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Reaction Kinetics of Levulinic Acid Synthesis from Glucose Using Bronsted Acid Catalyst

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Catalyst

Abstract—Glucose is the primary derivative of lignocellulosic biomass, which is abundantly available. Glucose has excellent potential to be converted into valuable compounds such as ethanol, sorbitol, gluconic acid, and levulinic acid (LA). Levulinic acid is a very promising green platform chemical. It is composed of two functional groups, ketone and carboxylate groups which can act as highly reactive electrophiles for nucleophilic attack so it has extensive applications, including fuel additives, raw materials for the pharmaceutical industry, and cosmetics. The reaction kinetics of LA synthesis from glucose using hydrochloric acid catalyst (bronsted acid) were studied in a wide range of operating conditions, i.e., temperature of 140-180 °C, catalyst concentration of 0.5-1.5 M, and initial glucose concentration of 0.1-0.5 M. The highest LA yield is 48.34 %wt at 0.1 M initial glucose concentration, 1 M HCl, and temperature of 180 °C. The experimental results show that the bronsted acid catalyst's reaction pathway consists of glucose decomposition to levoglucosan (LG), conversion of LG to 5-hydroxymethylfurfural (HMF), and rehydration of HMF to LA. The experimental data yields a good fitting by assuming a first-order reaction model.

Keywords: Bronsted Acid, Glucose, Hydrochloric Acid, Kinetics, Levulinic Acid.

INTRODUCTION

Many kinds of materials in industries still originate from fossils, whereas they are not the only feedstock used. Hazardous materials emission and global warming are environmental problems from fossils [1]. Fossils, which are currently popular material widely used, experience a continuous decline in quantity. Lignocellulosic biomass, a renewable raw material, can be the solution as an alternative for energy and chemical production.

Lignocellulosic biomass is generally available from forest and agricultural residues [2]. It can reduce inorganic carbon from the environment through photosynthesis. Biomass production via photosynthesis can reach 150 million tons per year [3]. It fits with the goal of sustainable resource development [4]. Recently, researchers have begun to focus on converting biomass into various types of materials. The research conducted aims to develop more environmentally friendly technology. Biomass conversion can also solve problems related to agricultural residue waste [5]. Furthermore, biomass as residue with low or even negative value has an advantage from not competing with food needs [6].

Cellulose, hemicellulose, and lignin are the main components of lignocellulosic biomass. Each of these components can be cracked or derived to many other beneficial compounds. Cellulose is a stable polymer composed of anhydroglucose units in linear glucan chains [2]. Cellulose, a natural polymer, is a core component of raw materials synthesis in the chemical industry [4]. In general, cellulose undergoes hydrolysis to produce glucose, the smallest and most abundant sugar unit [7]. Glucose is a C6 sugar that can be reacted with an acid catalyst to form levulinic acid (LA) as the final product [8].

Levulinic acid, commonly called 4-oxopentanoic acid, is easily soluble in water and ethanol [9]. This colorless crystalline compound has a melting point of 33-37 °C, a boiling point of 245-246 °C, and a density of around 1.14 g/cc [10]. Levulinic acid or gamma-ketovaleric acid is composed of two functional groups, ketone and carboxylate groups which can act as highly reactive electrophiles for nucleophilic attack [11]. Because of those functional groups' high reactivity, LA can undergo esterification, oxidation-reduction, substitution, and condensation [12]. The nature of the ketone and carboxylate contained in LA makes it one of the top bio-based chemicals that can be converted into various other compounds, such as gamma-valerolactone [5], 2-methyl tetrahydrofuran [13], diphenolic acid [14], and delta-aminolevulinic acid [15]. The derivatives of LA have extensive applications, including fuel additives, raw materials for the pharmaceutical industry, and cosmetics [16].

Levulinic acid needs are projected to increase with certainty from year to year. In 2020, LA market demand increased significantly to 3,820 tons, from 2,606.2 tons in 2013. This production is estimated to generate revenue over 19.65 million

USD with an annual growth rate of 4.8% [17]. Levulinic acid's price ranges from 5-8 USD/kg and can be decreased to 0.09-0.22 USD/kg if the raw material is biomass or the derivatives [18]. The decline in prices is caused by the cheapness and abundant availability of biomass raw materials. When the production price falls, the selling price of the product will be lower. Thus, it is expected that LA's use as a precursor for other compounds will be more efficient.

A variety of methods can synthesize LA. One way is to heat the C6 sugar or carbohydrates containing C6 sugar with a dilute mineral acid catalyst for a specific time [19]. Mineral acid catalysts usually provide a relatively higher yield because of the easy interaction between reactants and catalysts [5]. In general, the catalyst used for LA synthesis is Bronsted acid or Lewis acid. Levulinic acid synthesis occurs through several stages of reactions involving several complex essential intermediate compounds, depending on the type of catalyst used.

Signoretto et al. [20] stated that a pathway of LA synthesis is through fructose as an intermediates. Glucose undergoes isomerization to fructose. Hydroxymethylfurfural is formed from fructose, which can occur cyclically or acyclically. The fructose route will happen when Lewis acid is used as a catalyst. Unfortunately, Lewis acid also catalyzes more by-products, including humin [7]. Another study by Mukherjee and Raghavan [10] explained that initially, the C6 sugar catalyzed by bronsted acid is dehydrated to form an intermediate called HMF by losing three water molecules. Furthermore, HMF undergoes rehydration to form the final products, namely LA.

