

Research Article

Evaluation of Separate and Simultaneous Kinetic Parameters for Levulinic Acid and Furfural Production from Pretreated Palm Oil Empty Fruit Bunches

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Palm oil empty fruit bunches (POEFBs) can be converted into levulinic acid (LA) and furfural, which are among the top building-block chemicals. The purpose of this study was to investigate separate and simultaneous kinetic model parameters for LA and furfural production from POEFBs, which were pretreated by soaking in aqueous ammonia (SAA). The highest LA yield, which was obtained at a reaction temperature of 170°C after 90 min in an acidic solution with a concentration of 1 M, was 52.1 mol%. The highest furfural yield was 27.94 mol%, which was obtained at a reaction temperature of 170°C after 20 min in an acidic solution with a concentration of 0.5 M. SAA pretreatment affected activation energy in glucose degradation reactions and favoured direct conversion of hemicellulose to furfural. The activation energy of LA production ($E_a k_{\text{HMF}}$) increases with higher acid catalyst concentration, and the activation energy of furfural production ($E_a k_{\text{XYN}}$) decreases with higher acid concentration. These trends in the activation energy occurred in both separate and simultaneous kinetic models. Simultaneous kinetic model is better to calculate kinetic parameters of LA and furfural production than separate kinetic models because the simultaneous kinetic model had a lower sum of square error (SSE) when estimating kinetic parameters.

1. Introduction

The palm oil industry continues to grow in response to increased consumption and demand for palm oil. Thus, the palm oil industry represents a major potential source of biomass. During the processing of palm oil, palm oil empty fruit bunches (POEFBs), which are a type of lignocellulosic biomass, are produced as waste. Lignocellulosic biomass consists of cellulose, hemicellulose, lignin, and minor components, such as ash, proteins, and extractives [1].

The largest component of POEFBs is cellulose. Cellulose chains dissociate to produce cellulose fibrils in wood components [2]. Cellulose is surrounded by hemicellulose and lignin, which are the other major fractions from lignocellulosic biomass [3]. Hemicellulose is a branched amorphous polymer compound, of which the main monomer is xylose [4].

Lignin consists of a complex and amorphous three-dimensional network of phenolic polymers; it acts as a support structure for plant cell walls, making these walls resistant to microbial attack [5].

Pretreatment of lignocellulosic biomass is necessary to facilitate hydrolysis of its cellulose and hemicellulose fractions. The pretreatment process is important because it affects production costs. Due to its low boiling point, ammonia can potentially be used for pretreatment of lignocellulosic biomass by the processing industry, and it can easily be recycled back into the process via ventilation [6]. In addition, ammonia is favoured by many studies, including this one, because it is inexpensive and reduces the formation of by-products [7].

Hydrolysis of lignocellulose to produce sugar monomers or other degradation compounds generally uses acid as

a catalyst. Acid hydrolysis of lignocellulosic biomass produces solid and liquid fractions. The solid fraction is rich in cellulose and can be used for bioethanol production. The liquid fraction is rich in hemicellulose, hydrolysate (xylose and arabinose), and fermentation inhibitor compounds [8]. The two fermentation inhibitors produced from acid hydrolysis are levulinic acid (LA) and furfural. LA and furfural are two of the top 12 chemicals, with their potential uses as building blocks for a variety of chemicals and derivatives [9].

LA is a short-chain fatty acid with a ketone carbonyl group and an acidic carboxyl group, enabling it to produce a variety of chemical substances [10]. LA production commences with depolymerisation of the biomass cellulose fraction into oligosaccharides and glucose [11]. Next, six-carbon sugars are hydrolysed to 5-hydroxymethylfurfural (HMF), which is then dehydrated into LA and formic acid [12, 13]. LA has applications in biofuels, in which it is converted into γ -valerolactone, 2-methyltetrahydrofuran, and levulinate esters. Both γ -valerolactone (GVL) and 2-methyltetrahydrofuran can be blended directly with gasoline as alternative fuel for vehicles. Levulinate esters can be used in biodiesel because they have the same properties as fatty acid methyl esters (FAME) [14].

Biofine technology refers to a traditional technology used to produce LA from lignocellulosic biomass [15]. The technology consists of a two-stage process. In the first stage, hexose sugar is converted to HMF using a sulfuric acid catalyst (1–4%) at temperatures of 200–230°C and ambient pressure (20–25 bar) for a few seconds [12]. In the second stage, the product produced in the first stage is hydrolysed into LA at temperatures of around 190–220°C and 10–15 bar pressure for 15–30 min [12].

Furfural derived from lignocellulose has two functional groups: aldehyde and a furan ring system. Furfural can be utilized in various applications, including the production of chemicals and fuels [16]. Furfuryl alcohol is one of the most widely used furfural derivatives. Furfural production generally commences with the initial hydrolysis of the hemicellulose fraction of lignocellulose into pentose, which is then dehydrated into furfural [17]. In this process, in the batch mode, a sulfuric acid catalyst reacts with the biomass at temperatures of 170–185°C to obtain a furfural yield of approximately 40–50%. Examples of commercial furfural production processes are Quaker Oats, Westpro-modified Huaxia Technology, SupraYield, and Vedernikov [15].

Many parameters, such as temperature, acid concentration, and biomass characteristics, influence the rate of LA and furfural reactions. Previous studies have investigated the kinetic reactions of LA and furfural production in various types of biomass using sulfuric acid catalysts [16–26]. Chin et al. [20] performed a kinetic study of POEFB acid hydrolysis, which produced xylose decomposition products and LA. Dussan et al. [21] performed a kinetic study of furfural and LA production from *Miscanthus x giganteus*. These kinetic studies used separate kinetic models; the LA kinetic model was evaluated using a cellulose degradation kinetic model, and the furfural kinetic model was evaluated using a hemicellulose degradation kinetic model. However, LA and furfural kinetic models should be evaluated using

a combined kinetic model because they can be produced simultaneously from biomass in the acid hydrolysis process. Therefore, evaluation of the kinetic model of simultaneous production of furfural and levulinic acid in acid hydrolysis process is important.

There have been no studies evaluating the kinetic parameters of LA and furfural from POEFBs pretreated with ammonia in both separate and simultaneous kinetic models. Therefore, the purpose of this study was to investigate separate and simultaneous kinetic parameters of LA and furfural production using the sulfuric acid hydrolysis process from POEFBs pretreated (soaked) with aqueous ammonia.

