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Experimental and Kinetic Study on the Production of Furfural and HMF from Glucose

Ouwen He ¹, Yangfan Zhang ¹, Pan Wang ², Lina Liu ^{1,*} , Qian Wang ¹, Nan Yang ¹, Wenjie Li ³, Pascale Champagne ⁴ and Hongbing Yu ^{1,*}

¹ College of Environmental Science and Engineering, Nankai University, 38 Tongyan Road, Jinnan District, Tianjin 300350, China; heouwen@mail.nankai.edu.cn (O.H.); zhangyf@mail.nankai.edu.cn (Y.Z.); 170h1@queensu.ca (Q.W.); yangnan@nankai.edu.cn (N.Y.)

² Key Laboratory of Cleaner Production and Integrated Resource Utilization of China National Light Industry, Beijing Technology and Business University, Beijing 100048, China; wangpan@th.btbu.edu.cn

³ School of Ecology and Environment, Zhengzhou University, Zhengzhou 450001, China; wenjieli@zzu.edu.cn

⁴ Department of Civil Engineering, Queen's University, Kingston, ON K7L 3N6, Canada; pascale.champagne@queensu.ca

* Correspondence: liulin@nankai.edu.cn (L.L.); yuhb@nankai.edu.cn (H.Y.); Tel.: +86-18526446994 (L.L.); +86-13920683244 (H.Y.)

Abstract: Furfural and 5-hydroxymethylfurfural (HMF) have been identified as promising bio-platform furans that have a wide range of potential applications as biofuels, bioplastics, and biochemicals. Furfural and HMF are typically synthesized from the substrates of C₅ sugars and C₆ sugars, respectively. Furfural can also be produced from C₆ sugars, which is technically more challenging owing to the higher energy requirement for carbon–carbon bond cleavage. In this study, the simultaneous production of furfural and HMF from glucose was conducted over different binary catalyst systems of Brønsted acids and Lewis acids using γ -valerolactone (GVL) as the solvent. A promising performance was achieved by a SnSO₄–H₂SO₄ coupling catalyst, with an optimized furfural yield of 42% and an HMF yield of 34% at 443 K in GVL. In addition, a kinetics study was performed in order to understand the mechanism of the simultaneous formation of furfural and HMF from glucose at different temperatures and GVL/water ratios. The results showed that the ratio of furfural to HMF production rate at different temperatures (433 to 463 K) or GVL/water ratios (90 to 80%) was constant close to 1, suggesting that the production of furfural and HMF might follow similar reaction pathways. Finally, the reaction pathway of glucose conversion to furfural and HMF was proposed based on the experimental and kinetics studies.

Keywords: glucose conversion; bio-platform chemicals; furfural; 5-HMF; γ -valerolactone; kinetics

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1. Introduction

The development of human society has been highly dependent on fossil carbon reserves, which are finite and have a negative environmental impact. Therefore, there is now a growing interest in the development of renewable energy resources, including primary biomass, hydropower, wind energy, and solar energy [1]. Among these, biomass-derived chemicals have been widely studied as a potential alternative to petroleum-based fuels and chemicals. Biomass can be agricultural, commercial, domestic, or industrial wastes [2,3]. Among the various biomass-derived products, furfural and 5-hydroxymethylfurfural (HMF) have received significant attention as promising platform chemicals since they can be utilized as versatile building blocks in the synthesis of various commodity chemicals and fuels [4]. For example, furfural can be converted into biofuels such as 2-methylfuran, 2-methyltetrahydrofuran, and other furans, in which 2-methyltetrahydrofuran can be directly used as a base material for the production of gasoline [5–7]. 2,5-furandioic acid (FDCA), a derivative of HMF, can be used in the polyethylene terephthalate (PET) industry to produce biodegradable plastic materials as a greener alternative [8].

Biomass has three main compositions of ~40–50% cellulose, ~20–30% hemicellulose, and ~10–30% lignin. Cellulose primarily comprises hexoses, such as glucose, while hemicellulose substantially comprises pentoses, such as xylose [9,10]. HMF is mainly formed from glucose, whereas furfural is mainly formed from xylose [11]. However, the low abundance of xylose in biomass remains the main problem for furfural synthesis. Therefore, the synthesis of furfural from hexoses provides a new way to overcome this problem by providing a single product stream from the total carbohydrate content of biomass, which accounts for a maximum of 80% of biomass by weight [12]. It should be noted that HMF formation from glucose involves two reaction procedures of isomerization and dehydration. Differently, furfural formation from glucose needs to undergo three processes of isomerization, decarboxylation, and dehydration, which require more energy for the selective decarboxylation from glucose [13]. Therefore, the yield of furfural using glucose as a substrate is generally lower than the HMF yield [14]. To date, the reported studies for furfural production from hexoses showed that a careful selection of solvent and catalyst is crucial in order to reduce the activation energy and improve the yield of furfural from glucose conversion.

