acid concentration increased the yield, as shown in the yield values for acid concentrations of 0.25 M to 0.5 M throughout the reaction time under consideration, the increase in the yield based on experimental data differed at acid concentrations of 0.5 M to 0.75 M. As shown by Figure 4(b), the equilibrium value of the LA yielded was relatively the same for both 0.5 M and 0.75 M acid concentrations. However, at different times, 0.75 M catalyst was faster. This finding showed that the increase in acid concentration does not change the equilibrium but speeds up its achievement. This data also implies that adding an acid catalyst to the decomposition of galactose does not lead to the desired reaction by producing more yield but to an undesired reaction for the formation of by-products. Such effect of the acid catalyst also occurred in the decomposition of fructose and glucose [16,28–30], where galactose produced insoluble by-products more than fructose and glucose did [21].

### 3.1.3 Initial substrate loading

Figures 3(c), 4(c) and 5(c) show the effect of initial substrate loading on galactose conversion, LA yield and 5-HMF yield. The effect of initial substrate loading was studied at temperature  $T = 170\text{ }^\circ\text{C}$  and acid catalyst concentration  $C_H = 0.75\text{ M}$ . As shown in Figure 3(c), the lower the concentration of galactose as the initial substrate loading, the higher its conver-

Table 3. Coefficient of acid concentration ( $k_0$ ).

Temperature ( $^\circ\text{C}$ )	$C_{gal}$ (M)	$C_H$ (M)	Coefficient of acid concentration ( $k_{i0}$ )			
			$k_{10}$	$k_{20}$	$k_{30}$	$k_{40}$
170	0.15	0.25	0.0660	0.0728	2.3552	0.6808
		0.5	0.0946	0.0732	2.5126	0.8606
		0.75	0.1671	0.0965	2.2785	1.1149



sion yield and the faster its process to be decomposition products despite no significant difference between the three concentration ranges used. The lower concentration of galactose as the initial substrate loading gives the higher its conversion yield, because of calculation. Calculation of conversion based on initial galactose, in which divided by initial galactose. At the beginning of the reaction (the first 3 min), the three galactose feeds showed relatively high conversion levels, namely 60%, 46%, and 41%, for the initial substrate loadings of 0.05, 0.15, and 0.25 M, respectively. This data indicated that the temperature of 170 °C and the concentration of 0.75 M acid catalyst have a significant influence on the conversion rate of galactose into its decomposition products. The lower the initial substrate loading, the easier it is to convert completely. Galactose, with the initial substrate loadings of 0.05, 0.15, and 0.25 M, were completely converted at 15, 20, and 40 min, respectively.

An increase in the substrate amount lowers the LA yielded, as shown in Figure 4(c). The three variations of initial substrate loadings of galactose gave relatively similar LA yield trends in reaching equilibrium conditions, but with different amounts of the LA yielded. At the beginning of the reaction, the LA yielded increased until the reaction time of 15 min to reach equilibrium. Equilibrium conditions for the three substrate variations resulted in different yield amounts. Lower galactose substrate resulted in a higher yield. Based on the experiment the substrate loadings of 0.05, 0.15, and 0.25 M yielded LA of 37.37%, 27.86%, and 21.19%, respectively.

As shown in Figure 5(c), an increase in the substrate amount lowers the 5-HMF yielded. The three variations of initial substrate loadings of galactose gave relatively similar profile trends in formation and degradation of 5-HMF. Maximum 5-HMF yield was achieved in the initial time reaction, then decreased with reaction time. Maximum formation and completely decomposed (rehydrated and degraded) were achieved relatively on same time. This effect was agreed with Fachri [29] who converted C6-sugar fructose in the range of initial substrate loading 0.1–1.0 M, temperature of 160 °C and concentration of sulfuric acid 0.1 M. They found the highest yield of 5-HMF at 48%mol at 0.1 M of initial fructose intakes at 2.5 min. In the range of initial substrate loading that used in this experiment, the highest yield of 5-HMF was achieved only 1.5%wt. It was obviously lower. Possibility because of using the acid concentration in our system higher. It has been re-

ported that acid concentrations will accelerate the decomposition reaction of HMF, both rehydration and degradation reaction [16]. So that 5-HMF detected was lower. Besides that, fructose had a much better selectivity in converting into HMF than galactose [21,40].

