

Catalytic Conversion of Glucose to Levulinate Ester Derivative in Ethylene Glycol

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A comprehensive, kinetic experiment on the conversion of glucose to 2-hydroxyethyl levulinate ethylene ketal (HLEK), in a cascade of reactions in ethylene glycol, catalyzed by low-concentration sulfuric acid, was conducted. The ethylene glycol/sulfuric acid system was found to be tolerant of a high glucose concentration, and no solid humins were created. At a high initial glucose concentration (30 wt %), an HLEK yield of 27.6% was achieved at a moderate temperature (433 K) after a 330-min reaction with dilute sulfuric acid (0.15 mol/L). In ethylene glycol, more than half of the initial glucose was converted into glucosides within 5 min, and a dynamic equilibrium between these species was achieved; thus, it is reasonable to assume that the ratio of glucosides to glucose was constant (1.35:1) during the entire reaction process. The production of HLEK from glucose via glucosides as a function of the process variables was well-represented by a simplified first-order kinetic model, and the rate expressions were applied to determine the optimum conditions for batch processing.

Keywords: Glucose; Levulinate ester derivative; Ethylene glycol; Kinetic study

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INTRODUCTION

Biomass, which is abundant, renewable, and can be converted to high quality chemicals and fuels, has received worldwide attention because of the depletion of fossil resources and the deterioration of environmental quality (Huber *et al.* 2006; Ragauskas *et al.* 2006). An attractive option for the use of biomass is the production of levulinic acid (LA) and levulinate esters from biomass-derived carbohydrates via multiple homogeneous or heterogeneous, acid-catalyzed systems (Kunkes *et al.* 2008; Lin *et al.* 2012; Maldonado *et al.* 2012; Huang and Ramaswamy 2013). LA and its esters are suitable to be used as additives for gasoline and diesel in the transportation sector (Christensen *et al.* 2011; Joshi *et al.* 2011; Windom *et al.* 2011) and have potential applications in the flavoring and fragrance industries (Bloom 2010). Particularly, LA and its esters are versatile, with the potential to be building blocks for the production of value-added chemicals (Tang *et al.* 2014c); these moieties can also be easily upgraded to liquid hydrocarbon fuels (Serrano-Ruiz *et al.* 2010; Braden *et al.* 2011) as a possible replacement for their fossil-based counterparts in biorefinery processes.

Recently, much research has focused on the acid-catalyzed conversion of carbohydrates into LA/esters in aqueous/alcoholic media, with a typical product yield of about 60% (Fizpatrick 1997; Farone *et al.* 2000; Girisuta *et al.* 2006; Lake *et al.* 2010;

Girisuta *et al.* 2012; Choudhary *et al.* 2013; Yang *et al.* 2013). In aqueous media, glucose and its intermediate product, 5-(hydroxymethyl) furfural (HMF), can be easily polymerized into solid humins. The hydroxyl group of the anomeric carbon in glucose and the 2,5-substituted functional groups in HMF have high reactivity and play important roles in humin formation (Hu and Li 2011; Hu *et al.* 2011; Zhang and Weitz 2012; Qiao *et al.* 2014). In alcoholic media, these reactive functional groups could be stabilized by etherification with solvents such as methanol (MeOH) or ethanol, minimizing the formation of humins during the acid-catalyzed alcoholysis process. Previous research has led to the development of several catalytic strategies for the production of alkyl levulinates from carbohydrates by alcoholysis and their upgrading in alcoholic media (Peng *et al.* 2011, 2012; Tang *et al.* 2013, 2014a). The formation of solid humins is partially suppressed during the acid-catalyzed alcoholysis of carbohydrates, although larger-scale production of alkyl levulinates from carbohydrates by alcoholysis is still hindered by low substrate/product concentration and harsh reaction conditions (Chang *et al.* 2012; Wu *et al.* 2012). For instance, Rataboul and Essayem (2011) have presented an efficient catalyst system for the synthesis of methyl levulinate from cellulose in a MeOH-H₂O (90:10, wt/wt) mixture. Under supercritical conditions for MeOH (573 K and 10 MPa), solid acid catalysts such as C_{S_x}H_{3-x}PW₁₂O₄₀ gave a methyl levulinate yield of around 20% from cellulose, but the concentration of the desired product in the reaction mixture was only 0.28 wt%. Apparently, the harsh reaction conditions and the low concentration of the target product would require excessive energy for both the production of alkyl levulinates by alcoholysis and their purification by distillation (Tang *et al.* 2014b). Thus, exploring a catalytic reaction system with a high feedstock input under mild reaction conditions is highly desirable to decrease the manufacturing cost of alkyl levulinates from biomass.