2. Materials and Methods

2.1. Biomass and Chemicals. POEFBs were obtained from the palm oil industry PTPN 5 Kertajaya, Banten, Indonesia. The particle size of POEFBs was reduced to 20 mesh, and the POEFBs were washed, dried at temperature 100°C until the moisture content reached 1–5%, and then stored in a plastic bag until further use. Ammonia solution (25%), which was supplied by Merck, Germany, was used as the pretreatment chemical. Sulfuric acid (96.1%) from Mallinckrodt, England, was used as the acid catalyst. Standard analytical grades of glucose, xylose, HMF, furfural, and LA were purchased from Sigma-Aldrich, United States.

2.2. Soaking in Aqueous Ammonia (SAA) Pretreatment. POEFBs were soaked with aqueous ammonia solution (13.13%) for 14 hours at room temperature (27°C) [27]. The solid-to-liquid ratio was 1 : 6. After soaking for 14 hours, the pretreated POEFBs were washed with water to remove ammonia until neutrality and dried until the moisture content reached 1–5%.

2.3. Kinetic Experiments. The kinetic experiments were performed using a pressurized reactor (1 L volume, 16-bar max pressure, and 100 rpm impeller velocity). The reactants were pretreated POEFBs and 0.5 M and 1 M sulfuric acid solution with a mass ratio of 1 : 20. First, pretreated POEFBs and water were added to the reactor. Next, the reactor was tightly sealed and heated. After the reactor reached the desired temperature, a sulfuric acid catalyst was injected into the reactants. The start of the reaction time was when the sulfuric acid catalyst was released into the reactor. Duplicate samples were obtained after 10, 20, 30, 45, 90, and 120 min at 150°C, 160°C, and 170°C (120 min reaction).

2.4. Analytical Methods. Sample compositional analysis of POEFBs before and after the ammonia pretreatment was determined by referring to the method of the National Renewable Energy Laboratory (NREL) [28, 29], and scanning electron microscopy (SEM) of POEFBs was performed to determine the condition of the fibres. The liquid product concentration from kinetic experiments such as glucose, xylose, HMF, furfural, and LA was analysed using high-performance liquid chromatography (HPLC), with an

Aminex HPX-87H ion exclusion column (Bio-Rad, Life Science Group Hercules, CA). The eluent was 0.006 N of H_2SO_4 , and the flow rate was 0.6 ml/min. HPLC detector was a refractive index detector, and the temperatures of the detector and column were 60°C.

2.5. Kinetic Modeling. This research used two steps to evaluate kinetic parameters of LA and furfural production which are separate kinetic evaluation and simultaneous kinetic evaluation in the same experimental data. Separate kinetic evaluation assumed that there is no interference between LA and furfural kinetic reaction, so the kinetic parameter calculation of LA and furfural would be done in a separate kinetic model. On the other side, the simultaneous kinetic evaluation calculated LA and furfural kinetic reaction in one kinetic model. The effects of other components in POEFBs such as lignin and ash were negligible from LA and furfural kinetic models, and kinetic parameter calculation since ammonia pretreatment was done before kinetic experiments.

2.6. Separate Kinetic Model of LA and Furfural. In separate kinetic evaluation, LA production was independently evaluated using kinetic model of Girisuta et al. [22], who examined the kinetics of acid hydrolysis of sugarcane bagasse in the production of LA. The reaction model of Girisuta et al. [22] is consecutive reactions from glucan to glucose and humin, then to HMF before finally transforming to LA + FA. The model can be computed with the following kinetic equations:

$$\begin{aligned}\frac{dC_{\text{glucan}}}{dt} &= -k_{\text{GLN}} \cdot C_{\text{glucan}}, \\ \frac{dC_{\text{glucose}}}{dt} &= k_{\text{GLN}} \cdot C_{\text{glucan}} - k_{\text{GLC1}} \cdot C_{\text{glucose}} - k_{\text{GLC2}} \cdot C_{\text{glucose}}, \\ \frac{dC_{\text{HMF}}}{dt} &= k_{\text{GLC2}} \cdot C_{\text{glucose}} - k_{\text{HMF}} \cdot C_{\text{HMF}}, \\ \frac{dC_{\text{LA(+FA)}}}{dt} &= k_{\text{HMF}} \cdot C_{\text{HMF}}, \\ \frac{dC_{\text{HUM}}}{dt} &= k_{\text{GLC2}} \cdot C_{\text{glucose}}.\end{aligned}\quad (1)$$

As the HPLC analysis of xylose and furfural did not reveal the presence of xylose in most of the samples, xylose was not included in this furfural kinetic model. The furfural kinetic model reaction scheme for the first stage is shown in Figure 1. From Figure 1, we can compute the following kinetic equations:

$$\begin{aligned}\frac{dC_{\text{xytan}}}{dt} &= -k_{\text{XLN}} \cdot C_{\text{xytan}}, \\ \frac{dC_{\text{furfural}}}{dt} &= k_{\text{XYN}} \cdot C_{\text{xytan}} - k_{\text{FUR}} \cdot C_{\text{furfural}}, \\ \frac{dC_{\text{RES}}}{dt} &= k_{\text{FUR}} \cdot C_{\text{furfural}}.\end{aligned}\quad (2)$$

2.7. Simultaneous Kinetic Model of LA and Furfural. Simultaneous kinetic evaluation would calculate LA and furfural production in one kinetic model. The reaction

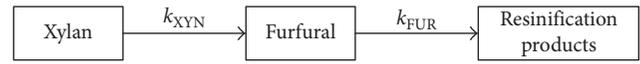


FIGURE 1: Reaction scheme of furfural production.

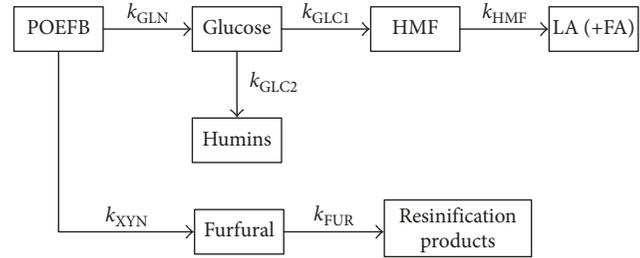


FIGURE 2: Simultaneous reaction scheme of LA and furfural production.

