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Conversion of Hemicellulose Sugars Catalyzed by Formic Acid: Kinetics of the Dehydration of D-Xylose, L-Arabinose, and D-Glucose

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The pre-treatment of lignocellulosic biomass produces a liquid stream of hemicellulose-based sugars, which can be further converted to high-value chemicals. Formosolv pulping and the Milox process use formic acid as the fractionating agent, which can be used as the catalyst for the valorisation of hemicellulose sugars to platform chemicals. The objective of this study was to investigate the reaction kinetics of major components in the hemicelluloses fraction of biomass, that is, D-xylose, L-arabinose and D-glucose. The kinetics experiments for each sugar were performed at temperatures between 130 and 170 °C in various formic acid concentrations (10–64 wt %). The implications of these kinetic models on the selectivity of each sugar to the desired products are discussed. The models were used to predict the reaction kinetics of solutions that resemble the liquid stream obtained from the fractionation process of biomass using formic acid.

Introduction

Furanic compounds, for example, furfural and 5-hydroxymethylfurfural (HMF), as well as organic acids, for example, levulinic and formic acids, are important renewable bulk chemicals derived from lignocellulosic materials, such as agricultural wastes and energy crops. Approximately 60–62 % of the worldwide production of furfural is used to produce furfuryl alcohol, an important polymer precursor that is obtained mainly through the hydrogenation of furfural in the gas phase over Cu catalysts at mild temperatures.[1] Other furfural derivatives, such as 2-methylfuran and 2-methyltetrahydrofuran, have been designated as fuel additives.[2] Lange et al.[2] studied the production of ethyl furfuryl ether derived from furfuryl alcohol and its utilisation as a gasoline additive because of its high octane number and high energy density (28 MJ kg^{-1}). The carbonyl and hydroxyl groups of HMF can be transformed through oxidation and esterification reactions to various bulk and fine chemicals for a wide range of applications, such as 2,5-furandicarboxylic acid, 2,5-diformylfuran and others. Additionally, base-catalysed aldol condensation reactions of furfural and HMF with other aldehydes or ketones at moderate temperatures (50–120 °C) are considered as a promising route for the production of C_8–C_{13} alkanes through a subsequent reduction of the condensed molecules.[3,4] Levulinic acid (LA) has been recognised as a versatile building block and highly valuable precursor of biofuels. LA derivatives, such as ethyl and *n*-butyl levulinates, have been blended with fossil-based diesel successfully up to 20 %.[5] LA can also be hydrogenated selectively to γ-valerolactone, which can be further transformed to alkane fuel mixtures.[6]

Furfural, HMF and LA can be produced by a complex reaction network of the hemicelluloses fraction of biomass in acidic aqueous media (Scheme 1). Initially, the glycosidic linkages of the hemicellulose are protonated and subsequently hydrolysed to release pentoses (i.e., xylose and arabinose) and hexoses (i.e., glucose, mannose and galactose). The conversion of D-xylose to furfural is initiated by the protonation of the hydroxyl groups of D-xylose in its pyranose form. Some investigations have suggested that once one molecule of water is eliminated from the D-xylose molecule, an intermediate dehydrofuranose is formed, which would dehydrate further to form furfural.[7,8] The intermediate dehydrofuranose may react with various functional groups present in the reaction medium, for example, the aldehyde group in furfural or the nucleophilic groups in lignin-derived compounds, to lead to non-valuable byproducts.[9] Likewise, furfural is known to undergo resinification and decomposition reactions through the hydrolytic cleavage of its saturated ring. These undesired side reactions are promoted by acid catalysts and high temperatures[10] and eventually lead to low selectivity for furfural production in aqueous acidic media. Although L-arabinose is not especially abundant in most common crops and agricultural residues (~15 % of total hemicelluloses), its content in bark fractions of pine wood (*Pinus sylvestris*, *Picea abies*) and spruce wood (*Picea abies*) can be much higher than in other lignocellulosic biomass. The studies of Hosia et al. and Eskilsson and Hartler (cited by Hayes[11]) reported that L-arabinose corresponded to approximately 50–70 % of the total pentoses found in the stem bark of these wood species. Heartwood from species

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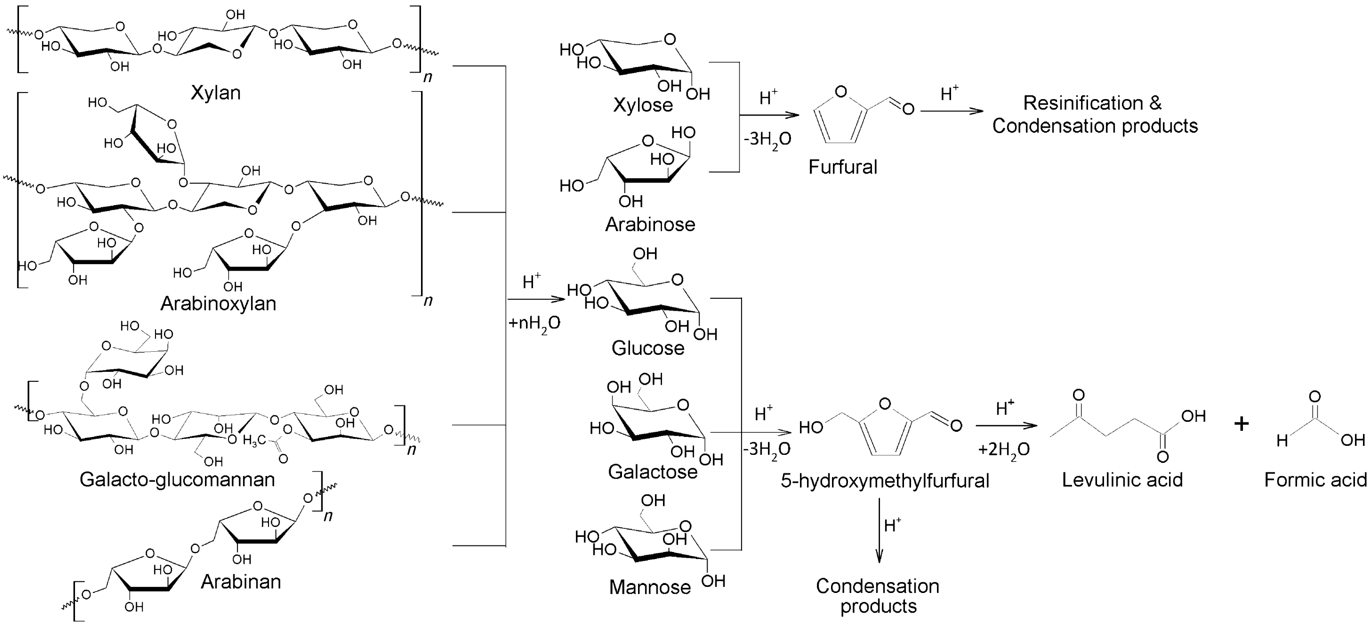


Scheme 1. Reaction network of the acid-catalysed hydrolysis of hemicellulose in lignocellulosic biomass.

such as Larix lariciana also has relatively high amounts of arabinose (~40% of total pentoses).[12] The furfural production from these wood species can be mostly attributed to the dehydration of arabinose to furfural. Therefore, comprehensive studies on the conversion of D-xylose and L-arabinose to furfural in acidic media are essential for the development of lignocellulosic biorefineries that comprise a wide range of feedstocks, which include wood and wood residues.

The total amount of hexoses from the hydrolysis reaction of hemicellulose is generally low in grasses and hardwood materials; however, depending on the type of lignocellulosic material and the conditions of hydrolysis reaction, the amount of glucose release can account for up to 40% of the glucan content in cellulose with high formic acid concentrations at high temperatures.[13] As a result of the low activity of hexoses towards the enolisation reaction in water, all hexoses show generally low selectivities to HMF[14] and require high temperatures and strong acid catalysts to obtain significant yields of HMF.[15] HMF can be hydrated easily in the aqueous phase at low temperatures to form LA and formic acid.[16] However, undesired side reactions of HMF to the condensation products also occur easily, which decrease the yields of LA and formic acid.

Although numerous kinetic studies have been performed in the past, most of these studies simplify the conversion reactions of hemicellulose sugars to pseudo-first-order kinetics.[17–19] Weingarten et al.[20] found that the kinetics of the D-xylose dehydration reaction catalysed by hydrochloric acid (0.1 M) in a biphasic system (water/methyl isobutyl ketone) followed a second-order reaction mechanism in which D-xylose and furfural reacted to form the decomposition products. Lamminpää et al.[21] proposed a more complex reaction mechanism for the kinetics of the xylose dehydration reaction in an aqueous medium catalysed by formic acid (<30 wt%) at temperatures between 160 and 200 °C. The reaction mechanism presented by Lamminpää includes the formation of an unknown intermediate from D-xylose before the formation of furfural, which reacts subsequently with this intermediate to form the condensation products.[20] Kupiainen et al.[22] investigated the conversion of glucose catalysed by formic acid (<20 wt%) at high temperatures (>180 °C). They found that HMF was formed via an intermediate compound through first-order reaction kinetics.

Biomass fractionation processes that use formic acid as the fractionation solvent (i.e., Formosolv pulping and the Milox process) have been implemented not only as technologies for paper production but also as a pre-treatment process for the biochemical conversion of cellulosic pulps.[13,22–24] The hemicellulose sugars released from these types of fractionation processes can be further valorised in the formic acid solvent that also acts as the catalyst to form platform chemicals such as furfural, HMF and LA.[25] The aim of this study was to evaluate the kinetics of the dehydration reactions of D-xylose, L-arabinose and D-glucose in formic acid solution (10–64 wt%) at temperatures between 130 and 170 °C. Additionally, the effects of the initial concentrations of substrates and products on the selectivity of the dehydration reactions to the desired products were also investigated and taken into account to validate the reaction mechanisms. Finally, the kinetic models developed for each sugar were combined and used to model the reaction kinetics of solutions that resemble the liquors obtained from the fractionation process using formic acid.

Results and Discussion

Reaction mechanisms

Despite the number of studies on xylose dehydration, a reaction mechanism for the kinetics determination has not yet been collectively agreed. Three of the most common reaction mechanisms found in the literature for the conversion of pentoses are described in Scheme 2. The most significant difference in these mechanisms is related to the side reactions that affect the selectivity of the dehydration reactions of D-xylose (XYL) or L-arabinose (ARA). The first mechanism involves first-order reaction rates for the conversion of XYL/ARA to furfural and to condensation products (COND). The second mechanism implies the conversion of XYL/ARA to furfural via an intermediate species, as proposed from mechanistic and molecular modelling studies.[7,8] This intermediate compound (INT) reacts with furfural to form condensation products following a second-order reaction rate. The third mechanism describes the formation of condensation products between furfural and XYL/ARA. These three reaction mechanisms propose that furfural would undergo a self-degradation reaction to form resinification products (RES).

The reaction rate equations used for the modelling of the kinetics that follow the mechanisms described in Scheme 2 for D-xylose are presented as follows:

Formation of resinification products from furfural (FUR) [Eq. (1)]:

$$\frac{\mathrm{d}[\mathrm{RES}]}{\mathrm{d}t} = k_\mathrm{R}[\mathrm{FUR}] \tag{1}$$

Mechanism 1 [Eqs. (2)–(4)]:

$$\frac{\mathrm{d}[\mathrm{XYL}]}{\mathrm{d}t} = -(k_\mathrm{X1} + k_\mathrm{X2})[\mathrm{XYL}] \tag{2}$$

$$\frac{\mathrm{d}[\mathrm{FUR}]}{\mathrm{d}t} = k_\mathrm{X1}[\mathrm{XYL}] - k_\mathrm{R}[\mathrm{FUR}] \tag{3}$$

$$\frac{\mathrm{d}[\mathrm{COND}]}{\mathrm{d}t} = k_\mathrm{X2}[\mathrm{XYL}] \tag{4}$$

Mechanism 2 [Eqs. (5)–(8)]:

$$\frac{\mathrm{d}[\mathrm{XYL}]}{\mathrm{d}t} = -k_\mathrm{X1}[\mathrm{XYL}] \tag{5}$$

$$\frac{\mathrm{d}[\mathrm{INT}]}{\mathrm{d}t} = k_\mathrm{X1}[\mathrm{XYL}] - k_\mathrm{X2}[\mathrm{INT}][\mathrm{FUR}] - k_\mathrm{X3}[\mathrm{INT}] \tag{6}$$

$$\frac{\mathrm{d}[\mathrm{FUR}]}{\mathrm{d}t} = k_\mathrm{X3}[\mathrm{INT}] - k_\mathrm{X2}[\mathrm{INT}][\mathrm{FUR}] - k_\mathrm{R}[\mathrm{FUR}] \tag{7}$$

$$\frac{\mathrm{d}[\mathrm{COND}]}{\mathrm{d}t} = k_\mathrm{X2}[\mathrm{INT}][\mathrm{FUR}] \tag{8}$$

Mechanism 3 [Eqs. (9)–(11)]:

$$\frac{\mathrm{d}[\mathrm{XYL}]}{\mathrm{d}t} = -k_\mathrm{X1}[\mathrm{XYL}] - k_\mathrm{X2}[\mathrm{XYL}][\mathrm{FUR}] \tag{9}$$

$$\frac{\mathrm{d}[\mathrm{FUR}]}{\mathrm{d}t} = k_\mathrm{X1}[\mathrm{XYL}] - k_\mathrm{X2}[\mathrm{XYL}][\mathrm{FUR}] - k_\mathrm{R}[\mathrm{FUR}] \tag{10}$$

$$\frac{\mathrm{d}[\mathrm{COND}]}{\mathrm{d}t} = k_\mathrm{X2}[\mathrm{XYL}][\mathrm{FUR}] \tag{11}$$

Equations (1)–(11) also represent the rate equations for the modelling of the kinetics of ARA, in which XYL can be replaced with the corresponding concentration of ARA, and the reaction rate constants will correspond to the arabinose system (k_A1, k_A2, k_A3).