In this article, an efficient and low-cost catalytic strategy for converting glucose to HLEK in ethylene glycol was developed. Ethylene glycol was selected as the reaction solvent mainly due to its high boiling point (470.3 K), which could convert glucose in an open atmospheric pressure reactor, rather than a high-pressure one. Most importantly, the solubility of glucose in ethylene glycol can be greater than 300 g/100 g, as opposed to less than 10 g/100g in methanol and ethanol, thus ensuring a satisfactory initial substrate concentration. Studies concerning HLEK have been extremely few. The first related study was published in 1976, and then HLEK was found and identified in the liquefied cellulose oil by the Amarasekara and Wiredu (Bulat and Liu 1976; Amarasekara and Wiredu 2015). In this paper, the effects of different acid catalysts and varied process parameters (*e.g.*, temperature, acid concentration, or initial glucose concentration) on the reaction behavior were investigated to optimize the yield of HLEK. Based on the experimental results, a plausible reaction pathway is proposed, and a kinetic study on the conversion of glucose to HLEK and byproducts is also conducted.

EXPERIMENTAL

Materials

Ethyl levulinate (98%) was obtained from Aladdin Reagent Co. Ltd. (Shanghai, China). Ethylene glycol, sulfuric acid, and all other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and used without further treatment.

Methods

Typical procedure for the production of HLEK from glucose

The experiments were carried out in a 100-mL flask. In a typical experiment, 15 g of glucose, 0.25 g of sulfuric acid, and 35 g of ethylene glycol were added to the flask. The reaction mixture was heated in an oil bath at 433 K with reflux condensation and stirred at a speed of 500 rpm for 3 h. After the desired reaction time was reached, the flask was quickly cooled to room temperature, and the sample was collected for further analysis.

Analytical methods

High-performance liquid chromatography (HPLC) analysis of glucose was performed using a Waters 2695 Separation Module (Waters, USA) equipped with a refractive index detector and a Bio-Rad Aminex HPX-87P carbohydrate analysis column (Bio-Rad, USA, 300 × 7.8 mm). The column was operated at 85 °C, and the mobile phase was ultrapure water at a flow rate of 0.65 mL/min. The concentration of HLEK was determined on an Agilent 7890 series gas chromatograph (GC) equipped with an HP-5 capillary column (Agilent, USA, 30.0 m × 320 μm × 0.25 μm) and a flame ionization detector (FID) operating at 270 °C. The glucose conversion and HLEK yield were calculated using Eqs. 1 and 2:

$$\text{Glucose conversion (\%)} = \left(1 - \frac{\text{mole of glucose in products}}{\text{initial mole of glucose}}\right) \times 100 \quad (1)$$

$$\text{HLEK yield (\%)} = \frac{\text{mole of HLEK in products}}{\text{initial mole of glucose}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