The studied initial substrate loading of galactose and operating condition range showed that a higher substrate produced a lower yield, indicating the presence of side reactions and by-products. The results obtained due to the effect of initial substrate loading of galactose were in line with the results studied by Kim and Jeong [39] in converting galactose with sulfuric acid catalyst. This parameter also gave the same effect on the decomposition of C6-sugar glucose which was carried out by other researchers: Girisuta [16] who studied the decomposition of glucose with HCl as the catalyst.

### 3.2 Kinetics

Table 2 shows that increasing the acid catalyst concentration and reaction temperature increased the reaction rate coefficients of the dehydration reaction of galactose to 5-HMF ( $k_1$ ), degradation of galactose into by-products ( $k_2$ ), rehydration reaction of 5-HMF to LA ( $k_3$ ), and degradation reaction of 5-HMF into by-product ( $k_4$ ). Increasing temperature gives a higher coefficient of reaction rate, so that the reaction rate increases.

The rates of both the desired reaction (the rate of formation of LA) and the undesired reaction (the rate of formation of side products) increased simultaneously during the reaction time under consideration. However, the magnitude of the increase in the reaction rate coefficients due to the effect of increasing temperature were greater than that of the increase in acid concentration, indicating that temperature is an important parameter in the decomposition of galactose to LA. This indication is supported by the high effect of galactose conversion results and the LA yielded found in this experiment due to the effect of temperature. Kim and Jeong [39] also found the same thing, that with a constant acid catalyst, temperature gives a higher amount of yield and a higher conversion level.

The reaction rate coefficient due to the effect of increasing the substrate shown in Table 2 has a different effect from other reaction parameters (temperature and acid concentration). The effect of initial substrate loading on LA production is more complex. At constant acid concentration and temperature, the higher the