Higher furfural production from hexoses has been achieved in the presence of acid catalysts and polar aprotic solvents. Polar aprotic solvents such as lactones and sulfolane were especially active for furfural synthesis. For example, glucose was isomerized to fructose, which was then dehydrated to HMF over Sn-Beta zeolite in the aqueous phase [15]. However, a furfural yield of 69.2% was achieved from glucose in γ -valerolactone (GVL) [16]. Given the published studies for converting hexoses to furfural, acid catalysts such as zeolite and H_2SO_4 presented an improvement for the selectivity of furfural formation. Particularly, the ratio of Lewis acid and Brønsted acid sites is essential for the conversion of glucose to furfural, and a higher ratio contributed to a higher selectivity of furfural [13,16].

Earlier studies showed that furfural formation competed with HMF formation from hexoses. The distribution patterns of furfural and HMF products varied significantly by changing the catalysts or solvents. For example, the changes of the water proportion in the sulfolane from 0.5 to 0 increased furfural yield from 10% to 51% [17]. However, the competition mechanism for furfural and HMF formation was complex and rarely reported. A kinetic study is favorable for the understanding of the complex mechanism. The kinetic study in this work could not only provide access for the understanding of the complex mechanism but also depict their relationship.

In this study, therefore, a few combinations of different homogeneous Brønsted acids and Lewis acids were employed in glucose conversion using GVL as the solvent. In addition, co-catalysts of SnSO_4 and H_2SO_4 were selected to study the kinetic models for the conversion of glucose into furfural and HMF in GVL at a range of temperatures and GVL/water ratios. Furthermore, a possible reaction pathway for the co-production of furfural and HMF was proposed.

2. Results

2.1. Synergistic Effect of Lewis and Brønsted Acids

The furfural and HMF yields achieved in the presence of Brønsted acids (H_2SO_4 , HCl , HNO_3 and H_3PO_4) and Lewis acids (SnSO_4 , CuSO_4 , and MnSO_4) as co-catalysts are presented in Table 1. The coupling of Lewis acid and Brønsted acid achieved higher furfural and HMF yields than the single-acid systems. Regarding the single-acid systems, the presence of only Lewis acid of SnSO_4 (0.014 mol/L and 0.028 mol/L) showed a negligible effect on the conversion of glucose to furfural or HMF under the same reaction conditions, suggesting the poor activity of SnSO_4 as a Lewis acid [18]. However, H_2SO_4 as a Brønsted acid catalyst gave a small yield of furfural and HMF. The same result has been published, in which a furfural yield of 10% was obtained from glucose conversion in GVL over H_2SO_4 at 448 K for 30 min [19]. Despite the slight decrease in HMF yield and glucose conversion, the increase in H_2SO_4 concentration from 0.009 to 0.018 mol/L led to an obvious increase in furfural yield and selectivity from 7% and 13% to 12% and 24%, respectively. The result indicates that H_2SO_4 played an important role in furfural production.

Table 1. Glucose conversion into furfural and 5-hydroxymethylfurfural (HMF) using single and mixed catalysts. Reaction conditions: 0.0555 mol L^{−1} glucose; 1.8 mL γ -valerolactone (GVL); 0.2 mL water; temperature: 443 K; reaction time: 25 min.