Initial Glucose Concentration

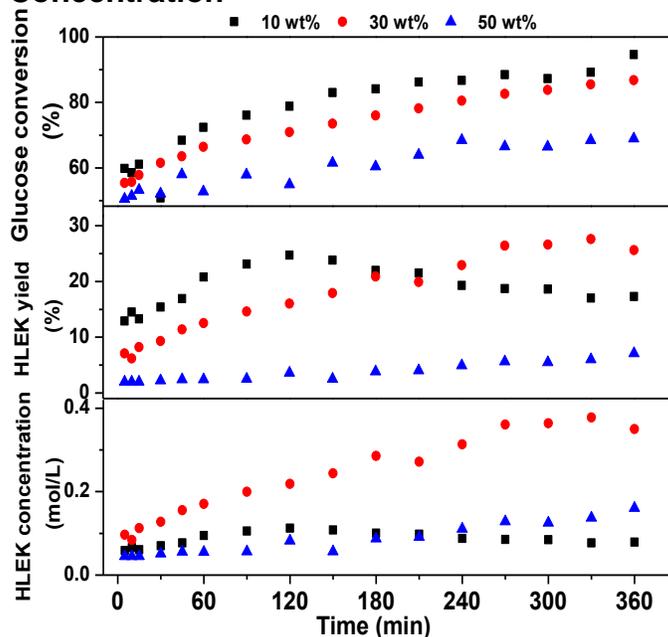


Fig. 1. The effect of initial glucose concentration on glucose conversion, HLEK yield, and HLEK concentration. Reaction conditions: 433 K, sulfuric acid concentration of 0.15 mol/L

A high initial substrate concentration was crucial for raising the concentration of HLEK in the reaction mixture (Peng *et al.* 2012; Chang *et al.* 2012). In this work, the influence of the initial concentration on the yield and concentration of HLEK was investigated. As shown in Fig. 1, the glucose conversion decreased with increasing initial glucose concentration over the same reaction time. The maximum glucose conversion reached 94.6%, 86.8%, and 68.9% after 6 h when the initial glucose concentration was 10 wt%, 30 wt%, and 50 wt%, respectively. The HLEK yield increased, peaked at 24.7%, then dropped to 17.3% with prolonged reaction time when the initial glucose concentration was 10 wt %; the maximum HLEK yield could be increased to 27.6% when 30 wt% glucose was fed. In addition, the HLEK concentration rose dramatically when the initial glucose concentration was increased from 10 to 30 wt %. However, a further increase in the glucose concentration to 50 wt% led to an HLEK yield of only 7.1%, even after a reaction time of 6 h, and a drop in HLEK concentration was observed. In that case the fluidity of reaction solution was lower than the others', leading to weakened mass transfer. Apparently, a longer reaction time is required to achieve the equilibrium HLEK yield at a high initial glucose input, as upward tendency of the HLEK concentration shown in page 4 Fig.1. Besides, such a high concentration of initial glucose introduced a large amount of water into the reaction system, and this was not conducive to HLEK formation, as shown in Fig. S5. Compared to previous studies conducted in aqueous or alcoholic media (such as methanol or ethanol) (Chang *et al.* 2012; Peng *et al.* 2012; Ya'aini *et al.* 2013), ethylene glycol, used here, was found to be an outstanding solvent to convert glucose at a high initial concentration without solid humins formation. After the reaction, all products were totally dissolved in solvent to create a solution with good fluidity, avoiding the problems of coking and pipe plugging that often appear during the acid-catalyzed conversion of carbohydrates.

