



Thermo-kinetic assessment of glucose decomposition to 5-hydroxymethyl furfural and levulinic acid over acidic functionalized ionic liquid



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ABSTRACT

Decomposition of biomass feedstock is a promising technique for producing versatile chemicals such as 5-hydroxymethyl furfural (5-HMF) and levulinic acid (LA). Glucose, the model compound of cellulose, is one of the most important starting components for bio-based chemical synthesis. Herein, the kinetics of glucose decomposition catalyzed by an acidic functionalized ionic liquid, 1-sulfonic acid-3-methyl imidazolium tetrachloroferrate ([SMIM][FeCl₄]) was studied in the temperature range of 110–170 °C. A simplified kinetic model was developed based on pseudo-homogeneous first-order reactions. The kinetic model consists of four main key steps: (1) dehydration of glucose to 5-HMF; (2) degradation of glucose to humins; (3) rehydration of 5-HMF to LA; and (4) degradation of 5-HMF to humins. The proposed model was in a good agreement with the experimental results. The evaluated activation energies for glucose decomposition to 5-HMF and 5-HMF decomposition to LA were 37 and 30 kJ·mol⁻¹, respectively. The first-order rate constants were also used to calculate the thermodynamic activation parameters. The kinetic and thermodynamic parameters obtained can be applied to provide insights on the biomass decomposition to 5-HMF and LA using acidic ionic liquid.

1. Introduction

Non-renewable energy generation from primary energy sources has compels the chemical industry to explore alternatives for energy and basic chemical productions [1]. Selective conversion of renewable biomass resources into fuels and chemicals are challenging. Extensive studies are being carried out to investigate the conversion of carbohydrates biomass into bio-based chemicals [2]. As such, utilization of glucose as the model compound of biomass for the production of 5-hydroxymethylfurfural (5-HMF) and levulinic acid (LA) chemicals has drawn significant attention [3–5]. 5-HMF and LA have been recognized as versatile platform chemicals for synthesizing a broad range of chemical compounds [6–8]. 5-HMF can be applied for the production of fine chemicals, polymers, and bio-fuels and is also an intermediate for LA production [1]. LA can be used for the production of fuel additives, food flavouring agents, fragrances, and resins [9,10].

The reaction pathway of glucose decomposition to 5-HMF and LA is illustrated in Fig. 1. The pathway includes triple dehydration of glucose to produce 5-HMF, rehydration of 5-HMF with two water molecules to produce LA, and decomposition of glucose and 5-HMF to produce humins - the insoluble dark brown byproduct [11,12]. From an environmental and economical point of view, a selective glucose conversion to

5-HMF and LA can be attained with the use of effective catalyst for the respective reactions. Until now, various types of homogeneous and heterogeneous acid catalysts have been employed [13–19]. In addition, there has been an increasing tendency of using ionic liquids in lignocellulosic biomass processing for sugars production and subsequently for 5-HMF and LA production where ionic liquids can be used as either catalysts or solvents [20–22].

Modification of ionic liquid through the inclusion of different types of functional groups on the anion and cation confers a new ionic liquid called functionalized ionic liquid. The modification could alter the ionic liquid properties such as acidity as demonstrated for SO₃HCl and metal halide [23,24]. In the search for an ionic liquid that can improve the conversion of glucose to 5-HMF and LA, acidic functionalized ionic liquid has reported some encouraging results. Recently, SO₃HCl and low cost and non-toxic metal halide, FeCl₃, were introduced to imidazolium based ionic liquid to synthesize an acidic functionalized ionic liquid for glucose conversion to 5-HMF and LA [25].

Substantial interests in application of glucose for 5-HMF and LA production have led to the kinetic study of glucose decomposition in order to elucidate the mechanistic of the chemical reaction [14,26–29]. The kinetic model of acid catalyzed glucose decomposition incorporated the formation reactions of 5-HMF, LA, and humins. As

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glucose is available in polymer of cellulose, some studies have emphasized the kinetics of cellulose and lignocellulosic biomass hydrolysis to glucose [30–34]. The current reaction models of lignocellulosic biomass and cellulose hydrolysis [35–38] were tailored from Saeman's first order pseudo-homogeneous kinetic model of cellulose hydrolysis to glucose [39], which consisted of two consecutive reactions: cellulose to glucose, and glucose to decomposition products. The thermodynamic parameters for cellulose hydrolysis have been determined accordingly [38,40]. However, reports on kinetic and thermodynamic parameters for glucose conversion reaction are very limited. Thus, it is of great interest to obtain the thermo-kinetic parameters for energy assessment of glucose conversion reaction. Besides, the thermo-kinetic modeling can help to elucidate practical conversion processes and subsequently optimize the design of efficient reactors.

In our earlier work, three different acidic functionalized ionic liquids have been prepared and applied as catalyst for glucose conversion to 5-HMF and LA [25]. From the analysis, 1-sulfonic acid-3-methyl imidazolium tetrachloroferrate ([SMIM][FeCl₄]) with the highest acidity offered a prominent catalytic performance. Thus, a kinetic study of glucose decomposition catalyzed by [SMIM][FeCl₄] was inevitable. The kinetic model was developed based on pseudo homogeneous reaction. In this paper, the kinetic parameters for glucose decomposition to 5-HMF and LA were reported, including reaction rate constants at different temperatures, activation energy, as well as the pre-exponential factor. Furthermore, the thermodynamic energy assessment of the present methodology was also presented by considering the activation enthalpy, activation entropy, and Gibbs energy. The outputs from this work will provide important basic information for process development of catalytic biomass conversion to 5-HMF and LA using [SMIM][FeCl₄] in particular and acidic functionalized ionic liquids in general.

2. Materials and methods

2.1. Materials

All chemicals were used as received without any further purification. 1-Methylimidazole, chlorosulfonic acid (SO₃HCl), dichloromethane (CH₂Cl₂), and iron (III) chloride hexahydrate (FeCl₃·6H₂O) were used for the preparation of [SMIM][FeCl₄]. In the catalytic test and product analysis steps, glucose, 5-HMF (99%), LA (98%), sodium hydroxide (NaOH), 3,5-dinitrosalicylic acid, potassium sodium tartrate tetrahydrate, sodium sulfite, and sulfuric acid (H₂SO₄; 96%) were employed. All chemicals were obtained from Merck, Germany and Sigma Aldrich, United States.

2.2. [SMIM][FeCl₄] preparation

[SMIM][FeCl₄] was prepared by mixing the as-synthesized 1-sulfonic acid-3-methyl imidazolium chloride, [SMIM][Cl], and FeCl₃·6H₂O. Meanwhile, the synthesis of [SMIM][Cl] accorded with the procedure elucidated in [25]. For the preparation of [SMIM][FeCl₄], equimolar [SMIM][Cl] and FeCl₃·6H₂O were mixed and stirred vigorously for 24 h, then dried overnight at 80 °C. The properties of [SMIM][FeCl₄] were characterized using several techniques such as CHNS elemental analysis, ¹H and ¹³C NMR, pyridine-FTIR, Hammett acidity function, and acid-base titration method [25].