Entry	Brønsted Acid (mol/L)	Lewis Acid (mol/L)	Furfural Production (%)	HMF Production (%)	Glucose Conversion (%)	Furfural Selectivity (%)	HMF Selectivity (%)
1	n.a	n.a	n.a	n.a	n.a	n.a	n.a
2	H ₂ SO ₄ (0.009)	n.a	7 ± 0.8	8 ± 1.4	54 ± 3.9	13 ± 0.6	15 ± 1.5
3	H ₂ SO ₄ (0.018)	n.a	12 ± 1.4	6 ± 0.5	49 ± 4.3	24 ± 0.7	12 ± 0.1
4	H ₂ SO ₄ (0.018)	MnSO ₄ (0.014)	4 ± 0.6	15 ± 1.2	58 ± 7.2	14 ± 0.2	26 ± 1.2
5	H ₂ SO ₄ (0.018)	CuSO ₄ (0.014)	24 ± 0.1	32 ± 0.3	92 ± 2.4	26 ± 0.6	35 ± 0.6
6	H ₂ SO ₄ (0.018)	SnSO ₄ (0.014)	33 ± 2.5	21 ± 1.8	99 ± 0.2	33 ± 2.5	22 ± 1.3
7	H ₂ SO ₄ (0.018)	SnSO ₄ (0.028)	29 ± 1.4	12 ± 0.3	84 ± 2.9	36 ± 0.5	14 ± 0.1
8	HCl (0.018)	SnSO ₄ (0.014)	15 ± 1.7	37 ± 2.3	79 ± 4.2	19 ± 1.1	47 ± 0.4
9	H ₃ PO ₄ (0.018)	SnSO ₄ (0.014)	1 ± 0.5	1 ± 0.6	10 ± 0.5	10 ± 4.5	10 ± 5.5
10	HNO ₃ (0.018)	SnSO ₄ (0.014)	20 ± 2.1	36 ± 3.0	76 ± 1.9	27 ± 3.2	48 ± 5.0
10	n.a	SnSO ₄ (0.014)	n.a	n.a	Trace	n.a	n.a
11	n.a	SnSO ₄ (0.028)	n.a	n.a	Trace	n.a	n.a

n.a: means no applicable.

Adding SnSO₄ (0.014 mol/L) into the solvent with H₂SO₄ (0.018 mol/L) contributed to the almost complete conversion of glucose with a conversion efficiency of 99%, as well as a 2.75 times higher furfural yield of 33% and 3.5 times higher HMF yield of 21% (Table 1, entry 6) than those achieved by applying only H₂SO₄ as a catalyst in the same reaction condition (Table 1, entry 3). The obvious synergistic effect of SnSO₄ and H₂SO₄ could be observed during the degradation of glucose to furfural and HMF. The possible reason is that the active Lewis acid of SnSO₄ was proven to be more active in promoting the isomerization of C6 sugar to the intermediates [18], while a Brønsted acid of H₂SO₄ was mainly responsible for the dehydration and the protonation of hydroxyl groups to form furfural and HMF [20,21]. As a consequence, a synergy was created for the selective conversion of glucose to furfural and HMF with the co-existence of SnSO₄ and H₂SO₄.

The effect of other different Brønsted acids is also presented in Table 1. HCl and HNO₃ can effectively achieve decent glucose conversions of 79% and 76%, respectively (entry 8 and 10). In contrast, H₃PO₄, the weakest and non-oxide acid, suppressed the conversion of glucose (Entry 9). On the other hand, the highest and second-highest furfural selectivities were obtained using oxidizing acids such as H₂SO₄ and HNO₃, while HCl as the strongest acid promoted HMF selectivity. This indicates that oxygenates were more promising in promoting the C-C bond cleavage and, subsequently, the furfural production, compared with a non-oxide acid like HCl. In brief, the selection for Brønsted acids determines glucose conversion efficiency and selectivity of furfural and HMF.

Additionally, the yield of HMF and furfural and even their ratio were affected by the metal cations of Lewis acids, such as Sn²⁺, Cu²⁺, and Mn²⁺, with the same valance state. Comparatively, the CuSO₄/H₂SO₄ system obtained the highest HMF conversion and selectivity, while SnSO₄/H₂SO₄ achieved the highest furfural conversion and selectivity. Therefore, the substitution of Sn²⁺ by Cu²⁺ resulted in the increase in HMF yield from 21% (Table 1, entry 6) to 32% (Table 1, entry 5), but furfural yield was decreased from 33% (Table 1, entry 6) to 24% (Table 1, entry 5). Besides, the MnSO₄/H₂SO₄ system provided much lower furfural (4%, Table 1, entry 4) and HMF (15%, Table 1, entry 4) yields. The result suggested that different metal cations could also alter the main reaction pathway of glucose degradation.

2.2. Kinetics Model

Based on the catalyst filtering results, the SnSO₄/H₂SO₄ catalytic system was selected to study the kinetics, mechanism, and GVL effect for glucose conversion into furfural and HMF. Figure 1 presents the fitting results between the experimental data and the simulated data from models for glucose conversion, furfural production, and HMF production at various temperatures (433 to 463 K). The R-squared values for all simulations are greater than 0.9, indicating a good fit between the model and experimental data.