Bronsted acid catalyst can provide sufficient protons for reactant hydrolysis to LA, as in the study conducted by Feng et al. (2020) [21]. The study on the LA synthesis from cellulose and xylan shows that using Bronsted acid as the catalyst will give effective catalytic activity to obtain a high LA yield. Different study regarding mineral acids, powerful Bronsted acids, also showed an excellent ability to convert cellulose to LA [22].

Some of the Bronsted acids are HCl, H₂SO₄, and H₃PO₄. Hydrochloric acid is 12 times more reactive than H₂SO₄, however the selectivity is almost the same. It happens because of the better proton activity of HCl. Another acid catalyst, H₃PO₄ is too weak for LA synthesis [23]. Hydrochloric acid produces better selectivity than H₂SO₄, shown by LA's production from paper sludge [6]. Hydrochloric acid is the most preferred catalyst for converting various materials into LA because HCl is easy to recover and recycle, and can be separated by simple vacuum distillation [10].

This research will study LA synthesis from pure glucose, the main monosaccharide of biomass, as the starting part of our big project, LA synthesis from lignocellulosic biomass. The catalyst used in this experiment is HCl, a bronsted acid.

Previous researchers have developed several kinetics models. Saeman (1945) [24] was the first researcher to propose a kinetics model of glucose conversion into decomposition products. Generally, the models proposed by researchers include the immediate reaction of glucose to HMF followed by the reaction of HMF to LA [2,11,25-27]. Hereinafter, Liu et al. (2020) [4] more clearly explained that glucose is directly dehydrated to HMF (without going through fructose) when the type of catalyst used is bronsted acid.

Boonyakarn et al. [7] said that dehydration to HMF directly from glucose is more difficult than from fructose. It is intended to find out in more detail the reason that dehydration of glucose to HMF is difficult. It is believed that the presence of another intermediate involved in converting glucose to LA, namely levoglucosan (LG), which other similar studies have not been mentioned before. Therefore, revelation of new reaction pathway will comprise of the conversion of glucose to LG, LG to HMF, and HMF to LA. These simultaneous reactions that occurred will be modeled by the first-order reaction equation.

MATERIALS AND METHODS

1. Materials

The materials used in this study include (1) glucose, levoglucosan (LG), 5-HMF, and LA obtained from Sigma Aldrich; (2) 37% HCl obtained from Merck.

2. Experimental Procedure

The reaction was carried out on a glass tube with an inner diameter of 15 mm and a length of 10 cm. The glass tube was filled with a glucose solution and a certain amount of catalyst. The glass tube was placed in a stainless-steel tube for safety reasons. The series of tubes was placed on an oil bath shaker where the temperature was set as desired. After reaching a particular time, the tube was removed from the oil bath and immediately cooled until it reached room temperature. The reaction product was separated using filter paper to obtain the filtrate (liquid phase) and the remaining solid. The operating conditions used were 0.1-0.5 M for initial glucose concentration, 0.1-1.5 M for catalyst concentration, the temperature of 140-180 °C, and reaction time of 0-110 minutes.

Liquid sample analysis was conducted by HPLC. This analysis was used to determine the concentration of glucose, LG, HMF, and LA in the filtrate. The column used was Waters Nova-Pak C18 with a refractive index detector. The operating condition was at a temperature of 30 °C. The mobile phase used was 5 mM H₂SO₄ with a flow rate of 0.6 cm³/minute. The

compounds' concentration was obtained using a standard curve made from several known concentrations of chemical standards.

3. Modeling

The kinetic model is developed to understand the effect of temperature, initial reactant concentration, catalyst concentration, and reaction time on products, intermediates, and reactants' concentration profiles. The conversion of glucose using the HCl catalyst in this experiment is simplified in the reaction network, as shown in Figure 1.

Please insert Figure 1

Fig. 1. Reaction Network of Glucose Conversion to LA

Unlike the existing models, it is assumed that there is LG as intermediate included in the kinetic modeling. The reactions that occur in the LA synthesis from glucose include (1) R_1 : glucose to LG and $R_{1'}$: glucose to by-products, (2) R_2 : LG to HMF and $R_{2'}$: LG to by-products, and (3) R_3 : HMF to LA and $R_{3'}$: HMF to by-products. The following reaction equations are used to estimate the kinetic parameters:

$$R_1 = k_1 C_G \quad (1)$$

$$R_{1'} = k_{1'} C_G \quad (2)$$

$$R_2 = k_2 C_{LG} \quad (3)$$

$$R_{2'} = k_{2'} C_{LG} \quad (4)$$

$$R_3 = k_3 C_{HMF} \quad (5)$$

$$R_{3'} = k_{3'} C_{HMF} \quad (6)$$

$$k_i = A_i \exp\left[-\frac{E_i}{RT}\right] \quad (7)$$

$$\frac{dC_G}{dt} = -R_1 - R_{1'} \quad (8)$$

$$\frac{dC_{LG}}{dt} = R_1 - R_2 - R_{2'} \quad (9)$$

$$\frac{dC_{HMF}}{dt} = R_2 - R_3 - R_{3'} \quad (10)$$

$$\frac{dC_{LA}}{dt} = R_3 \quad (11)$$

The kinetic parameters of all reactions were determined using the MATLAB software package. Estimation was done by calculating the minimization of errors between experimental data and the model results, called the sum of squared error (SSE). The fminsearch toolbox was used to minimize these errors.