2.3. Experimental procedures

A closed 100 ml Schott bottle equipped with a thermocouple, stood as a batch reactor, was used for all experiments. The reactor was filled with predetermined amount of feedstock (glucose or 5-HMF), [SMIM][FeCl₄] catalyst, and distilled water, then heated to a set temperature. The initial concentration of feedstock was 5000 ppm, with the presence of 10 g of [SMIM][FeCl₄] and 20 mL of water. 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 reaction time was

started once the reaction mixture reached the set temperature. 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 using 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 H₂SO₄, detector = UV 210 nm; retention time = 40 min; column temperature = 60 °C. Meanwhile, glucose concentration in the liquid product was determined using DNS method. DNS reagent was prepared according to method described elsewhere [41]. Feedstock conversion and product yield were calculated according to Eqs. (1) and (2), respectively.

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

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

2.5. Determination of kinetic and thermodynamic parameters

Fig. 1 depicts the reaction scheme for glucose decomposition employed in the development of the kinetic model. The reaction scheme consisted of four main reactions include (1) conversion of glucose to 5-HMF, (2) degradation of glucose to humins, (3) conversion of 5-HMF to LA, and (4) degradation of 5-HMF to humins. As glucose decomposition in the presence of [SMIM][FeCl₄] is a homogeneous catalytic system, the effect of mass transfer diffusion is considered negligible. Additionally, several assumptions were considered to develop the kinetic model. These assumptions were in agreement with previously reported kinetic models [26,30,32,42]:

- 1) Glucose decomposition using [SMIM][FeCl₄] is a pseudo homogeneous first-order reaction.
- 2) Glucose decomposition reaction is a series of irreversible reactions from glucose to 5-HMF (Reaction 1) then subsequently to LA (Reaction 3).
- 3) Formation of intermediates from glucose and 5-HMF decompositions is negligible.
- 4) All humins and other soluble products are by-products (Reaction 2 and 4).
- 5) LA is the main product from 5-HMF decomposition and other possible reactions are negligible.

Eqs. (3) and (4) represent the rate of reactions for glucose and 5-HMF decompositions, respectively, as pseudo first-order kinetic approach was used. R_G and R_H are the reaction rates of glucose and 5-HMF decomposition, respectively. k_G, k_H, k₁, k₂, k₃, and k₄ are the kinetic constants of glucose decomposition, 5-HMF decomposition, reactions 1, 2, 3, and 4, respectively. The kinetic parameters were determined using software package Polymath 6.10.

$$R_G = (k_1 + k_2)C_G \quad (3)$$

$$R_H = (k_3 + k_4)C_H \quad (4)$$

where

$$k_G = k_1 + k_2 \quad (5)$$

$$k_H = k_3 + k_4 \quad (6)$$

A set of differential Eqs. (7–9) were derived based on the rate of

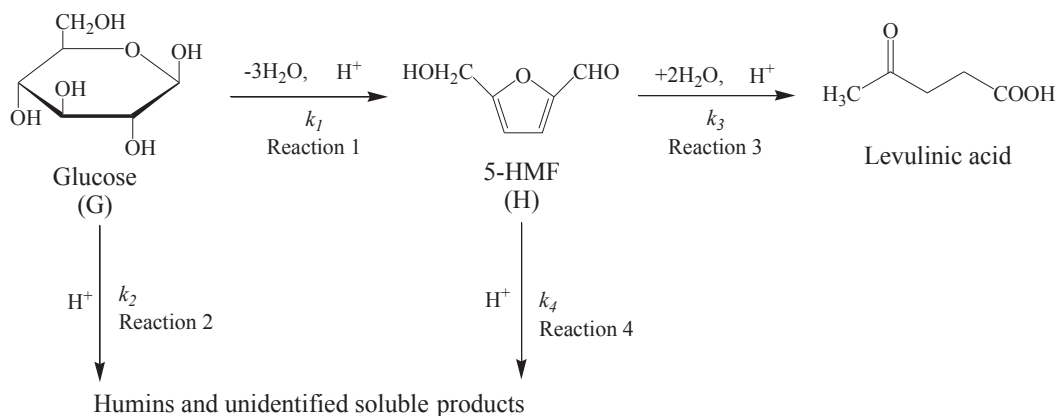


Fig. 1. Reaction pathways of glucose decomposition to 5-HMF and LA.

reactions; Eqs. (3) and (4).

$$\frac{-dC_G}{dt} = (k_1 + k_2)C_G = k_G C_G \quad (7)$$

$$\frac{dC_H}{dt} = k_1 C_G - (k_3 + k_4)C_H = k_1 C_G - k_H C_H \quad (8)$$

$$\frac{dC_{LA}}{dt} = k_3 C_H \quad (9)$$

The analytical expressions of glucose, 5-HMF and LA concentration were obtained as in equations (10), (11), and (12), respectively, by solving the differential Eqs. (7–9). The experimental data were fitted into the expressions accordingly. C_G , C_H , C_{LA} , and C_{G0} refer to the concentrations of glucose, 5-HMF, LA, and initial glucose, respectively.

$$C_G = C_{G0} e^{-k_G t} \quad (10)$$

$$C_H = \frac{k_1 C_{G0}}{k_H - k_G} (e^{-k_G t} - e^{-k_H t}) \quad (11)$$

$$C_{LA} = \frac{k_1 k_3 C_{G0}}{k_H - k_G} \left[\frac{k_H (1 - e^{-k_G t}) - k_G (1 - e^{-k_H t})}{k_G k_H} \right] \quad (12)$$

The reaction rate constants were then fitted to the Arrhenius plot of $\ln k$ versus $1/T$ based on the Eq. (13) to acquire the values of activation energies (E_a) and exponential factors (A) of the respective reactions.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (13)$$

Based on the transition state theory, Eyring equation which is similar to Arrhenius's expression was used to relate rate constant to temperature. The Eyring equation (Eq. (14)) was applied to determine the thermodynamic parameter; the activation enthalpy (ΔH^\ddagger) and the activation entropy (ΔS^\ddagger). Eq. (14) gives a plot of $\ln(k/T)$ against $1/T$ for evaluating both ΔH^\ddagger and ΔS^\ddagger . The Gibbs free energy of activation was determined from Eq. (15). From the equations, k_B is the Boltzmann's constant ($1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$), h is Planck's constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}$), and R is gas constant ($8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (14)$$

$$\Delta G^\ddagger = -RT \ln\left(\frac{kh}{T k_B}\right) \quad (15)$$

3. Results and discussion

3.1. Catalytic performance of [SMIM][FeCl₄]

The prepared [SMIM][FeCl₄] is a stiff solid at room temperature

that melts at higher temperature ($\sim 70^\circ\text{C}$). The properties of [SMIM][FeCl₄] have been examined using several methods and the detail characterization analyses can be found elsewhere [25]. High performance of glucose conversion to 5-HMF and LA has been achieved when [SMIM][FeCl₄] was employed as catalyst. From the catalyst screening, [SMIM][FeCl₄] prevailed among the other acidic functionalized ionic liquids, as the catalyst acidity registered a large effect on glucose conversion and product yields, where the catalyst with stronger acidity led to higher activity [25]. The presence of Brønsted and Lewis acid sites from [SMIM][FeCl₄] were deemed suitable for glucose conversion to 5-HMF and LA, as both Brønsted and Lewis acid sites played important roles in the reaction. The isomerization of glucose to fructose is catalyzed by the Lewis acid sites [43], and Brønsted acid sites are required for 5-HMF rehydration to LA [43]. In addition, [SMIM][FeCl₄] can be reused and exhibited favorable catalytic activity over five successive cycles of glucose decomposition reaction [25].