scheme is shown in Figure 2. From Figure 2, we can compute the following kinetic equations:

$$\begin{aligned}\frac{dC_{\text{POEFB}}}{dt} &= -k_{\text{GLN}} \cdot C_{\text{POEFB}} - k_{\text{XLN}} \cdot C_{\text{POEFB}}, \\ \frac{dC_{\text{glucose}}}{dt} &= k_{\text{GLN}} \cdot C_{\text{POEFB}} - k_{\text{GLC1}} \cdot C_{\text{glucose}} \\ &\quad - k_{\text{GLC2}} \cdot C_{\text{glucose}}, \\ \frac{dC_{\text{HMF}}}{dt} &= k_{\text{GLC2}} \cdot C_{\text{glucose}} - k_{\text{HMF}} \cdot C_{\text{HMF}}, \\ \frac{dC_{\text{LA(+FA)}}}{dt} &= k_{\text{HMF}} \cdot C_{\text{HMF}}, \\ \frac{dC_{\text{HUM}}}{dt} &= k_{\text{GLC2}} \cdot C_{\text{glucose}}, \\ \frac{dC_{\text{furfural}}}{dt} &= k_{\text{XYN}} \cdot C_{\text{POEFB}} - k_{\text{FUR}} \cdot C_{\text{furfural}}, \\ \frac{dC_{\text{RES}}}{dt} &= k_{\text{FUR}} \cdot C_{\text{furfural}}.\end{aligned}\quad (3)$$

2.8. Kinetic Parameter Estimation for Separate Kinetic Model of LA and Furfural. Reaction rate constants were optimized by minimizing errors between the experimental data, such as the concentrations of glucose, xylose, HMF, furfural, and LA at various temperatures and concentrations of acid catalyst with kinetic models. The concentrations were transformed into yields to compensate the large spread in concentrations. The sum of square error (SSE) of LA and furfural model prediction was formulated:

$$\text{SSE} = \sum_x \sum_n (Y_{n,\text{predicted}} - Y_{n,\text{experiment}})^2, \quad (4)$$

where $Y_{n,\text{predicted}}$ is the model yield predicted for every sampling time (mol/mol)%, $Y_{n,\text{experiment}}$ is the experimental yield for every sampling time (mol/mol)%, and x is the data of glucose, xylose, HMF, furfural, and LA.

The yield of LA from the POEFBs on a molar basis (Y_{LA}) was defined as the ratio of the LA concentration in the acid hydrolysis product (C_{LA}) to the initial C6 sugar concentration in the POEFBs (C_6):

$$Y_{LA} \text{ (mol/mol)\%} = \frac{C_{LA}}{C_6} \times 100\%. \quad (5)$$

The yield of furfural from the POEFBs on a molar basis (Y_F) was defined as the ratio of the furfural in the acid hydrolysis product ($C_{furfural}$) to the initial C5 sugar concentration in the POEFBs (C_5):

$$Y_F \text{ (mol/mol)\%} = \frac{C_{furfural}}{C_5} \times 100\%. \quad (6)$$

Minimization of the sum of square error values was done by fminsearch optimization using MATLAB optimization routine to get LA and furfural reaction rate constants at optimum slope. The value of the reaction rate constants was used to determine the value of the preexponential factor (A) and activation energy (E_a), using the Arrhenius equation. Systematically, the relationship between the reaction rate constant (k) and temperature (T) was expressed by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right), \quad (7)$$

where k is the reaction rate constant, A is the preexponential factor, E_a is the activation energy (kJ/mol), R is the gas constant (kJ/mol·K), and T is the temperature (K).

The effect of acid concentration on LA and furfural production can be predicted using acid reaction order equation that in this equation, there is correlation between reaction rate constant and acid concentration, which can be formulated:

$$k = A_x [C]^n, \quad (8)$$

where k is the reaction rate constant, A_x is the preexponential factor from acid reaction order equation, C is the acid concentration (M), and n is the acid reaction order. The calculation of acid reaction order was counted based on (8) from the average value of kinetic experiment temperature.

2.9. Kinetic Parameter Estimation for Simultaneous Kinetic Model of LA and Furfural. The calculation of kinetic parameters for simultaneous kinetic model of LA and furfural was same with the separate kinetic model, but the yield from experimental data was obtained from mass basis.

The yield of LA and furfural from the POEFBs on mass basis was defined as the ratio of the LA and furfural mass concentration in the acid hydrolysis product (m_{LA} and $m_{furfural}$) to the mass of cellulose and hemicellulose in the POEFBs (m_b):

$$Y_{LA} \text{ (gr/gr)\%} = \frac{m_{LA}}{m_b} \times 100\%, \quad (9)$$

$$Y_F \text{ (gr/gr)\%} = \frac{m_{furfural}}{m_b} \times 100\%.$$

3. Results and Discussion

3.1. SAA Pretreatment. The purpose of the pretreatment process was to improve the conversion of cellulose and hemicellulose to LA and furfural. The results of the compositional analysis of different types of biomass with SAA pretreatment are shown in Table 1.

According to Table 1, the composition of the POEFBs before and after the SAA pretreatment did not differ greatly, with just a small reduction in lignin composition (from 22.8% to 21.8%). The composition of cellulose and hemicellulose in the untreated POEFBs increased slightly from 39.3% to 29.8%, as compared to the SAA pretreated POEFBs (42% and 32.0%, resp.). As shown in Table 1, previous studies also reported insignificant changes in lignin composition in untreated and SAA pretreated samples at various temperatures, soaking times, and ammonia concentrations [30–33].

Lignin can affect LA and furfural production. However, according to Daorattanachai et al. [34], lignin can promote the isomerization reaction of glucose to fructose, which can then be dehydrated to HMF using a phosphoric acid catalyst. As is well known, lignin removal from lignocellulose biomass is difficult and costly. Therefore, in this study, lignin was not removed from the biomass.

In this study, based on Zulkiple et al. [27], SSA pretreatment produced more sugar than raw POEFBs after enzyme hydrolysis. Ammonia pretreatment is an alkali pretreatment. The alkali agent saponifies the ester bonds in the xylan backbone, resulting in the production of carboxyl groups and the breakdown of lignin-hemicellulose bonds [6].

SEM images before and after the SAA pretreatment are presented in Figure 3. As shown in Figure 3(a), prior to the SSA pretreatment, the POEFB fibres looked hard and stiff, with a flat, smooth surface structure. After the SAA pretreatment, the lignin-carbohydrate bonds in the POEFB fibres broke down and the surface contained pores, indicating that the surface area of the POEFBs had increased (Figure 3(b)). Thus, SAA pretreatment appears able to break the bonds between lignin and carbohydrate. As reported earlier, ammonia will also increase the accessibility of cellulose because it acts as a swelling agent [35].