RESULTS AND DISCUSSION

There was a total of 18 batches of experiments with various operating conditions. The parameters studied were the effect of operating conditions on glucose conversion, LA yield, and reaction kinetics values. Most experimental batches are capable of achieving up to 100% glucose conversion. The highest LA yield that can be obtained from this experiment is 48.34% wt at the initial concentration of 0.1 M glucose, 1 M HCl, and a temperature of 180 °C.

1. The Effects of Operating Conditions

Temperature

The effect of temperature on glucose conversion is shown in Figure 2(a). As the reaction temperature increases, the rate of glucose decomposition also increases significantly. The higher the operating temperature, the faster the glucose conversion will be. To achieve complete conversion, it takes only about 50 minutes for temperature of 180 °C and about 110 minutes for 160 °C to reach almost full conversion. At the lowest temperature used in this experiment, 140 °C, 100% conversion is not achieved until the longest reaction time. This effect of temperature on glucose conversion is in line with the experiment conducted by Ma et al. [28] and Toif et al. [29].

Please insert Figure 2

Fig. 2. (a) Glucose Conversion and (b) LA Yield ($CG_0=0.25M$; $CH=0.5M$)

The higher the operating temperature, the higher LA yield will be achieved at a faster time. It is demonstrated in Figure 2(b). At 140 °C, the LA yield at 110 minutes is only about 15%. When the temperature is raised to 160 °C and 180 °C, the maximum yield can reach around 35%. However, at 180 °C, the maximum yield is gained faster than at lower temperatures. The results are consistent with Shen and Wyman [30]. Unfortunately, very high temperatures cause lower LA yield. Chang et al. [31] stated that temperatures higher than 210 °C would cause side reactions to occur more rapidly, thus lowering the LA yield. LA concentrations can drop when the temperature is too high or more than 190 °C due to further reactions [18]. It is also supported by Yan et al. [32] that LA will dehydrate to unsaturated lactone temperatures above 230 °C.

Catalyst Concentration

The effect of catalyst concentration on glucose conversion is shown in Figure 3(a). Complete glucose conversion will be achieved faster when the catalyst concentration used is higher. At the highest catalyst concentration of 1.5 M, achieving complete conversion is only about 80 minutes. A similar result was obtained by Kupiainen et al. [2]. Otherwise, the low catalyst concentration causes a lack of H^+ ions to hydrolyze the reactants so that the reaction rate is slow [32].

Please insert Figure 3

Fig. 3. (a) Glucose Conversion and (b) LA Yield ($C_{G_0}=0.1M$; $T=160^\circ C$)

Figure 3(b) shows that the formation of LA is affected by the concentration of the catalyst. The maximum yield achieved at different catalyst concentrations is almost the same for 1 and 1.5 M HCl, but the speed to achieve the maximum yield is different. The higher the catalyst concentration, the faster and the higher the yield will be. The maximum yield of LA in the reaction carried out with the lowest catalyst concentration is reached in about 110 minutes. A similar result was also obtained by Anggorowati et al. [33], which states that at the same time, the higher the catalyst concentration, the higher the LA yield.

Initial Glucose Concentration

Another parameter affecting glucose conversion and LA yield is the initial glucose concentration. Figure 4(a) shows its effect on glucose conversion. The higher initial glucose concentration will speed up the time to achieve complete glucose conversion. However, the LA yield would be lower when the initial glucose concentrations were higher, as shown in Figure 4(b). Too much glucose causes other reactions such as polymerization and rehydration, resulting in by-products formation [28].

Please insert Figure 4

Fig. 4. (a) Glucose Conversion and (b) LA Yield ($CH=1M$; $T=160^\circ C$)

The main by-product formed from the glucose hydrolysis to LA is humin, a visible dark solid material [5,8,34]. Humin mainly consists of furan-type fragments with nearly 60% carbon [2]. Humin will be formed more and more when the operating temperature is too high [32], the catalyst concentration and initial concentration are too high [26], and the reaction time is getting longer [35]. Several other side products were also detected in the liquid phase. However, the limited facilities make it difficult for us to identify it. According to Girisuta et al. [8], a reversion product 1,6-anhydro-beta-D-glucofuranose appears. Besides, isomaltose and gentibiose appear, resulting from an intermolecular condensation reaction between 2 glucose units.

2. Kinetic Model

Hydrochloric acid, a Bronsted acid, was used in this experiment. From the analysis using HPLC, there was no fructose as one of the reaction pathways, as was found by Jiang et al. [36] and Feng et al. [21]. If fructose is an intermediate of glucose dehydration, fructose should be detectable because the ability to analyze fructose is sufficient and suitable. The direct dehydration pathway of glucose without passing through fructose is indeed a characteristic of the Bronsted acid-catalyzed conversion route. Isomerization of glucose to fructose cannot be catalyzed by Bronsted acid but requires Lewis acid or Bronsted base [7]. Unfortunately, Lewis acid increases the formation of by-products. Kuster and Temmink [37]

studied the effect of pH on glucose conversion. They observed no isomerization of glucose to fructose at pH <4.5, as was done in this experiment.