3.2. Glucose and 5-HMF decompositions

Glucose decomposition reactions catalyzed by [SMIM][FeCl₄] were conducted at a temperature range of 110–170 °C from 0 to 300 min. Besides, decomposition reactions of 5-HMF were carried out in order to comprehend the degradation rate of 5-HMF. 5-HMF and LA were the main products from glucose decomposition (Fig. 1, Reaction 1), while LA was the main compound from 5-HMF decomposition (Fig. 1, Reaction 3). Humins and other soluble products can also be obtained from glucose and 5-HMF decompositions (Fig. 1, Reaction 2 and 4). Humins are dark brown insoluble byproduct formed through polymerization reaction in the presence of water which initiated from glucose, glucose intermediate, and 5-HMF decompositions [14,44]. Nonetheless, humins did not originate from LA [15,28].

Alongside the formation of LA, 5-HMF dehydration has resulted in the emergence of formic acid. In the acidic and high temperature reaction media, formic acid has high chance to decompose to CO₂, H₂, CO, and H₂O [45]. Besides, formic acid could also be produced from furfural, which originated from 5-HMF [46]. The decomposition of formic acid and its formation from furfural have caused the formic acid concentration to fluctuate throughout the reactions. Other than formic acid and humins, traces amounts of furfural and lactic acid were detected and regarded as byproducts. The formation of furfural was initiated via formaldehyde loss from 5-HMF [27], while the Lewis acid sites in the reaction system boosted lactic acid formation from glucose decomposition [47,48].

Fig. 2 illustrates the glucose conversions, 5-HMF yields, and LA yields from glucose decomposition using [SMIM][FeCl₄] as catalyst at various reaction temperatures (110–170 °C). Glucose conversion varied from 6 to 100%. It is known that reaction temperature had a strong effect on glucose decomposition, as high reaction rate could be

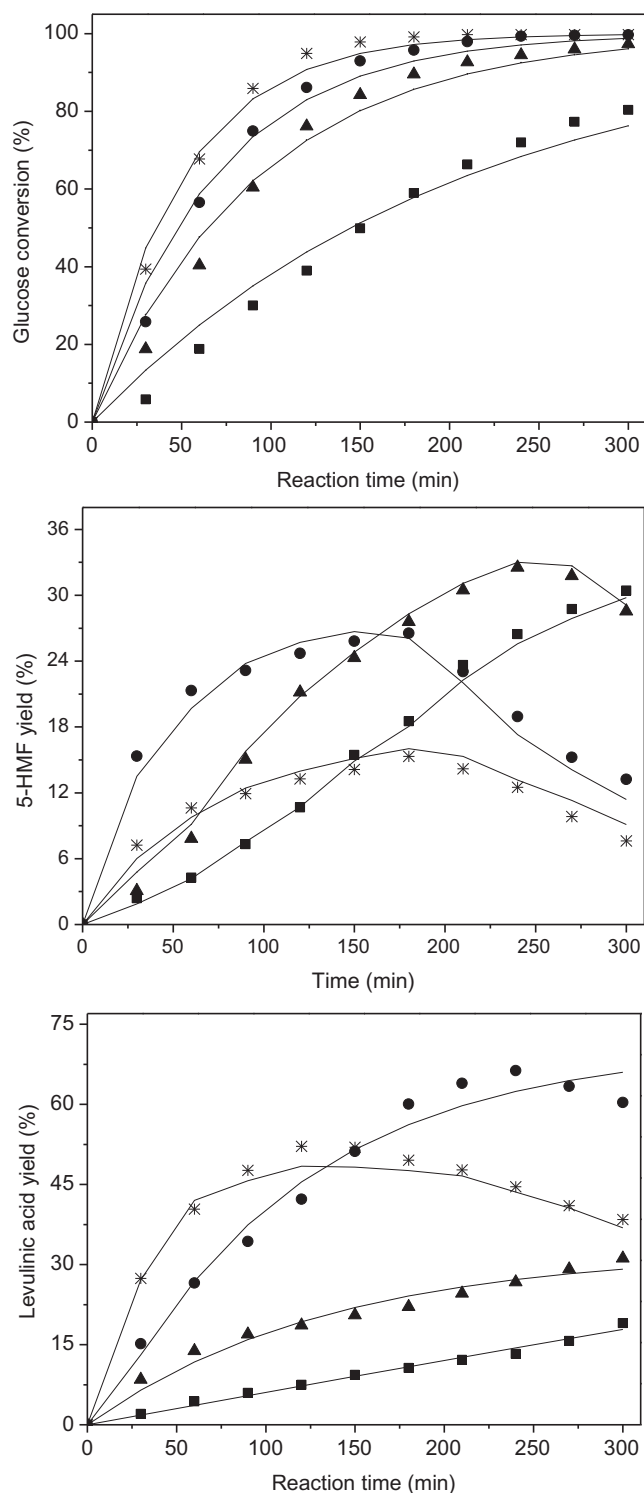


Fig. 2. Glucose decomposition – effect of reaction temperature on glucose conversion, 5-HMF yield, and LA yield. ■ 110 °C, ▲ 130 °C, ● 150 °C, * 170 °C.

accomplished at elevated temperature. For instance, glucose conversion of 70% was achieved in less than 120 min for reaction conducted at 130 °C, compared to 240 min for glucose conversion at lower temperature; 110 °C. The maximum 5-HMF yield of 24% was attained at 110 °C in 300 min. Enhanced 5-HMF formation from glucose decomposition was achieved either at low temperature – prolonged time or high temperature – shortened time. Higher reaction temperature (up to 150 °C) could boost the LA formation, giving the maximum LA yield of

