Kinetic study of glucose conversion to levulinic acid over Fe/HY zeolite catalyst

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HIGHLIGHTS

- A kinetic model developed to describe glucose conversion to LA.
- Fe/HY zeolite was used as catalyst.
- The first-order model and the experimental data fitted-well.

ABSTRACT

The glucose conversion using Fe/HY zeolite catalyst in a batch reactor has been investigated. The main products within the temperature range between 120 and 200 °C were 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA). The highest LA yield of 66% was obtained from 100% glucose conversion at 180 °C. After eliminating the influence of internal and external diffusions, a kinetic model was developed based on the pseudo homogeneous model. The kinetic model consisted of four key steps: (1) glucose dehydration to form 5-HMF; (2) glucose degradation to produce humins; (3) 5-HMF rehydration to form LA; and (4) 5-HMF degradation to form humins. The first-order model and the experimental data fitted-well. The reactions rates increased with temperature, and the activation energies of glucose conversion to 5-HMF and 5-HMF conversion to LA were 64 and 61 kJ mol⁻¹, respectively, comparatively lower than previously reported values.

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1. Introduction

Exacerbating energy demands have caused for the search of fossil resource alternatives to supply chemicals and energy in the future. With annual production up to 2 × 10¹¹ tons worldwide, biomass is an important source for energy source [1]. Levulinic acid (LA), a versatile chemical that can be derived from biomass, is an important basic chemical with various potential uses [2]. From energy to manufacturing, LA can be used as fuel additives, coating material, solvent, fragrance, and food flavouring agent. The other applications include pharmaceutical compound, resins, and biofuels. The first commercial-scale plant for the synthesis of LA was built in Caserta, Italy through a process developed by Biofine Renewables [3,4]. The Biofine process involves two stages of acid-catalyzed hydrolysis for the optimum product yield and minimum product degradation and tar formation [3].

Glucose, the most abundant sugar, has been widely employed as a model compound for the study of lignocellulosic biomass conversion. The formation of LA from glucose decomposition consists of a series of consecutive reactions, which includes a triple dehydration of glucose to produce 5-hydroxymethyl furfural (5-HMF), and the rehydration of 5-HMF with to produce LA and formic acid (Fig. 1). Various studies have reported on LA production using homogeneous and heterogeneous catalysts [5–8]. Heterogeneous solid acid catalysts attracted substantial interests to overcome the problems associated with homogeneous catalytic system. Generally, solid acid catalysts used for the production of LA are reusable, with tolerable reduction in product yield until five to six runs [9,10]. Consequently, equipment corrosiveness and cost required for the overall process will be less in a heterogeneous system. Reviews on LA production using various feedstock and catalysts have been summarized before [11,12].

Previously, zeolite has been tested as catalyst for glucose dehydration reaction [5,6,13–15]. Zeolite has good potential to be used in glucose dehydration since the pore structures exert significant influence on the reaction [6,16,17]. Meanwhile, metal halide has...
been applied as catalyst for LA production. Earlier research have mostly reported on the use of CrCl$_2$ and CrCl$_3$ [10,18–20]. Modification of porous zeolite with metal halide to form a new catalyst could enhance the glucose dehydration to LA. The new catalyst has the additional benefit of being easily separated from reaction products [21]. Recently, CrCl$_2$ and HY zeolite were combined to form a ‘hybrid catalyst’ for LA production from glucose [22,23]. The hybrid catalyst offered better performance compared to the parent HY zeolite since the hybrid catalyst possessed higher acidity. However, high price, toxicity and environmental pollution caused by Cr based catalyst have necessitated the search for a non-toxic and low cost catalyst. Instead of using Cr, other metal chlorides such as the low cost, extensively available, and non toxic FeCl$_3$ [24] can be considered. Thus, Fe modified zeolite (Fe/HY zeolite) was prepared and applied as catalyst for glucose conversion to LA [25]. The Fe/HY zeolite catalyst was found to be active and reusable for LA production.