Following a similar approach, several reaction mechanisms were investigated for the conversion of D-glucose (GLC) to HMF, which is converted subsequently to LA and formic acid (Scheme 3). Mechanism 1 follows a reaction network in which the formations of humin-type byproducts from GLC and HMF follow first-order reaction rates. Mechanism 2 considers the conversion of GLC to an intermediate compound, which is converted to HMF and reacts subsequently with HMF following a second-order reaction rate to form the condensation byproducts. Mechanism 3 includes a second-order reaction in which GLC and HMF react to form the condensation byproducts. The intermediate compounds considered in Mechanism 2 for XYL, ARA and GLC were not isolated or identified in the analytical systems used in this study.

The reaction rate equations used for the modelling of the kinetics that follow the mechanisms described in Scheme 3 for D-glucose are presented as follows:

Mechanism 1:

$$\frac{\mathrm{d}[\mathrm{GLC}]}{\mathrm{d}t} = -(k_\mathrm{G1} + k_\mathrm{G3})[\mathrm{GLC}] \tag{12}$$

$$\frac{\mathrm{d}[\mathrm{HMF}]}{\mathrm{d}t} = k_\mathrm{G1}[\mathrm{GLC}] - (k_\mathrm{G2} + k_\mathrm{G4})[\mathrm{HMF}] \tag{13}$$

$$\frac{\mathrm{d}[\mathrm{LA}]}{\mathrm{d}t} = k_\mathrm{G2}[\mathrm{HMF}] \tag{14}$$

$$\frac{\mathrm{d}[\mathrm{COND}]}{\mathrm{d}t} = k_\mathrm{G3}[\mathrm{GLC}] + k_\mathrm{G4}[\mathrm{HMF}] \tag{15}$$

Mechanism 2:

$$\frac{\mathrm{d}[\mathrm{GLC}]}{\mathrm{d}t} = k_\mathrm{G1}[\mathrm{GLC}] \tag{16}$$

$$\frac{\mathrm{d}[\mathrm{INT}]}{\mathrm{d}t} = k_\mathrm{G1}[\mathrm{GLC}] - k_\mathrm{G2}[\mathrm{INT}\cdot\mathrm{G}] - k_\mathrm{G3}[\mathrm{INT}\cdot\mathrm{G}][\mathrm{HMF}] \tag{17}$$

$$\frac{\mathrm{d}[\mathrm{HMF}]}{\mathrm{d}t} = k_\mathrm{G2}[\mathrm{INT}\cdot\mathrm{G}] - k_\mathrm{G3}[\mathrm{INT}\cdot\mathrm{G}][\mathrm{HMF}] - k_\mathrm{G4}[\mathrm{HMF}] \tag{18}$$

$$\frac{d[\mathrm{LA}]}{dt} = k_\mathrm{G4}[\mathrm{HMF}] \tag{19}$$

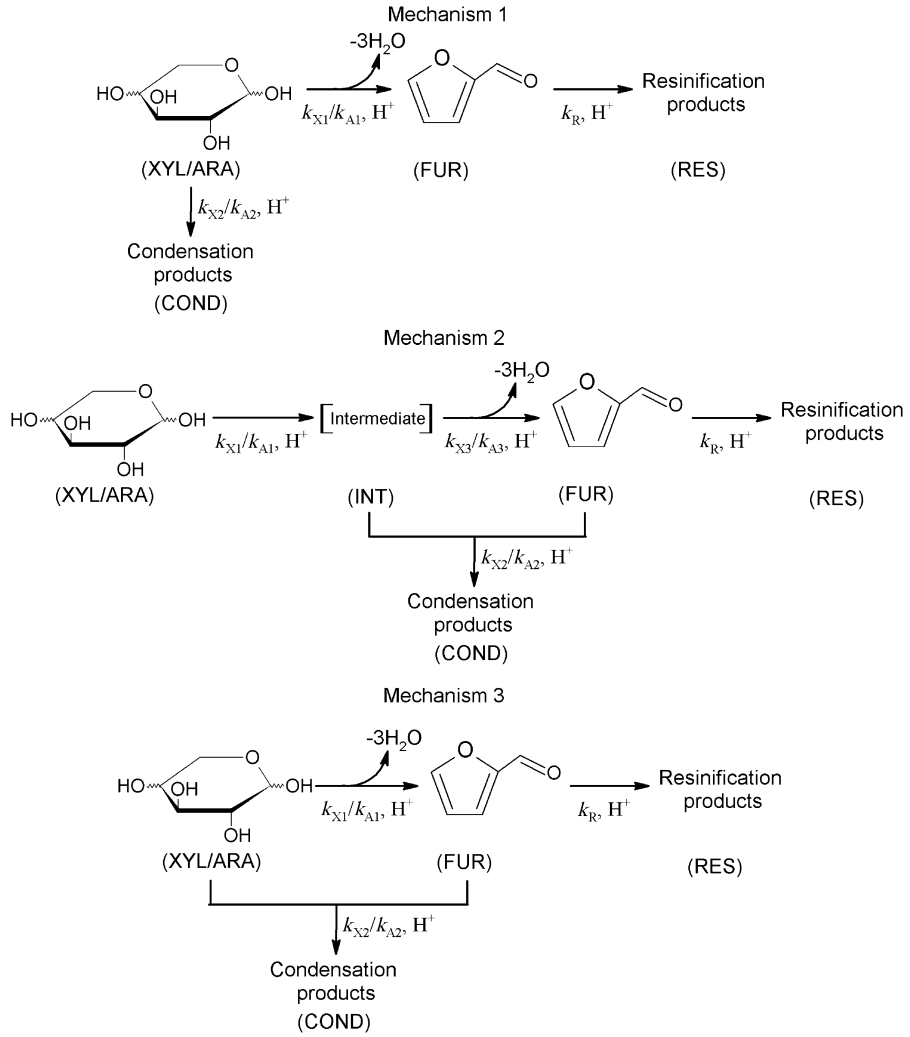
$$\frac{\mathrm{d}[\mathrm{COND}]}{\mathrm{d}t} = k_\mathrm{G3}[\mathrm{INT}\cdot\mathrm{G}][\mathrm{HMF}] \tag{20}$$

Mechanism 3:

$$\frac{\mathrm{d}[\mathrm{GLC}]}{\mathrm{d}t} = -k_\mathrm{G1}[\mathrm{GLC}] - k_\mathrm{G3}[\mathrm{GLC}][\mathrm{HMF}] \tag{21}$$

$$\frac{\mathrm{d}[\mathrm{HMF}]}{\mathrm{d}t} = k_\mathrm{G1}[\mathrm{GLC}] - k_\mathrm{G2}[\mathrm{HMF}] - k_\mathrm{G3}[\mathrm{GLC}][\mathrm{HMF}] \tag{22}$$

$$\frac{\mathrm{d}[\mathrm{LA}]}{\mathrm{d}t} = k_\mathrm{G2}[\mathrm{HMF}] \tag{23}$$



Scheme 2. Reaction mechanisms for the kinetic study of the acid-catalysed dehydration of D-xylose (XYL) and L-arabinose (ARA) and the degradation of furfural (FUR).

$$\frac{d[COND]}{dt} = k_{G3}[GLC][HMF] \qquad (24)$$

Furfural degradation in concentrated formic acid

A series of nine experiments was performed to assess the degradation rates of furfural at various concentrations of formic acid (27–60 wt%). The degradation of furfural was barely affected by the formic acid concentration. For example, the degradation of furfural (100 mM) at 170 °C after 100 min of reaction time was 14.2, 15.2 and 12.0 mol% in formic acid solutions of 30, 47 and 62 wt%, respectively. Additional experiments were performed in concentrated formic acid (98 wt%) and deionised water to validate whether the furfural degradation reaction was independent of the concentration of formic acid. These experimental results are presented in Figure 1.

If concentrated formic acid (98 wt%) was used as the reacting solvent, only 5% of the furfural was degraded after 160 min. This indicated that furfural is stable in concentrated formic acid solution, that is, with a very low concentration of water in the mixture. The degradation of furfural in deionised water was similar to that observed in the dilute solutions of formic acid. The presence of the dissociated hydronium ion (0.020–0.045 M) in the solutions of formic acid (30–62 wt%) used in this study barely enhanced the degradation rate of furfural. This observation is in line with previous studies on the degradation of furfural in dilute solutions of formic acid (<30 wt%).[21] However, if we used significantly high formic acid concentrations (>60 wt%), the effects of water as a solvent on the rate constant of the degradation of furfural must be taken into account.

The kinetics of the furfural degradation reaction was modelled following a first-order reaction rate in which the reaction rate constant was expressed as a function of temperature following the Arrhenius equation [Eq. (25)]:

$$k_R = A_R \exp\left(\frac{-E_{A,R}}{RT}\right) \qquad (25)$$

in which A_R corresponds to the frequency factor (min^{-1}), $E_{A,R}$ is the activation energy ($kJ\,mol^{-1}$), and R is the universal gas constant. The kinetic parameters

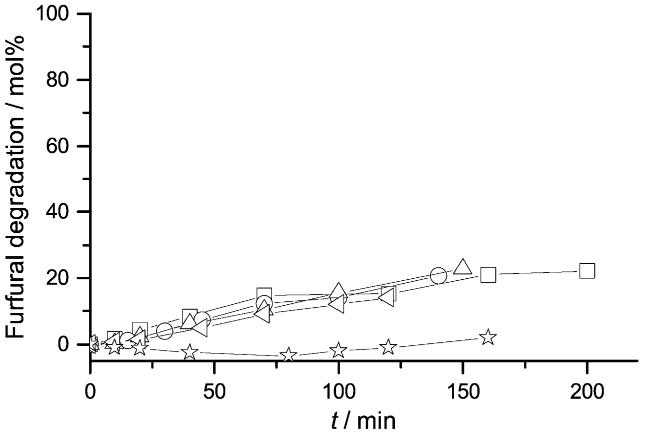
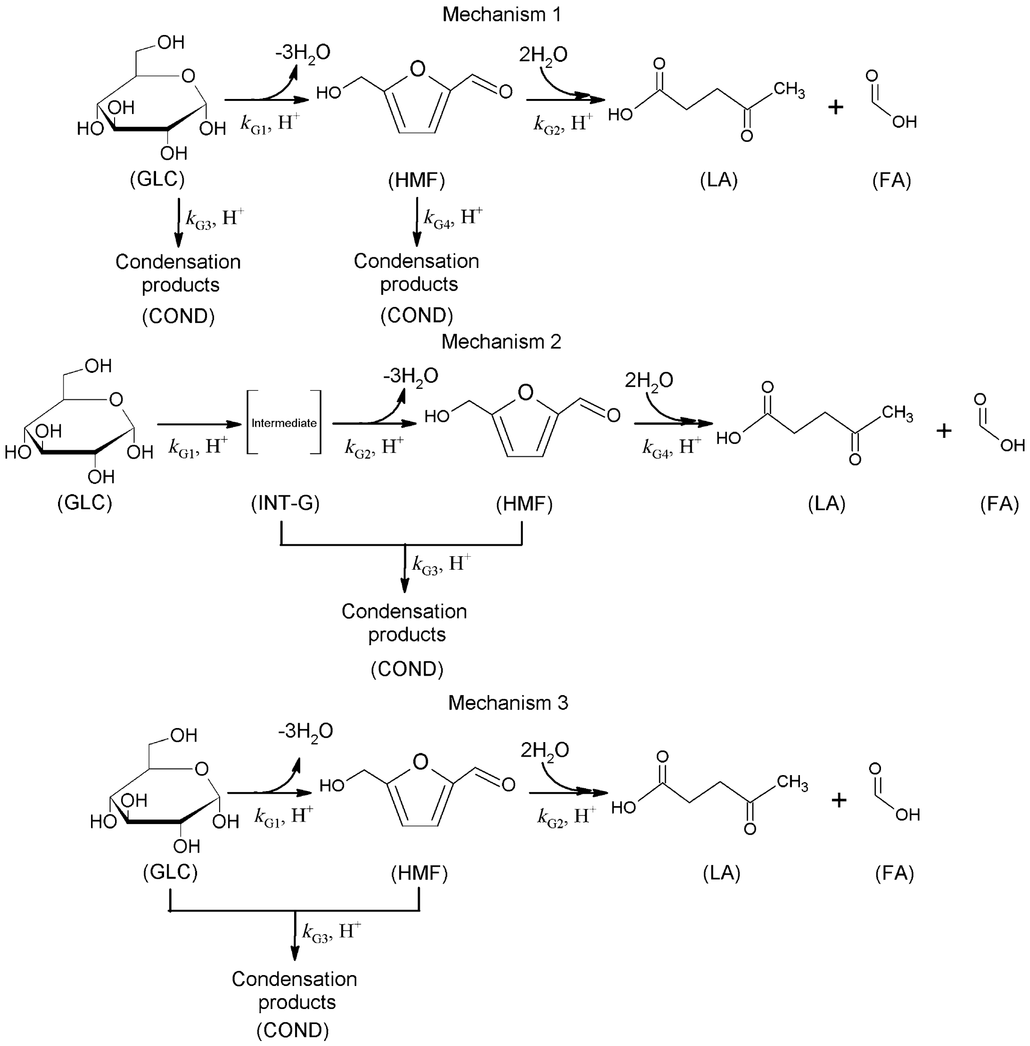


Figure 1. The degradation of the furfural ($C_{FUR,i}$ = 100 mM) at 170 °C in various reacting solvents: □, deionised water; ○, 29.5 wt% HCOOH; △, 46.5 wt% HCOOH; ◁, 62.1 wt% HCOOH; ★, concentrated formic acid (98 wt% HCOOH).