According to the experimental results, LG was proven to be involved in the hydrolysis reaction of glucose to LA. Takahashi et al. [38] explained that glucose decomposes into LG, and then LG becomes an unknown degradation product. Going more advanced, Weingarten et al. [39] could explain that LG is formed from glucose dehydration, which would go through double dehydration to HMF. Furthermore, Herbs and Janiak [40] reported that the LG route would occur when the reaction is carried out using a Bronsted acid catalyst, as was done in this study.

Please insert Figure 5

Fig. 5. Typical Concentration Profile of Glucose Hydrolysis to LA ($CG_0=0.5M$; $CH=0.5M$; $170^\circ C$)

Essential compounds from the glucose conversion could be identified with HPLC, including glucose, HMF, LG, and LA. Based on Figure 5, it can be seen that the trend in the concentration of the compounds involved implies a consecutive reaction. The rate of glucose decomposition can be assumed to be a first-order reaction. It is consistent with what was reported by Xiang et al. [41], Chun et al. [11], Girisuta et al. [8], and Kupiainen et al. [2]. In this reaction model, the rate is directly proportional to the concentration of each reactant. The results of the kinetic parameter estimation can be seen in Table 1.

Table 1. Kinetic Parameter of LA Synthesis from Glucose

Please insert Table 1

Please insert Figure 6

Fig. 6. Model Fitting at Various Operating Conditions

Figure 6 demonstrates the fitting data under a variety of operating conditions. Comparison of experimental data and kinetics model provides a good fit over a wide range of reaction conditions. It can be seen that the assumption of first-order reactions is suitable for LA synthesis reaction from glucose involving LG and HMF as intermediates.

Glucose conversion can reach 100%, but the maximum LA yield is only around 40%. It shows that there are other products besides LA that are derived from reactants and intermediates. LG and HMF were observed as intermediates in the reaction sequence. The concentrations of LG and HMF are generally small compared to both the LA product concentration and the initial glucose concentration. These observations indicate that LA products' formation is much faster than the conversion of glucose to intermediates. It can be seen from the value of k in Table 1.

Temperature was varied to determine its effect on the kinetic parameters. The temperature has a good influence on glucose decomposition seen from its k value in Table 1. The higher the temperature, the higher k in all reactions. The reaction will run faster when higher temperatures are used. However, it can be seen that the values of k_1' , k_2' , and k_3' are bigger. These results indicate that the reaction into by-products will occur more rapidly when high temperatures are used. The highest activation energy value is E_1' (glucose decomposition into by-products). So the decomposition of glucose to by-products is the most sensitive reaction of this sequence.

It can also be seen that decomposition of glucose increases with increasing acid concentration. The k values for the primary reaction almost invariably increase when the acid concentration is higher. However, all k values for side reactions also had a similar trend. The primary reaction goes faster as the side reaction rate increases. It is identical with Chun et al. [11]. Slightly diverse from the results obtained in this experiment, Xiang et al. [41] stated that acid concentration has minimal effect on the overall decomposition. Tarabanko et al. [23] reported more clearly. The kinetics of LA formation from glucose at medium temperature is slightly affected by the acid concentration. However, the LA formation rate increased markedly with increasing acid concentration when the reaction is carried out at elevated temperatures.

Glucose decomposition to LA can be done using certain temperatures and acids, specifically concentrated acid and low temperature or diluted acid and high temperature. Both of these can produce high LA yield. The condition of concentrated acid and low temperature will cause higher amounts of acid consumption, and the reaction time required is longer. Losses in terms of equipment corrosion and difficulty in acid recovery will occur when applied to the industry. Conversely, acid consumption and reaction time can be reduced very significantly at higher temperature conditions. It is also helpful in reducing side products [42]. Hydrolysis at high temperatures with dilute acid is considered better from an economic point of view.

The initial glucose concentration as a reactant also affects the reaction kinetics. When the initial glucose concentration used is too low, less than 0.3 M, HMF is undetectable and calculated very small in the reaction kinetics model. The values of k_3 and k_2 were also considered very large, compared to the values at the higher initial glucose concentration conditions. It shows that if the initial glucose concentration was too low, the decomposition rate of HMF is speedy. Nevertheless, in general, the higher the initial glucose concentration, the higher the value of the reaction rate constant, as shown in Table 1.

CONCLUSION

Glucose, the primary monosaccharide from lignocellulosic biomass, has been proven to be converted to LA. The reaction is influenced by temperature, catalyst concentration, and initial glucose concentration. The higher the temperature and the catalyst concentration used, the faster the glucose conversion and the higher the LA yield. On the contrary, the higher the initial glucose concentration will decrease the LA yield. The highest LA yield successfully obtained in this experiment is 48.34 %wt at 0.1 M initial glucose concentration, 1 M HCl, and temperature of 180 °C. The reaction with a bronsted acid catalyst will produce a reaction pathway through LG as an intermediate. Experimental data modeled with first-order reactions gives good fitting results. So, the LA synthesis reaction model from glucose that is proposed with the new pathway through LG can be applied.

DECLARATIONS

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Conflicts of interest

The author declares no competing interests.