An enormous interest in LA applications has led to numerous kinetic studies on the decomposition of carbohydrates to produce 5-HMF and LA [7,26–31]. Acid-catalyzed conversion of glucose to LA includes reactions of LA and 5-HMF formations, as well as humins formation reactions. Some studies have also incorporated a hydrolysis step into their kinetic models to produce glucose from cellulose or lignocellulosic biomass [4,32–34]. The first kinetic study of lignocellulosic biomass hydrolysis to glucose was performed by Saeman in 1945 [35]. Later, several later studies were conducted based on Saemans model [36–38]. Kinetic studies on the conversion of glucose in aqueous system using mineral acid as catalyst are widely reported [7,26–29]. However, there are limited reports on kinetic study of glucose conversion to LA using solid acid, particularly zeolite, while many of the kinetic studies were confined to glucose conversion to 5-HMF [39–41]. Herein, an attempt has been made to investigate the glucose decomposition to 5-HMF and LA by the heterogeneous acid catalyst; Fe/HY zeolite. A kinetic model of glucose decomposition was developed and the kinetic parameters were also reported. Furthermore, this work will provide inputs and important basic information for a full kinetic model for the solid acid catalyzed hydrolysis of biomass to LA using Fe/HY zeolite catalyst.

2. Materials and methods

2.1. Materials

NaY faujasite type zeolite (SiO$_2$/Al$_2$O$_3$ = 5) was purchased from Zeolyst International Inc. Iron chloride (FeCl$_3$), 3,5-dinitrosalicylic acid and glucose was supplied by Merck, Germany while potassium sodium tartrate tetrahydrate, sodium hydroxide (NaOH) were purchased from Sigma Aldrich, United States. Sulphuric acid (H$_2$SO$_4$), sodium sulphite and ammonium chloride (NH$_4$Cl) were supplied by QRec, New Zealand. A standard analytical grade of LA; 98% (Merck), 5-HMF; 99% (Sigma Aldrich), and formic acid 99% (Merck) were made available for product analysis. Distilled water was used as solvent in all experiments.

2.2. Fe/HY zeolite catalyst preparation and characterization

The acid form of NaY zeolite (HY zeolite) was prepared by ion exchange of Na$^+$ from NaY zeolite with NH$_4$Cl, followed by calcination at 500 °C for 5 h. The Fe/HY zeolite catalyst was prepared using wetness impregnation method following the procedure reported in [25]. Solution containing 10% weight ratio of FeCl$_3$ to HY zeolite was stirred at room temperature for 2 h. Then, the mixture was dried overnight at 120 °C. The Fe/HY catalyst was formed after calcination at 400 °C for 5 h. The properties of Fe/HY zeolite catalyst were characterized using several techniques [25].

2.3. Experimental procedures

A 100 ml stirred high pressure reactor was used for experiments. The reactor was filled with predetermined amount of feedstock (glucose or 5-HMF), catalyst, and distilled water, then heated to a set temperature. The initial concentration of feedstock was 5000 ppm. Different agitation speed on glucose conversion was studied from 0 to 300 rpm to evaluate the effect of external diffusion using Fe/HY zeolite catalyst. Besides, experiments were conducted at different Fe/HY zeolite particle sizes to determine if internal diffusion resistance was the controlling factor. A series of Fe/HY zeolite particle sizes used was 0.18, 0.21, 0.25, and 0.30 mm. For the typical experiment, the agitation speed was fixed at 200 rpm and the temperature was controlled within ±1 °C of the set value. The initial time for the reaction is taken once the set reaction temperature is reached. Randomly selected experimental runs were repeated to test the reproducibility of the data. All product samples were filtered through 0.45 μm nylon membrane filter to ensure particle free solution before further analysis.