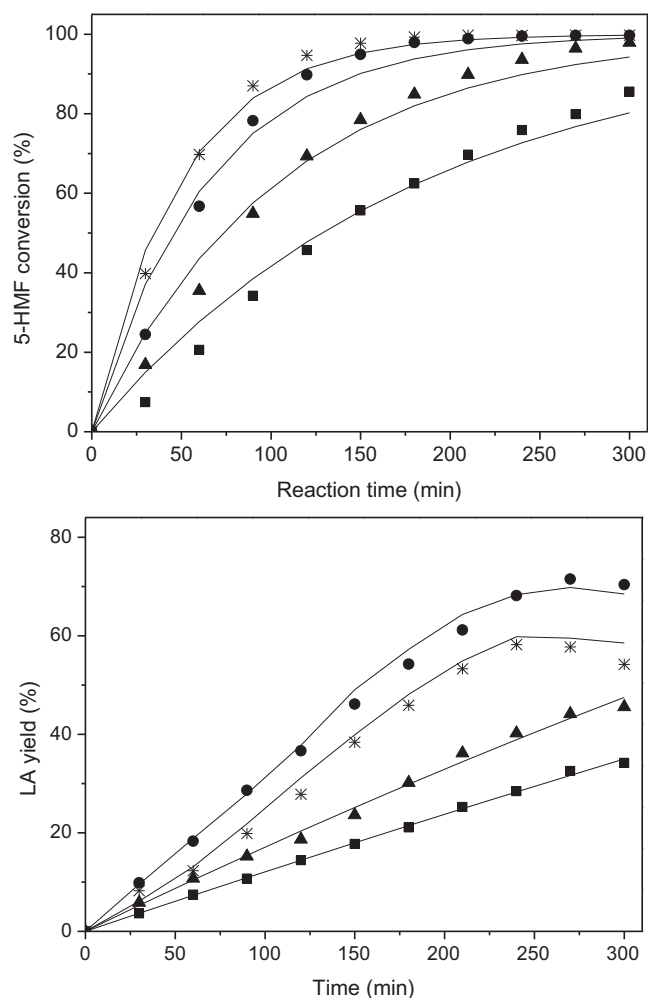


Fig. 3. 5-HMF decomposition – effect of reaction temperature on 5-HMF conversion and LA yield. ■ 110 °C, ▲ 130 °C, ● 150 °C, * 170 °C.

66%. Conversely, high temperature led to humins formation and lowered the LA production.

The 5-HMF conversions and LA yields from 5-HMF decomposition reactions at 110–170 °C are demonstrated in Fig. 3. Similar trends for the conversions of 5-HMF and glucose was observed, with higher decomposition rates of 5-HMF compared to glucose was scrutinized from the trend. The increase in reaction temperature and reaction time has resulted in the surge of 5-HMF conversion and LA yield. From the assessment, 5-HMF conversion was 34% in 90 min at 110 °C, and reached 78% in 90 min at 150 °C. In the meantime, the LA yield attained 25% in 210 min at 110 °C, and increased to 46% in 120 min at 150 °C. Notable amount of humins were observed at high reaction temperature and consequently decreased the LA production.

3.3. Kinetic modeling and thermo-kinetic assessment

Fig. 4 displays the concentration profile of relevant compounds in glucose decomposition reaction using [SMIM][FeCl₄] at 150 °C. The compounds include glucose, 5-HMF, and LA. Glucose concentration decreased with increasing time as glucose dehydrated to 5-HMF and decomposed to humins. The concentration of 5-HMF was low throughout the reaction, as 5-HMF was converted to LA once formed and decomposed to humins.

The first order dependence of glucose and 5-HMF decomposition reactions using [SMIM][FeCl₄] were supported by the linearity of $-\ln(1-X)$ versus time plots in Fig. 5. Besides, the previously reported

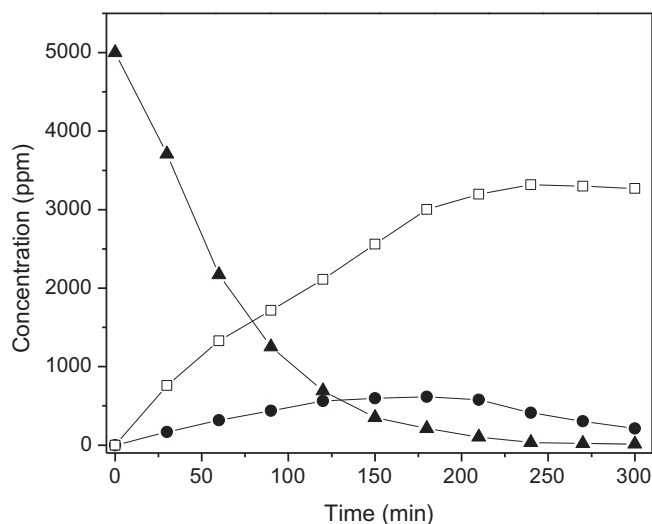


Fig. 4. Typical concentration profile of glucose decomposition at 150 °C. ▲ Glucose, ● 5-HMF, □ LA.

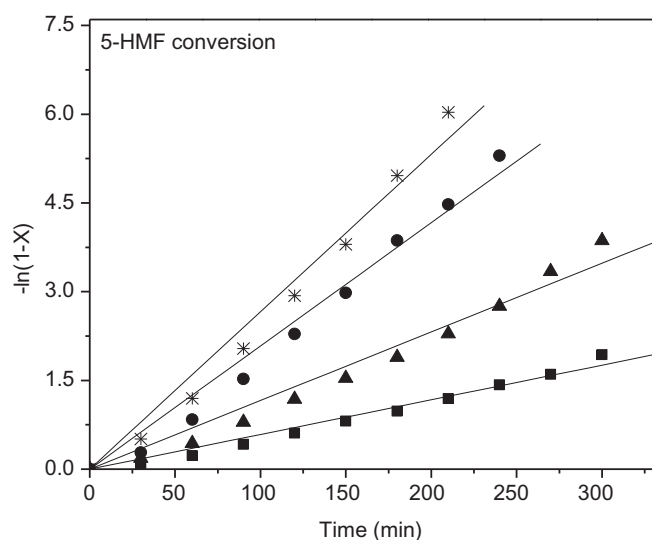
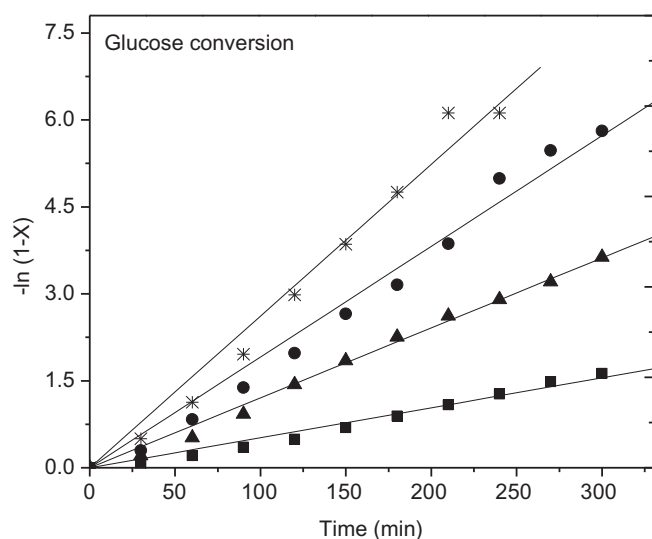