Reaction Temperature and Acid Concentration

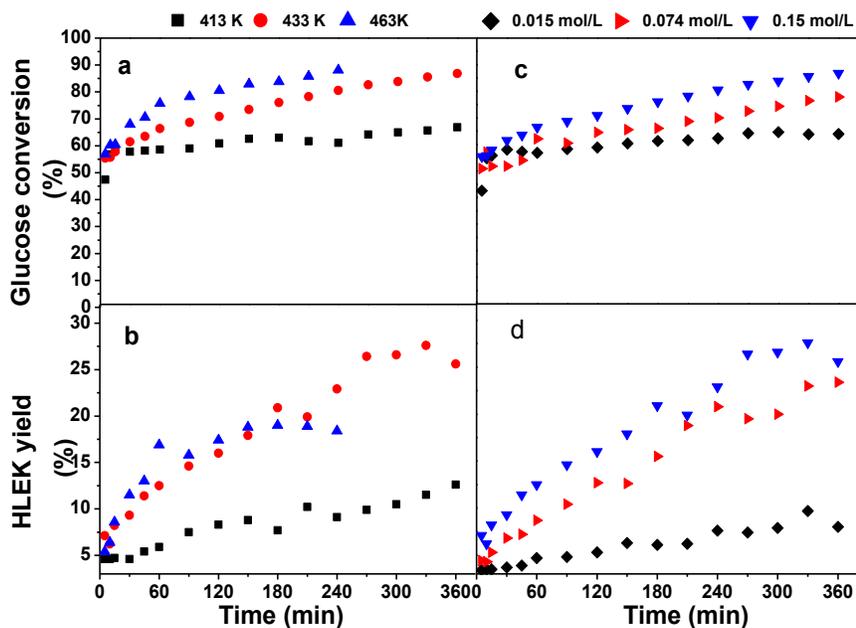


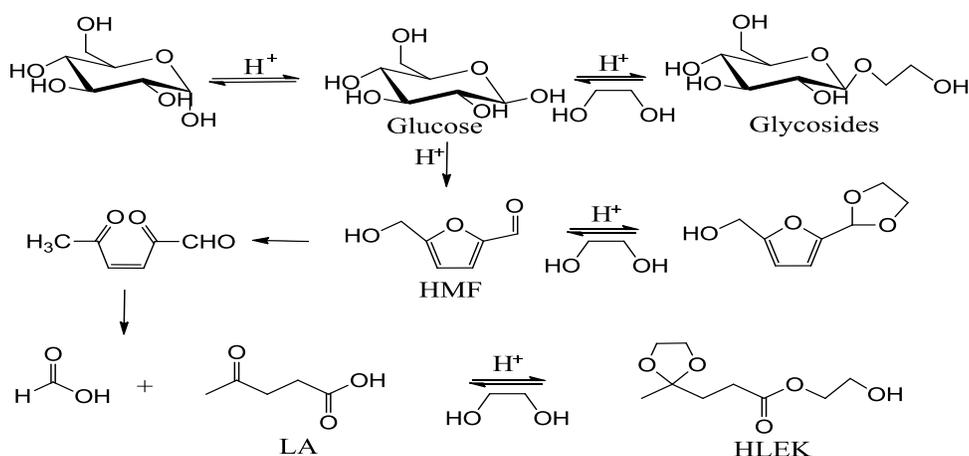
Fig. 2. The effect of reaction temperature and acid concentration on glucose conversion and HLEK production. Reaction conditions: (a, b) glucose concentration of 30 wt %, sulfuric acid concentration of 0.15 mol/L; (c, d) glucose concentration of 30 wt%, 433 K

In general, the reaction temperature had a great influence on the reaction rate and conversion efficiency. Figures 2a and 2b illustrate the temporal evolution of the glucose conversion and HLEK yield at three different temperatures: 413, 433, and 453 K. In every case, almost 57.5% of the initial glucose was consumed within 5 min; then the glucose conversion increased at a comparatively low rate (Fig. 2a). This trend was probably due to the rapid transformation of glucose into glucosides through condensation with ethylene glycol during the initial reaction stage, and a similar situation was also observed using methanol/ethanol media (Peng *et al.* 2012). Meanwhile, the HLEK yield grew smoothly, then decreased with prolonged reaction time (Fig. 2b). There was a significant increase in the HLEK yield when the temperature was increased from 413 to 433 K over the same reaction time; when the reaction temperature was further increased to 453 K, only a slight increase in HLEK yield was observed. As the reaction progressed, however, the HLEK yield dropped gradually at 453 K, while the HLEK yield steadily increased, peaking at 27.6%, when the reaction was conducted at 433 K. Elevating the reaction temperature amplified the reaction rate, leading to a high glucose conversion and HLEK yield. However, a high reaction temperature would have also promoted side-reactions of glucose and intermediates, sacrificing the selectivity for HLEK.