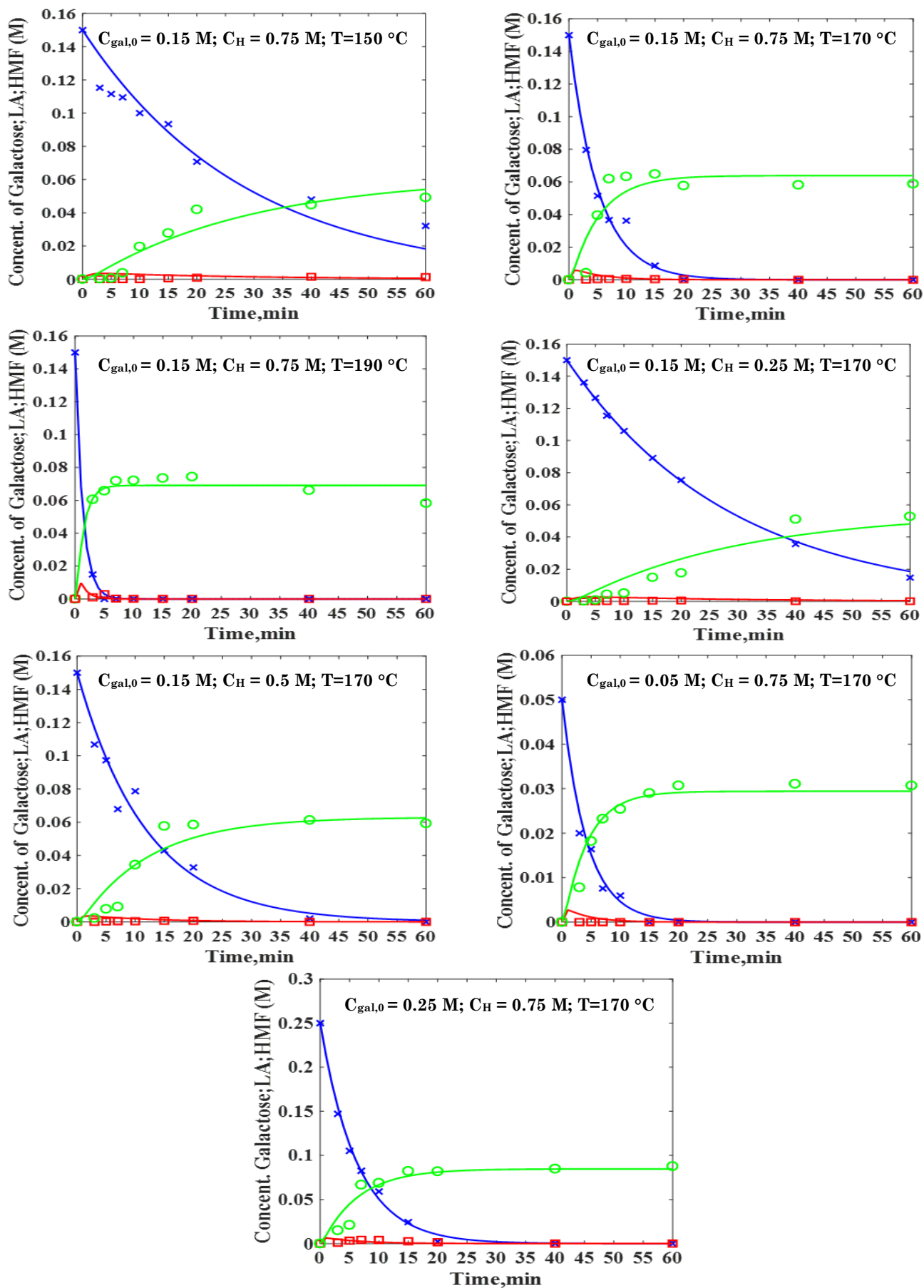


Figure 6. Comparison of experimental data ( $\times$  : galactose,  $\square$  : 5-HMF,  $\circ$  : LA) and kinetic model (solid lines).

substrate, the reaction rate of the dehydration of galactose to 5-HMF tends to decrease, as indicated by the reaction rate coefficient. However, the reaction rate towards the by-product of galactose degradation increased. The decrease in the reaction rate of the dehydration of galactose to 5-HMF is because the reaction rate which is more directed towards side reactions to produce humin products and soluble decomposition products of galactose. The lower 5-HMF formed resulted in a lower amount of LA as well. This is in line with the results of experiments carried out in this study. With the increase in substrate, the LA yielded tends to be lower. Meanwhile, the reaction rate coefficient of 5-HMF rehydration and degradation into by-products decreased from 0.05 to 0.15 M and increased for substrate concentrations of 0.15 to 0.25 M. In this condition, the rate of the rehydration reaction of 5-HMF to LA ( $r_3$ ) increased. This was in line with the understanding of the reaction rate which stated that the higher the reactant increases the reaction rate. The higher the concentration of initial substrate loading increased the contact of the galactose reactant with the acid catalyst, so that the reaction rate coefficient increased.

The reaction rate coefficient of the dehydration of galactose to 5-HMF ( $k_1$ ) produced, as the effects of the increase of temperature, acid catalyst concentration, and initial substrate loading, was much smaller than that of the rehydration of 5-HMF to LA ( $k_3$ ). This finding showed that the conversion of galactose to 5-HMF was much slower than that of 5-HMF to LA. Thus, the concentration of 5-HMF tended to be low. This is in line with the results of the experiments in this study.

Determination of the reaction rate coefficient by minimizing the errors (Sum of Squared Errors) of the kinetic model was based on the experimental data, while the activation energy ( $E_i$ ) and frequency factor ( $A_i$ ) for the decomposition of galactose into LA was determined for each reaction by applying the reaction rate and temperature coefficients at Arrhenius equation (Equation (10)). The values of the parameters  $E$

and  $A$  are shown in Table 4. It shows that the highest value was of  $E_2$ . The degradation of galactose to become a by-product was 130.69 kJ.mol<sup>-1</sup>, indicating that the high temperature produced a higher amount of humin. The next reaction sensitive to temperature was the dehydration reaction of galactose to 5-HMF, with  $E_2$  of 125 kJ.mol<sup>-1</sup>. With an increase in reaction temperature under acidic conditions, galactose was easily converted to 5-HMF.

Comparison of experimental data of the three galactose decomposition products obtained with the proposed model showed relatively good and fit result. The experimental data and the proposed model under various operating conditions carried out in this experiment are shown in Figure 6.

### 3.3 Comparison with Previous Kinetic Study on C6-sugar Hydrolysis

Comparison and summary of the kinetic studies result under various operating conditions on the LA production using C6-sugar as raw material are shown in Table 5. Previous kinetic study of C6-sugar hydrolysis had been studied by using sulfuric acid as homogeneous catalyst [15,29,36], solid acid [34], ionic liquid as Brønsted acid catalyst [38], and no catalyst using but the system used solvent other than water [37]. Based on literature overview in the same experimental temperature range, values of  $E_i$  in kinetic study for dehydration of C6-sugar to 5-HMF in the range of 47–152 kJ.mol<sup>-1</sup>, rehydration of 5-HMF to LA in the range of 34–111 kJ.mol<sup>-1</sup>, whereas by-product (humin and unidentified soluble product) formation from C6-sugar and 5-HMF degradations in the range of 23–165 kJ.mol<sup>-1</sup> and 42–111 kJ.mol<sup>-1</sup>. As those references, based on experimental and kinetic study of C6-sugar galactose that had been resulted is considered to be within the range.