Fig. 5. $-\ln(1-X)$ versus time for glucose and 5-HMF conversion. ■ 110 °C, ▲ 130 °C, ● 150 °C, * 170 °C.

kinetics of glucose decomposition involving ionic liquids as catalyst also obeyed the first-order kinetic approach [24,49]. As first order dependence of the reactions were validated, the reaction rate constants were computed as follows:

- 1) Reaction rate constants of glucose decomposition (k_G) were determined from the plots of $-\ln(1-X)$ versus reaction time, where X is the glucose conversion.
- 2) Reaction rate constants of 5-HMF decomposition (k_H) were determined from the plots of $-\ln(1-X)$ versus reaction time, where X is the 5-HMF conversion.
- 3) Reaction rate constants of Reaction 1 (k_1) and Reaction 3 (k_3) were obtained from Eqs. (10) and (11), respectively, using non-linear least square regression method.
- 4) Reaction rate constants of Reaction 2 (k_2) were computed from difference between k_G and k_1 , fitted using Eq. (7).
- 5) Reaction rate constants of Reaction 4 (k_4) were computed from difference between k_H and k_3 , fitted using Eq. (8).

Table 1 presents the kinetic parameters of glucose decomposition using [SMIM][FeCl₄] catalyst. The kinetic parameters include reaction rate constant (k), activation energy (E_a), and pre-exponential factor (A). The reaction rate constants were relied on the reaction temperature, where the rate constant increased with reaction temperature for all reactions. For glucose decomposition, the rate constants of glucose conversion to 5-HMF, k_1 were smaller compared to the rate constant of glucose decomposition, k_G at all temperatures. The smaller value of k_1 compared to k_G validated the fact that only a part of glucose was converted into 5-HMF, while the other part decomposed to other unwanted product such as humins.

The decomposition of 5-HMF is a fast reaction as can be demonstrated from low concentrations of 5-HMF throughout the reaction [31,32,50]. Moreover, higher reaction rate constant of 5-HMF decompositions, k_H compared to reaction rate of 5-HMF formation, k_1 shows that decomposition of 5-HMF is a fast reaction compared to its formation rate. LA is considered as the main product from 5-HMF decomposition [28,32]. As illustrated in Fig. 4, the concentration of LA increased initially, but gradually became constant after it reached a certain value. Thus, it is proposed that LA is the final product from glucose decomposition reaction under the experimental conditions.

For glucose decomposition reaction, lower reaction rate constants of humins formation, k_2 were accounted compared to the rate constant of 5-HMF formation, k_1 . In addition for 5-HMF decomposition reaction, the reaction rate constants of humis formation, k_4 was also lower than

Table 1
Kinetics and thermodynamic parameters of glucose decomposition using [SMIM][FeCl₄] catalyst.

Temperature (°C)	Reaction rate constant (min ⁻¹)					
	k_1	k_2	k_G	k_H	k_3	k_4
110	0.0035	0.0017	0.0059	0.0052	0.0037	0.0022
130	0.0065	0.0056	0.0116	0.0121	0.0067	0.0049
150	0.0127	0.0068	0.0195	0.0195	0.0108	0.0087
170	0.0157	0.0108	0.0266	0.0265	0.0127	0.0139
Parameter	Reaction					
	1	2	G	H	3	4
E_a (kJ·mol ⁻¹)	36.7	40.9	38.1	35.7	29.7	43.2
A (min ⁻¹)	371.7	803.8	925.0	467.5	44.9	1826.8
R^2 (Arrhenius plot)	97.4	90.6	96.8	98.6	96.4	99.4
ΔH^\ddagger (kJ·mol ⁻¹)	33.6	37.8	35.0	32.6	26.6	40.1
ΔS^\ddagger (J·mol ⁻¹ ·K ⁻¹)	-240.0	-233.7	-232.5	-238.2	-257.7	-226.9
R^2 (Eyring plot)	97.3	89.1	96.5	98.6	96.0	99.4
ΔG^\ddagger (kJ·mol ⁻¹)	128.18	129.77	126.41	126.48	128.44	129.23