Availability of data and material

All data and materials generated are included in this published article and are available upon reasonable request.

Code availability

LG : Levoglucosan
HMF : 5-hydroxymethylfurfural
LA : Levulinic acid

R_i	:	Reaction rate of i [mol/L/min]
k_i	:	Reaction kinetic of i [1/min]
C_i	:	Concentration of i [mol/L]
A_i	:	Arrhenius constant of i
E_i	:	Activation energy of i [kJ/mol]
R	:	Ideal gas constant [J/K/mol]
T	:	Temperature [K]
SSE	:	Sum of squared error

Authors' contribution

Arief Budiman conceived the main idea of this experiment. Rochmadi designed the detailed experiment. Meutia Ermina Toif performed the experiments, analyzed the data, and co-wrote the main manuscript. Muslikhin Hidayat worked on the mathematical calculation and modelling. All authors reviewed the manuscript.

Ethics approval

Not applicable.

Consent to participate

Informed consent was obtained from all individual participants included in the study.

Consent for publication

The authors have consented to the submission of this report to the journal.

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Figures

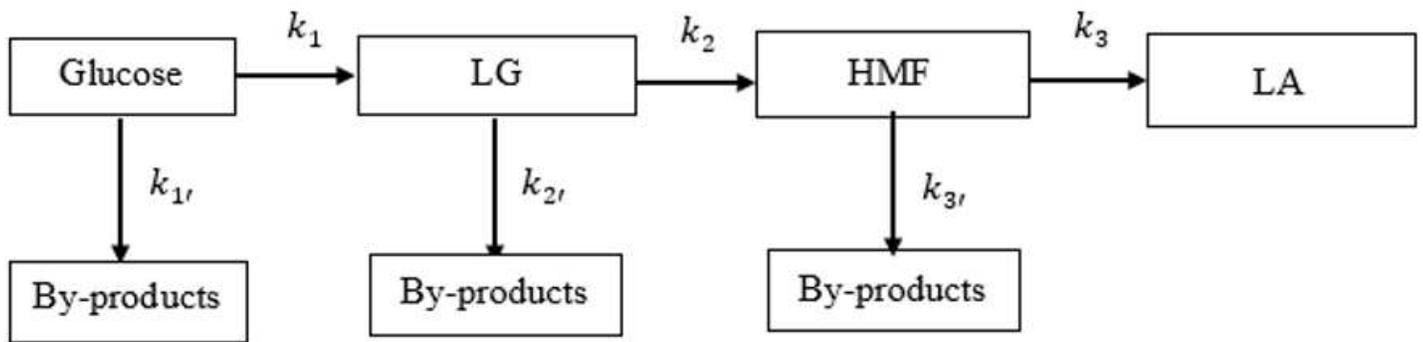
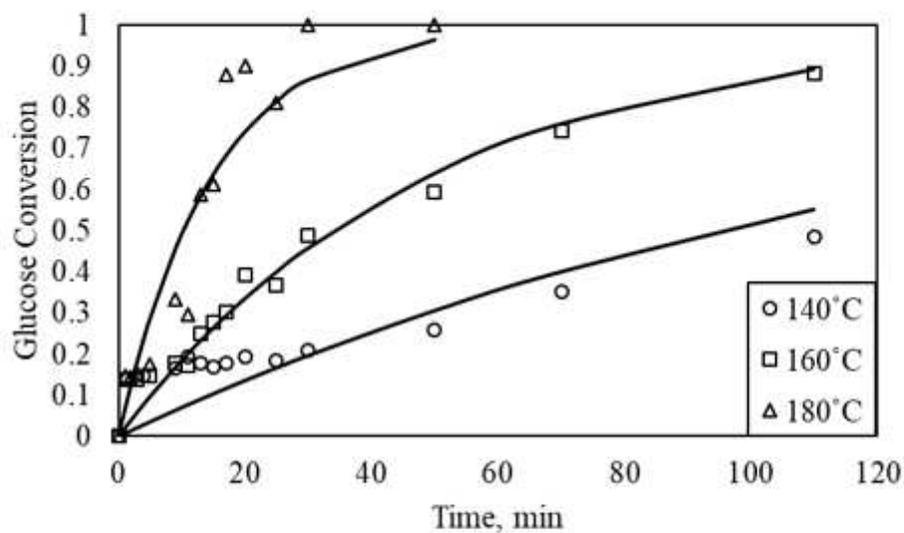
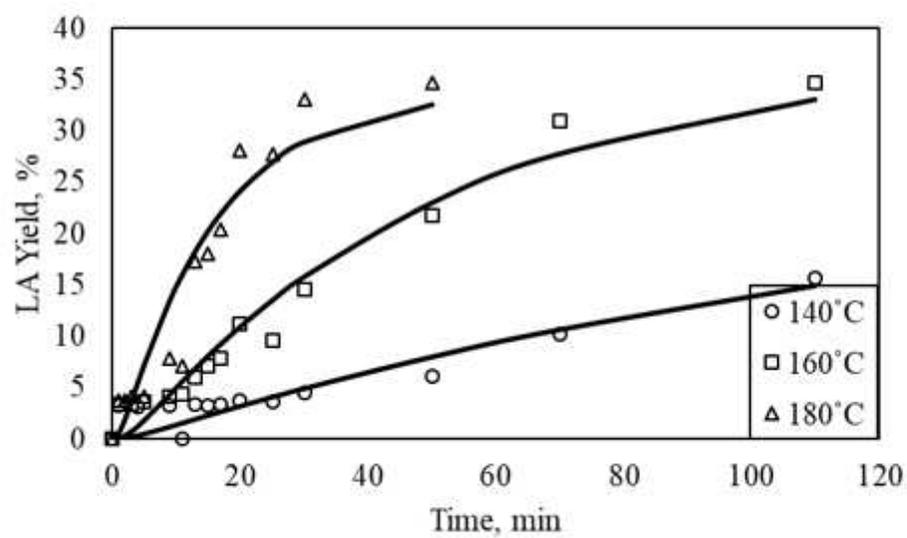