3.2. Evaluation of the Separate Kinetic Parameters of LA and Furfural Production

3.2.1. Evaluation of the Kinetic Parameters of LA Production. LA optimization results are presented in Figure 4. According to Figure 4(f), the highest yield of LA in the kinetic experiments was 52.1 mol%; this was obtained at a reaction temperature of 170°C, after a 90 min reaction, using an acid concentration of 1 M. Girisuta et al. [22] and Dussan et al. [21] examined the kinetics of LA production from sugarcane bagasse and a *Miscanthus giganteus* cross, respectively, at a temperature of 150–200°C, with a sulfuric acid catalyst (0.1–0.5 M), and obtained yields of around 60–70% mol. The lower yield found in the present study may be due to the operating temperature, which was quite low (150–170°C),

TABLE 1: Compositional analysis results of different types of biomass with SAA pretreatment.

Reference	[30]	[31]	[32]	[33]	This study					
Biomass	Barley hull	Switchgrass	Manure fibres	Poplar	POEFBs					
t^a	168	8	72	72	14					
T^b	30	40	22	22	27					
C^c (%)	30	15	15	32	13.13					
Composition (%)	Untreated	SAA	Untreated	SAA	Untreated	SAA	Untreated	SAA	Untreated	SAA
α -Cellulose (glucan)	33.6	33.6	37.0	33.2	17.1	18.7	32.7	29.1	39.3	42.0
Hemicellulose (xylan)	30.5	30.0	15.4	17.1	12.7	10.9	16.8	12.0	29.8	32.0
Lignin	19.3	13.4	25.0	22.1	24.8	22.3	34.2	34.4	22.8	21.8
Ash	NA	NA	NA	NA	NA	NA	NA	NA	1.7	1.8

^a t : soaking time (hours); ^b T : soaking temperature ($^{\circ}$ C); ^c C : ammonia concentration (%).

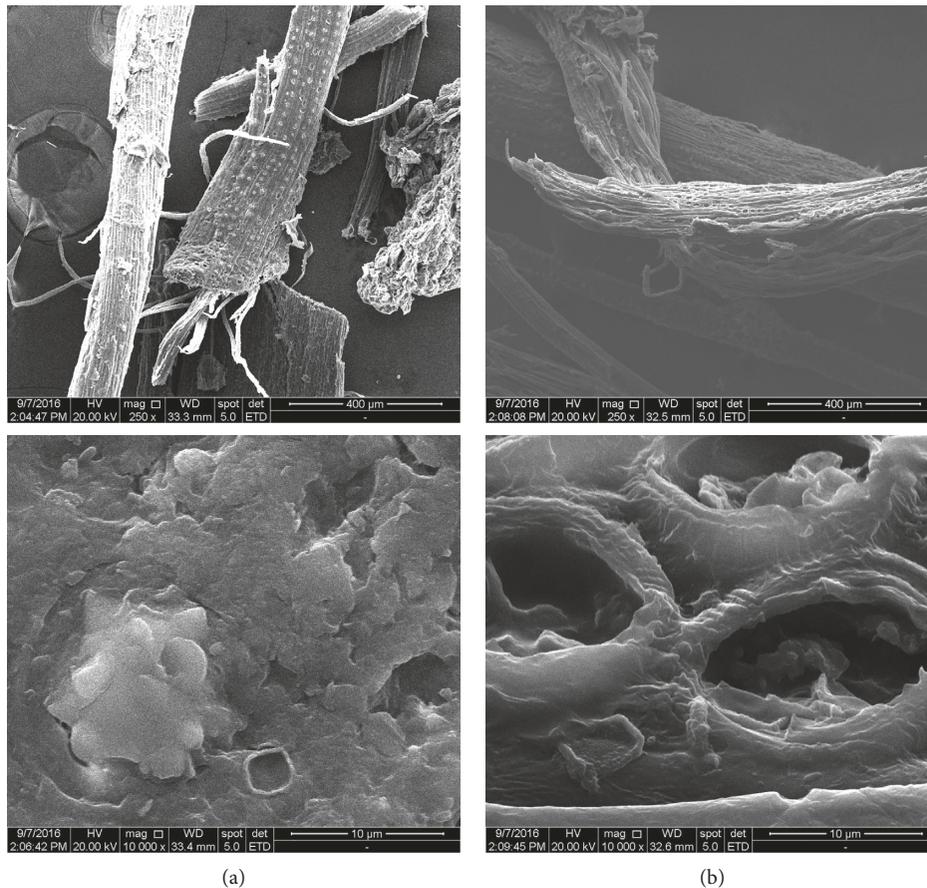


FIGURE 3: SEM images of OPEFB: (a) before the ammonia pretreatment; (b) after the ammonia pretreatment. Images of (a) and (b) have 2 different magnifications: with 400 μ m (upper images) and 10 μ m (lower images).

although the acid catalyst concentration was high (0.5–1 M) compared to that used by Girisuta et al. [22] and Dussan et al. [21]. This result shows that temperature affects LA production.

Comparison of activation energy values of LA production at different acid concentrations can be seen in Table 2. According to Table 2, activation energy tended to decrease in higher acid concentrations because sulfuric acid functioned as a catalyst to reduce the activation energy for LA production.

The activation energy for glucose formation was lower (132.37 kJ/mol and 108.48 kJ/mol) than the activation energy

for HMF formation (212.40 kJ/mol and 119.49 kJ/mol) in 0.5 and 1 M acid concentration, indicating that the glucose formation reaction was faster than the HMF formation reaction. This proved that higher temperature made the rate of the HMF formation reaction faster.

The HMF formation reaction at 0.5 and 1 M acid concentrations had higher activation energies (212.40 kJ/mol and 119.49 kJ/mol) and acid reaction order (2.00) than the activation energies (188.31 kJ/mol and 62.12 kJ/mol) and acid reaction order (1.66) of humin formation. These indicated that more glucose decomposed into HMF rather than into humins at higher temperatures. Likewise, the HMF