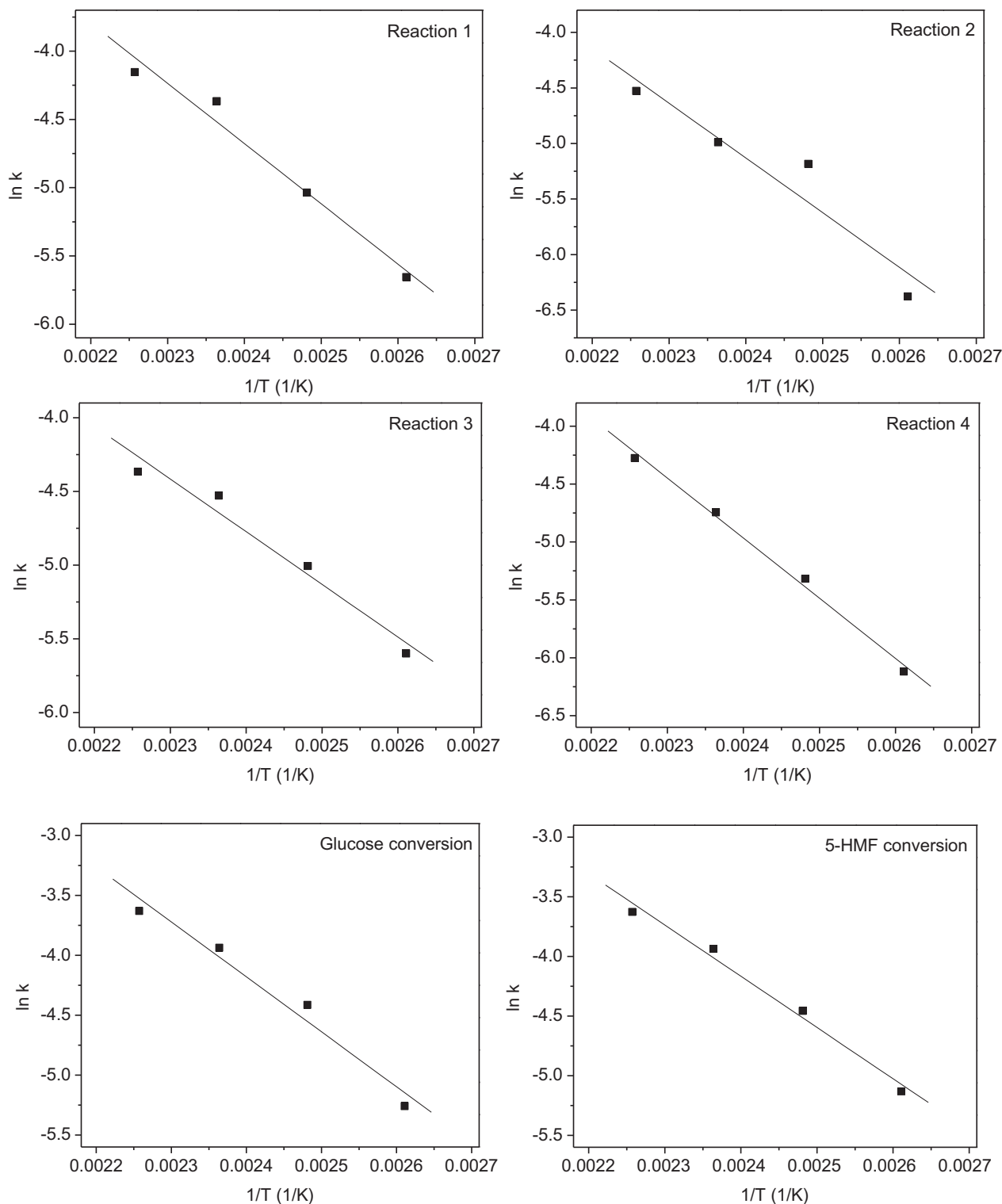


Fig. 6. Arrhenius plots of $\ln k$ versus $1/T$.

rate constant of LA formation, k_3 except at 170 °C. This elucidates that 5-HMF decomposition at higher temperature resulted in faster humins formation in contrast to LA formation. This supported the fact that higher temperature rendered unwanted side reaction and elevated humins formation [42,47].

The Arrhenius plots in Fig. 6 were drawn to determine the values of activation energies (E_a) and pre-exponential factors (A) as presented in Table 1. The highest activation energy registered by 5-HMF

decomposition to humins (Reaction 4) signified that this reaction was mostly affected by temperature. This implied that high temperature would enhance the formation of humins from 5-HMF. By comparing the activation energy of glucose decomposition (Reaction 1) with humins formation (Reaction 2), the activation energy of Reaction 2 was higher compared to the activation energy of Reaction 1. The same trend was perceived when comparing the activation energy of 5-HMF decomposition (Reaction 3) with humins formation (Reaction 4). This

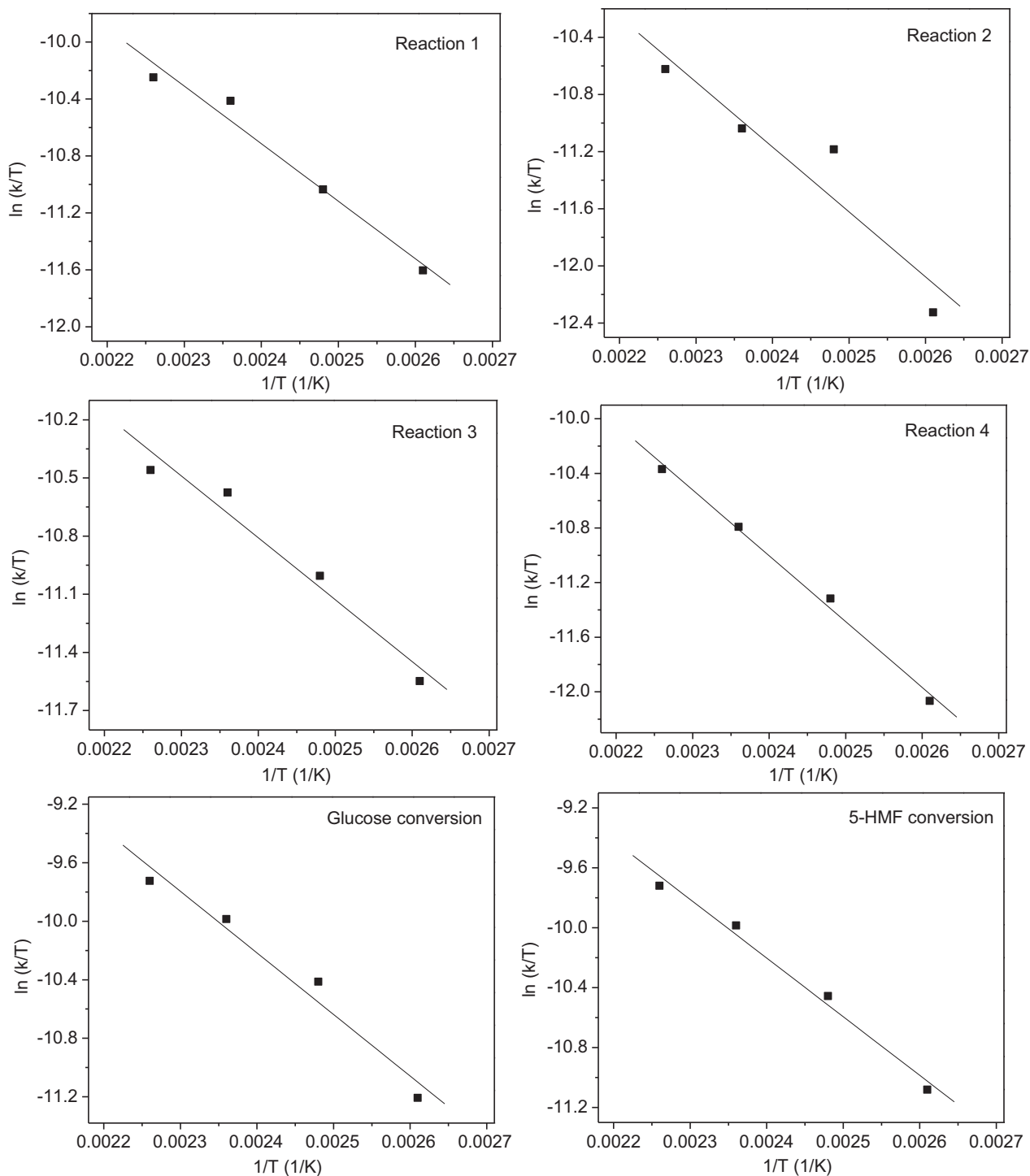


Fig. 7. Eyring plots of $\ln k/T$ versus $1/T$.

corroborates that high temperature is favorable for the formation of humins from glucose and 5-HMF. Thus, for glucose decomposition in the presence of $[\text{SMIM}][\text{FeCl}_4]$ as catalyst, lower reaction temperature ($< 170^\circ\text{C}$) was preferred to promote the 5-HMF and LA production, as high temperature elevates the tendency of humins formation.