2.4. Product analysis

The concentrations of LA and 5-HMF in the liquid product were determined with the high performance liquid chromatography (HPLC) (Perkin Elmer 2000) under the following conditions: column = Hi Plex H; flow rate = 0.6 ml/min, mobile phase 5 mM H$_3$PO$_4$, detector = UV 210 nm; retention time = 40 min; column temperature = 60 °C. Meanwhile, glucose conversion was determined using DNS method [25]. The concentrations of 5-HMF, LA, and glucose in the liquid product were determined using the standard calibration curve of respective compounds. Feedstock conversion, product yield, and product selectivity were calculated using Eqs. (1–3):

Feedstock conversion (%) = $\frac{\text{Initial feedstock amount} - \text{final feedstock amount}}{\text{Initial feedstock amount}} \times 100\%$  
(1)

Product yield (%) = $\frac{\text{Product amount}}{\text{Initial feedstock amount}} \times 100\%$  
(2)

Product selectivity (%) = $\frac{\text{Product yield}}{\text{Feedstock conversion}} \times 100\%$  
(3)
3. Results and discussion

3.1. Decomposition products

Glucose and 5-HMF decompositions using 10% Fe/HY zeolite catalyst were studied in a wide range of conditions. Experiments were carried out at 120–200 °C from 0 to 240 min. 5-HMF decomposition reactions were performed to understand its degradation rates. The main products from glucose conversion reaction were 5-HMF and LA, while the main product from 5-HMF conversion reaction was LA (Fig. 7, Reactions 1 and 3). Insoluble and dark brown material by-product, regarded as humins, was also produced from the reactions (Fig. 7, Reactions 2 and 4). It is proposed that humins originated from glucose, glucose intermediates, and 5-HMF [27,42]. Nevertheless, LA is not a source for the production of humins [7,31].

Besides, traces of soluble compounds such as furfural and lactic acid were detected and considered as by-products. It was reported that the formation of furfural was initiated via loss of formaldehyde from 5-HMF [28]. Meanwhile, lactic acid was produced from glucose decomposition due to the presence of Lewis acid sites in the reaction system [43,44]. As proposed by Horvat et al., the presence of water in the reaction system led to decarboxylation of 5-HMF to form LA and formic acid, and also prompted unwanted polymerization reactions to produce humins [45]. The production of formic acid was not consistent throughout the reaction which possibly be due to the tendency of formic acid decomposition to CO₂, H₂, CO, and H₂O in heat and acidic mediums [23].

3.2. Effect of external and internal diffusions

External and internal diffusions limitations should be examined in the study of the kinetics of heterogeneous reaction. The catalytic reaction system between glucose and Fe/HY zeolite in water solution may suffer from mass transfer limitations that affect the apparent reaction rate. Increasing the agitation speed might increase the interfacial area between glucose and catalyst, thus removing the external resistance to mass transfer [10]. The effect of agitation speed on glucose decomposition was studied from 0 to 300 rpm (Fig. 2a). From the inspection, there was no clear influence of agitation speed on glucose conversion. The results with the same trend have been reported previously [10]. Thus, the external resistance to mass transfer is negligible.

Additional experiments using different range of Fe/HY zeolite particle sizes (0.18, 0.21, 0.25, and 0.30 mm) were performed to determine if internal diffusion resistance was the controlling factor. The experimental results in Fig. 2b depict there is no effect on glucose conversion as well. These observations concluded that external and internal diffusions are not the rate limiting factors in glucose conversion reaction over Fe/HY zeolite catalyst. Thus, glucose conversion catalyzed by Fe/HY zeolite is not classify in diffusion limited regime. The pseudo homogeneous approach is applicable in the kinetic study of glucose conversion and will be used to represent the rate of reaction. Negligible internal and external diffusions have been reported for kinetic studies of fructose dehydration reactions over zeolites [39,46].