In the similar operating condition, by using sulfuric acid as the catalyst, the results of the kinetics study on the decomposition of galactose to LA were relatively similar to those on the decomposition kinetics of other C6-sugar, fructose [29] and glucose [16], which followed power law approach and the first-order reaction assumption. However, value of  $E_i$  that was gotten by Chun [36] in glucose degradation to by-product relatively higher ( $E_2 = 210$  kJ/mol), because of different model kinetic proposed. In the Chun's model, by-product just only come from C6-sugar degradation.

Water as solvent used in this work gave relatively higher  $E_i$  on C6-sugar dehydration to

Table 4. Estimated kinetic parameters from Arrhenius equation.

Reaction rate coefficient	$A_i$ (min <sup>-1</sup> )	$E_i$ (kJ.mol <sup>-1</sup> )	$R^2$
$k_1$	$6.96 \times 10^{13}$	125.00	0.9999
$k_2$	$1.45 \times 10^{14}$	130.69	0.9826
$k_3$	$2.12 \times 10^8$	69.26	0.9720
$k_4$	$1.79 \times 10^6$	53.66	0.9998

5-HMF and C-6 sugar degradation into by-product than  $\gamma$ -valerolactone as solvent ( $E_1 = 77$  kJ.mol<sup>-1</sup> and  $E_2 = 42$  kJ.mol<sup>-1</sup>). This solvent was used as co-catalyst of CH<sub>3</sub>-SBA-15-SO<sub>3</sub>H solid catalyst [34]. A lower  $E_i$  indicates that dehydration of C6-sugar to 5-HMF can occur more easily. However, this system provides by-product formation derived from C6-sugar degradation more easily as well. It was in line with Wang [37] who converted glucose without cata-

lyst aid but used LiCl.3H<sub>2</sub>O as solvent. The  $E_2$  value for the degradation of C6-sugar to by-product was 23 kJ.mol<sup>-1</sup>, which was almost the lowest values on activation energy of by-product formation from C6-sugar ( $E_2$ ). Meanwhile, based on the literature for the same experimental temperature range in Table 5, Kumar [38] who studied glucose conversion using ionic liquid Brønsted acid catalyst, [ILSO<sub>3</sub>H][Cl] and NiSO<sub>4</sub>.6H<sub>2</sub>O, got almost the

Table 5. Proposed kinetic models for acid catalyzed C6-sugars conversion to LA.