Figure 1. Comparison of experimental data and kinetic models for (a) glucose conversion and the production yields of (b) furfural production and (c) HMF production as a function of temperature. Reaction conditions: $0.0555 \text{ mol L}^{-1}$ glucose; 1.6 mL GVL; 0.4 mL water; 0.1 wt% H_2SO_4 ; and 0.014 mol L^{-1} SnSO_4 .

The temperature had a significant effect on glucose conversion and furfural and HMF production. The escalating temperature (from 433 to 463 K) shortened the reaction time from 40 min to 12 min to achieve a full glucose conversion (Figure 1a). However, higher temperatures were detrimental for furfural and HMF production. For example, the maximum furfural yield obtained at 443 K was 42%, higher than the 30% achieved at 463 K. The effect of temperature on the variety of glucose conversion and furfural and HMF production was demonstrated by the kinetic results (Tables 2 and 3).

Table 2. Kinetic parameters for the conversion of glucose into HMF and furfural at different temperatures.

Temp.	433 K	443 K	453 K	463 K
k_G	0.103	0.169	0.254	0.338
k_1	0.0518	0.0849	0.0976	0.121
k_2	0.0466	0.0713	0.076	0.124
k_3	0.0185	0.0194	0.0205	0.0213
k_4	0.0329	0.0761	0.115	0.138
k_5	0.0046	0.0128	0.0804	0.093
k_1/k_2	1.1	1.2	1.3	1.0
k_5/k_G	0.04	0.08	0.32	0.30
k_1/k_3	2.8	4.4	4.8	5.7
k_2/k_4	1.4	0.9	0.7	0.9
k_4/k_3	1.8	3.9	5.6	6.5

Table 3. Kinetic parameters for the conversion of glucose into furfural at different temperatures.

Temperature	k_G	k_1	k_2	k_3	k_4	k_5
E_a (kJ mol ^{−1})	66.9	44.9	49.9	8.0	79.0	181.5
A (min ^{−1})	1.17×10^7	1.49×10^4	5.02×10^4	5.91×10^0	1.32×10^8	3.92×10^{19}
R^2	0.991	0.935	0.932	0.997	0.921	0.927

All production and degradation rates (k_i) increased with the escalating temperatures (Table 2). Therefore, the comparisons between all reaction rates are significant for identifying which reaction rates decisively affected the furfural or HMF production. Given that, some factors were established, such as k_1/k_3 , k_2/k_4 , k_1/k_2 , k_4/k_3 , and k_5/k_G (Table 2). In detail, k_1/k_3 and k_2/k_4 were used to evaluate the furfural or HMF production efficiency; k_1/k_2 and k_4/k_3 were employed to compare furfural and HMF in terms of their production and degradation processes; the factor of k_5/k_G was used to show glucose side reactions.

It was observed from k_5/k_G that the glucose side reaction intensively competed with furfural and HMF production. k_5/k_G increased with rising temperature, suggesting that the glucose side reaction was enhanced with the increase in reaction temperature. As a result, the formation of furfural and HMF was suppressed, which could explain the reduction of furfural and HMF yield at higher temperatures, as displayed in Figure 1b,c. Furthermore, the decrease in HMF yield could be explained by another reason for the poor HMF thermal stability. It could be observed that after the maximum formation peak, furfural yields decreased gradually (Figure 1b), while HMF yields decreased sharply (Figure 1c). From the perspective of kinetics, k_2/k_4 was reduced from 1.4 to 0.9 with increasing temperatures, which indicates that HMF decomposition rates are quicker than its formation rates, especially at higher temperatures. The results of apparent activation energies (E_a) in Table 3 further support that the side reactions of glucose and HMF were easily promoted by increasing temperature. It could be observed that the highest apparent activation energy was achieved by glucose side reactions ($E_{a5} = 181.5$ kJ mol^{−1}) followed by HMF decomposition ($E_{a4} = 79.0$ kJ mol^{−1}), which implies that the side reactions of glucose and HMF are sensitive to the temperature changes. In contrast, the degradation of furfural to humin shows the lowest apparent activation energies of 8.0 kJ mol^{−1}. This suggests that changing temperature did not significantly promote the side reaction of furfural, which is consistent with the experimental result (Figure 1b).

Besides, the factor of k_1/k_2 was constantly kept at around 1, which was not evidently affected by the temperatures. This indicates that furfural and HMF might be produced through similar and non-interacting reaction pathways. More mechanism details will be presented in the following mechanism section. Overall, given the fact that long reaction time is detrimental for furfural and HMF production regardless of their better glucose conversion, the optimized reaction condition is registered at 443 K for 10 min. Therefore, a careful selection of reaction temperature is crucial to maximize the yields of furfural and HMF.