3.3. Effect of reaction temperature

Glucose conversions, 5-HMF yields, and LA yields from glucose conversion using Fe/HY zeolite at various temperatures (120–200 °C) are illustrated in Fig. 3. Since series of reactions are involved, the selectivity of 5-HMF and LA from glucose decomposition are exhibited in Fig. 4. From the analysis, the reactions of glucose conversion to 5-HMF and LA are determined to be in the kinetic limited regime. The glucose conversions varied between 8% and 100%. The reaction temperature has strong effect on glucose decomposition. It was observed that high reaction rate was achieved at elevated temperature. For example, the reaction time required to achieve a conversion of 34% decreased from 180 min to less than 90 min when the temperature was increased by 20 °C.

The maximum 5-HMF yield was 11.4% in 240 min at 120 °C. The 5-HMF formation favoured low temperature with prolonged reaction time, and high temperature with shortened reaction time. This can be verified from the trend of 5-HMF selectivity. High 5-HMF selectivity was obtained at 200 °C, since the LA precursor decomposed to CO₂, H₂, CO, and H₂O in heat and acidic mediums [23].
trend of 5-HMF conversion was similar as glucose conversion, and the decomposition rates of 5-HMF were substantially higher than those of glucose. The decomposition of 5-HMF and the formation of LA increased with increasing reaction temperature and at prolonged reaction time. The conversion of 5-HMF was 36.5% in 150 min at 120 °C, and reached 87.7% in 60 min at 180 °C. Meanwhile, LA yield attained 33% in 180 min at 120 °C, and increased to 52.6% in 120 min at 160 °C. At higher temperature (200 °C), humins was also generated from 5-HMF resulted in low LA yield.

3.4. Kinetic study

The concentration profile of compounds involved in glucose decomposition reaction using Fe/HY zeolite is shown in Fig. 6. Glucose concentration decreased with time as glucose was dehydrated to give 5-HMF. Then, 5-HMF rehydrated to the desired final product; LA. The 5-HMF concentrations measured for all experimental conditions were low, since 5-HMF was converted to LA and humins once formed. The traces amount of by-product was not computed, as other possible side reactions were considered negligible.

Fig. 7 exhibits the reaction scheme used for the development of the kinetic model of glucose decomposition. Glucose conversion reaction consists of four key steps (1) glucose dehydration to form 5-HMF, (2) glucose degradation to produce humins, (3) 5-HMF rehydration to form LA, and (4) 5-HMF degradation to produce humins. The kinetic model of glucose conversion reaction was proposed based on the following assumptions [4,33]:

![Fig. 3. Glucose decomposition-effect of reaction temperature on glucose conversion, 5-HMF yield, and LA yield.](image)

![Fig. 4. Glucose decomposition-effect of reaction temperature on 5-HMF selectivity and LA selectivity.](image)
The kinetic models were proposed based on the pseudo homogeneous first-order approach.

(2) All reactions are irreversible reactions.

(3) The formation of intermediates is negligible and the dehydration reaction is a series of irreversible reactions from glucose to 5-HMF then finally to LA.

(4) All humins and other soluble products are by-products.

(5) LA is the main product from 5-HMF decomposition and other possible reactions are negligible.

As pseudo first-order kinetic approach was used, the rate of reactions for decomposition of glucose and 5-HMF were defined as Eqs. (4) and (5), respectively.

\[ R_G = (k_1 + k_2)C_G \]  
\[ R_H = (k_3 + k_4)C_H \]

Based on the rate of reactions, the following set of differential Eqs. (6–8) were obtained:

\[ \frac{dC_G}{dt} = (k_1 + k_2)C_G = k_G C_G \]  
\[ \frac{dC_H}{dt} = k_1 C_G - (k_3 + k_4)C_H = k_1 C_G - k_H C_H \]  
\[ \frac{dC_{LA}}{dt} = k_3 C_H \]

where

\[ k_G = k_1 + k_2 \]  
\[ k_H = k_3 + k_4 \]

The differential Eqs. (6–8) were solved and the analytical expressions of concentration of glucose, 5-HMF and LA were obtained as in Eqs. (11–13), respectively.