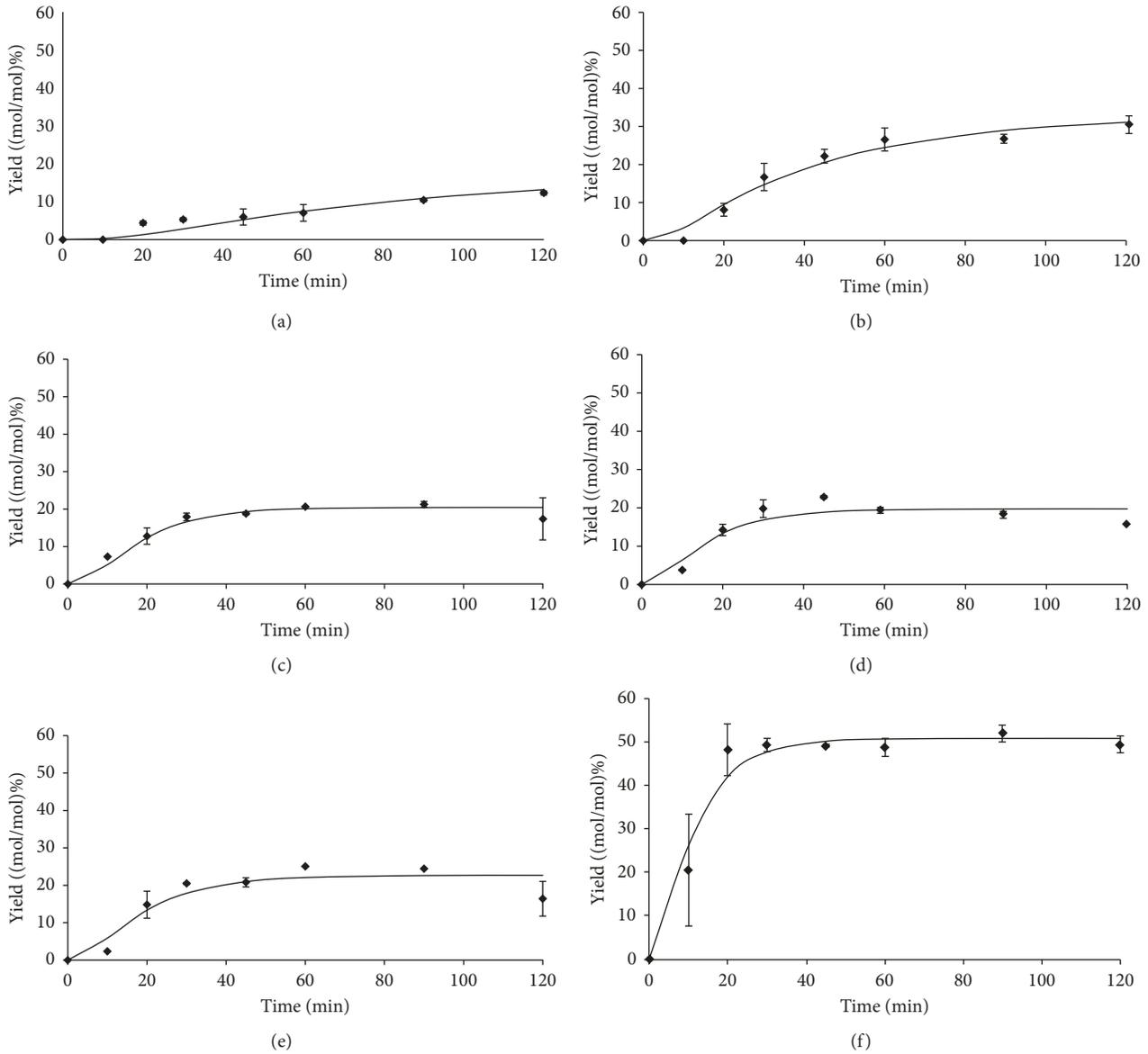


FIGURE 4: LA optimization results between experimental data (◆, LA) and kinetic model (lines): (a) 150°C and 0.5 M; (b) 150°C and 1 M; (c) 160°C and 0.5 M; (d) 160°C and 1 M; (e) 170°C and 0.5 M; and (f) 170°C and 1 M.

formation reaction had the highest activation energy and acid reaction order compared to all other reactions. These indicated that both temperature and acid concentration have greater effects on this reaction than on other reactions.

The effect of acid concentration also had an important role in humin formation, which can be seen from the second highest acid reaction order value after HMF formation. The higher acid concentration triggered the formation of humins. Humin formation is undesirable in the production of LA because this reaction competes with HMF formation when using glucose as the raw material. Therefore, temperature and acid concentration become important factors to prevent humin formation.

The lowest activation energy was recorded for LA formation (42.55 kJ/mol and 56.08 kJ/mol), suggesting that HMF was quickly converted into LA. The HMF concentration

TABLE 2: Kinetic parameters for LA production.

Reaction rate constants	Activation energy E_a (kJ/mol)		Acid reaction order n (-)
	0.5 M	1 M	
k_{GLN}	132.37	108.48	0.78
k_{GLC1}	212.40	119.49	2.00
k_{GLC2}	188.31	62.12	1.66
k_{HMF}	42.55	56.08	1.15

during the kinetic experiments was low due to rapid HMF degradation and LA formation.

The comparison of kinetic parameters in LA production (0.5 M acid concentration) with other research is shown in Table 3. The results from this study were compared with Girisuta et al. [22] and Dussan et al. [21], who examined the

TABLE 3: Comparison of kinetic parameters for LA production.

	Reaction rate constants	[22]	[21]	This study
Activation energy E_a (kJ/mol)	k_{GLN}	144.85	188.9	132.37
	k_{GLC1}	152.14	155.5	212.40
	k_{GLC2}	161.41	186.2	188.31
	k_{HMF}	101.63	121.3	42.55
Acid reaction order n (-)	k_{GLN}	1.57	1.40	0.78
	k_{GLC1}	1.14	1.39	2.00
	k_{GLC2}	1.08	0.90	1.66
	k_{HMF}	1.32	1.95	1.15

kinetics of LA production from sugarcane bagasse and a *Miscanthus giganteus* cross, respectively, at a temperature of 150–200°C with a lower sulfuric acid catalyst (0.1–0.5 M).

The activation energy of glucose formation in the present study (132.37 kJ/mol) was not too different from the studies by Girisuta et al. [22] and Dussan et al. [21], who reported figures of 144.85 kJ/mol and 188.9 kJ/mol, respectively. The differences could be due to the different characteristics of the biomass used.

In the present study, the lowest activation energy for LA formation was the same as that recorded in other research. Girisuta et al. [22] and Dussan et al. [21] reported low activation energies of about 101.63 kJ/mol and 121.3 kJ/mol, respectively. In this study, the activation energy conversion of LA formation was much smaller (42.55 kJ/mol), indicating that LA readily forms at a lower activation energy.

SAA pretreatment was the most likely cause of the higher activation energy in HMF formation (212.40 kJ/mol) as compared to humin formation (188.31 kJ/mol) in this study. In contrast, Girisuta et al. [22] and Dussan et al. [21] reported that the activation energy of HMF formation was lower than the activation energy of humin formation. The ammonia pretreatment likely improved the accessibility of the glucose, thereby resulting in increased production of HMF rather than humins. The results suggested that, at higher temperatures, the reaction pathway will tend to lead HMF formation rather than humins. The humins in this study may be products from cellulose conversions other than HMF.