2.3. Effect of Solvent

As mentioned, the increase in the solvent sulfolane proportion in water increased furfural yield from 10% to 51% [13], which is possible because the changes of the interactions between reactants and solvents alter the reaction pathway, reaction rate, and transition stability in glucose conversion [16,22–24]. Therefore, it is necessary to understand the effect and mechanism of solvents on glucose conversion into furfural and HMF. In this paper, solvents with various GVL/water ratios were employed and a kinetics study was conducted. Figure 2 shows the fitting results between experimental data and simulated data. The R-squared values for all simulations are greater than 0.9.

Figure 2. Comparison of experimental data and kinetic models for (a) glucose conversion, (b) furfural production, and (c) HMF production as a function of different ratios of GVL to water. Reaction conditions: temperature: 443 K; 0.0555 mol L^{−1} glucose; 0.1 wt% H₂SO₄; and 0.014 mol/L SnSO₄.

Figure 2a shows that a higher GVL content promoted glucose conversion, where glucose was rapidly consumed. However, a higher GVL content had an adverse effect on the total production of furfural and HMF. For instance, the total production was decreased from 42 to 33% for furfural, and from 35 to 11% for HMF with the increase in GVL contents from 80 to 90%. The reason could be revealed by the kinetic results in Table 4. The factor of k_5/k_G significantly increased with an increase in GVL content. In other words, glucose side reactions competed with furfural and HMF production, and these competitions became more vigorous as GVL contents increased.

Table 4. Kinetic parameters for the conversion of glucose to furfural at a different GVL content levels.

GVL/Water Ratio	90%	85%	80%
k_G	0.315	0.197	0.169
k_1	0.0578	0.07679	0.0849
k_2	0.0486	0.0695	0.0713
k_3	0.0006	0.00484	0.0194
k_4	0.0748	0.08966	0.0761
k_5	0.2186	0.0507	0.0128
k_1/k_2	1.2	1.1	1.2
k_5/k_G	0.69	0.26	0.08
k_1/k_3	96.3	15.9	4.4
k_2/k_4	0.6	0.8	0.9
k_4/k_3	124.7	18.5	3.9

Interestingly, the production of furfural did not show a sharp decrease after the maximum formation peak at higher GVL contents as HMF production did, suggesting that a higher GVL content could prevent the further degradation of furfural. The phenomenon could be explained by the kinetics results in Table 4. On the one hand, k_3 decreased visibly, while k_4 did not show obvious change with the increase in GVL content. This result suggested that the decomposition of furfural was inhibited at higher GVL content levels. On the other hand, a positive correlation was found between k_1/k_3 and GVL content, and the k_1/k_3 was increased from 4.4 to 96.3 with an increase in the GVL content, indicating that the effect of furfural decomposition on the furfural yield could be neglected at higher GVL contents.

Overall, it can be concluded that the distribution between the expected products and undesirable byproducts could be altered by changing the ratio of GVL to water. At the same time, a higher GVL content could suppress the further decomposition of furfural, contributing to the efficient and stable production of furfural.

2.4. Possible Reaction Pathway

Three reaction pathways (Pathway 1, 2, and 4) of glucose conversion into furfural have been proposed in previous studies, as presented in Figure 3. Gürbüz et al. have proposed that glucose could be initially converted to HMF, which then loses carbon as formaldehyde to form furfural (Pathway 1) [19]. However, in this study, when HMF was used as the feedstock in the $\text{SnSO}_4/\text{H}_2\text{SO}_4$ system, furfural was not detected in the final products (Table S4, Supplementary Materials), which excluded the possibility of this reaction pathway. Hu et al. applied density functional theory (DFT) calculations to study the formation mechanism of furfural from glucose. They proposed that the formation of HMF and furfural from glucose follows similar reaction pathways in theory, with 3-deoxyglucosone (Pathway 4) or fructose (Pathway 2) as the key intermediate [25]. Our kinetics results also showed that furfural and HMF have very similar production rate constants and reaction pathways. In Pathway 2, glucose is first transformed into fructose. Then, furfural is produced from fructose by losing carbon as formaldehyde and subsequently undergoing three dehydration processes [22,26,27]. However, fructose was not observed as an intermediate along with glucose conversion experiments in this study. In addition, the degradation of fructose as the substrate was conducted in the $\text{SnSO}_4/\text{H}_2\text{SO}_4$ system in this