\[ C_G = C_{Go} e^{-k_G t} \]  
\[ C_H = \frac{k_1 C_{Go}}{k_H - k_G} \left( e^{-k_H t} - e^{-k_G t} \right) \]  
\[ C_{LA} = \frac{k_1 k_3 C_{Go}}{k_H - k_G} \left[ \frac{k_H (1 - e^{-k_H t}) - k_G (1 - e^{-k_G t})}{k_G k_H} \right] \]

The nomenclature of the above Eqs. (4–13) are as follows. \( R_G \) and \( R_H \) are the reaction rates of glucose and 5-HMF decomposition, respectively. \( C_G, C_H, C_{LA} \), and \( C_{Go} \), refer to the concentration of glucose, concentration of 5-HMF, concentration of LA, and initial concentration of glucose, respectively. Meanwhile, \( k_G, k_H, k_1, k_2, k_3, \) and \( k_4 \) are the kinetic constants of glucose decomposition, 5-HMF decomposition, Reaction 1, Reaction 2, Reaction 3, and Reaction 4, respectively. The reaction rate constants for both kinetic studies were computed as follows:

(1) The glucose decomposition rate constant (\( k_G \)) was determined from the plot of \( -\ln(1 - X) \) versus reaction time, where \( X \) is the glucose conversion.

(2) The 5-HMF decomposition rate constant (\( k_H \)) was determined from the plot of \( -\ln(1 - X) \) versus reaction time, where \( X \) is the 5-HMF conversion.

(3) \( k_1 \) and \( k_4 \) were obtained from Eqs. (11) and (12), respectively using the method of non-linear least square regression method by Polymath 6.10 software.

Fig. 5. 5-HMF decomposition-effect of reaction temperature on 5-HMF conversion and LA yield. ■ 120 °C, ▲ 140 °C, ● 160 °C, ○ 180 °C, □ 200 °C.

Fig. 6. Concentration profile of glucose decomposition at 180 °C. ▲ Glucose, ● 5-HMF, □ LA.

Fig. 7. A reaction scheme for glucose decomposition.
was obtained from difference between $k_G$ and $k_1$, while $k_4$ was obtained from difference between $k_H$ and $k_3$, fitted using Eqs. (8) and (9), respectively.

(5) All the differential equations were used to fit the experimental data.

The activation energy ($E_a$) and exponential factor ($A$) were obtained by applying the following Arrhenius equation to the experimental data.

$$\ln k = \ln A - \frac{E_a}{RT}$$

The linearity of Fig. 8 supported the first order dependence of glucose and 5-HMF decomposition, therefore the validity of the selected kinetic model was confirmed, which enable the calculation of reaction rate constants. Kinetics performed for xylose conversion in the presence of HY zeolite by Moreau et al. also obeys the first-order kinetic law [47]. A good fit between the experimental data and kinetic modelling was achieved, as shown in Figs. 3 and 4.

The effects of reaction temperature on reaction rate constants of glucose conversion to LA using Fe/HY zeolite are given in Table 1. It can be seen that the glucose decomposition rate constant, $k_G$ increase as the temperature increase. The values of glucose conversion to 5-HMF rate constant, $k_1$ will always be smaller than the values of $k_G$, which signifies that only part of glucose decomposed into 5-HMF. Thus, the theoretical yield of LA cannot be reached from the glucose conversion reaction [26]. The low concentrations of 5-HMF in the glucose decomposition process suggested that the 5-HMF decomposition reaction is a fast reaction. The same explanation has been acknowledged in previous studies [32,33,48]. The fast decomposition of 5-HMF once formed can be validated from the higher decomposition rate of 5-HMF, $k_H$ compared to the formation rate of 5-HMF, $k_1$. The reaction rate constants of $k_1$ and $k_H$ increase with temperature.