Figure 1

Reaction Network of Glucose Conversion to LA



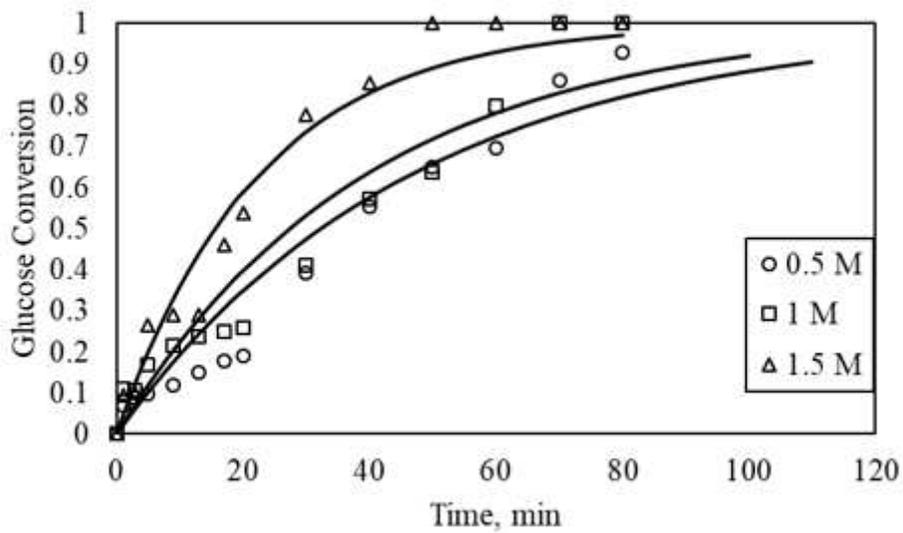
(a)



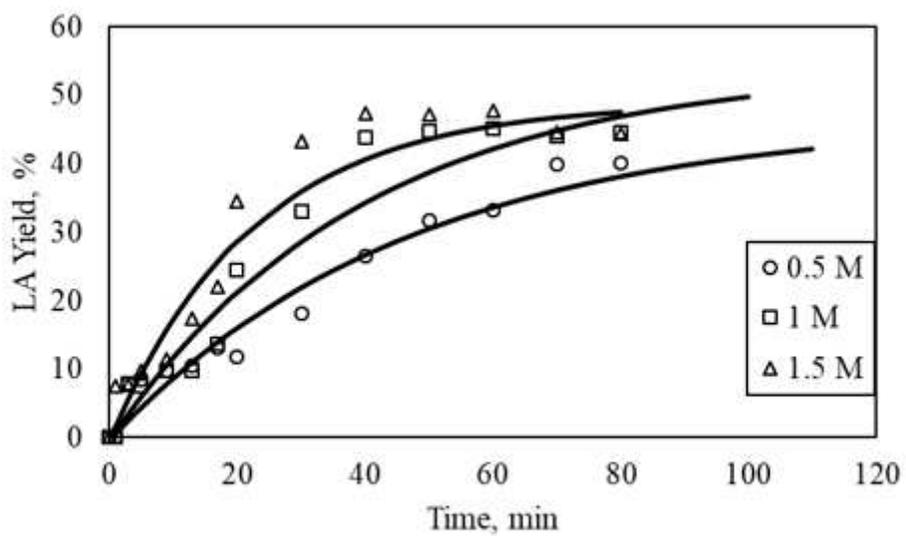
(b)

Figure 2

(a) Glucose Conversion and (b) LA Yield (CGo=0.25M ; CH=0.5M)



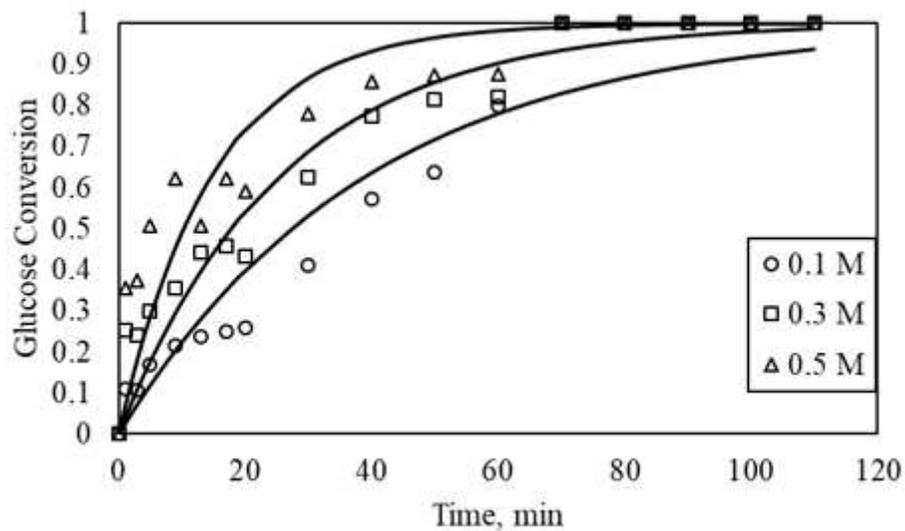
(a)