Subsequently, the influence of acid concentration (sulfuric acid selected to be the preferred acid in the given varied homogeneous catalysts as shown in Fig. S4), ranging from 0.015 to 0.15 mol/L, on glucose conversion and HLEK yield was studied, and the results are shown in Figs. 2c and 2d. A trend of temporal evolution of glucose conversion similar to that caused by changing the reaction temperature was also observed by varying the acid concentration. The optimal HLEK yield value increased remarkably, from 7.6% to 20.8%, when the acid concentration was increased from 0.015 mol/L to 0.074 mol/L. However, when the acid concentration was further increased to 0.15 mol/L, the HLEK yield increased only slightly.

Reaction Pathway for the Conversion of Glucose

Based on the above results and the related literature (Peng *et al.* 2012; Amarasekara and Wiredu 2015), a plausible mechanism for the conversion of glucose to HLEK in ethylene glycol is proposed, as shown in Scheme 1.

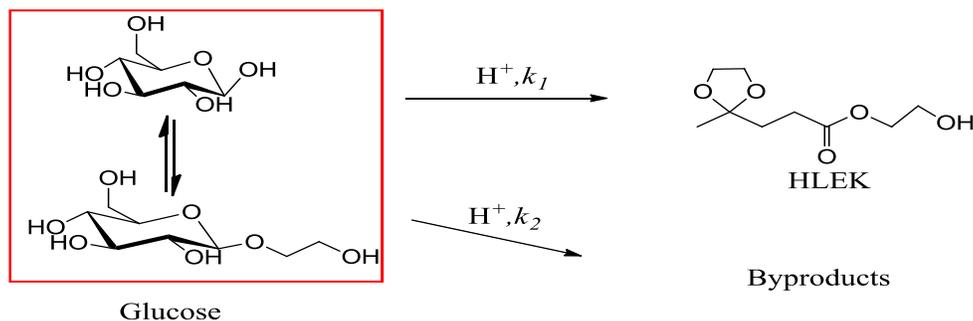


Scheme 1. Proposed mechanism for the conversion of glucose to HLEK in ethylene glycol

It should be noted that ethylene glycol played an important role not only as a solvent but also as a reactant in protecting reactive functional groups. Catalyzed by H^+ , the glycosidic hydroxyl of glucose initially reacted with the hydroxyl of ethylene glycol, forming glycosides, and equilibrium between these species was achieved. Glucose was dehydrated to HMF, and the carbonyl group of HMF was also condensed with the hydroxyl of ethylene glycol. Subsequently, HMF was converted into levulinic acid through sequential hydrolysis and rehydration. Ultimately, levulinic acid reacted with ethylene glycol to form the final products *via* condensation and esterification processes. Throughout this reaction process, reactive functional groups were protected by ethylene glycol, leading to fewer side reactions and eliminating humin formation to some degree.

A Kinetic Model for the Conversion of Glucose

The reaction kinetics for the conversion of glucose to HLEK in ethylene glycol were studied to clarify the reactivity of this system. The kinetic model was based on the equations given in Scheme 2. From the above results, more than half (almost 57.5%, as shown in Fig. 2) of the initial glucose was converted into glucoside in ethylene glycol within 5 min under the given conditions, and there was a dynamic equilibrium between glucose and glucoside. According to the experimental results it is reasonable to assume that the concentration ratio between glucoside and glucose was consistent with the initial value (1.35:1) during the entire conversion process. Glucose is believed to have decomposed to HLEK and byproducts in a parallel reaction, as the formation of intermediate products was negligible, and all of the unknown products were considered to be byproducts. According to the linear relationship between the natural logarithm of C_G ($\ln C_G$, where C_G (mol/L) is the concentration of glucose in ethylene glycol) and the corresponding reaction time (t), the first-order reaction kinetics proposed are suitable for the conversion of glucose in the present work.