LA is the main product from 5-HMF decomposition [7,33]. As shown in Fig. 5, the concentration of LA rose at the early stage, before it reached a plateau. Hence, it can be claimed that LA is the final product of the decomposition reactions under the experimental conditions. The reaction rate constants of LA formation, $k_3$ increased with temperature. The reaction rates for humins formation from glucose, $k_2$ were lower than 5-HMF formation, $k_1$. The same trend was also demonstrated when comparing the reaction rate of humins formation from 5-HMF, $k_4$ and LA formation, $k_3$, except at 200 °C. This indicates that at high temperature, humins formation rate increases more quickly than LA formation rate compared to reaction at lower temperatures.

The values of the activation energy, $E_a$ and pre-exponential factor, $A$ for glucose decompositions using Fe/HY zeolite are listed in Table 1. These constants were obtained from the Arrhenius plots in Fig. 9. The intercept of the plots gives the values of $A$, while the slope gives the values of activation energy. The decomposition reaction of glucose to humins had the highest activation energy, which indicates that this reaction is most affected by temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reaction rate constant (min⁻¹)</th>
<th>k₁</th>
<th>k₂</th>
<th>k₃</th>
<th>k₄</th>
</tr>
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<tbody>
<tr>
<td>120</td>
<td>0.0015</td>
<td>0.0008</td>
<td>0.0023</td>
<td>0.0032</td>
<td>0.0019</td>
</tr>
<tr>
<td>140</td>
<td>0.0029</td>
<td>0.0016</td>
<td>0.0045</td>
<td>0.0075</td>
<td>0.0043</td>
</tr>
<tr>
<td>160</td>
<td>0.0067</td>
<td>0.0041</td>
<td>0.0108</td>
<td>0.0205</td>
<td>0.0104</td>
</tr>
<tr>
<td>180</td>
<td>0.0128</td>
<td>0.0105</td>
<td>0.0233</td>
<td>0.0409</td>
<td>0.0217</td>
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<tr>
<td>200</td>
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<td>0.0435</td>
<td>0.0598</td>
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<tr>
<th>Parameter</th>
<th>Reaction</th>
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<th>2</th>
<th>G</th>
<th>H</th>
<th>3</th>
<th>4</th>
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<tbody>
<tr>
<td>$E_a$ (kJ mol⁻¹)</td>
<td>64.0</td>
<td>75.7</td>
<td>68.9</td>
<td>65.2</td>
<td>60.8</td>
<td>70.2</td>
<td></td>
</tr>
<tr>
<td>$A$ (min⁻¹)</td>
<td>$39.9 \times 10^4$</td>
<td>$69.3 \times 10^3$</td>
<td>$26.8 \times 10^3$</td>
<td>$14.3 \times 10^5$</td>
<td>$22.3 \times 10^4$</td>
<td>$27.0 \times 10^5$</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>96.9</td>
<td>96.7</td>
<td>96.7</td>
<td>99.8</td>
<td>99.4</td>
<td>99.5</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8. –ln(1 – X) versus time for (a) glucose conversion and (b) 5-HMF conversion. ■ 120 °C, ▲ 140 °C, ● 160 °C, ◯ 180 °C, ○ 200 °C.
This suggests that high temperature enhances the formation of humins from glucose. Thus, it is proposed that high 5-HMF selectivity not preferred at high temperature, as has been shown in the trend of 5-HMF selectivity (Fig. 4). The same trend has been reported for H$_2$SO$_4$ and non-catalyzed glucose conversion reaction [7,30]. High temperature will also enhances humins formation from 5-HMF due to high activation energy of 5-HMF decomposition to humins. This also suggested that high temperature was

Fig. 9. Arrhenius plots of ln$k$ versus $1/T$. 
not favorable for LA formation due to tendency of humins formation.