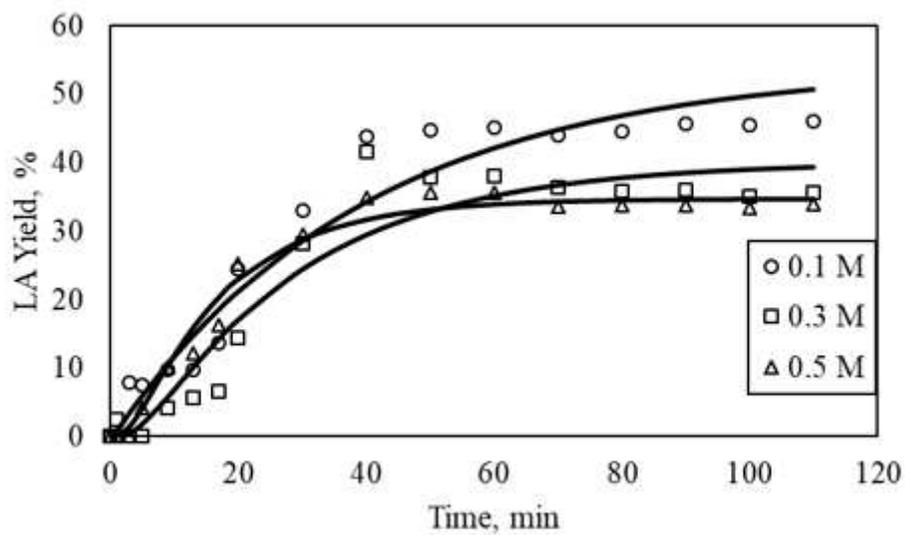
(b)

Figure 3

(a) Glucose Conversion and (b) LA Yield (CGo=0.1M ; T=160oC)



(a)



(b)

Figure 4

(a) Glucose Conversion and (b) LA Yield (CH=1M ; T=160oC)