Scheme 3. Reaction mechanisms for the kinetic study of the acid-catalysed dehydration of D-glucose (GLC) and the conversion of HMF to LA and formic acid.

Table 1. Kinetic parameters for the furfural degradation in concentrated formic acid.

Rate constant	Pre-exponential factor $\ln(A_R)$ [min^{-1}]	Activation energy $E_{A,R}$ [kJ mol^{-1}]	Fit to experimental data R^2
k_R	15.70 ± 1.26	81.70 ± 4.45	0.923

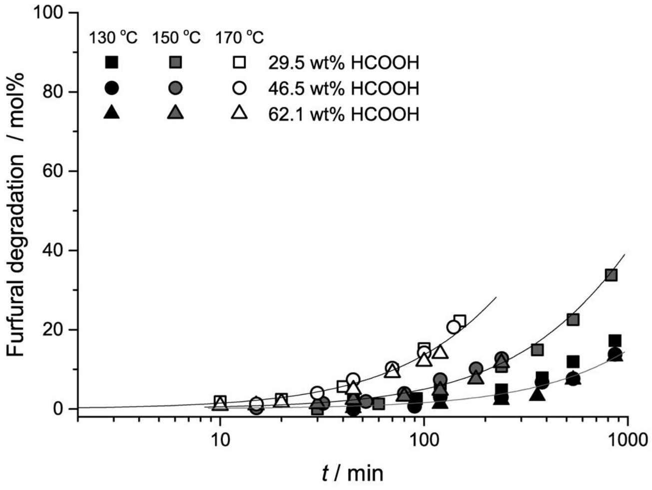


Figure 2. Comparisons between the experimental data and the kinetic model (solid lines) of furfural degradation reaction ($C_{FUR,i} = 100$ mM).

that fit the experimental values satisfactorily ($R^2 = 0.923$) are presented in Table 1 and Figure 2.

The activation energy agreed with the values obtained from previous studies on the kinetics of xylose dehydration and furfural destruction. Lamminpää et al.[21] reported an activation energy of 75.5 kJ mol^{-1} for the hydrothermal degradation of furfural at temperatures between 130 and 180 °C in formic acid solutions (7 and 30 wt %). Other reports gave activation energies for furfural degradation between 67 and 131 kJ mol^{-1} if catalysed by hydrochloric acid[17,20,26] and between 60 and 106 kJ mol^{-1} if catalysed by sulfuric acid.[17,26]

Dehydration of D-xylose to furfural

Kinetic modelling

The concentrations of D-xylose and furfural (200 data points in total), which were obtained from nine different sets of experimental conditions that combine three temperatures (130, 150, 170 °C) and three formic acid concentrations (30, 50, 64 wt %), were used to obtain the kinetic models based on the three proposed reaction mechanisms presented in Scheme 2. The kinetic parameters for all the experimental data were obtained through an estimation routine using the *fminsearch* optimisation function in Matlab. In this routine, the matrix determinant of the residual errors for D-xylose and furfural concentrations was used as the estimation criterion.[27] The kinetic model for the furfural degradation reaction was also included in the estimation routine. A modified Arrhenius equation that includes the effects of temperature T and the effective acid concentration $[\mathrm{H}^+]$ was used to fit the kinetic parameters [Eq. (26)]:

$$k_i = A_i \exp\left(\frac{-E_{A,i}}{RT}\right)[\mathrm{H}^+]^{m_i} \tag{26}$$

The kinetic parameters in Equation (26) are the frequency factor A_i [min^{-1}], the activation energy $E_{\mathrm{A},i}$ [$\mathrm{kJ\,mol}^{-1}$], and the reaction order of $[\mathrm{H}^+]^{m_i}$ (dimensionless). All the kinetic parameters determined for the three reaction mechanisms are listed in Table 2. The goodness-of-fit (GF %) between the experimental and modelled data for the concentrations of D-xylose and furfural are also reported in Table 2 and were calculated as follows [Eq. (27)]:

$$\mathrm{GF}\% = \left(1 - \frac{\sqrt{\sum_{i=1}^{n}(C_i - \hat{C})^2}}{\sqrt{\sum_{i=1}^{n}(C_i - \bar{C})^2}}\right) \times 100 \tag{27}$$

in which C_i corresponds to the concentration of D-xylose or furfural obtained from the experiments, $\hat{C}_i$ is the concentration of each compound predicted using the kinetic models, $\bar{C}_i$ is the mean value of the experimental data and n is the total number of data.

Table 2. Kinetic parameters for the acid-catalysed dehydration of D-xylose.

	GF %[a]	Parameters	Rate constants		
			k_{X1}	k_{X2}	k_{X3}
1	[XYL] = 89.4 % [FUR] = 85.0 %	$\mathrm{Ln}(A_{o,i})$ [$\mathrm{min}^{-1}\,\mathrm{M}^{-m_i}$]	40.2 ± 1.2	42.2 ± 2.1	–
		$E_{\mathrm{A},i}$ [$\mathrm{kJ\,mol}^{-1}$]	136.0 ± 3.0	140.5 ± 5.4	–
		m_i	1.9 ± 0.1	2.3 ± 0.2	–
2	[XYL] = 89.4 % [FUR] = 91.1 %	$\mathrm{Ln}(A_{o,i})$ [$\mathrm{min}^{-1}\,\mathrm{M}^{-m_i}$]	42.6 ± 0.9	26.9 ± 4.2[b]	27.3 ± 3.2
		$E_{\mathrm{A},i}$ [$\mathrm{kJ\,mol}^{-1}$]	140.3 ± 2.4	82.9 ± 11.1	91.5 ± 8.5
		m_i	2.1 ± 0.1	1.5 ± 0.5	1.1 ± 0.4
3	[XYL] = 88.3 % [FUR] = 76.3 %	$\mathrm{Ln}(A_{o,i})$ [$\mathrm{min}^{-1}\,\mathrm{M}^{-m_i}$]	41.2 ± 1.3	41.7 ± 3.4[b]	–
		$E_{\mathrm{A},i}$ [$\mathrm{kJ\,mol}^{-1}$]	137.6 ± 3.3	128.7 ± 9.0	–
		m_i	2.0 ± 0.2	2.4 ± 0.4	–

[a] Goodness-of-fit %. [b] $\mathrm{min}^{-1}\,\mathrm{M}^{-1-m_i}$.

The values of GF % determined for the three reaction mechanisms show significant differences, especially the GF % for furfural concentration. The kinetic models obtained from Mechanisms 1 and 2 gave higher GF % for furfural concentration (85.0 and 91.1 %, respectively) than that from Mechanism 3 (76.3 %). However, there was no significant difference for the GF % values for xylose concentration (88.3–89.4 %). Based on this statistical analysis, Mechanism 2 describes the dehydration reaction of D-xylose to furfural most suitably. To support this statistical analysis, additional experiments were performed at different initial concentrations of D-xylose and furfural. These experiments were performed at 150 and 170 °C using 40 and 64 wt % HCOOH as the catalyst. The experimental data and the prediction results obtained from the three sets of kinetic parameters given in Table 2 are shown in Figure 3. The kinetic model derived from Mechanism 1 failed to estimate the rate of furfural formation at a low initial concentration of D-xylose (Figure 3 a). If furfural was added at the beginning of the reaction (Figure 3 c and d), the kinetic model derived from Mechanism 1 overestimated the formation of furfural because this reaction mechanism does not include the undesired side reactions between xylose and furfural, which could occur from the beginning of the reaction. The kinetic models derived from Mechanisms 2 and 3 can predict the formation of furfural more accurately in every scenario shown in Figure 3. However, the concentrations of D-xylose predicted by the kinetic model derived from Mechanism 3 were lower than the experimental data that were obtained in the presence of furfural (Figure 3 c and d). In this case, the conversion of D-xylose was overestimated because the kinetic model derived from Mechanism 3 assumed that D-xylose was also consumed from the beginning of reaction following a second-order reaction between D-xylose and furfural. The fact that the conversion of D-xylose was not affected in the presence of significant amounts of furfural at the beginning of the reaction supports the hypothesis that furfural only reacts with the intermediate derived from D-xylose to form the condensation products. Based on this analysis, Mechanism 2 was chosen as the most appropriate model to describe the dehydration reaction of D-xylose to furfural in a solution of formic acid as the catalyst.

Implications of the kinetics

The experimental data and the predicted profiles of D-xylose conversion and furfural yields from the kinetics experiments are presented in Figure 4. Furfural yields of between 40 and 55 mol % were obtained at temperatures between 130 and 170 °C if initial D-xylose concentrations between 200 and 270 mM were used. The highest temperature used in this study (170 °C) gave the highest furfural yields (50–55 mol %). An increase of the formic acid concentration improved the furfural yield slightly, for example, an increase of the formic acid concentration from 30.0 to 63.5 wt % at 170 °C only enhanced the furfural yield by 5 %.

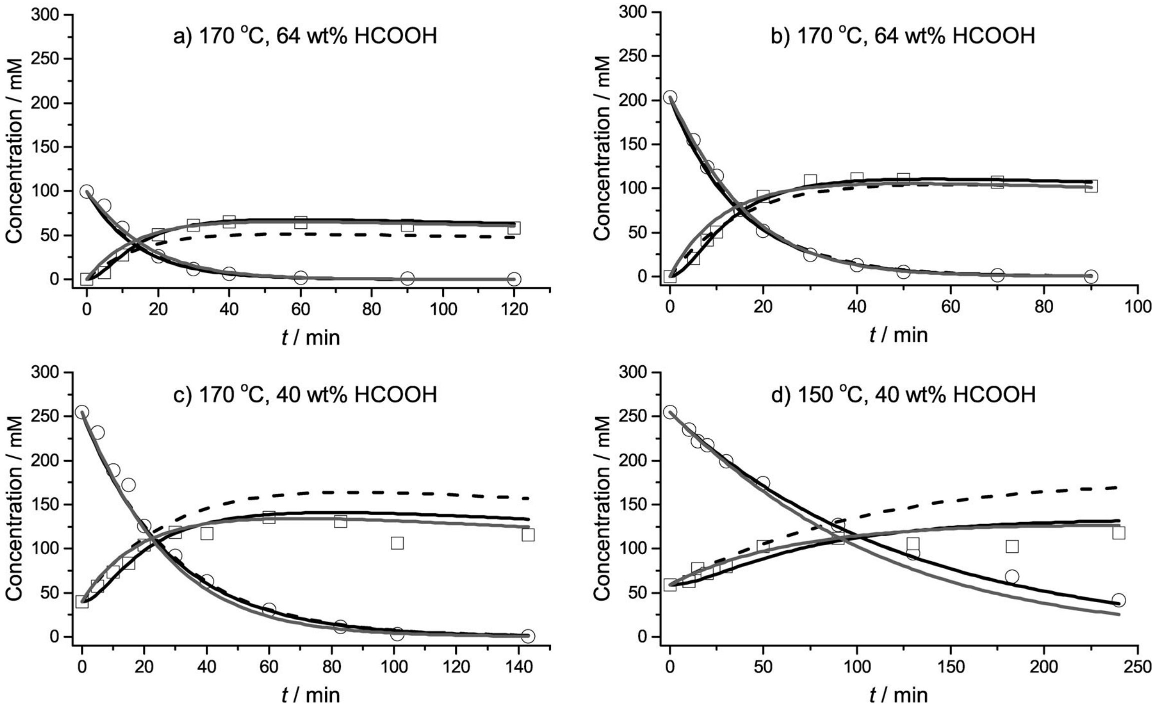


Figure 3. Concentrations of D-xylose (○) and of furfural (□) with different initial D-xylose/furfural compositions and profile predictions from Mechanisms 1 (dashed line), 2 (solid black line) and 3 (solid grey line).