C6-sugar	Proposed model	Reaction conditions	$E_i$ (kJ.mol <sup>-1</sup> )	Ref.
Glucose	$\begin{array}{ccc} \text{C6-sugar} & \xrightarrow{k_1} & \text{5-HMF} & \xrightarrow{k_3} & \text{LA} \\ \downarrow k_2 & & \downarrow k_4 & & \\ \text{humins and unidentified} & & \text{soluble products} & & \end{array}$	$T = 140\text{--}200$ °C Catalyst = H <sub>2</sub> SO <sub>4</sub> $C_H = 0.01\text{--}1$ M Solvent = water	$E_1 = 152$ $E_2 = 165$ $E_3 = 111$ $E_4 = 111$	[16]
	$\begin{array}{ccc} \text{C6-sugar} & \xrightarrow{k_1} & \text{5-HMF} & \xrightarrow{k_3} & \text{LA} \\ \downarrow k_2 & & & & \\ \text{humins and unidentified} & & & & \\ \text{soluble products} & & & & \end{array}$	$T = 170\text{--}190$ °C Catalyst = H <sub>2</sub> SO <sub>4</sub> $C_H = 0.1\text{--}0.5$ M Solvent = water	$E_1 = 86$ $E_2 = 210$ $E_3 = 57$	[36]
	$\begin{array}{ccc} \text{C6-sugar} & \xrightarrow{k_1} & \text{5-HMF} & \xrightarrow{k_3} & \text{LA} \\ \downarrow k_2 & & \downarrow k_4 & & \\ \text{humins and unidentified} & & \text{soluble products} & & \end{array}$	$T = 145\text{--}175$ °C Catalyst = [ILSO <sub>3</sub> H][Cl] + NiSO <sub>4</sub> .6H <sub>2</sub> O Solvent = water	$E_1 = 47$ $E_2 = 69$ $E_3 = 34$ $E_4 = 99$	[38]
	$\begin{array}{ccc} \text{C6-sugar} & \xrightarrow{k_1} & \text{5-HMF} & \xrightarrow{k_3} & \text{LA} \\ \downarrow k_2 & & \downarrow k_4 & & \\ \text{humins and unidentified} & & \text{soluble products} & & \end{array}$	$T = 140\text{--}170$ °C No catalyst Solvent = LiCl.3H <sub>2</sub> O	$E_1 = 161$ $E_2 = 23$ $E_3 = 72$ $E_4 = 42$	[37]
	$\begin{array}{ccc} \text{C6-sugar} & \xrightarrow{k_1} & \text{5-HMF} & \xrightarrow{k_3} & \text{LA} \\ \downarrow k_2 & & \downarrow k_4 & & \\ \text{humins and unidentified} & & \text{soluble products} & & \end{array}$	$T = 140\text{--}180$ °C Catalyst = CH <sub>3</sub> -SBA-15-SO <sub>3</sub> H Solvent = $\gamma$ -valerolactone	$E_1 = 77$ $E_2 = 42$ $E_3 = 63$ $E_4 = 62$	[34]
Fructose	$\begin{array}{ccc} \text{C6-sugar} & \xrightarrow{k_1} & \text{5-HMF} & \xrightarrow{k_3} & \text{LA} \\ \downarrow k_2 & & \downarrow k_4 & & \\ \text{humins and unidentified} & & \text{soluble products} & & \end{array}$	$T = 140\text{--}180$ °C Catalyst = H <sub>2</sub> SO <sub>4</sub> $C_H = 0.005\text{--}1$ M Solvent = water	$E_1 = 123$ $E_2 = 148$ $E_3 = 110$ $E_4 = 111$	[29]
	$\begin{array}{ccc} \text{C6-sugar} & \xrightarrow{k_1} & \text{5-HMF} & \xrightarrow{k_3} & \text{LA} \\ \downarrow k_2 & & \downarrow k_4 & & \\ \text{humins and unidentified} & & \text{soluble products} & & \end{array}$	$T = 120\text{--}170$ °C No catalyst Solvent = LiCl.3H <sub>2</sub> O	$E_1 = 139$ $E_2 = 50$ $E_3 = 73$ $E_4 = 54$	[37]
Galactose	$\begin{array}{ccc} \text{C6-sugar} & \xrightarrow{k_1} & \text{5-HMF} & \xrightarrow{k_3} & \text{LA} \\ \downarrow k_2 & & \downarrow k_4 & & \\ \text{humins and unidentified} & & \text{soluble products} & & \end{array}$	$T = 150\text{--}190$ °C Catalyst = H <sub>2</sub> SO <sub>4</sub> $C_H = 0.25\text{--}0.75$ M Solvent = water	$E_1 = 125$ $E_2 = 131$ $E_3 = 69$ $E_4 = 54$	This study

lowest values of activation energies on the main route of C6-sugar decomposition ( $E_1$  and  $E_3$ ). Activation energies of 5-HMF and LA formations were  $E_1 = 47.3 \text{ kJ.mol}^{-1}$  and  $E_3 = 34.28 \text{ kJ.mol}^{-1}$ . It seems good system. However, this system provides drawbacks. Higher LA yield can be achieved at the long reaction time and difficulty in recovering catalyst [34].

#### 4. Conclusions

Acid treatment as well as kinetic studies using sulfuric acid as a catalyst on C6-sugar galactose to yield LA has been investigated. From the three reaction parameters studied in LA production, reaction temperature has a greater influence on LA production than acid concentration and initial substrate loading. A lower initial substrate with higher acid concentration and reaction temperature resulted in more LA. In this experiment, the highest amount of LA of 40 wt% was got at an initial substrate loading of 0.05 M, a temperature of 170 °C, and an acid catalyst concentration of 0.75 M, at 40 min. An increase in temperature and acid concentration in a long reaction time drove the reaction to the formation of by-products directly, as indicated by the results of the reaction kinetics parameters. The galactose decomposition reaction kinetics model under acidic conditions and a temperature range of 150–190 °C has been developed using a pseudo-first-order irreversible approach, the results of which fitted the experimental data.