A reaction can be classified as diffusion limited or kinetically controlled reaction. As glucose decomposition in the presence of $[\text{SMIM}][\text{FeCl}_4]$ is a homogeneous catalytic system, the mass transfer diffusion is considered negligible. It has been reported that kinetically controlled reactions show activation energy higher ($> 14 \text{ kJ}\cdot\text{mol}^{-1}$), while E_a for a diffusion limited reaction is much lower ($< 14 \text{ kJ}\cdot\text{mol}^{-1}$) [51,52].

Hence, it is certified that the present case of glucose decomposition reaction using $[\text{SMIM}][\text{FeCl}_4]$ catalyst is kinetically controlled, based on the high E_a values (Table 1).

The first order rate constants for glucose decomposition reaction were applied in the Eyring plot (Fig.7), and the activation enthalpies (ΔH^\ddagger), activation entropies (ΔS^\ddagger), and Gibbs free energy of activation (ΔG^\ddagger) obtained are summarized in Table 1. The ΔH^\ddagger values from the Eyring plots are nearly equal to the E_a values from the Arrhenius plots, as evident by the similar trend observed for both Eyring and Arrhenius plots. The positive values of ΔH^\ddagger indicated the endothermic nature of glucose decomposition in the present reaction system. The lower ΔH^\ddagger

Table 2
Kinetics overview of glucose decomposition reaction.

Proposed model	Reaction conditions	Ea (kJ·mol ⁻¹)	A (min ⁻¹)	References
$\begin{array}{ccccc} \text{Glucose} & \xrightarrow{1} & 5\text{-HMF} & \xrightarrow{3} & \text{LA} \\ \downarrow 2 & & \downarrow 4 & & \downarrow 5 \\ \text{Humins} & & \text{Humins} & & \text{Decomposition} \\ & & & & \text{product} \end{array}$	180–280 °C Non catalyzed	Ea ₁ = 108 Ea ₂ = 136 Ea ₃ = 89 Ea ₄ = 109 Ea ₅ = 31	A ₁ = 5.1 × 10 ⁹ A ₂ = 4.3 × 10 ¹² A ₃ = 2.6 × 10 ⁶ A ₄ = 3.6 × 10 ⁹ A ₅ = 0.031	[54]
$\begin{array}{ccc} \text{Glucose} & \xrightarrow{1} & 5\text{-HMF} \xrightarrow{2} \text{LA} \\ \downarrow 3 & & \\ \text{Humins} & & \end{array}$	170–210 °C H ₂ SO ₄	Ea ₁ = 86 Ea ₂ = 57 Ea ₃ = 209	N.A	[26]
$\begin{array}{ccccc} \text{Glucose} & \xrightarrow{1} & 5\text{-HMF} & \xrightarrow{3} & \text{LA} \\ \downarrow 2 & & \downarrow 4 & & \\ \text{Humins} & & \text{Humins} & & \end{array}$	98–200 °C H ₂ SO ₄	Ea ₁ = 152 Ea ₂ = 165 Ea ₃ = 111 Ea ₄ = 111	N.A	[28]
$\begin{array}{ccccccc} \text{Glucose} & \xrightarrow{1} & \text{Int.} & \xrightarrow{5} & 5\text{-HMF} & \xrightarrow{2} & \text{LA} \\ & & \downarrow 3 & & \downarrow 4 & & \\ & & \text{Humins} & & \text{Humins} & & \end{array}$	180–220 °C Formic acid	Ea ₁ = 153 Ea ₂ = 107 Ea ₃ = 117 Ea ₄ = 127 Ea ₅ = 110	N.A	[14]
$\begin{array}{ccccc} \text{Glucose} & \xrightarrow{1} & 5\text{-HMF} & \xrightarrow{3} & \text{LA} \\ \downarrow 2 & & \downarrow 4 & & \\ \text{Humins} & & \text{Humins} & & \end{array}$	140–180 °C HCl	Ea ₁ = 160 Ea ₂ = 51 Ea ₃ = 95 Ea ₄ = 142	A ₁ = 10.2 × 10 ⁷ A ₂ = 47.5 A ₃ = 98.7 × 10 ³ A ₄ = 20.4 × 10 ⁶	[27]
$\begin{array}{ccccc} \text{Glucose} & \xrightarrow{1} & 5\text{-HMF} & \xrightarrow{2} & \text{LA} \\ \downarrow & & \downarrow & & \\ \text{Humins} & & \text{Humins} & & \end{array}$	170–230 °C H ₃ PO ₄	Ea ₁ = 121 Ea ₂ = 56	N.A	[56]
$\begin{array}{ccccc} \text{Glucose} & \xrightarrow{1} & 5\text{-HMF} & \xrightarrow{3} & \text{LA} \\ \downarrow 2 & & \downarrow 4 & & \\ \text{Humins} & & \text{Humins} & & \end{array}$	120–200 °C Fe/HY zeolite	Ea ₁ = 64 Ea ₂ = 76 Ea ₃ = 61 Ea ₄ = 70	A ₁ = 39.9 × 10 ⁴ A ₂ = 69.3 × 10 ⁵ A ₃ = 22.3 × 10 ⁴ A ₄ = 27.0 × 10 ⁵	[42]
$\begin{array}{ccccc} \text{Glucose} & \xrightarrow{1} & 5\text{-HMF} & \xrightarrow{3} & \text{LA} \\ \downarrow 2 & & \downarrow 4 & & \\ \text{Humins} & & \text{Humins} & & \end{array}$	150–180 °C H ₃ PO ₄ and CrCl ₃	Ea ₁ = 65 Ea ₂ = 86 Ea ₃ = 61 Ea ₄ = 82	A ₁ = 9.16 × 10 ⁵ A ₂ = 7.21 × 10 ⁷ A ₃ = 2.88 × 10 ⁵ A ₄ = 6.79 × 10 ⁷	[29]
$\text{Glucose} \xrightarrow{1} 5\text{-HMF}$	140–180 °C [C ₂ OHMIM][BF ₄]	Ea ₁ = 56	A ₁ = 1.6 × 10 ⁴	[49]
$\text{Glucose} \xrightarrow{1} 5\text{-HMF}$	110–170 °C Cr ₃ -SO ₃ H-polymeric ionic liquids	Ea ₁ = 22	N.A	[24]
$\text{Glucose} \xrightarrow{1} 5\text{-HMF}$	80–120 °C CrCl ₃ in [AMIM][Cl]	Ea ₁ = 135	A ₁ = 1.28 × 10 ¹⁶ (mol/L) ⁻¹ s ⁻¹	[55]
$\begin{array}{ccc} \text{Glucose} & \xrightarrow{1} & \text{LA} \\ \downarrow 2 & & \\ \text{Humins} & & \end{array}$	160–180 °C [C ₃ SO ₃ HMIM][HSO ₄]	Ea ₁ = 202 Ea ₂ = 167	N.A	[57]
$\begin{array}{ccccc} \text{Glucose} & \xrightarrow{1} & 5\text{-HMF} & \xrightarrow{3} & \text{LA} \\ \downarrow 2 & & \downarrow 4 & & \\ \text{Humins} & & \text{Humins} & & \end{array}$	110–170 °C [SMIM][FeCl ₄]	Ea ₁ = 37 Ea ₂ = 41 Ea ₃ = 30 Ea ₄ = 43	A ₁ = 371.7 A ₂ = 803.8 A ₃ = 44.9 A ₄ = 1826.8	This study