The activation energy of the conversion of D-xylose reported in this study (140.3 kJ mol^{-1}) was in agreement with values reported by Lavarack et al.[17] (111.2–118.9 kJ mol^{-1}), Nabarlatz et al.[28] (122.5 kJ mol^{-1}), Morinelly et al.[26] (106–132 kJ mol^{-1}), Weingarten et al.[20] (123.9 kJ mol^{-1}) and Lamminpää et al.[21] (153 kJ mol^{-1}). The reaction orders of [H$^+$] indicated that the formic acid concentration affects the conversion rate of D-xylose and the formation rate of furfural significantly. This is presented in Figure 4, which shows that faster conversions of D-xylose were observed at higher concentrations of formic acid, particularly at low temperatures. However, the selectivity of furfural formation was not increased extensively with the increase of the acid concentration because of competing side reactions, which were also promoted by the acid to a similar extent. The semi-empirical models demonstrated that the reaction orders of the acid concentration for the rate constants k_{X1} and k_{X2} varied between 1.5 and 2.1; nevertheless, the mechanistic pathway associated with this is yet unclear and requires further investigation.

Dehydration of L-arabinose to furfural

Kinetic modelling

The kinetics of the L-arabinose dehydration reaction was studied following a similar protocol as used for D-xylose. Nine sets of experiments were performed at 130, 150 and 170 °C in solutions of formic acid (10.8, 42.8 and 61.8 wt %). The initial L-arabinose concentration (~20 mM) was selected according to the proportion of arabinose and xylose in an energy crop such as Miscanthus x *giganteus* (~10:1 ratio). A total of 180 experimental data points that consist of L-arabinose and furfural concentrations obtained from these experiments were used to determine the kinetic parameters for the kinetic models according to the reaction mechanisms shown in Scheme 2 and the modified Arrhenius equation [Eq. (26)]. The kinetic parameters of the L-arabinose conversion to furfural are listed in Table 3. The values of GF % for L-arabinose in all three reaction mechanisms are higher than 86 %; however, only Mechanisms 1 and 2 gave a value of GF % higher than 80 % for the furfural concentration.

Table 3. Kinetic parameters for the acid-catalysed dehydration of L-arabinose.

	GF %[a]	Parameters	Rate constants		
			k_{A1}	k_{A2}	k_{A3}
1	[ARA] = 86.7 % [FUR] = 83.7 %	Ln($A_{o,i}$) [min^{-1} M$^{-m_i}$]	36.9 ± 1.4	32.1 ± 3.6	–
		$E_{A,i}$ [kJ mol^{-1}]	130.2 ± 4.0	125.8 ± 11.7	–
		m_i	1.6 ± 0.1	0.8 ± 0.2	–
2	[ARA] = 86.7 % [FUR] = 85.4 %	Ln($A_{o,i}$) [min^{-1} M$^{-m_i}$]	36.3 ± 1.2	20.1 ± 7.9[b]	30.4 ± 4.5
		$E_{A,i}$ [kJ mol^{-1}]	129.4 ± 3.6	88.6 ± 25.8	100.0 ± 14.6
		m_i	1.3 ± 0.1	0.5 ± 0.5	1.4 ± 0.5
3	[ARA] = 86.4 % [FUR] = 76.5 %	Ln($A_{o,i}$) [min^{-1} M$^{-m_i}$]	35.5 ± 1.4	18.6 ± 4.5[b]	–
		$E_{A,i}$ [kJ mol^{-1}]	127.6 ± 4.4	94.2 ± 16.3	–
		m_i	1.3 ± 0.1	0	–

[a] Goodness-of-fit %. [b] min^{-1} M$^{-1-m_i}$.

To select the most suitable reaction mechanism from these two options, additional experiments were performed at different initial concentrations of L-arabinose and furfural at 170 °C

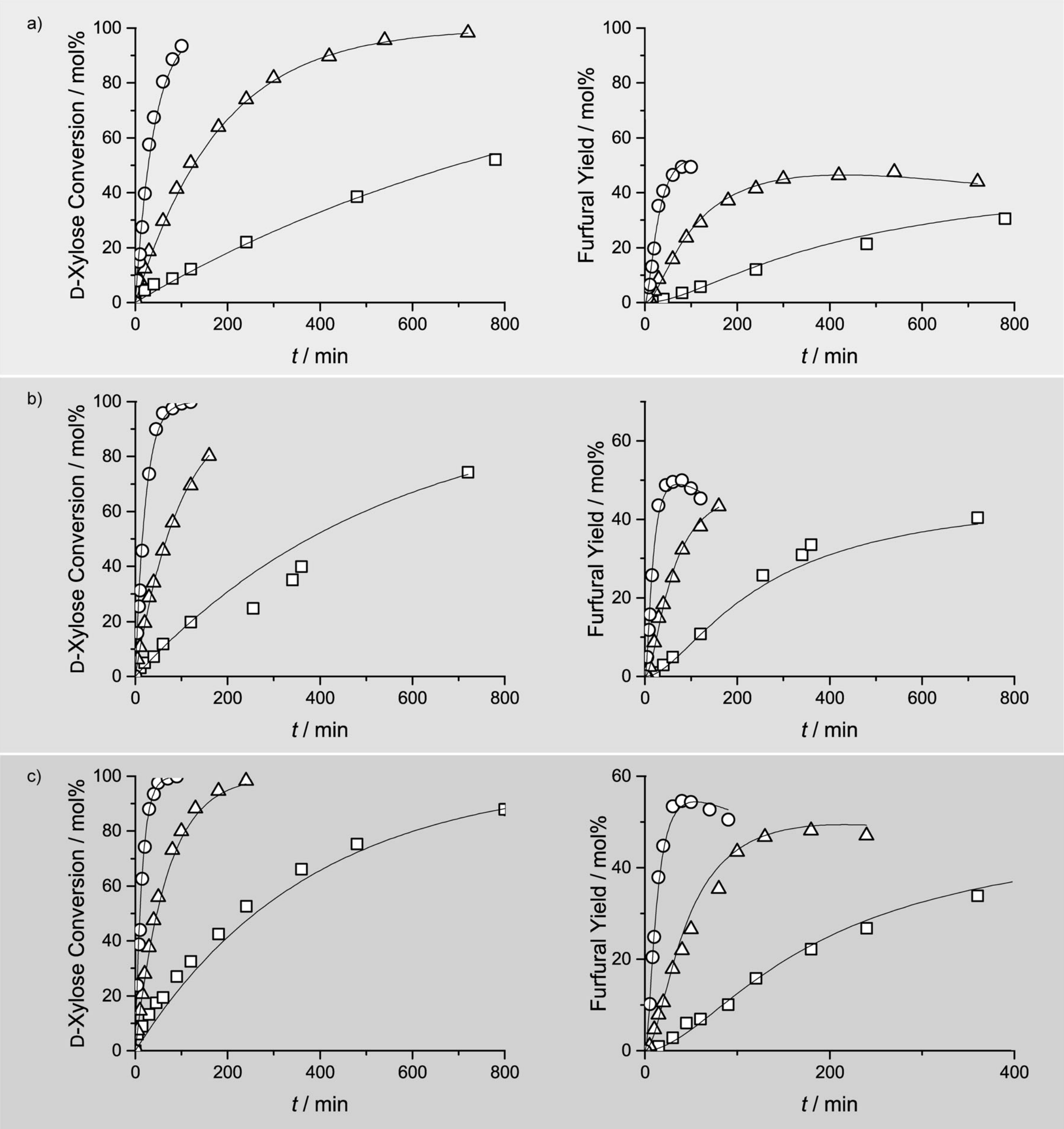


Figure 4. Experimental and modelled (solid lines) D-xylose conversion and furfural yield at 130 (□), 150 (△) and 170°C (○) with $C_{XYL,o}$ = 200–270 mM and different formic acid concentrations: a) 30 wt% HCOOH, b) 49 wt% HCOOH, c) 64 wt% HCOOH

in formic acid solutions (60–62 wt%). The experimental and predicted data for these additional experiments are shown in Figure 5. There were no significant differences between the L-arabinose concentrations predicted by the kinetic models and the experimental data. That means that the presence of furfural had no significant effect on the conversion rate of L-arabinose. However, differences between the experimental data and the predicted values for furfural concentrations were evident. In Mechanisms 2 and 3, furfural also reacted with L-arabinose or the intermediate from L-arabinose following a second-order reaction rate. As a result, the furfural concentrations calculated using these reaction mechanisms were much lower than the experimental data (Figure 5b–d). This behaviour was more evident if furfural was added at the beginning of the reaction (Figure 5c and d).

Based on these experimental results and the statistical analysis, a simple first-order reaction mechanism with only one side reaction (i.e., Mechanism 1) describes the dehydration reaction of L-arabinose to furfural satisfactorily and was selected for further study.

Implications of the kinetics

The experimental data and the predicted profiles of L-arabinose conversion and furfural yields at various reaction conditions are presented in Figure 6. Maximum furfural yields between 57 and 62 mol% were observed at 170°C and formic

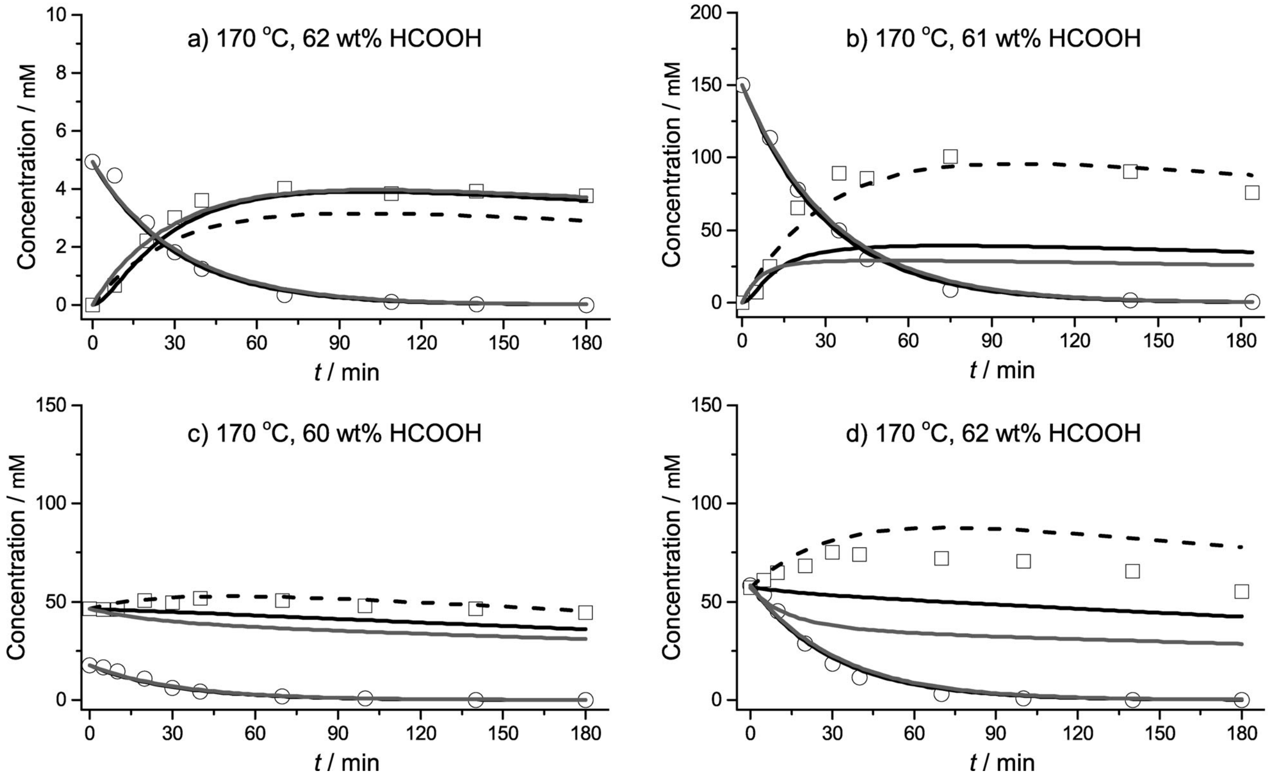


Figure 5. Concentrations of L-arabinose (○) and of furfural (□) with different initial compositions and profile predictions from Mechanisms 1 (dashed line), 2 (solid black line) and 3 (solid grey line).

acid concentrations between 42.8 and 61.8 wt%. As a result of the low initial concentration of L-arabinose used in these experiments (20 mM), the maximum furfural yields obtained from L-arabinose were higher than those obtained from D-xylose. In line with the experimental results using D-xylose, the highest temperature used in this study (170 °C) gave the highest furfural yields.