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#### References

[1] Meinita, M.D.N., Amron, A., Trianto, A., Harwanto, D., Caesarendra, W., Jeong, G.T., Choi, J.S. (2021). Review: Levulinic acid production from macroalgae: Production and promising potential in Industry”. *Sustainability*, 13, 13919. DOI: 10.3390/su132413919.

[2] Jamilatun, S., Suhendra, S., Budhijanto, B., Rochmadi, R., Taufikurahman, T., Yuliestyan, A., Budiman, A. (2020). Catalytic and non-catalytic pyrolysis of *Spirulina platensis* residue (SPR): Effects of temperature and catalyst content on bio-oil yields and its composition. *AIP Conference Proceedings*, 2248, 060003. DOI: 10.1063/5.0013164.

[3] Jeong, G.T., Kim, S.K. (2021). Thermochemical conversion of defatted microalgae *Scenedesmus obliquus* into levulinic and formic acids. *Fuel*, 283, 118907. DOI: 10.1016/j.fuel.2020.118907.

[4] Listyaningrum, N.B., Azis, M.M., Sarto, Rosdi, A.N., sHarun, M.R. (2021). Kinetic Study of Subcritical Water Extraction of Carbohydrates from Microalgae *Nannochloropsis sp.* *ASEAN Journal of Chemical Engineering*, 21(1), 11-18. DOI: 10.22146/ajche.60015.

[5] Ringgani, R., Azis, M.M., Rochmadi, R., Budiman, A. (2022). Kinetic study of levulinic acid from spirulina platensis residue. *Applied Biochemistry and Biotechnology*, 194, 2684–2699. DOI: 10.1007/s12010-022-03806-x.

[6] Signoretto, M., Taghavi, S., Ghedini, E., Menegazzo, F. (2019). Catalytic Production of Levulinic Acid (LA) from Actual Biomass. *Molecules*, 24(15), 2760. DOI: 10.3390/molecules24152760.

[7] Toif, M.E., Hidayat, M., Rochmadi, R., Budiman, A. (Article In Press). Heterogeneous Reaction Model for Evaluating the Kinetics of Levulinic Acid Synthesis from Pretreated Sugarcane Bagasse. *International Journal of Technology*.

[8] Mthembu, L.D., Lokhat, D., Deenadayalu, N. (2021). Esterification of levulinic acid to ethyl levulinate: optimization of process conditions using commercial levulinic acid and extension to the use of levulinic acid derived from depithed sugarcane bagasse. *Biomass Conversion and Biorefinery*, DOI: 10.1007/s13399-021-01632-5.

[9] Huang, X., Liu, K., Vrijbur, W.L., Ouyang, X., Dugulan, A.I., Liu, Y., Verhoeven, M.W.G.M.T., Kosinov, N.A., Pidko, E.A., Hensen, E.J.M. (2020). Hydrogenation of Levulinic Acid to  $\gamma$ -Valerolactone over Fe-Re/TiO<sub>2</sub> Catalysts. *Applied Catalysis B: Environmental*, 278, 119314. DOI: 10.1016/j.apcatb.2020.119314

[10] Kawasumi, R., Narita, S., Miyamoto, K., Tominaga, K., Takita, R., Uchiyama, M. (2017). One-step conversion of levulinic acid to succinic acid using I<sub>2</sub>/t-BuOK System: The Iodoform Reaction Revisited. *Scientific Report*, 7, 17967. DOI: 10.1038/s41598-017-17116-4.

[11] Xie, Z., Chen, B., Wu, H., Liu, M., Liu, H., Zhang, J., Yang, G., Han, B. (2019). Highly efficient hydrogenation of levulinic acid into 2-methyltetrahydrofuran over Ni-Cu/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> bifunctional catalysts. *Green Chemistry*, 21, 606-613. DOI: 10.1039/c8gc02914h.