The acid concentration had a larger effect on LA formation, which is consistent with the data in earlier studies. Girisuta et al. [22] and Dussan et al. [21] reported acid reaction orders of approximately 1.32 and 1.95, respectively, which were relatively similar to the acid reaction order in the present study (1.15). Therefore, higher acid concentration will enhance LA formation.

3.2.2. Evaluation of the Kinetic Parameters of Furfural Production. Furfural optimization results are presented in Figure 5. As shown in Figure 5(e), the largest furfural yield in this study (27.94 mol%) was obtained at a temperature of 170°C, with a 20 min reaction and a 0.5 M acid concentration. The furfural yield in this study was low. This was likely due to the high temperature (170°C), resulting in the formation of degradation products (formic acid and tar), as reported previously by Danon et al. [36]. In addition, the presence of lignin may have affected furfural production. Lamminpaa

et al. [37] showed that lignin can increase the pH of a reactant solution, leading to low conversion of xylose into furfural.

In the present study, xylose was detected only at a temperature of 150°C, after a 60 min reaction time in a 0.5 M acid concentration. Xylose was undetectable at higher temperatures, higher acid concentrations, and longer reaction times, in contrast to the findings of Dussan et al. [21] and Chin et al. [20]. Both studies detected xylose at higher reaction temperatures of about 200°C and 180°C, respectively. The kinetic model by Dussan et al. [21], which incorporated xylose, was not in line with the experimental data. Therefore, xylose was not included in the furfural kinetic model.

The SAA pretreatment explains the differences between xylose production in this study as compared to those observed in the kinetic experiments conducted by Dussan et al. [21] and Chin et al. [20]. Hemicellulose is an amorphous polymer, which is more easily degraded than cellulose. In the presence of ammonia pretreatment, the increased accessibility of hemicellulose means it is likely to be converted into a variety of products. Therefore, during acid hydrolysis, xylose located in hemicellulose amorphous fibres will be directly converted into furfural.

In this study, according to Table 4, the activation energy of furfural formation (76.76 kJ/mol) was higher than the activation energy of furfural decomposition (9.89 kJ/mol) in 0.5 M acid concentration. This means that, at higher temperatures, reactions can produce more furfural. The largest furfural yield in this study (27.94 mol%) was obtained at a temperature of 170°C in 0.5 M acid concentration.

In contrast, the higher acid concentration (1 M) made the activation energy of furfural formation (59.22 kJ/mol) lower than the activation energy of furfural decomposition (77.08 kJ/mol). This means that, at higher temperatures, reactions can degrade furfural, as indicated by the fact that the furfural yield was lower at a temperature of 170°C in 1 M acid concentration in the present study.

3.3. Evaluation of Simultaneous Kinetic Parameters of LA and Furfural Production. The results of the evaluation of simultaneous kinetic parameters of LA and furfural are presented in Figure 6, and the comparison of separate and simultaneous LA and furfural kinetic parameters at different acid concentrations can be seen in Table 5, which shows that the activation energy of LA production was reduced because of the sulfuric acid catalyst. The LA activation energy trends are the same in separate and simultaneous LA production, except for $E_a k_{GLN}$.

As shown in Table 5, the activation energy of glucose formation ($E_a k_{GLN}$) in the simultaneous kinetic model tended to increase when the acid concentration was higher. The higher activation energy of the glucose formation ($E_a k_{GLN}$) indicated that there were complex hydrolysis interaction reactions of pretreated POEFBs when LA and furfural kinetic parameters were calculated simultaneously. Glucose was the main monomer derived from the pretreated POEFB cellulose fraction, which was the highest fraction (42%) in pretreated POEFBs; therefore, glucose was the largest monomer composition in pretreated POEFBs.