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

value signified easy formation of the catalyst-substrate complex, hence lower the amounts of energy needed for chemical bonds to attain the transition state [52]. Lower ΔH^\ddagger values were deduced from desired product formation reactions (Reaction 1 and 3) compared to humins formation reactions (Reaction 2 and 4). ΔS^\ddagger represents the extent of disorder between transition and ground state of a reaction, which the ease of reaction is associated with the lower ΔS^\ddagger value and vice versa [52]. In the present glucose decomposition reaction, ΔS^\ddagger values were found to be lower for glucose to HMF and HMF to LA reactions (Reaction 1 and 3), which indicated more feasible environment for the corresponding reactions, compared to glucose to humins and 5-HMF to humins reactions (Reaction 2 and 4). Besides, the positive values of ΔG^\ddagger for glucose conversions to HMF and humins (Reaction 1 and 2) as well as 5-HMF conversions to LA and humins (Reaction 3 and 4) certified the endergonic or non-spontaneous of the respective reactions [53].

3.4. Overview of kinetic studies on glucose conversion reaction

The experimental data for glucose decomposition catalyzed by [SMIM][FeCl₄] were best described using a first order kinetic model. The first order kinetic model also has been applied to represent glucose decomposition reactions in previous studies [14,24,29,42,49,54,55]. There were also other approaches used to elucidate the kinetic model of glucose decomposition reaction. For instance, a power law was used to model the experimental data, where the kinetic model was developed for a wide range of acid concentrations [27]. Besides, a modified Arrhenius equation was employed to determine the temperature dependence of the rate constants where the dissociation constant of catalyst was considered in the kinetic model [28].

Table 2 compares the kinetics of glucose decomposition including non-catalyzed reaction and glucose conversion reaction using various catalysts. The kinetic models of glucose decomposition were developed based on several individual reaction schemes, while some of the models did not considered the individual reaction of each products. Besides, the parallel reactions of humins formation from glucose and 5-HMF have been proposed and integrated in the kinetic models.

As revealed in Table 2, a wide range of activation energy for glucose conversion to 5-HMF have been reported: 108 kJ·mol⁻¹ for non-catalyzed reaction [54], 86–160 kJ·mol⁻¹ for reactions involving mineral acid [14,26–28,56], ~65 kJ·mol⁻¹ for reaction catalyzed by modified zeolite and synergy of mineral acid and chromium chloride [29,42], and 22–202 kJ·mol⁻¹ for reactions using ionic liquids [24,49,55,57]. This current study reported an activation energy of 37 kJ·mol⁻¹ for glucose conversion to 5-HMF catalyzed by [SMIM][FeCl₄], which is lower compared to earlier work on non-catalyzed conversion reaction and reactions employing various catalysts.

Kinetics of glucose decomposition normally reported the direct conversion of glucose to 5-HMF, without taking into account the formation of intermediates. Nevertheless, intermediates formation has been considered throughout the conversion of glucose to 5-HMF catalyzed by formic acid [14]. The kinetics implied that the use of intermediate compound is beneficial since the best fit between experimental data and model could be achieved. From the model, the activation energies for intermediate formation from glucose and intermediate conversion to 5-HMF were 153 and 110 kJ·mol⁻¹, respectively.

In most kinetic models, 5-HMF has been accounted as the intermediate compound for LA production from glucose decomposition. Thus, the activation energy for 5-HMF conversion to LA was determined accordingly. When [SMIM][FeCl₄] was applied as catalyst, the activation energy for 5-HMF decomposition to LA was 30 kJ·mol⁻¹. It is worthy to note the activation energy for 5-HMF conversion to LA was not reported for reactions involving ionic liquids in previous studies [24,49,55,57]. For reaction catalyzed by modified zeolite, the activation energy for 5-HMF conversion to LA was comparable with H₃PO₄, H₂SO₄, and mixture of H₃PO and CrCl₃ as catalysts [26,29,42,56]. In addition, higher activation energies were reviewed for other

homogeneous acid catalysis reactions [14,27,28]. As mentioned before, humins originated from glucose and 5-HMF decomposition. The activation energies for humins formation from glucose and 5-HMF in this study were 41 and 43 kJ·mol⁻¹, respectively. Conversely, higher activation energies in the range of 109–209 kJ·mol⁻¹ for humins formation were previously reported [14,26,28,54,56,57].

A kinetic model of glucose decomposition was developed by considering only two reactions: decomposition of glucose to LA and humins, without including the formation of 5-HMF [57]. From this model, the activation energy of glucose conversion to LA was 202 kJ·mol⁻¹, and the activation energy for glucose decomposition to humins was 167 kJ·mol⁻¹ [57]. In another study, the non-catalyzed reaction of glucose decomposition at high temperature (180–280 °C) has incorporated the decomposition of LA in the kinetic model with its activation energy accounted as 31 kJ·mol⁻¹ [54]. As the reaction was carried out at high temperature up to 280 °C, the decomposition of LA was included in the kinetic model since it would decompose at high temperature and dehydrated to unsaturated lactones [58].

A broad range of activation energy and pre-exponential factor was reported for glucose decomposition reaction. Several factors have led to the variation in the activation energy and pre-exponential factor including types of catalyst and solvent, heating method, reaction time, and temperature range [59]. Relatively lower values of activation energy and pre-exponential factor were obtained in this work compared to previous studies focusing on kinetic study of glucose conversion. This highlights the feasibility of [SMIM][FeCl₄] in the glucose conversion process, where the reaction can be conducted at lower energy requirement.

4. Conclusion

In this study, the decomposition of glucose catalyzed by acidic functionalized ionic liquid [SMIM][FeCl₄] has been investigated. The thermo-kinetic study is performed for glucose conversion reaction at temperature range of 110–170 °C. Subsequent to several consideration and assumptions, the kinetic study is based on pseudo homogeneous model, which fitted-well with the experimental data. The kinetic model consists of four reactions, and the main decomposition products are 5-HMF and LA while humins is the insoluble by-product. The kinetics is in accordance to first-order reaction and various kinetic parameters (k, E_a, A) are deduced based on the Arrhenius theory. Moreover, the thermo activation parameters (ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger) are also determined based on the Eyring equation for energy assessment. From the analysis, the rate of reactions increase with temperature and the E_a is fairly lower than previous studies using different catalysts. The proposed kinetic model and the thermo-kinetic assessment of glucose conversion reaction in this work will be useful in the design of reactor for biomass-based conversion to 5-HMF and LA in presence of acidic ionic liquid.

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