The difference in activation energies between the furfural formation reaction and the undesired condensation reactions reported in this study is only 4 kJ mol^{-1}. As a result, the reaction temperature could not play a significant role to change the selectivity of the dehydration reaction of L-arabinose to furfural. However, an increase of the concentration of formic acid would not only enhance the conversion rate of L-arabinose, but more importantly would enhance the furfural yield from L-arabinose significantly. As an example, the furfural yield increased from 10 to 60 mol% on increasing the formic acid concentration from 10 to 62 wt% at 130 °C. This result can be explained by comparing the reaction orders of [H$^+$] for the formation reactions of furfural and of condensation products, that is, 1.6 and 0.8, respectively. These results indicate that the reaction rate of furfural formation is affected more profoundly by [H$^+$], and an increase of the formic acid concentration would enhance the yields of furfural eventually.

The activation energy for the dehydration reaction of L-arabinose reported in this study (130.2 kJ mol^{-1}) agreed with the values reported in other studies on the degradation of L-arabinose catalysed by mineral acids (HCl or H_2SO_4). These studies were reported by Lavarack et al.[17] (135.1 kJ mol^{-1}), Nabarlatz et al.[28] (125.2 kJ mol^{-1}), Danon et al.[29] (121.4 kJ mol^{-1}) and Carvalheiro et al.[30] (114–117 kJ mol^{-1}). The activation energies of the auto-catalysed dehydration reaction of L-arabinose reported by Gairola and Smirnova[31] (109 kJ mol^{-1}) and Zheng et al.[32] (130–135 kJ mol^{-1}) were also in line with this study. The activation energy of L-arabinose conversion to the condensation products (125.8 kJ mol^{-1}) was also in line with that reported by Gairola and Smirnova[31] (123 kJ mol^{-1}) and Danon et al.[29] (120.2 kJ mol^{-1}).

Comparison of the dehydration reactions of D-xylose and L-arabinose

The combined effects of temperature and acid concentration on the maximum furfural yields obtained from D-xylose (200 mM) and L-arabinose (20 mM) are depicted in Figure 7. The selectivity of the D-xylose conversion to furfural was improved mainly by reaction temperature. At reaction temperatures above 235 °C and using formic acid concentrations between 25 and 55 wt%, the maximum furfural yields from D-xylose were around 68 mol%. If dilute formic acid solutions (~14 wt%) are used, reaction temperatures above 170 °C are essential to maintain furfural yields above 50 mol%. However, furfural yields greater than 50 mol% can be obtained readily at reaction temperatures above 150 °C if more concentrated formic acid solutions (> 64.4 wt%) are used.

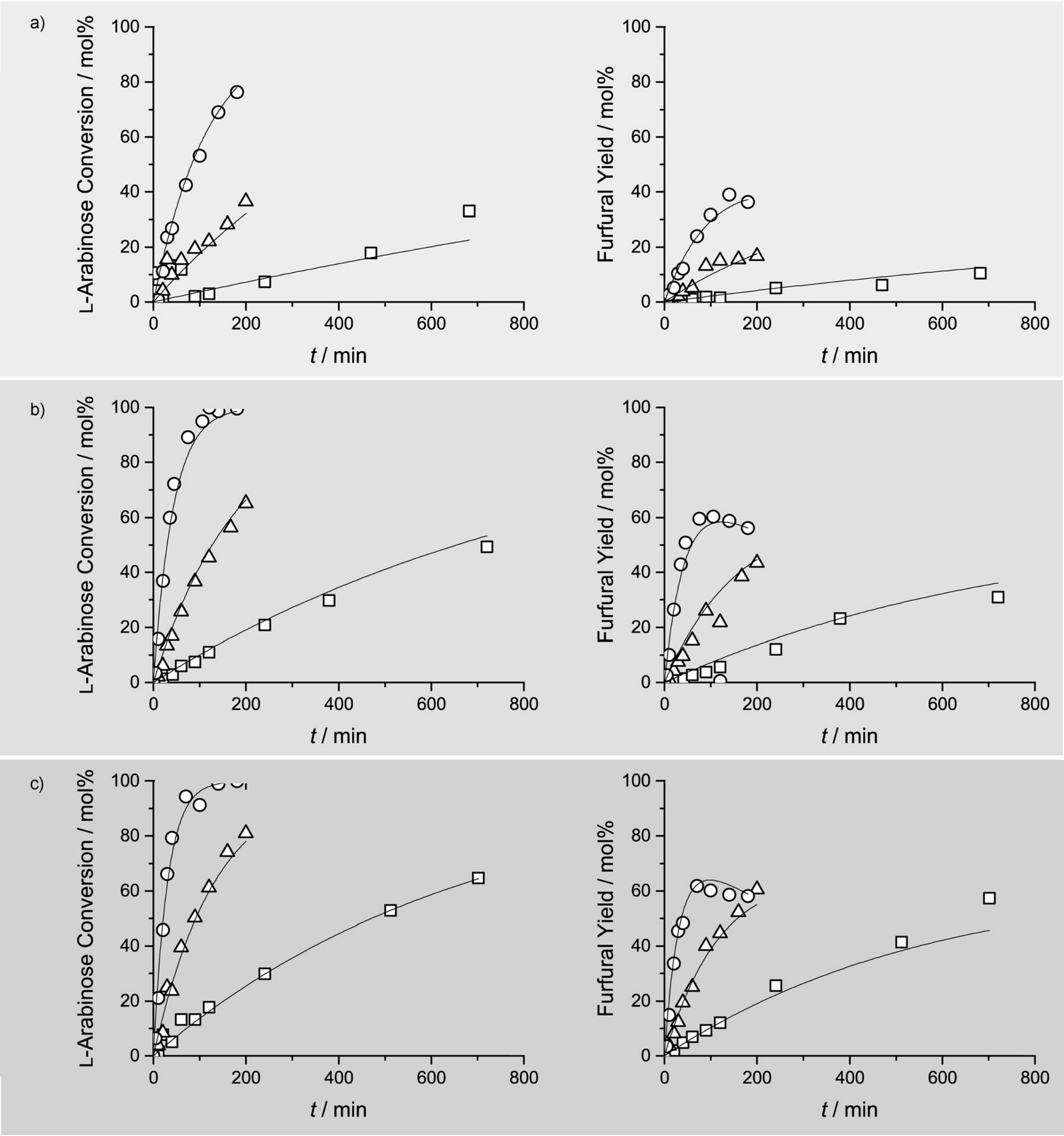


Figure 6. Experimental and modelled (solid lines) L-arabinose conversion and furfural yield at 130 (□), 150 (△) and 170°C (○) with $C_{ARA,o} = 20$ mM and different formic acid concentrations: a) 10 wt% HCOOH, b) 43 wt% HCOOH, c) 62 wt% HCOOH

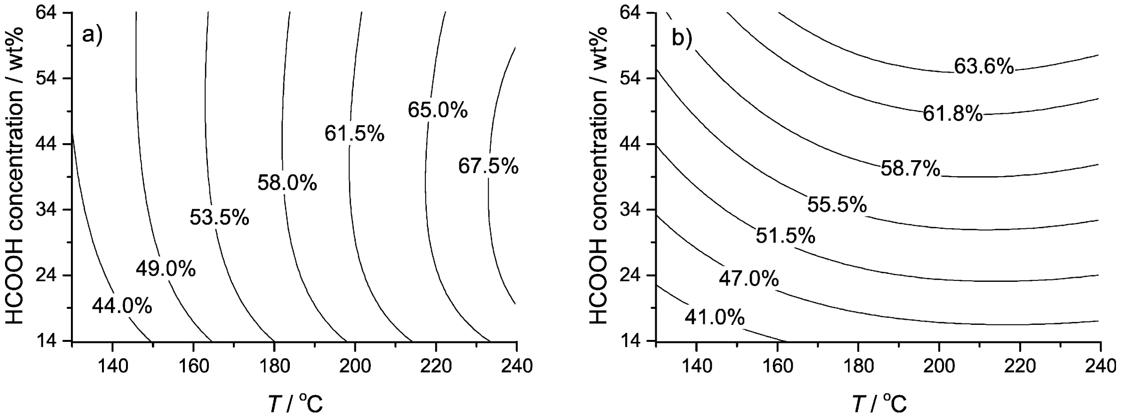


Figure 7. Maximum furfural yields as a function of temperature and formic acid concentration: a) D-xylose (200 mM) and b) L-arabinose (20 mM).

Furfural yields greater than 50 mol% can be obtained from L-arabinose at reaction temperatures lower than 150 °C if formic acid concentrations above 30 wt% are used as the catalyst. As opposed to D-xylose, a gradual increase in the reaction temperature up to 240 °C does not increase the furfural yields from L-arabinose gradually. The highest furfural yield (~63.6 wt%) from L-arabinose can be obtained only at formic acid concentrations higher than 55 wt% and temperatures above 162 °C. The concentration of formic acid plays a more important role in the selectivity of the dehydration reaction of L-arabinose to furfural than that of D-xylose (Figure 7). Although the initial concentration of L-arabinose (20 mM) was lower than that of D-xylose (200 mM), the highest furfural yields predicted from L-arabinose (62.1–63.6%) were lower than the furfural yields from D-xylose (65.0–67.7%).

The estimated loss of pentoses [mol%] through condensation or resinification reactions as a function of temperature in solutions of 13.8 and 50.6 wt% HCOOH is shown in Figure 8. These losses were estimated by simultaneously solving a system of differential equations that describe the concentrations of pentoses and furfural as a function of time, temperature and acid concentration using initial concentrations of xylose and arabinose of 200 and 20 mM, respectively.

The amounts of condensation and resinification products presented in Figure 8 were evaluated at a definite reaction time when the maximum furfural formation was observed. The loss of pentoses through either condensation or resinification reactions was calculated as shown in Equation (28):

$$\text{Loss through side reactions} = \frac{v_{SR} \times n_{SR}}{n_{C_5,o}} \times 100 \tag{28}$$

in which ν_{SR} corresponds to the amount of D-xylose or L-arabinose required to form 1 mol of condensation or resinification products, that is, 2 mol XYL (1 mol of INT-X and 1 mol of FUR) forms 1 mol COND, 1 mol ARA forms 1 mol COND, and 1 mol of pentose forms 1 mol of furfural, which ultimately forms 1 mol of RES, n_{RX} refers to the number of moles of condensation or resinification products formed and $n_{C_5,o}$ corresponds to the initial number of moles of xylose or arabinose.

An increase of the reaction temperature generally inhibits the formation of resinification products from furfural (Figure 8 a and b). A more concentrated acidic medium is beneficial to suppress the formation of resinification products, that is, the loss of D-xylose in the solution of 50.6 wt% HCOOH was only between 3–5%, compared to 9–13% loss in the solution of 13.8 wt% HCOOH. In a more concentrated solution of HCOOH (50.6 wt%), the formation of resinification products from L-arabinose was higher than that from D-xylose because of the lower rate of furfural formation from L-arabinose (1.2–168.6 $\text{mol}_{FUR}\,\text{mol}_{ARA,o}^{-1}\,\text{min}^{-1}$) than from D-xylose (1.8–187.8 $\text{mol}_{FUR}\,\text{mol}_{XYL,o}^{-1}\,\text{min}^{-1}$). As a result, the maximum yield of