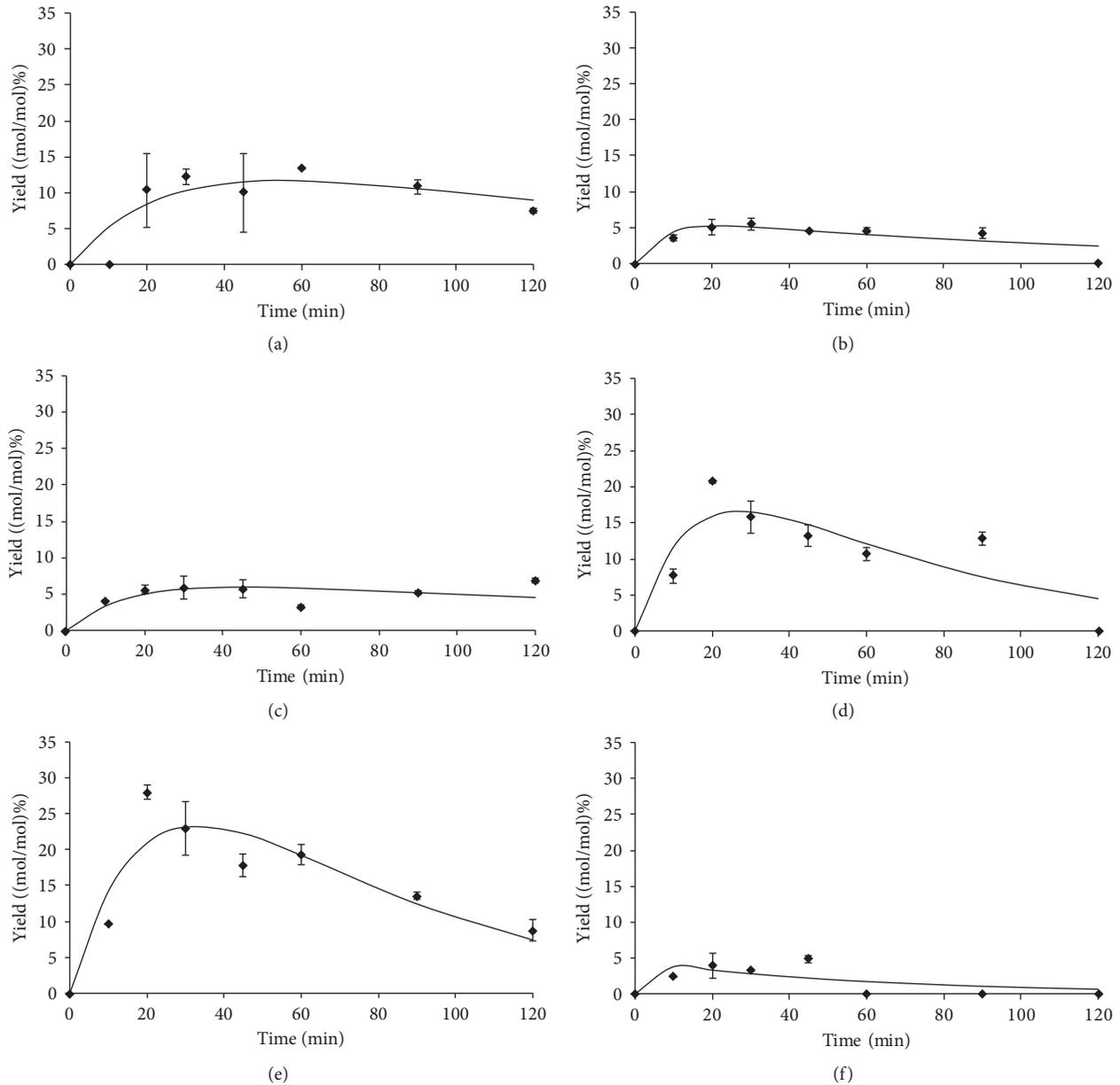


FIGURE 5: Furfural optimization results between experimental data (◆, furfural) and kinetic model (lines): (a) 150°C and 0.5 M; (b) 150°C and 1 M; (c) 160°C and 0.5 M; (d) 160°C and 1 M; (e) 170°C and 0.5 M; and (f) 170°C and 1 M.

The degradation process from cellulose fraction into glucose was a complex reaction in biomass hydrolysis. In contrast, LA was the product of a series of reaction steps in the acid hydrolysis of biomass. LA formation was a complex reaction produced from C6 sugars (glucose and fructose) in lignocellulose biomass [12]. Therefore, the activation energy of glucose formation ($E_a k_{GLN}$) depends on reaction conditions and the interaction between compounds that affect its degradation into other products (HMF and humins).

According to Table 5, the activation energy of furfural formation (171.74 kJ/mol) was higher than the activation energy of furfural decomposition (98.21 kJ/mol) in 0.5 M acid concentration, and the activation energy of furfural formation (88.81 kJ/mol) was lower than the activation energy of furfural

TABLE 4: Kinetic parameters for furfural production.

Reaction rate constants	Activation energy E_a (kJ/mol)		Acid reaction order n (-)
	0.5 M	1 M	
k_{XYN}	76.76	59.22	1.02
k_{FUR}	9.89	77.08	1.64

decomposition (175.14 kJ/mol) in 1 M acid concentration. This means that, at higher temperatures, reactions can produce more furfural in 0.5 acid concentration, but furfural would be degraded in 1 M acid concentration. Therefore, it was shown that the interaction effect on biomass hydrolysis is very low for furfural formation because hemicellulose is

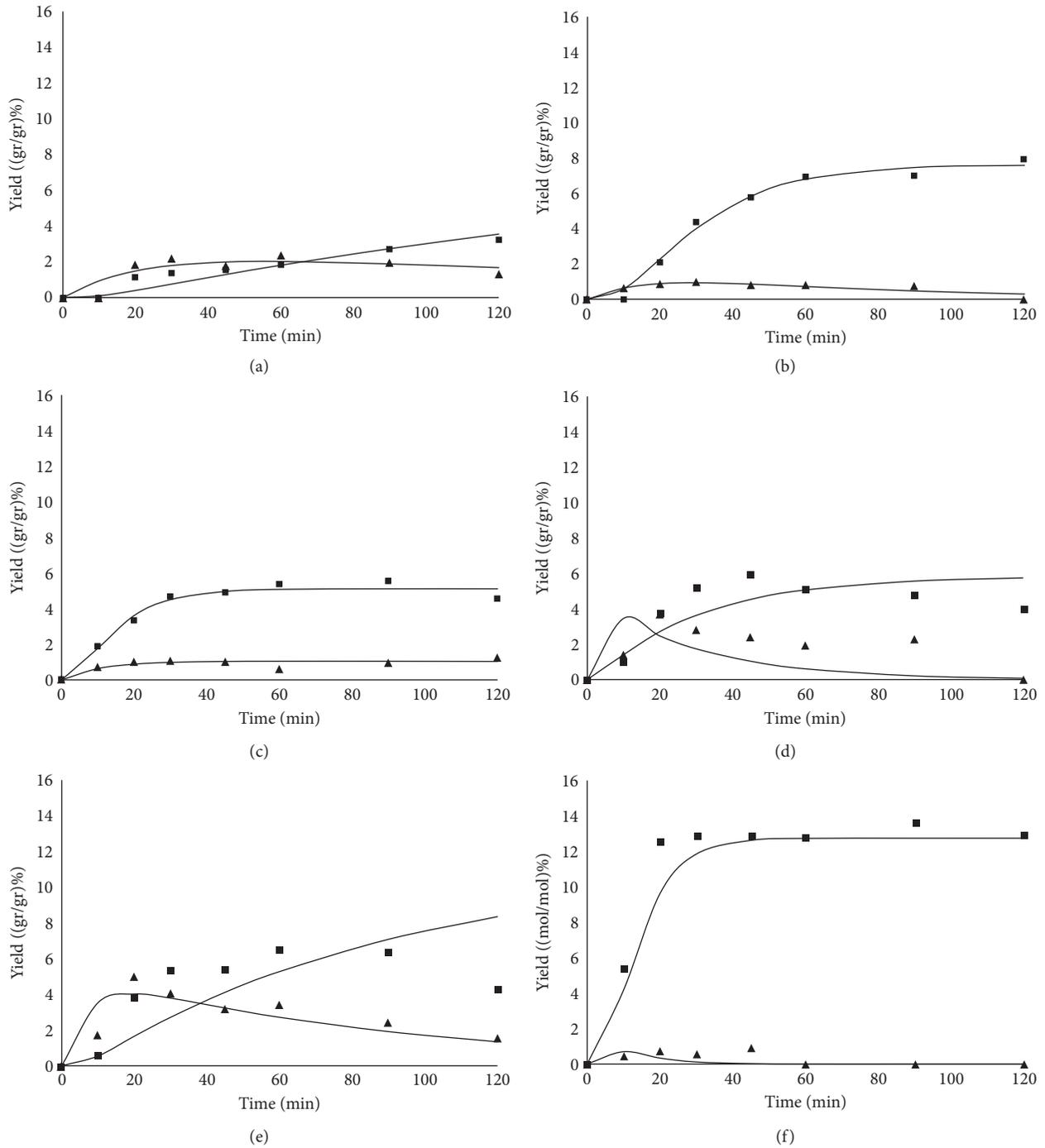


FIGURE 6: LA and furfural simultaneous optimization results between experimental data (■, LA; ▲, furfural) and simultaneous kinetic model (lines): (a) 150°C and 0.5 M; (b) 150°C and 1 M; (c) 160°C and 0.5 M; (d) 160°C and 1 M; (e) 170°C and 0.5 M; and (f) 170°C and 1 M.

comprised of amorphous fibres that are easily degraded in the biomass hydrolysis process.