- [12] Ha, H., Lee, S., Ha, Y., Park, J. (1994). An International Journal for Rapid Communication of Synthetic Organic Chemistry Selective Bromination of Ketones. A Convenient Synthesis of 5-Aminolevulinic Acid. *Synthetic Communications*, 24(18), 2557–2562. DOI: 10.1080/00397919408010567.
- [13] Morone, A., Apte, M., Pandey, R.A. (2015). Review: Levulinic acid production from renewable waste resources: Bottlenecks, potential remedies, advancements and applications. *Renewable and Sustainable Energy Reviews*, 51, 548–565. DOI: 10.1016/j.rser.2015.06.032.
- [14] Antonetti, C., Licurci, D., Fulignati, S., Valentini, G., Galetti, A.M.R. (2016). Review: New Frontiers in the Catalytic Synthesis of Levulinic Acid: From Sugars to Raw and Waste Biomass as Starting Feedstock. *Catalysts*, 6, 196. DOI: 10.3390/catal6120196.
- [15] Son, P.A., Nishimura, S., Ebitani, K. (2012). Synthesis of levulinic acid from fructose using Amberlyst-15 as a solid acid catalyst. *Reaction Kinetics, Mechanisms and Catalysis*, 106, 185-192. DOI: 10.1007/s11144-012-0429-1.
- [16] Girisuta, B., Janssen, L.P.B.M., Heeres, H.J. (2006). Green chemicals: A kinetic study on the conversion of glucose to levulinic acid. *Chemical Engineering Research and Design*, 84, 339-349. DOI: 10.1205/cherd05038.
- [17] Shi, N., Liu, Q., Cen, H., Ju, R., He, X., Ma, L. (2019). Formation of humins during degradation of arbohydrates and furfural derivatives in various solvents. *Biomass Conversion and Biorefinery*, 10, 277–287. DOI: 10.1007/s13399-019-00414-4.
- [18] Ahlkvist, J. (2014). Formic & Levulinic Acid from Cellulose via Heterogeneous Catalysis. *PhD Thesis*. Umeå: Umeå universitet, Sweden, ISBN: 978-91-7459-798-1.
- [19] Yu, I.K.M., Tsang, D.C.W. (2017). Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms. *Bioresource Technology*, 238, 716-732. DOI: 10.1016/j.biortech.2017.04.026.
- [20] Weiqi, W., Shubin, W. (2018). Experimental and kinetic study of glucose conversion to levulinic acid in aqueous medium over Cr/HZSM-5 catalyst. *Fuel*, 225, 311-321. DOI: 10.1016/j.fuel.2018.03.120.
- [21] Hu, X., Wu, L., Wang, Y., Song, Y., Mourant, D., Gunawan, R., Gholizadeh, M., Zhu Li, C. (2013). Acid-catalyzed conversion of mono- and poly-sugars into platform chemicals: Effects of molecular structure of sugar substrate. *Bioresource Technology*, 133, 469–474. DOI: 10.1016/j.biortech.2013.01.080.
- [22] Kang, M., Kim, S.W., Kim, J.W., Kim, T.H., Kim, J.S. (2013). Optimization of levulinic acid production from *Gelidium amansii*. *Renewable Energy*, 54, 173-180. DOI: 10.1016/j.renene.2012.08.028.
- [23] Park, M.R., Kim, S.K., Taek Jeong, G.T. (2018). Optimization of the levulinic acid production from the red macroalga, *Gracilaria verrucosa* using methanesulfonic acid. *Algal Research*, 31, 116-122. DOI: 10.1016/j.algal.2018.02.004.
- [24] Jeong, G.T., Ra, C.H., Hong, Y.K., Kim, J.K., Kong, I.S., Kim, S.K., Park, D.H. (2015). Conversion of red-algae *Gracilaria verrucosa* to sugars, levulinic acid and 5-hydroxymethylfurfural. *Bioprocess and Biosystems Engineering*, 38, 207–218. DOI: 10.1007/s00449-014-1259-5.
- [25] Wang, B., Liu, Q., Huang, Y., Yuan, Y., Ma, Q., Du, M., Cai, T., Cai, Y. (2018). Extraction of Polysaccharide from *Spirulina* and Evaluation of Its Activities. *Hindawi Evidence-Based Complementary and Alternative Medicine*, 2018, 3425615. DOI: 10.1155/2018/3425615.
- [26] Chaiklahan, R., Chirasuwan, N., Triratana, P., Loha, V., Tia, S., Bunnag, B. (2013). Polysaccharide extraction from *Spirulina* sp. and its antioxidant capacity. *International Journal of Biological Macromolecules*, 58, 73–78. DOI: 10.1016/j.ijbiomac.2013.03.046.
- [27] Weingarten, R., Cho, J., Xing, R., Conner Jr, W.C., Huber, G.W. (2012). Kinetics and Reaction Engineering of Levulinic Acid Production from Aqueous Glucose Solutions. *ChemSusChem*, 5(7), 1280-1290. DOI: 10.1002/cssc.201100717.
- [28] Asghari, F.S., Yoshida, H. (2007). Kinetics of the Decomposition of Fructose Catalyzed by Hydrochloric Acid in Subcritical Water: Formation of 5-Hydroxymethylfurfural, Levulinic, and Formic Acids. *Industrial & Engineering Chemistry Research*, 46, 7703-7710. DOI: 10.1021/ie061673e.
- [29] Fachri, B.A., Abdilla, R., Bovenkamp, H., Rasrendra, C., Heeres, H.J. (2016). Experimental and Kinetic Modeling Studies on the Sulphuric Acid Catalyzed Conversion of D-Fructose to 5-Hydroxymethylfurfural and Levulinic acid in Water. *ACS Sustainable Chemistry Engineering*, 3(12), 3024–3034. DOI: 10.1021/acssuschemeng.5b00023.
- [30] Toif, M.E., Hidayat, M., Rochmadi, R., Budiman, A. (2021). Reaction Kinetics of Levulinic Acid Synthesis from Glucose Using Brønsted Acid Catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, 16(4), 904-915. DOI: 10.9767/bcrec.16.4.12197.904-915.