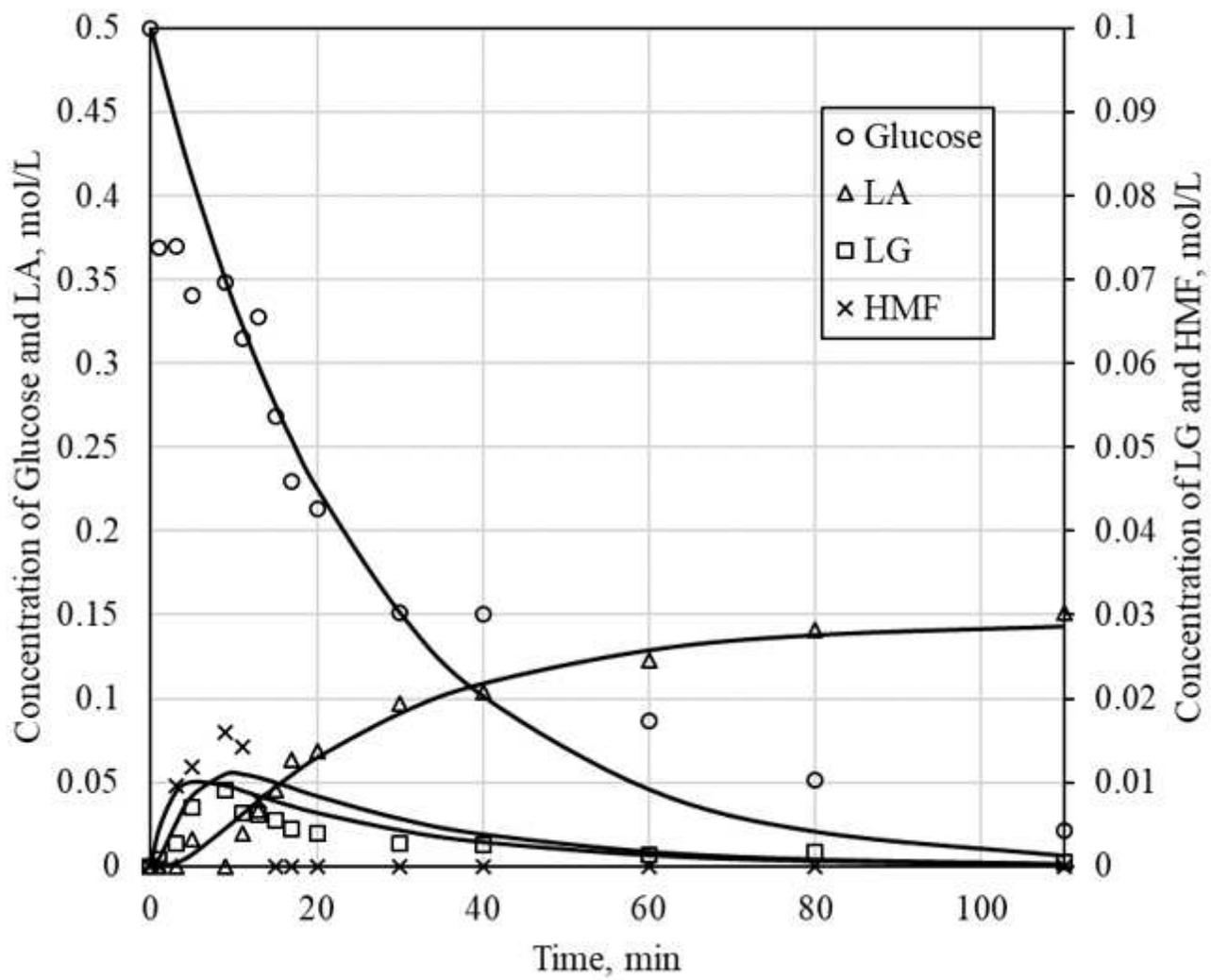


Figure 5

Typical Concentration Profile of Glucose Hydrolysis to LA (CG0=0.5M ; CH=0.5M ; 170oC)

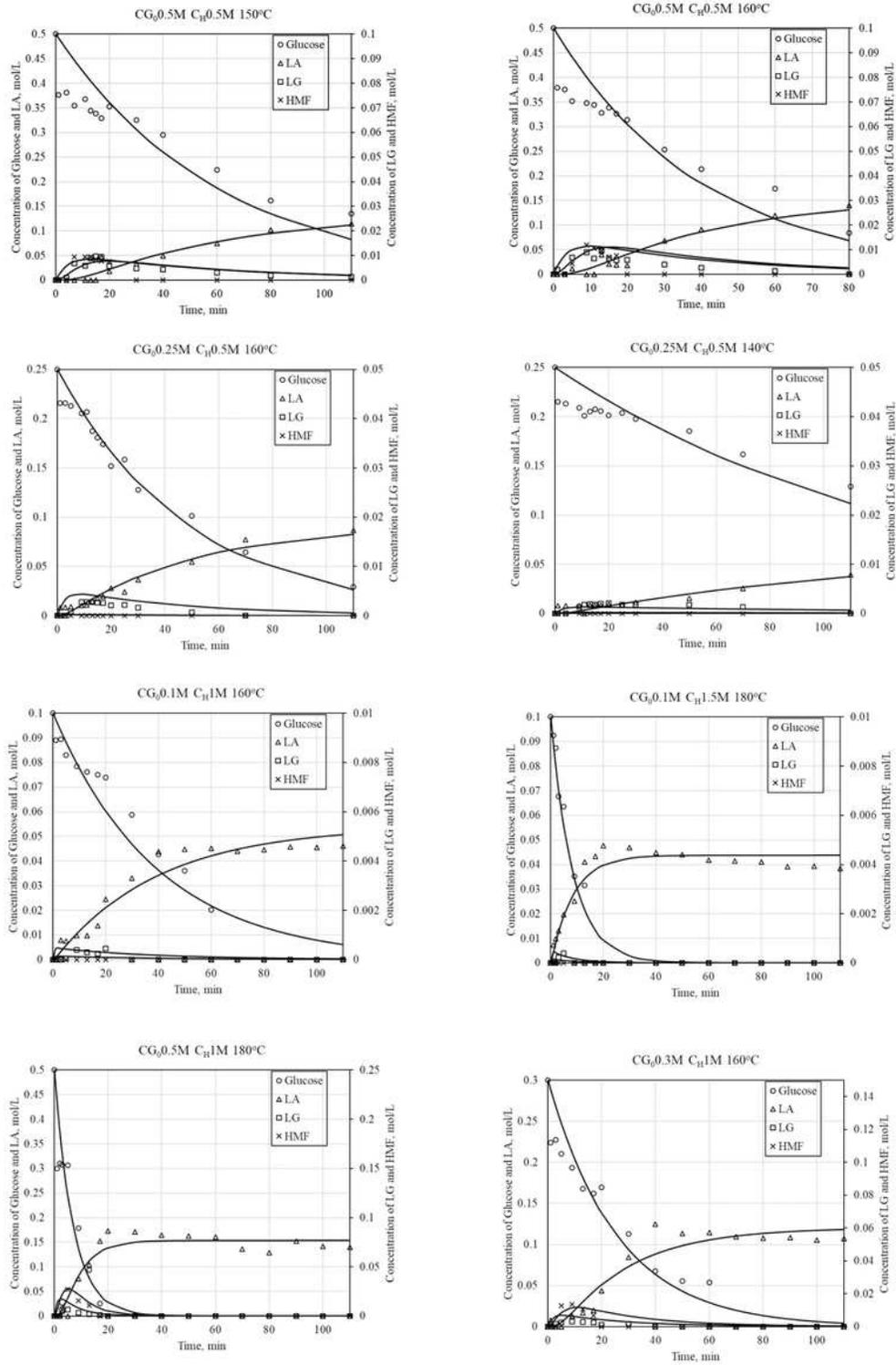


Figure 6

Model Fitting at Various Operating Conditions