The acid reaction order in the simultaneous kinetic model of LA and furfural production showed higher values than that in the separate kinetic model. This suggested that acid had an important role as a catalyst in the hydrolysis reaction of pretreated POEFBs and LA-furfural production.

According to Table 5, the activation energy of LA and furfural acid production from simultaneous kinetic model

calculation had the same trend as the separate kinetic model calculation. In separate and simultaneous kinetic models, the activation energy of LA production ($E_a k_{\text{HMF}}$) increased with higher acid catalyst concentration and the activation energy of furfural production ($E_a k_{\text{XYN}}$) decreased with higher acid concentration.

Simultaneous kinetic model is better than separate kinetic models for evaluating kinetic parameters in LA and furfural production. Glucan and xylan in separate kinetic

TABLE 5: Kinetic parameters for separate and simultaneous LA and furfural production.

Reaction rate constants	Activation energy (E_a) (kJ/mol)				Acid reaction order n (-)	
	Separate		Simultaneous		Separate	Simultaneous
	0.5 M	1 M	0.5 M	1 M		
k_{GLN}	132.37	108.48	25.95	61.18	0.78	4.75
k_{GLC1}	212.40	119.49	99.27	60.36	2.00	3.51
k_{GLC2}	188.31	62.12	18.38	4.25	1.66	1.37
k_{HMF}	42.55	56.08	33.27	83.97	1.15	2.18
k_{XYN}	76.76	59.22	171.74	88.81	1.02	2.37
k_{FUR}	9.89	77.08	98.21	175.14	1.64	1.35

models of LA and furfural were combined into one kinetic model (Figure 2) because glucan and xylan are fractions in POEFBs; this is the main reason simultaneous kinetic model was developed in this study. The sum of square error (SSE) of the optimization result between the experimental data and the models in the kinetic parameter estimation was lower in the simultaneous kinetic model (14.32) compared to those in the separate kinetic models (88.23 for LA and 44.04 for furfural). Therefore, the simultaneous kinetic model is better than separate kinetic models.

4. Conclusion

This study evaluated separate and simultaneous kinetic models of LA and furfural production from POEFBs that were pretreated with ammonia. A kinetic experiment was performed using a pressurized reactor at a temperature of 150–170°C, with a sulfuric acid catalyst at concentrations of 0.5 M and 1 M. In the kinetic experiments, the greatest LA yield was 52.1 mol%, which was obtained at a reaction temperature of 170°C, after a 90 min reaction, using an acid concentration of 1 M. The highest furfural yield was 27.94 mol%, which was obtained at a temperature of 170°C, after a 20 min reaction, using an acid concentration of 0.5 M. SAA pretreatment affected activation energy in glucose degradation reactions and favoured direct conversion of hemicellulose to furfural. Based on the evaluation of the kinetic parameters, the simultaneous kinetic model has been shown to have the same trends as the separate kinetic models in LA and furfural production: the activation energy of LA production ($E_a k_{HMF}$) increases with higher acid catalyst concentration, and the activation energy of furfural production ($E_a k_{XYN}$) decreases with higher acid concentration. Higher reaction temperature and acid concentration will increase LA production. However, higher acid concentration can reduce furfural production because of furfural decomposition. Based on the lower sum of square error (SSE) of the optimization result between the experimental data and the models in the kinetic parameter estimation, simultaneous kinetic model is better to calculate kinetic parameters of LA and furfural production than separate kinetic models.

Nomenclature

A:	Preexponential factor (s^{-1})
C_5 :	C5 sugar concentration (mol/L)
C_6 :	C6 sugar concentration (mol/L)

$C_{furfural}$:	Furfural concentration (mol/L)
C_{glucan} :	Glucan concentration (mol/L)
$C_{glucose}$:	Glucose concentration (mol/L)
C_{HMF} :	5-Hydroxymethylfurfural concentration (mol/L)
C_{HUM} :	Humin concentration (mol/L)
C_{LA} :	Levulinic acid concentration (mol/L)
C_{RES} :	Resinification product concentration (mol/L)
C_{xylan} :	Xylan concentration (mol/L)
E_a :	Activation energy (kJ/mol)
FA:	Formic acid
FAME:	Fatty acid methyl esters
GVL:	γ -Valerolactone
H_2SO_4 :	Sulfuric acid
HCl:	Hydrochloric acid
HMF:	5-Hydroxymethylfurfural
HPLC:	High-performance liquid chromatography
k :	Reaction rate constant (s^{-1})
k_{FUR} :	Furfural reaction rate constant (s^{-1})
k_{GLC1} :	Glucose reaction rate constant 1 (s^{-1})
k_{GLC2} :	Glucose reaction rate constant 2 (s^{-1})
k_{GLN} :	Glucan reaction rate constant (s^{-1})
k_{HMF} :	5-Hydroxymethylfurfural reaction rate constant (s^{-1})
k_{XLN} :	Xylan reaction rate constant (s^{-1})
LA:	Levulinic acid
n :	Acid reaction order
NREL:	National Renewable Energy Laboratory
POEFBs:	Palm oil empty fruit bunches
R:	Gas constant (kJ/mol \cdot °C)
SAA:	Soaking in aqueous ammonia
SEM:	Scanning electron microscopy
SSE:	Sum of square error
T:	Temperature (°C)
Y_F :	Furfural yield (mol%)
Y_{LA} :	Levulinic acid yield (mol%)
$Y_{n,experiment}$:	Experimental yield for every sampling time (mol/mol)%
$Y_{n,predicted}$:	Model yield predicted for every sampling time (mol/mol)%

Data Availability

The authors confirm that all data underlying the findings in the paper are fully available without restriction.

The calculations and data used to support the findings of this study are included within the paper and supplementary information file.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

LA and furfural reaction rate constant data at optimum slope after MATLAB optimization can be seen in supplementary materials. (*Supplementary Materials*)

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