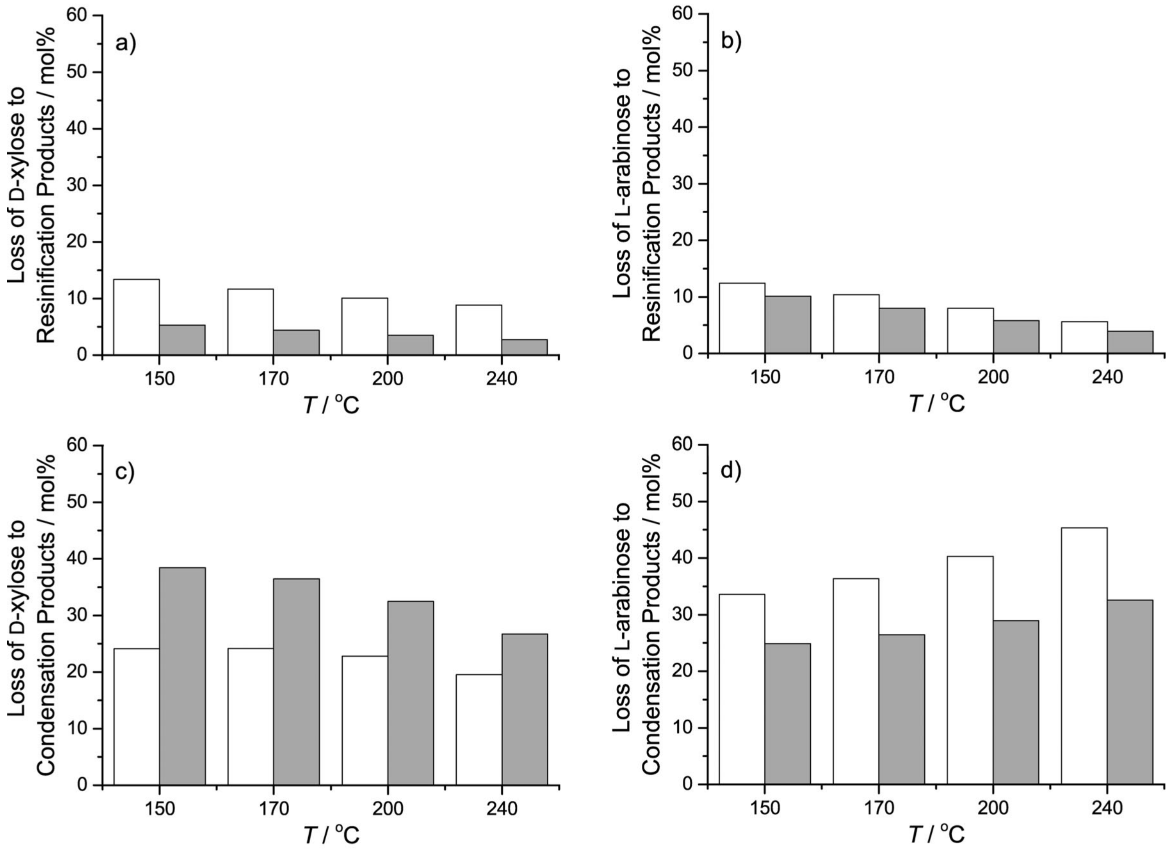
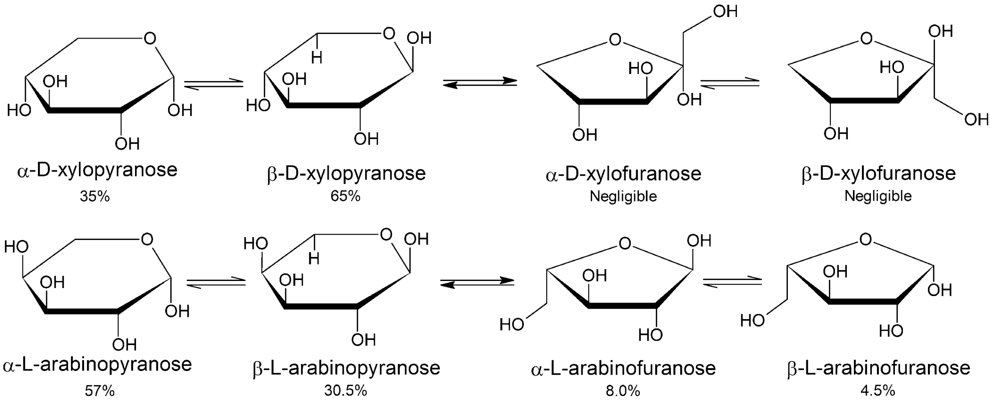


Figure 8. Effect of the temperature on the loss of D-xylose (200 mM) and of L-arabinose (20 mM) through condensation and resinification products with 13.8 (white bar) and 50.6 wt% HCOOH (grey bar).



Scheme 4. Distribution of isomers in the aqueous dilution of D-xylose and L-arabinose at 20 and 25 °C, respectively.[35,36]

furfural from L-arabinose could only be obtained at longer reaction times, which allowed the furfural to form more resinification products than in the case of D-xylose. No significant differences were observed for the reactions in a solution of 13.8 wt% HCOOH.

The loss of D-xylose or L-arabinose through condensation reactions showed a distinct trend as a function of temperature and acid concentration (Figure 8c and d). For D-xylose, an increase in temperature led to a lower amount of condensation products. The formation reaction of the condensation products, which can be also referred to as humins or humic products, may be categorised as a polymerisation reaction. Consequently, it is expected that higher temperatures would inhibit the formation of these byproducts by preventing bond formation between the xylose-derived intermediate and furfural. The loss of the D-xylose was 7–14% higher if the acid concentration was increased from 13.8 to 50.6 wt% at temperatures between 150 and 240 °C. This indicates that the condensation reaction between the xylose intermediate and furfural was catalysed significantly by formic acid as observed by the high reaction orders of [H$^+$] of the condensation reaction ($m_{X2}=1.5$). However, L-arabinose showed the opposite trends to D-xylose. The increase in temperature led to a greater loss of L-arabinose through condensation reactions. This suggests that these condensation products were formed through a direct thermal degradation reaction of L-arabinose rather than from the polymerisation between L-arabinose and furfural, which occurred with D-xylose. As shown in the previous section, the formic acid concentration had a beneficial effect on the selectivity of the dehydration of L-arabinose to furfural. The loss of L-arabinose was 9–13% lower if the acid concentration increased from 13.8 to 50.6 wt% at temperatures between 150 and 240 °C.

The differences in pentoses reactivity found in this study are in agreement with previous studies that have compared the reactivity of pentoses in different types of reactions, such as enzymatic conversion and acid or thermal degradations.[33,34] Garret and Dvorchik[33] compared the HCl-catalysed degradation of various aldopentoses (ribose, D-xylose, lyxose, L-arabinose) in the aqueous phase. Arabinose was the least reactive of the pentoses they used, and the authors attributed this to the particular steric position of the hydroxyl groups in arabinose and their role during the dehydration reaction. Notably, the tautomeric distributions of L-arabinose and D-xylose are remarkably different (Scheme 4). The predominant form of D-xylose in aqueous solutions is known to be mostly the β-pyranose form (~65%), whereas for L-arabinose the α-pyranose form is predominant (~57%) with significant amounts of α- and β-furanoses (~12.5%) at 25 °C.[35,36] The presence of a more stable tautomer (α-pyranose) in L-arabinose may hinder the dehydration of this molecule, and consequently L-arabinose would be more vulnerable to thermal degradation at temperatures over 150 °C. As a result, the selectivity towards furfural decreased as observed in this study.

Dehydration of D-glucose to HMF and LA

Kinetic modelling

The calculation routine described previously was followed, and the three sets of kinetic parameters, which fit the kinetic models of the glucose dehydration reaction shown in Scheme 3, are presented in Table 4 as well as the GF% for the concentrations of D-glucose, HMF and LA. The GF% for D-glucose concentrations obtained from the three reaction mechanisms did not differ significantly (77–78%). Mechanism 3 gave the poorest fit (57%) for HMF concentrations; however, it gave the highest GF% for LA concentrations (86%). Mechanism 2, which involves the formation of an intermediate compound,

Table 4. Kinetic parameters for the acid-catalysed dehydration of D-glucose.

	GF%[a]	Parameters	Rate constants			
			k_{G1}	k_{G2}	k_{G3}	k_{G4}
	[GLC] = 78.6%	Ln($A_{o,i}$) [min^{-1} M$^{-m_i}$]	36.4±5.5	25.8±1.8	27.1±5.8	28.5±6.3
1	[HMF] = 68.9%	$E_{A,i}$ [kJ mol^{-1}]	132.2±17.2	90.7±5.6	106.0±17.4	112.6±22.1
	[LA] = 81.3%	m_i	1.6±0.4	1.4±0.1	1.0±0.4	0.7±0.3
	[GLC] = 77.1%	Ln($A_{o,i}$) [min^{-1} M$^{-m_i}$]	36.9±3.8	26.2±1.0	15.8±1.4[b]	22.5±2.3
2	[HMF] = 73.5%	$E_{A,i}$ [kJ mol^{-1}]	132.4±11.4	95.2±3.1	71.6±4.4	79.3±7.3
	[LA] = 84.3%	m_i	1.4±0.3	0.7±0.1	0.4±0.1	1.3±0.2
	[GLC] = 77.1%	Ln($A_{o,i}$) [min^{-1} M$^{-m_i}$]	34.6±3.5	22.9±1.8	20.5±10.1[b]	–
3	[HMF] = 57.0%	$E_{A,i}$ [kJ mol^{-1}]	126.1±10.6	81.0±5.7	90.2±32.3	–
	[LA] = 86.1%	m_i	1.4±0.3	1.3±0.1	1.0±0.7	–

[a] Goodness-of-fit%. [b] min^{-1} M$^{-1-m_i}$.

fitted the experimental data of the three compounds involved in the dehydration reaction of D-glucose satisfactorily.

To support the selection of this reaction mechanism and the validation of the kinetic parameters, additional experiments with various initial concentrations of D-glucose and HMF were performed at temperatures between 165 and 170 °C in formic acid solutions of 34–35 and 60–61 wt %. The experimental data obtained from these validation experiments as well as the predicted data calculated from the three sets of kinetic parameters given in Table 4 are presented in Figure 9.

Although the second-order reaction rate proposed in Mechanisms 2 and 3 can describe the kinetic data satisfactorily, these kinetic models could not fit the concentration of HMF if the initial concentration of D-glucose was varied (Figure 9). The kinetic models obtained from Mechanisms 2 and 3 over- and underestimated the HMF concentrations, respectively, if the initial D-glucose concentration was much lower (12 mM; Figure 9 a) and much higher (210 mM; Figure 9 b) than the initial concentration used in the kinetic experiments (~100 mM). Consequently, the predicted LA concentrations were higher (Mechanism 2) or lower (Mechanism 3) than the experimental data. These two reaction mechanisms also overestimated the LA concentration if equimolar amounts of D-glucose and HMF were reacted at 170 °C in a solution of 60 wt % HCOOH (Figure 9 d). However, Mechanism 1 predicted each of the experimental scenarios presented in Figure 9 accurately and was selected as the most suitable reaction mechanism for further study.

Implications of the kinetics

The concentration profiles of D-glucose, HMF and LA obtained from the kinetic experiments along with the predicted values obtained from the kinetic model derived from Mechanism 1 are presented in Figure 10. Low conversions of D-glucose ($<$ 40 %) were observed at a reaction temperature of 130 °C, although the reaction times were extended to 12 h. The HMF yield reached a maximum as soon as a significant amount of D-glucose was converted. Higher temperatures led to higher yields of HMF, and the highest HMF yield of 12 mol % was obtained at 170 °C. An increase of the concentration of formic acid also had a positive effect on the maximum yield of HMF. As a result of the slow reaction rates of D-glucose at 130 °C, the yields of LA did not exceed 20 mol % after 12 h. The highest LA yield of 40 mol % was obtained at 170 °C.

The activation energy for the dehydration reaction of D-glucose to HMF obtained in this study (132 kJ mol^{-1}) is lower than that reported in previous studies. In their kinetics studies, Girisuta et al.[37,38] and Weingarten et al.[39] reported activation energies between 152 and 160 kJ mol^{-1} for the dehydration of D-glucose to HMF using mineral acids (H_2SO_4 or HCl) as the catalyst. This means that the catalytic activity of formic acid is less sensitive to changes in the reaction temperature than that of mineral acids. Interestingly, the activation energy for the formation reaction of condensation products from D-glucose obtained in this study (106 kJ mol^{-1}) is much lower than the reported values from previous studies (150–160 kJ mol^{-1}). This relatively lower value is beneficial to suppress the formation of condensation products by shifting the reaction temperature to

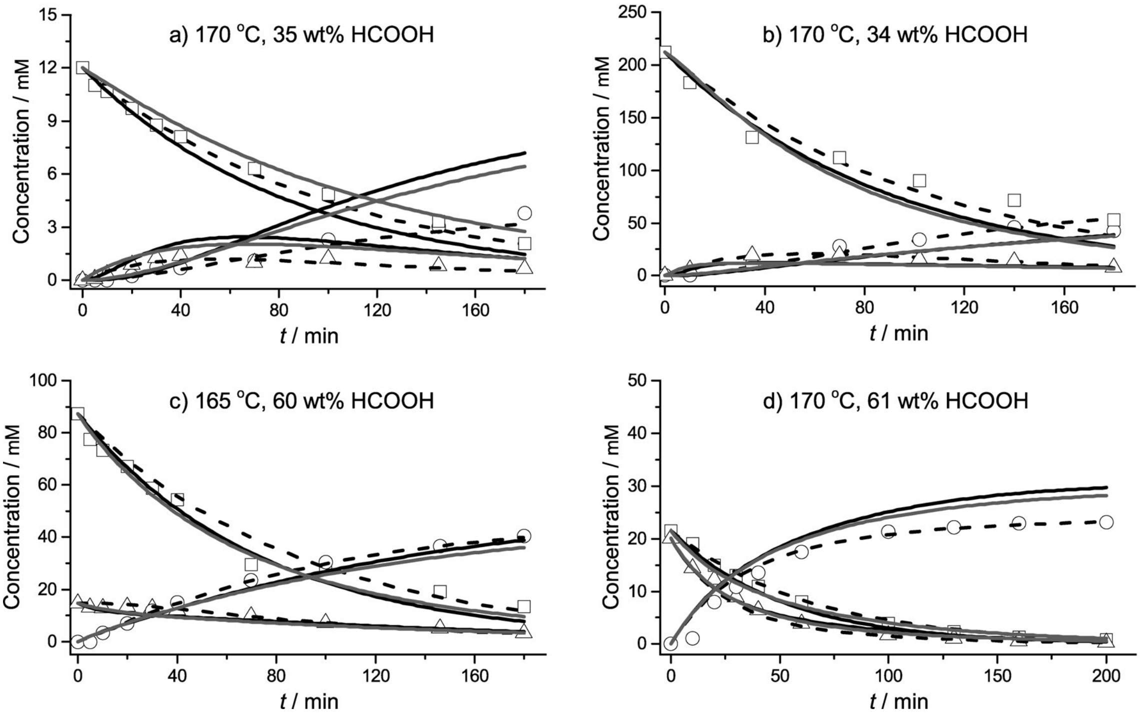


Figure 9. Concentrations of D-glucose (□), HMF (△) and LA (○) with different initial ratios of D-glucose/HMF and profile predictions from Mechanisms 1 (dashed line), 2 (solid black line) and 3 (solid grey line).