- [31] Thapa, I., Mullen, B., Saleem, A., Leibig, C., Baker, R.T., Giorgi, J.B. (2017), Efficient green catalysis for the conversion of fructose to levulinic acid. *Applied Catalysis A: General*, 539, 70-79. DOI: 10.1016/j.apcata.2017.03.016.
- [32] Son, A.A., Nishimura, S., Ebitani, K. (2012). Synthesis of levulinic acid from fructose using Amberlyst-15 as a solid acid catalyst. *Reaction Kinetics, Mechanisms and Catalysis*, 106, 185-192. DOI: 10.1007/s11144-012-0429-1.
- [33] Hes, N., Mylin, A., Prudius, S. (2022). Catalytic production of levulinic and formic acid from fructose over superacid ZrO<sub>2</sub>-SiO<sub>2</sub>-SnO<sub>2</sub> catalyst. *Colloids and Interfaces*, 6(1), 4. DOI: 10.3390/colloids6010004.
- [34] Cheng, X., Feng, Q., Ma, D., Xing, F., Zeng, X., Huang, X., Teng, J., Feng, L., (2022). Kinetics for glucose conversion to levulinic acid over solid acid catalyst in  $\gamma$ -valerolactone solution. *Biochemical Engineering Journal*, 180, 108360. DOI: 10.1016/j.bej.2022.108360.
- [35] Rackemann, D.W. (2014). Production of Levulinic acid and Other Chemicals From Sugarcane Fibre, Centre for Tropical Crops and Biocommodities. *PhD Thesis*. School of Chemistry, Physics and Mechanical Engineering, Faculty of Science and Technology, Queensland University of Technology".
- [36] Chun, C., Xiaojian, M.A., Peilin, C. (2006). Kinetics of Levulinic Acid Formation from Glucose Decomposition at High Temperature. *Chinese Journal of Chemical Engineering*, 14(5), 708-712. DOI: 10.1016/S1004-9541(06)60139-0.
- [37] Wang, J., Cui, H., Wang, J., Li, Z., Wang, M., Yi, W. (2021). Kinetic insight into glucose conversion to 5-hydroxymethyl furfural and levulinic acid in LiCl·3H<sub>2</sub>O without additional catalyst. *Chemical Engineering Journal*, 415, 128922. DOI: 10.1016/j.cej.2021.128922.
- [38] Kumar, K., Pathak, S., Upadhyayula, S., (2020). 2<sup>nd</sup> generation biomass derived glucose conversion to 5-hydroxymethylfurfural and levulinic acid catalyzed by ionic liquid and transition metal sulfate: Elucidation of kinetics and mechanism. *Journal of Cleaner Production*, 256, 120292. DOI: 10.1016/j.jclepro.2020.120292.
- [39] Kim, H.S., Jeong, G.T. (2018). Valorization of galactose into levulinic acid via acid catalysis. *Korean Journal of Chemical Engineering*, 35(11), 2232-2240. DOI: 10.1007/s11814-018-0126-5.
- [40] Flannelly, T, Lopes, M., Kupiainen, L., Dooley, S., Leahy, J., (2015). Non-Stoichiometric Formation of Formic and Levulinic Acids from the Hydrolysis of Biomass Derived Hexose Carbohydrates. *RSC Advances*, 6, 5797-5804. DOI: 10.1039/C5RA25172A.