study. A distinguished product composition with 49% HMF and 9% furfural was obtained (Table S4, Supplementary Materials), compared with 21% HMF and 33% furfural using glucose as a substrate. Therefore, the production of furfural from glucose is also unlikely to follow the fructose pathway in this study. Moreover, the possibility of Pathway 3 in which HMF is generated from fructose is also quite low due to the absence of fructose as an intermediate. Furthermore, 3-deoxy-glucosone was detected in the reacted mixture using Liquid Chromatography with tandem mass spectrometry (LC-MS/MS) (Figures S4–S7, Supplementary Materials). Therefore, we proposed that furfural and HMF were formed from glucose via 3-deoxy-glucosone as a key intermediate in this system via pathway 4. Then, 3-deoxy-glucosone was transformed into a double-bond intermediate with poor stability, which would quickly lose carbon as formaldehyde to form furfural [28].

Figure 3. Possible reaction pathway for the furfural and HMF production from glucose.

3. Materials and Methods

3.1. Materials

D(+)-Glucose (Sigma–Aldrich, St. Louis, MO, USA, 99.5%), fructose (Macklin, Shanghai, China, 99%), HMF (Sigma–Aldrich, St. Louis, MO, USA, 99%), furfural (Macklin, Shanghai, China, 99%), GVL (Macklin, Shanghai, China, 98%), 2,4-Dinitrophenylhydrazine (DNPH)-silica cartridges (Energy Chemical, Shanghai, China, 37%), formaldehyde (Energy Chemical, Shanghai, 37%), sulfuric acid (Meryer, Shanghai, China, $\geq 98\%$), hydrochloric acid (Meryer, Shanghai, China, $\geq 36\%$), phosphoric acid (Meryer, Shanghai, China, $\geq 95\%$), SnSO_4 (Meryer, Shanghai, China, 99%), MnSO_4 , and CuSO_4 were all purchased from Tianjin Jiangtian Co., Tianjin, China.

3.2. Catalytic Reactions

All experiments, including glucose conversion, furfural production, and HMF production, were conducted in a thick-walled glass reactor (8 mL) with a Teflon screw top. Different ratios of GVL and water and the required amount of feedstock (glucose, furfural, and HMF) and catalysts, as well as a 5 cm stir bar, were added into the reactor in sequence. Then, the reactor was put in a preheated oil bath at different temperatures for the target reaction time. After each reaction, the sample was directly quenched in an ice bath and subsequently diluted using water. Then, the sample was filtered through a $0.22\ \mu\text{m}$ syringe filter and analyzed using a high-performance liquid chromatography (HPLC) system. All experiments were performed in duplicate or triplicate. The formaldehyde collection set-up

was used to collect the formaldehyde product in the gas phase (Scheme 1). After the reaction, N_2 with a flow rate of 5 mL min^{-1} was employed to purge the reactor, which, together with the products, was then passed through DNPN-silica cartridges for 30 min. After collection, the DNPN-silica cartridges were washed with 5 mL acetonitrile (HPLC purity) at approximately 0.5 mL min^{-1} , and the solvent was analyzed by HPLC.

Scheme 1. Formaldehyde gas collection set-up diagram (reaction condition: glucose: 1.11 mol L^{-1} , 32 mL GVL, 8 mL water; 0.1 wt% H_2SO_4 ; $0.014 \text{ mol L}^{-1} \text{ SnSO}_4$).

3.3. Determination of Glucose, Furfural, HMF, and Formaldehyde

Glucose was analyzed using an HPLC apparatus equipped with a refractive index detector and an Agilent (Santa Clara, California, UAS) Zorbax Amide column at a sample injection volume of $20 \mu\text{L}$. A solution of acetonitrile/distilled water (60:40, v/v) was used as the mobile phase at a flow rate of 1.0 mL min^{-1} .

Furfural, HMF, and formaldehyde were analyzed using a 1200 HPLC system equipped with an Agilent XDB-C18 column and a UV-Vis photodiode array detector with a sample injection volume of $20 \mu\text{L}$. A solution of acetonitrile/water (15:85, v/v) was used as the mobile phase for furfural (280 nm) and HMF (280 nm) analysis at a flow rate of 1 mL min^{-1} , whereas acetonitrile/water (40:60, v/v) was used for formaldehyde quantification (355 nm).