Scheme 2. Simplified reaction scheme for the conversion of glucose

Based on the model, the concentrations of glucose and HLEK as functions of time were represented by a set of differential equations in a bath system (Eqs. 3 and 4):

$$-\frac{dC_G}{dt} = k \cdot C_G \quad (3)$$

$$\frac{dC_{\text{HLEK}}}{dt} = k_1 \cdot C_G \quad (4)$$

Solving the differential equations, the analytical expressions for the concentration of glucose and HLEK were obtained (Eqs. 5 and 6):

$$C_G = C_{G,0} \cdot \exp(-kt) \quad (5)$$

$$C_{\text{HLEK}} = C_{G,0} \cdot \frac{k_1}{k} \cdot [1 - \exp(-kt)] \quad (6)$$

The kinetic rate constants were defined in terms of modified Arrhenius equations, which combined the effects of temperature (T) and acid concentration (C_H) (Eqs. 7 and 8):

$$k_1 = A_1 \cdot C_H^\alpha \exp\left(-\frac{E_{a1}}{RT}\right) \quad (7)$$

$$k_2 = A_2 \cdot C_H^\beta \exp\left(-\frac{E_{a2}}{RT}\right) \quad (8)$$

In these expressions, k_1 and k_2 correspond to reaction rate constant, A_1 and A_2 to the frequency factor, E_{a1} and E_{a2} to the activation energy, α and β to the reaction order of acid concentration, and R to the ideal gas constant. The best estimates of the kinetic parameters, as determined by minimization of the errors between all experimental data and the kinetic model, are shown in Tables 1 and 2. A good fit between the experimental data and the kinetic model was obtained and confirmed by a parity plot, as shown in Fig. 3.

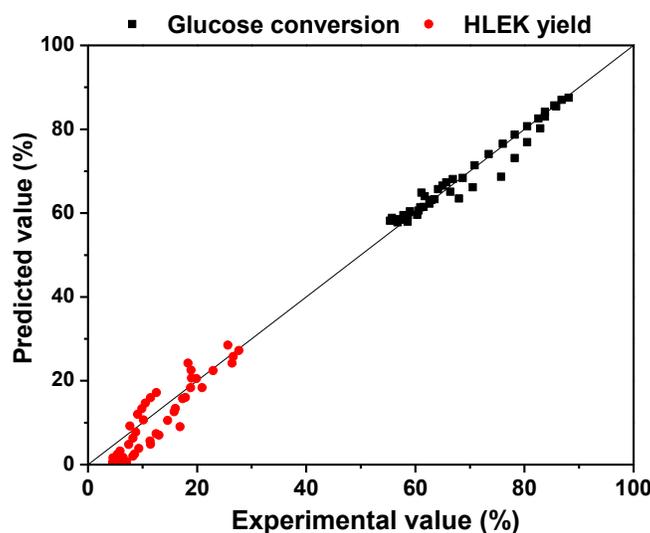


Fig. 3. Parity plot of the experimental and model values of glucose conversion and HLEK yield

Table 1. Rate Constants of Glucose Decomposition and HLEK Formation with Different Acid Concentrations *via* Various Reaction Temperatures

T (K)	H ₂ SO ₄ (mol/L)	k (min ⁻¹)	k_1 (min ⁻¹)	k_2 (min ⁻¹)	k_1/k
413	0.15	0.0008	0.00045	0.00035	0.56
433	0.015	0.0008	0.00034	0.00046	0.43
433	0.074	0.0021	0.00100	0.00109	0.48
433	0.15	0.0033	0.00144	0.00186	0.44
453	0.15	0.0051	0.00175	0.00335	0.34