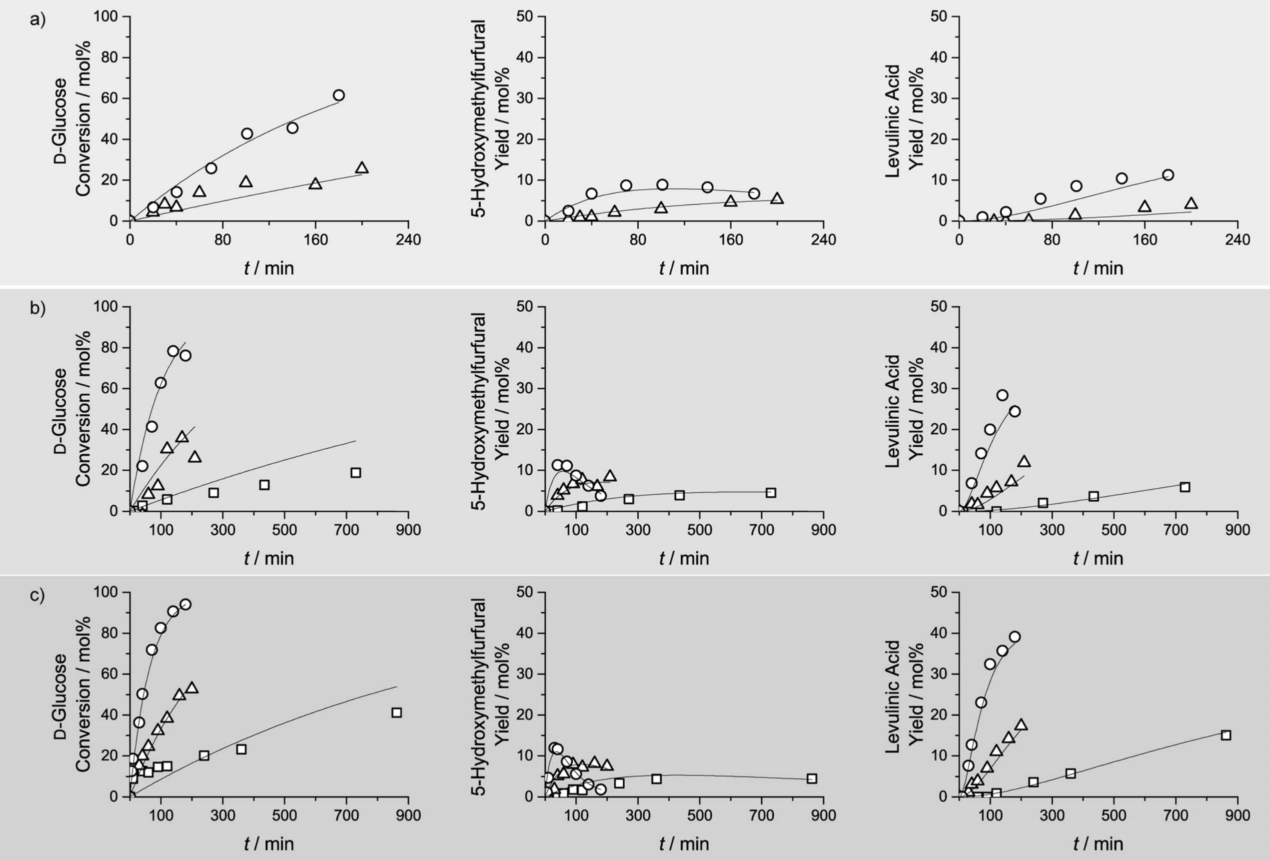


Figure 10. Experimental and modelled (solid lines) D-glucose conversion and HMF and LA yields at 130 (□), 150 (△) and 170 °C (○) with $C_{GLC,o}=82–103$ mM and different formic acid concentrations a) 12.8, b) 34.2 and c) 60.8 wt % HCOOH.

a higher value. This analysis is also supported by the experimental data, which show that the selectivity to HMF was improved at the highest reaction temperature used in this study. The activation energies obtained in this study for the conversion of HMF to the desired products (LA and formic acid) and to the undesired condensation products were in agreement with the values reported in previous studies.

In this study, the reaction orders of the effective acid concentration for the conversion of D-glucose to HMF ($m_1=1.6$) and the conversion of HMF to LA ($m_2=1.4$) were higher than the reaction orders for the conversion of glucose and HMF to the condensation products ($m_3=1.0$ and $m_4=0.7$, respectively). Therefore, an increased acid concentration would favour the selectivity of the dehydration reaction of D-glucose towards valuable products, that is, HMF, LA and formic acid.

The maximum yields of HMF and LA as a function of reaction temperature (130–240 °C) and formic acid concentration (14–64 wt %) are shown in Figure 11. HMF yields as high as

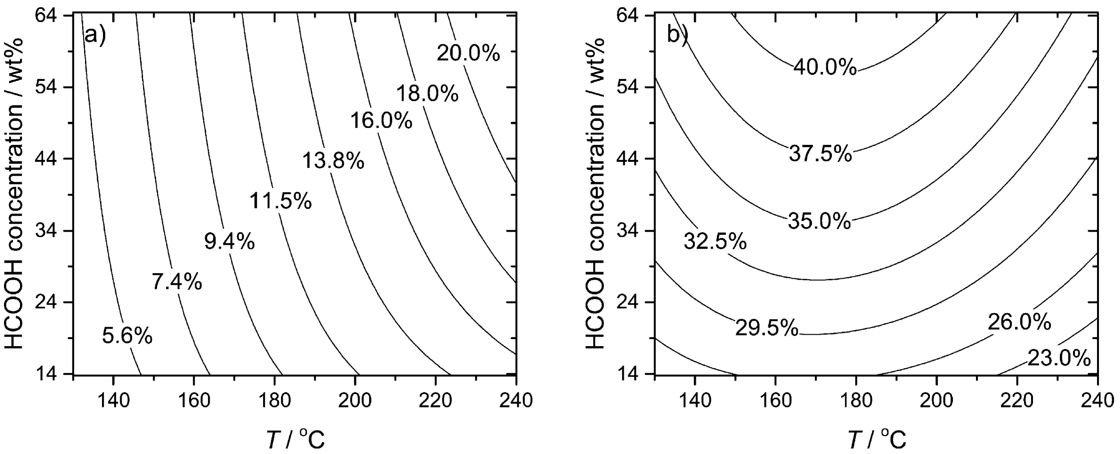


Figure 11. Maximum molar yields of a) HMF and b) LA as a function of temperature and formic acid concentration ($C_{GLC,o}=200$ mM).

18 mol % can be obtained at reaction temperatures over 212 °C and formic acid concentrations over 28 wt % (Figure 11 a). However, reaction temperatures lower than 170 °C would give a maximum yield of HMF of 11 mol %, which can only be achieved using the most concentrated solution of formic acid (64 wt %). The HMF yields obtained in this study were substantially higher than those obtained using mineral acids (0.05–0.5 M H_2SO_4 or HCl) as the catalyst, which only gave a maximum HMF yield between 2–6 mol % at 170–175 °C.[38,39]

The formation of LA was particularly promoted at reaction temperatures between 150 and 200 °C and in concentrated solutions of formic acid (> 56 wt %; Figure 11 a). The maximum LA yields estimated in this study ranged between 37 and 40 mol %. However, these yields of LA were lower than those obtained from the dehydration of D-glucose catalysed by H_2SO_4, which gave LA yields between 64–68 mol % at a reaction temperature of 140 °C.[40] At reaction temperatures over 200 °C, LA yields obtained by using formic acid as the catalyst could reach 40 mol %. Conversely, LA yields obtained at these temperatures by using H_2SO_4 with an equivalent acidity were only 30 mol %.[40] Under these circumstances, that is, reaction temperatures above 200 °C and formic acid concentrations between 25 and 64 wt %, it would be preferable to use formic acid over sulfuric acid to catalyse the dehydration reaction of D-glucose to LA.

Simultaneous dehydration of D-xylose, L-arabinose and D-glucose in aqueous mixtures of formic acid

To evaluate the applicability of the kinetic models presented in this work, two solutions that contained D-xylose, L-arabinose, D-glucose and furfural were reacted at three different temperatures (150, 160, 170 °C) and two formic acid concentrations (23 and 37 wt % HCOOH). The reaction solutions were prepared to resemble the expected composition of the liquid phase obtained from the fractionation process of lignocellulosic materials using formic acid.[13] The initial compositions of the solutions and the reaction conditions of the experiments presented in this section are listed in Table 5.

Table 5. Initial conditions of the experiments for simultaneous dehydration by formic acid of xylose, arabinose and glucose.

Sample	Concentration [mM]				Formic acid [wt %]
	xylose	arabinose	glucose	furfural	
A1	50	6	15	20	23.0
A2	50	5	10	20	37.0

The experimental pentoses and furfural concentrations as well as the predicted data obtained from the kinetic models are shown in Figure 12. Although the initial D-xylose concentration used in these experiments (50 mM) was lower than that used in the aforementioned kinetic study (200–270 mM), the kinetic model predicts the dehydration reaction of D-xylose to furfural satisfactorily. This also confirms that the kinetic models developed in this study can be applied satisfactorily in a wide range of reaction conditions.

A previous study performed by Danon et al.[41] has shown that the presence of D-glucose can promote the degradation

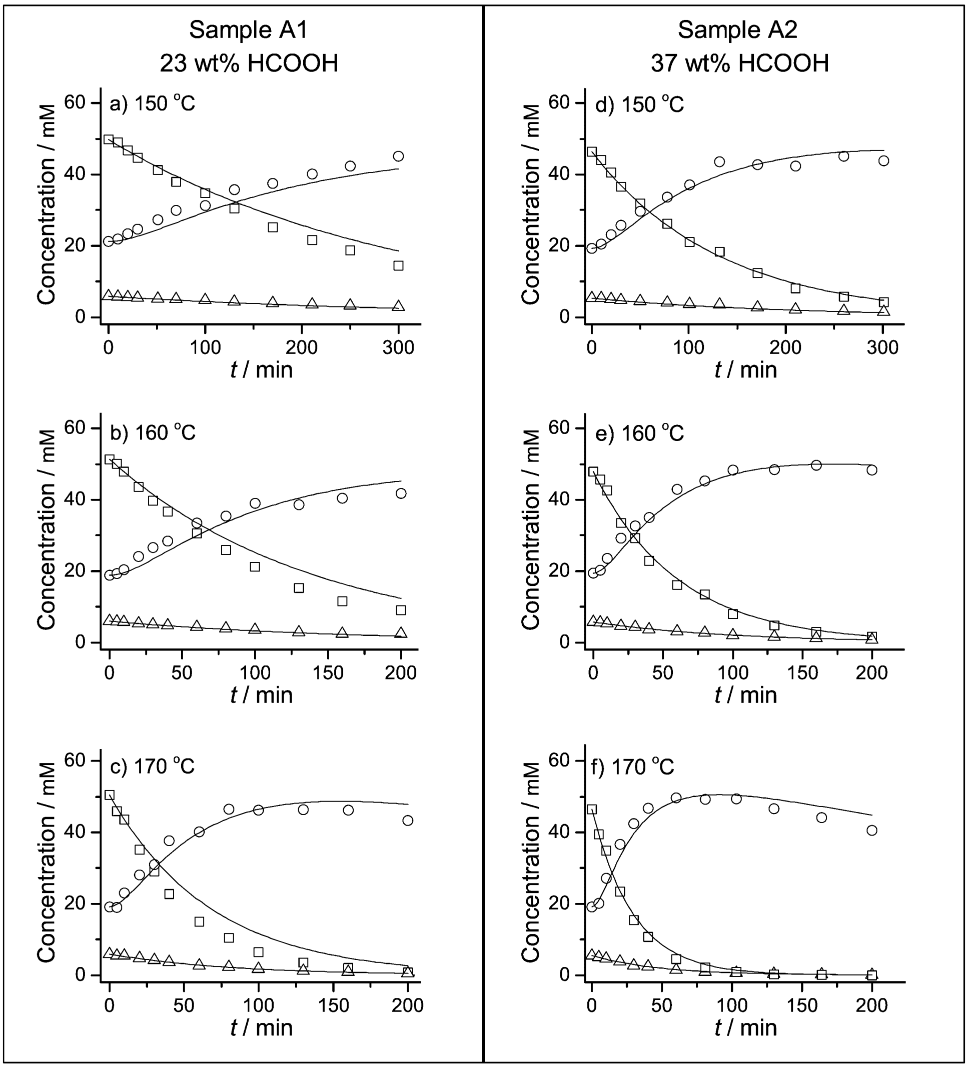


Figure 12. Concentrations of D-xylose (□), L-arabinose (△) and furfural (○) as a function of time for experiments at different temperatures. Solid lines correspond to the predictions by the kinetic models.