The glucose conversion, furfural degradation, HMF degradation, furfural yield, HMF yield, furfural selectivity, and 5-HMF selectivity were calculated by Equations (1)–(5), as follows.

$$\text{Glucose conversion } (X_{\text{GLU}} \%) = \frac{\text{moles of converted glucose}}{\text{moles of starting glucose}} \times 100\% \quad (1)$$

$$\text{Furfural yield } (\%) = \frac{\text{moles of produced furfural}}{\text{moles of starting glucose}} \times 100\% \quad (2)$$

$$\text{HMF yield } (\%) = \frac{\text{moles of produced HMF}}{\text{moles of starting glucose}} \times 100\% \quad (3)$$

$$\text{Furfural selectivity } (\%) = \frac{\text{moles of produced furfural}}{\text{moles of converted glucose}} \times 100\% \quad (4)$$

$$\text{HMF selectivity } (\%) = \frac{\text{moles of produced HMF}}{\text{moles of converted glucose}} \times 100\% \quad (5)$$

3.4. Kinetic Calculation

Based on the reported study on furfural and HMF formation, the simplified reaction in Scheme 2 was developed to describe the behavior of glucose, furfural, and HMF degradation as well as furfural and HMF production. The kinetic model with a pseudo first-order mechanism was considered. The validity of the model was tested by fitting the proposed rate equations to the experimental data [29–31]. As reference, similar published kinetic models were presented and compared in Table S5.

Scheme 2. Simplified reaction scheme for the conversion of glucose.

Five key chemical reaction steps for glucose conversion have been considered in the kinetic model: (1) the conversion of glucose to HMF; (2) the conversion of glucose to furfural; (3) the conversion of glucose to other degradation products; (4) the further degradation of HMF; and (5) the further degradation of furfural.

The kinetic model of the glucose conversion reaction was proposed on the following assumptions.

(1) The intermediates of furfural production and HMF production have not been included in the kinetic model.

(2) All unidentified products are considered to be degradation products (humins).

(3) All reactions are irreversible.

The degradation rates of glucose, furfural, and HMF in Equations (6)–(9) are developed.

$$\frac{dC_{GLU}}{dt} = (k_1 + k_2 + k_5)C_{GLU} \quad (6)$$

$$\frac{dC_{FUR}}{dt} = k_1C_{GLU} - k_3C_{FUR} \quad (7)$$

$$\frac{dC_{HMF}}{dt} = k_2C_{GLU} - k_4C_{HMF} \quad (8)$$

$$k_{GLU} = k_1 + k_2 + k_5 \quad (9)$$

where GLU represents glucose, HMF represents HMF, and FUR represents furfural.

The concentrations of glucose, furfural, and HMF over time were described as Equations (10)–(12) with $C_{GLU0} = 0.0555 \text{ mol L}^{-1}$ and $C_{HMF} = C_{FUR} = 0$ at $t = 0$:

$$C_{GLU} = C_{GLU0} \left(1 - e^{-k_{GLU}t} \right) \quad (10)$$

$$C_{FUR} = \frac{k_1 C_{GLU0}}{k_3 - k_{GLU}} \left[e^{-k_{GLU}t} - e^{-k_3t} \right] \quad (11)$$

$$C_{HMF} = \frac{k_2 C_{GLU0}}{k_4 - k_{GLU}} \left[e^{-k_{GLU}t} - e^{-k_4t} \right] \quad (12)$$

The Arrhenius equation in Equation (13) was used to calculate the activation energy (E_a) and evaluate the effect temperature (T) on the rate constants (k):

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

where A corresponds to pre-exponential factor (min^{-1}), k is the reaction rate constant (min^{-1}), E_a is the activation energy (kJ mol^{-1}), R is the universal gas constant ($\text{kJ}^{-1} \text{mol}^{-1} \text{K}^{-1}$), and T is the temperature (K).

The reaction rate constants (k_i) are determined according to previous studies, as follows [29–31]:

(1) The conversion rate constants for glucose (k_G) were obtained using a nonlinear curve fitting, as Equation (10), where the data are from Figure 1a.

(2) The formation rate constants of furfural (k_1) and HMF (k_2) and the degradation rate constants of furfural (k_3) and HMF (k_4) were obtained using a nonlinear curve fitting, as Equations (11) and (12), where the data are from Figure 1b,c.

(3) The formation of other degradation products (k_5) was calculated using Equation (9) by subtracting the sum of k_1 and k_2 from k_G .