Table 1 illustrates that the rate constants of glucose decomposition and the formation of HLEK and byproducts evidently increased with increasing temperature, meaning that higher temperature led to a high conversion rate. However, it does not mean that a high selectivity could be achieved at the same conditions, as indicated by the k_1/k_2 ratio. When the reaction temperature increased, the k_1/k_2 ratio decreased; thus, the formation rate of HLEK relative to the rate of glucose decomposition was decreased, which hindered the selectivity of HLEK. The activation energy for byproducts formation ($E_{a2} = 88.4$ KJ/mol) from glucose was higher than that of HLEK production ($E_{a1} = 53.4$ KJ/mol), which implied that higher temperature had a negative influence on the HLEK selectivity. To inhibit byproducts formation, reactions at a low temperature are favored. Hence, an appropriate reaction temperature must be determined to achieve both a high reaction rate and selectivity. The activation energy of HLEK formation from glucose in ethylene glycol was lower than the values reported using other media, such as levulinic acid from glucose in an aqueous system and methyl levulinate converted from glucose in methanol media (Girisuta *et al.* 2006; Peng *et al.* 2012). This phenomenon suggests that glucose conversion in ethylene glycol media required a lower temperature than other reaction systems, which will lead to a lower energy consumption and economic cost.

Table 2. Kinetic Parameters for the Conversion of Glucose

Parameter	Value
the activation energy for HLEK production (E_{a1})	53.4 KJ/mol
the activation energy for byproducts formation (E_{a2})	88.4 KJ/mol
the reaction order of acid concentration for HLEK production (α)	0.64
the reaction order of acid concentration for byproducts formation (β)	0.59
the frequency factor for HLEK production (A_1)	13847 min ⁻¹
the frequency factor for byproducts formation (A_2)	2.6E+08 min ⁻¹

As can be observed from Table 1, a higher acid concentration could enhance both glucose decomposition and HLEK formation, as α was 0.64 and β was 0.59, as shown in Table 2. The changes in the k_1/k_2 ratio indicated that the formation rate of HLEK relative to the rate of glucose decomposition increased when the acid concentration increased from 0.015 to 0.074 mol/L, then decreased with a further increase in acid concentration. A moderate acid concentration was favorable to this reaction.

With the model available, it was possible to optimize the yields of HLEK in a batch reactor as a function of reaction conditions. For this purpose, t was defined as infinite in Eq. 6, leading to a new expression when combined with Eq. 2:

$$\text{HLEK yield (\%)} = \frac{k_1}{k_1 + k_2} \times 100 \quad (9)$$

The combination of Eqs. 7 and 8 with the differentiated form of Eq. 9 leads to an expression of HLEK yield as a function of reaction temperature and acid concentration (Eq. 10):

$$\text{HLEK yield (\%)} = \frac{A_1 \cdot C_H^\alpha \exp\left(-\frac{E_{a1}}{RT}\right)}{A_1 \cdot C_H^\alpha \exp\left(-\frac{E_{a1}}{RT}\right) + A_2 \cdot C_H^\beta \exp\left(-\frac{E_{a2}}{RT}\right)} \times 100 \quad (10)$$