3.5. Comparison with previous kinetic models

Herein, the experimental data for glucose decomposition reaction were best described using the first-order kinetic model. The same trend has been previously reported [27,30,40,41,49]. In a study by Weingarten et al., the experimental data was modelled using a power law approach [28], where the kinetic model has been made for a wide range of acid concentrations. Meanwhile, a modified Arrhenius equation was used to determine the temperature dependence of the rate constants [7]. The dissociation constant of the catalyst (H₂SO₄) was also considered in the kinetic model.

Table 2 summarizes the kinetic studies from the literature for glucose decomposition reaction to compare with the current studies reported by Girisuta and team, a modified Arrhenius equation was used to determine the temperature dependence of the rate constants [7]. The dissociation constant of the catalyst (H₂SO₄) was also considered in the kinetic model.

Table 2
Summary of kinetic study on glucose decomposition.

<table>
<thead>
<tr>
<th>Proposed model</th>
<th>Reaction conditions</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
<th>( A ) (min(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose (\rightarrow) 5-HMF (\rightarrow) LA</td>
<td>180–280°C Non catalyzed</td>
<td>( E_a = 108 )</td>
<td>( A = 5.1 \times 10^7 )</td>
<td>[30]</td>
</tr>
<tr>
<td>Humins</td>
<td></td>
<td>( E_a = 136 )</td>
<td>( A = 4.3 \times 10^{12} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_a = 89 )</td>
<td>( A = 2.6 \times 10^8 )</td>
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<tr>
<td></td>
<td></td>
<td>( E_a = 109 )</td>
<td>( A = 3.6 \times 10^9 )</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>( E_a = 31 )</td>
<td>( A = 0.031 )</td>
<td></td>
</tr>
<tr>
<td>Glucose (\rightarrow) 5-HMF (\rightarrow) LA</td>
<td>170–210°C H₂SO₄</td>
<td>( E_a = 86 )</td>
<td>N.A</td>
<td>[26]</td>
</tr>
<tr>
<td>Humins</td>
<td></td>
<td>( E_a = 57 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_a = 209 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose (\rightarrow) 5-HMF (\rightarrow) LA</td>
<td>98–200°C H₂SO₄</td>
<td>( E_a = 152 )</td>
<td>N.A</td>
<td>[7]</td>
</tr>
<tr>
<td>Humins</td>
<td></td>
<td>( E_a = 165 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_a = 111 )</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>( E_a = 111 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose (\rightarrow) Int. 5-HMF (\rightarrow) LA</td>
<td>180–220°C Formic acid</td>
<td>( E_a = 153 )</td>
<td>N.A</td>
<td>[27]</td>
</tr>
<tr>
<td>Humins</td>
<td></td>
<td>( E_a = 107 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_a = 127 )</td>
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<tr>
<td></td>
<td></td>
<td>( E_a = 110 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose (\rightarrow) 5-HMF (\rightarrow) LA</td>
<td>140–180°C HCl</td>
<td>( E_a = 160 )</td>
<td>( A = 10.2 \times 10^7 )</td>
<td>[28]</td>
</tr>
<tr>
<td>Humins</td>
<td></td>
<td>( E_a = 51 )</td>
<td>( A = 47.5 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_a = 95 )</td>
<td>( A = 98.7 \times 10^3 )</td>
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<tr>
<td></td>
<td></td>
<td>( E_a = 142 )</td>
<td>( A = 20.4 \times 10^6 )</td>
<td></td>
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<tr>
<td>Glucose (\rightarrow) 5-HMF (\rightarrow) LA</td>
<td>170–230°C H₃PO₄</td>
<td>( E_a = 121 )</td>
<td>N.A</td>
<td>[29]</td>
</tr>
<tr>
<td>Humins</td>
<td></td>
<td>( E_a = 56 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose (\rightarrow) 5-HMF</td>
<td>140–180°C [C₂OHMIM][BF₄]</td>
<td>( E_a = 56 )</td>
<td>( A = 1.6 \times 10^4 )</td>
<td>[49]</td>
</tr>
<tr>
<td>Glucose (\rightarrow) 5-HMF</td>
<td>110–170°C Cr₃-SO₃H-polymeric ionic liquids</td>
<td>( E_a = 22 )</td>
<td>N.A</td>
<td>[41]</td>
</tr>
<tr>
<td>Glucose (\rightarrow) 5-HMF</td>
<td>80–120°C CrCl₃ in [AMIM][Cl]</td>
<td>( E_a = 135 )</td>
<td>( A = 1.28 \times 10^{10} \text{ (mol/L)}^{-1} \text{ s}^{-1} )</td>
<td>[40]</td>
</tr>
<tr>
<td>Glucose (\rightarrow) LA</td>
<td>160–180°C [C₃SO₃HMIM][HSO₄]</td>
<td>( E_a = 202 )</td>
<td>N.A</td>
<td>[50]</td>
</tr>
<tr>
<td>Humins</td>
<td></td>
<td>( E_a = 167 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose (\rightarrow) 5-HMF (\rightarrow) LA</td>
<td>120–200°C Fe/HY zeolite</td>
<td>( E_a = 64 )</td>
<td>( A = 39.9 \times 10^6 )</td>
<td>[This study]</td>
</tr>
<tr>
<td>Humins</td>
<td></td>
<td>( E_a = 76 )</td>
<td>( A = 69.3 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_a = 61 )</td>
<td>( A = 22.3 \times 10^6 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( E_a = 70 )</td>
<td>( A = 27.0 \times 10^5 )</td>
<td></td>
</tr>
</tbody>
</table>