The A and E_a were obtained from Arrhenius rate data plots, as shown in Figure S1, Supplementary Materials.

As a comparison, another reported method was also employed to calculate the above parameters from experimental data as given in Figure S1 to S3 and Table S2, Supplementary Materials [30].

4. Conclusions

In this study, the performance of different co-catalyst systems of Brønsted acid and Lewis acid on the selective conversion of glucose to furfural and HMF was studied, as well as the effect of temperature and solvent composition (different ratios of GVL/water mixtures). In addition, a kinetic model, based on the pseudo first-order kinetics, was proposed to understand the complex mechanism for glucose conversion to furfural and HMF. The result demonstrated that the co-catalyst systems could effectively promote the selective conversion of glucose into furfural and HMF within a short time in GVL/water mixtures. It has been found that strong oxidizing Brønsted acid such as H_2SO_4 coupling with appropriate Lewis acid such as $SnSO_4$ could enhance furfural production while a combination of HCl with $SnSO_4$ or H_2SO_4 with $CuSO_4$ was more favorable for HMF production. Given that, the selection for Brønsted acids determines glucose conversion efficiency and the selectivity of furfural and HMF. The highest furfural and HMF yields of 42% and 34% were obtained in the $SnSO_4/H_2SO_4$ -catalyzed system at 80% GVL, for 10 min at 443 K. Besides, the reaction temperature and ratios of GVL to water also exhibited complex effects on the conversion of glucose and the production of furfural and HMF. High temperatures provided a low yield of furfural and HMF, which is mainly due to an increased humin production rate from glucose and HMF based on the kinetics study. Meanwhile, GVL could change the product distribution by altering the ratio of glucose conversion into expected products to degradation products. A higher ratio of GVL/water promoted the conversion of glucose, which, in contrast, resulted in a lower yield of furfural and HMF due to the rapid increase in HMF and glucose side reactions. In addition, the activation energies in this study are lower than in previous reports. Kinetics results showed that the ratio of furfural and HMF production rate at different temperatures (433 to 463 K) or water/GVL ratio (90 to 80%) was constant close to 1, suggesting that the production of furfural and HMF might follow similar reaction pathways. Based on the results of kinetic and experiments, it is proposed that the reaction pathway of furfural and HMF production from glucose is via 3-deoxy-glucosone as the key intermediate.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4344/11/1/11/s1>, Figure S1: Arrhenius plots of $\ln(k_i)$ versus $1/T$; Figure S2: $-\ln(1-X)$ versus reaction time for (a) furfural degradation and (b) HMF degradation over different temperatures; Figure S3: $-\ln(1-X)$ versus reaction time for (a) furfural conversion and (b) 5-HMF conversion based on the mixed catalyzed system over different ratios of GVL to water; Figure S4: 3-DG determination mechanism; Figure S5: LC-MS spectra of m/z 285.12 (DAN-3-DG) and its fracture process; Figure S6: MS spectra of m/z 285.12 (DAN-3-DG) and corresponding structures; Figure S7: Fragments of DAN-3-DG; Table S1: Kinetic parameters for the conversion of glucose into HMF and furfural at different temperatures; Table S2: Kinetic parameters for the conversion of glucose to furfural at a different water content; Table S3: Glucose conversions into furfural and 5-HMF using single and mixed catalysts; Table S4: Glucose conversions into furfural and 5-HMF using single and mixed catalysts; Table S5: Comparison with previous kinetic models.

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Nomenclature

A	pre-exponential factor (min^{-1})
k	reaction rate constant (min^{-1})
E	activation energy (kJ/mol)
R	($\text{kJ mol}^{-1} \text{K}^{-1}$)
T	temperature (K)
k_G	glucose degradation rate constant (min^{-1})
k_1	furfural formation rate constant (min^{-1})
k_2	HMF formation rate constant (min^{-1})
k_3	degradation rate constant for furfural (min^{-1})
k_4	degradation rate constant for HMF (min^{-1})
C_{GLU}	initial concentration of glucose (mol L^{-1})
C_{HMF}	initial concentration of HMF (mol L^{-1})
C_{FUR}	initial concentration of furfural (mol L^{-1})
E_{a1}	activation energy for furfural production (kJ mol^{-1})
E_{a2}	activation energy for HMF production (kJ mol^{-1})
E_{a3}	activation energy for furfural degradation (kJ mol^{-1})
E_{a4}	activation energy for HMF degradation (kJ mol^{-1})
E_{a5}	activation energy for glucose degradation (kJ mol^{-1})

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