rate of furfural if equivalent amounts of furfural and D-glucose (50 mM furfural/50 mM D-glucose) were reacted at temperatures between 160 and 200 °C using a mixture of 50 mM HCl/500 mM NaCl as the catalyst. Based on their results at 170 °C, the furfural loss after 1 h was only 6 % in the absence of D-glucose, whereas the furfural loss increased to 22 % if an equimolar mixture of furfural and D-glucose was used as the reactant. They attributed this effect to the formation of LA, which would enhance the degradation rate of furfural. In this study, however, the formation and degradation rates of furfural were not affected by the presence of D-glucose, which was present either in sample A1 or A2 at a molar ratio of 20 mM furfural/10–15 mM D-glucose. This could be explained by the differences in the type of catalyst and also the lower concentrations of furfural and D-glucose in the solutions, which were 2–5 times lower than those used in the study reported by Danon et al.[41]

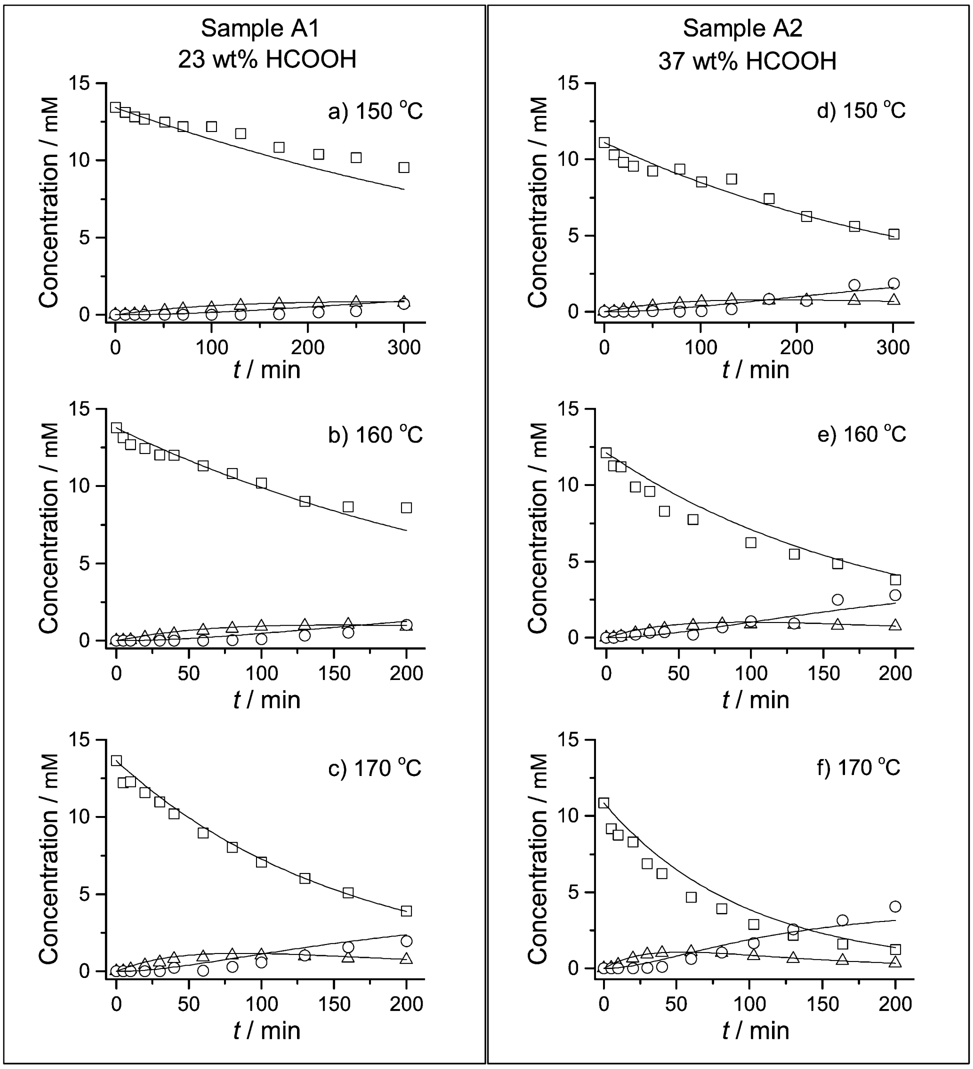


Figure 13. Concentrations of D-glucose (□), HMF (△) and LA (○) as a function of time for experiments at different temperatures. Solid lines correspond to the predictions by the kinetic models.

The concentrations of D-glucose, HMF and LA obtained by the reaction of the samples A1 and A2 at temperatures between 150 and 170 °C and formic acid concentrations between 23 and 37 wt % are shown in Figure 13. The predicted data calculated from the kinetic model fit well with the experimental data. These results support the fact that the presence of furfural in the reaction mixture had no significant effects on the conversion rate of D-glucose as well as on the selectivity to HMF and LA.

Table 6. Estimated production of furfural, HMF and LA from the hydrolysed carbohydrates in different biomass feedstocks.

Biomass	Miscanthus[37]	Wheat straw[43]	Norway spruce[44,45]
Carbohydrate composition [wt % dry basis]			
Arabinan	2.2	2.1	2.0
Xylan	19.6	21.5	6.2–9.0
Glucan	40.7	34.6	50–65
Galactomannan	1.0	0.7	15–25
Lignin	23.8	16.1	~30
Estimated yields [kg $\text{ton}_{\text{biomass}}^{-1}$] (molar yield %)[a]			
Furfural	94 (59.3)	99 (57.8)	43–56 (72.2–69.6)
HMF[b]	5 (9.4)	4 (9.5)	15–24 (8.7–9.0)
LA[b]	9 (18.6)	8 (18.3)	34–50 (20.8–20.1)

[a] Only 15 % of the glucan content was considered to be hydrolysed before conversion to HMF and LA. Reaction time to attain the maximum production of furfural with 60 wt % HCOOH and 100 g L^{-1} of biomass at 170 °C. [b] The kinetic parameters for the conversion of glucose were used for the estimation of product formation from galactose/mannose.

If we take into account the previous observations, the production of furfural, HMF and LA can be estimated in aqueous streams obtained from different types of biomass in the presence of formic acid. An estimation of the formation of these products in aqueous streams obtained from Miscanthus, wheat straw and Norway spruce is presented in Table 6. In general, high hydrolysis yields (> 80 %) can be attained during the extraction of hemicellulose sugars at high temperatures with weak acids.[42] Molar yields of furfural between 50 and 60 mol % are expected from the conversion at 170 °C of feedstocks with high arabinoxylan content, such as Miscanthus, wheat straw and hardwoods. However, softwoods, such as spruce, would lead to relatively higher furfural yields

(> 70 mol %) because of the lower amount of pentose carbohydrates present in these materials. Similarly, as a result of the high content of hexose sugars, that is, glucose, galactose and mannose, greater amounts of HMF and LA can be formed from hemicellulose hydrolysates obtained from softwoods (up to 24 kg HMF and 50 kg levulinic acid ton^{-1} of Norway spruce).

Conclusions

This report presents a comprehensive study on the conversions of the monosaccharides found in the hemicellulose fraction of biomass to high-value chemicals, such as furfural, 5-hydroxymethylfurfural and levulinic acid. We started with a systematic investigation of the kinetics of major components in the hemicelluloses fraction of biomass, that is, D-xylose, L-arabinose and D-glucose. The kinetics experiments for each sugar were performed at temperatures between 130 and 170 °C in various formic acid solutions (10–64 wt %) that act as the reaction solvent as well as the catalyst. In this study, three of the reaction mechanisms reported most commonly for the conversion of pentoses and hexose were examined thoroughly and fitted to the experimental data. Based on the statistical analyses and the kinetic model validation using additional experimental data, the kinetic models for the dehydration reactions of D-xylose, L-arabinose and D-glucose were selected. The implications of these kinetic models on the selectivity of each sugar to the desired products were discussed extensively. Finally, the kinetic models developed for each sugar were combined and used to model the reaction kinetics of solutions that resemble the liquid phase obtained from the fractionation process using formic acid. The kinetic models developed in this study provide detailed insights on the conversion of the hemicellulose fraction of biomass to valuable chemicals, and further optimisation studies can utilise these kinetic models to design and develop efficient processes for the fractionation and valorisation of lignocellulosic biomass.

Experimental Section

Materials and chemicals

D-Xylose, D-glucose, L-arabinose, formic acid (> 98.0 %), LA (> 98), HMF (> 99.0 %) and furfural (> 99.0 %) were of analytical grade and purchased from Sigma–Aldrich. All reaction solutions and dilutions for HPLC analysis were prepared with deionised water (18.2 MΩ cm).

Dehydration experiments

The dehydration reactions were performed in ACE glass pressure tubes (2.54 cm O.D. × 10.2 cm) that comprised polytetrafluoroethylene (PTFE) plugs and fluoroelastomer with tetrafluorolethylene additives (FETFE) O-rings. The tube reactors can hold an operational pressure up to 1.0 MPa. An aqueous solution of the model compound (5 mL, 2–250 mM) was mixed with the corresponding amount of formic acid and was poured into the pressure tubes. The tubes were sealed, and each tube was placed for a defined period of time in an oil bath set at the particular reaction temperature (130–170 °C). On completion, each tube was removed from the oil bath and immersed in a cold water bath to quench the reaction. The effective concentration of acid as hydronium ion [H^+] was calculated from the dissociation equilibrium constant and the activity coefficients evaluated at the reaction temperature using the Debye–Hückel equation and the temperature-dependent function of the dissociation constant of formic acid as proposed by Kim et al.[46]

Analytical measurements

The concentrations of D-xylose, L-arabinose, D-glucose, HMF, LA and furfural in the samples were quantified using HPLC. The measurement of sugars was conducted by using an ICS-3000 system (Dionex Corp., Sunnyvale, CA) equipped with an AS50 autosampler (10 μL sample-loop injection), dual pump, column oven, and integrated electrochemical detector for the quantification of the carbohydrates. An ion exchange column (Hi-Plex H 0.77 × 30.0 cm, 8 μm) was used for the combined elution of the monosaccharides. The column was operated at 65 °C by isocratic elution with deionised water (0.65 mL min^{-1}) and a post-column flow of sodium hydroxide (0.3 M, 0.1 mL min^{-1}) for detection in the electrochemical detector. In addition, a diode array detector (DAD-3000RS) set at 278 nm was used for the measurement of furfural and HMF. LA was separated in a Dionex Acclaim Organic Acid (5 μm, 0.4 × 25.0 cm) column, which was operated at 30 °C and was eluted using 100 mM Na_2SO_4 at pH of 2.65 at a flow rate of 0.8 mL min^{-1}.

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Keywords: biomass · carbohydrates · hydrolysis · kinetics · reaction mechanisms

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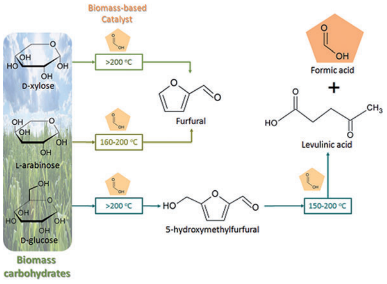
Hemicellulose’s next top model: The pretreatment of lignocellulosic biomass produces liquid streams with hemicellulose sugars, which can be further converted to high-value chemicals. This study investigates the reaction kinetics of the conversion of major hemicellulose sugars of biomass using formic acid as catalyst. Kinetic models are used to model the conversion of sugars in solutions obtained from the fractionation of biomass.



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Conversion of Hemicellulose Sugars Catalyzed by Formic Acid: Kinetics of the Dehydration of D-Xylose, L-Arabinose, and D-Glucose