Int = intermediate compound, N.A = not available.

Table 2 summarizes the kinetic studies from the literature for glucose decomposition reaction to compare with the current studies reported by Girisuta and team, a modified Arrhenius equation was used to determine the temperature dependence of the rate constants [7]. The dissociation constant of the catalyst (H₂SO₄) was also considered in the kinetic model.
The activation energy for 5-HMF conversion to LA using Fe/HY zeolite (61 kJ mol$^{-1}$) was comparable with some kinetic studies of glucose decomposition using H$_2$PO$_4$ and H$_2$SO$_4$ as catalysts [26,29]. Meanwhile, higher activation energies were attained for other homogeneous acid catalysis reactions. As shown in Table 2, the activation energy for 5-HMF conversion to LA was not reported for reactions involving ionic liquids [40,41,49,50]. On the other hand, the activation energy of glucose conversion directly to LA was reported (202 kJ mol$^{-1}$) as the formation reaction of 5-HMF was not included in the kinetic model [50]. For the formation of humins from glucose and 5-HMF, this study reported values of 76 and 70 kJ mol$^{-1}$, respectively. Meanwhile, higher activation energies were obtained from previous studies (109–209 kJ mol$^{-1}$) [7,26,27,29,30,50]. The values acquired for activation energies of humins formation in this study and in a study reported by Weingarten et al. [28] do not concur with those reported values.

The values of activation energies and pre-exponential factors for this study were comparatively lower than previously reported results focusing on kinetic studies of glucose conversion. This highlights the feasibility of Fe/HY zeolite in the glucose conversion process, where the reaction can be conducted at lower temperature. In addition, the variation in the activation energy and pre-exponential factor of a reaction is possibly due to several factors including types of catalyst and solvent, and heating method [51].

4. Conclusion

The decomposition of glucose is investigated at temperatures of 120–200°C for 0–240 min in a batch reactor using heterogeneous Fe/HY zeolite catalyst. A kinetic model is developed to investigate the kinetics of glucose conversion to LA. The model involves four reactions, and the main decomposition products are 5-HMF and LA with humins as the insoluble by-product. After eliminating the effect of external and internal diffusions, a pseudo homogenous reaction model is used for the kinetic modelling. The kinetic is first-order with a good agreement between the experimental and modelling data. The activation energies derived from our model are comparatively lower than the value previously reported in the literatures. The findings from this study are useful for process modelling applications.

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References