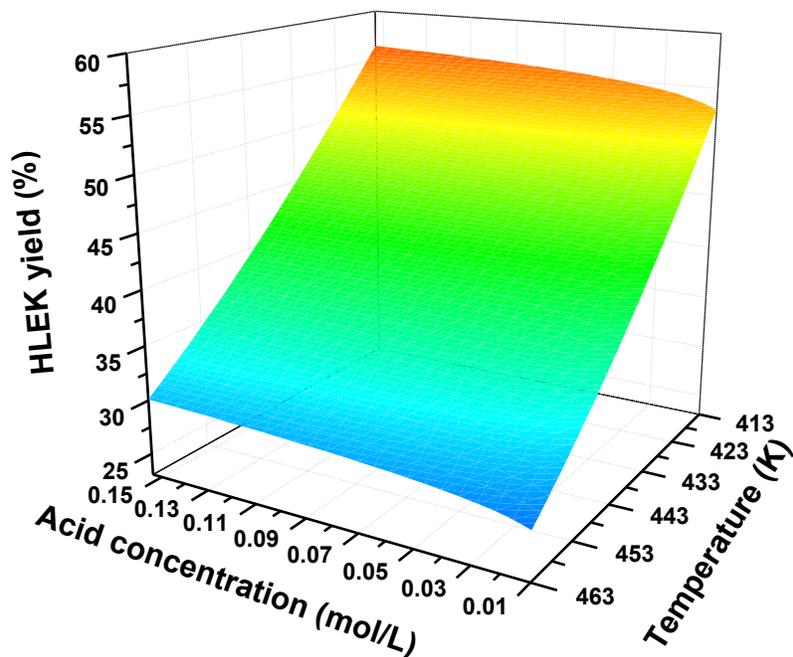


Fig. 4. Effects of temperature and acid concentration on HLEK yield

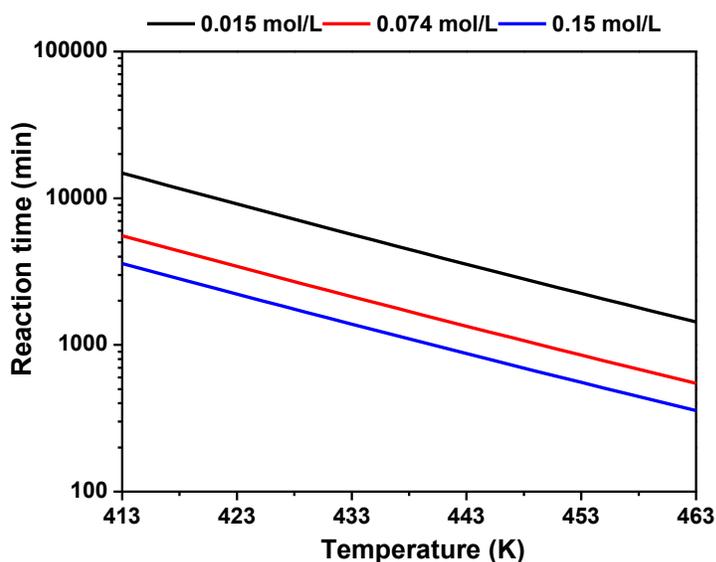


Fig. 5. Modeled reaction time to achieve 90% glucose conversion as function of temperature and acid concentration

Figure 4 shows the effects of acid concentration and reaction temperature on the HLEK yield. It is obvious that lower operating temperatures and moderate acid concentration led to a higher HLEK yield. However, the production rate of HLEK would be decreased dramatically at low temperature. By using the kinetic model developed in this study, an equation was developed to calculate the reaction time until 90% conversion of glucose was achieved as a function of temperature and acid concentration (Eq. 11):

$$t = \frac{\ln(0.1)}{-(k_1 + k_2)} \quad (11)$$

Figure 5 illustrates the reaction time needed to reach 90% conversion of glucose in a batch reactor as a function of the temperature and acid concentration. It clearly shows that the HLEK formation rate strongly depended on the reaction conditions applied in the acid catalyzed decomposition of glucose.

CONCLUSIONS

1. This study described an efficient and economical strategy for the acid-catalyzed conversion of samples with a high initial glucose concentration into a novel levulinate ester derivative (HLEK) in ethylene glycol.
2. High glucose conversion and HLEK yield were achieved under the catalysis of sulfuric acid. The trial at an initial glucose concentration of 30 wt % saw efficient catalysis by 0.5 wt % sulfuric acid at 433 K for 4.5 h to obtain a high HLEK yield.
3. It should be noted that no insoluble solid waste (solid humins) was generated at the high initial substrate concentrations tested, which would lessen the difficulties in manufacturing operations.
4. There was a dynamic equilibrium between glucose and glucosides when glucose was reacted with ethylene glycol in the presence of sulfuric acid, and it was assumed that the ratio of glucosides to glucose was a constant (1.35:1) during the reaction.
5. A simplified kinetic model for the glucose decomposition reaction agreed with a first-order rate equation. The rates of the main reaction to HLEK and the side reaction to byproducts were modeled as functions of acid concentration and reaction temperature, and the experimental data exhibited a good fit to the modeling results.

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