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Bioenergy II: Furfural Destruction Kinetics during Sulphuric Acid-Catalyzed Production from Biomass*

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Abstract

The interest for furfural has increased in the last years due to its potential for competing with oil derivatives as platform chemical. In addition, furfural, derived from C_5 sugars, can play a key role in the valorization of the hemicellulose contained in biomass when considering the development of a modern biorefinery concept. The development of such new and competitive biorefinery processes must be based on accurate kinetic data for the reactions involving furfural in the conditions used for its production.

This work addresses the determination of furfural destruction kinetics in aqueous acidic environment, using sulphuric acid as catalyst, in the temperature range 150 - 200°C, acid concentration range 36.4 - 145.5 mM and furfural initial concentration between 60.4 and 72.5 mM. These studies were carried out using a recently built lab-scale titanium reactor that enables liquid phase reactions in a relatively broad range of conditions.

The obtained results show that destruction of furfural follows first-order reaction kinetics within the range of temperature and acid concentration evaluated. Moreover, the proposed kinetic model takes into account the effects of temperature and acid dilution on the ions activity, and thus H_3O^+ , by using the electrolyte Non-Random Two-Liquid (eNRTL) model. By using this approach, the rate constant dependence on temperature could be described by the Arrhenius law and thus the activation energy could be estimated as being 125.1 [kJ/mol] and the preexponential factor $3.71 \cdot 10^{11}$ [s⁻¹]. Separation of different reaction products was

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achieved by means of HPLC, these products were not yet completely identified. Contrarily to what is reported in previous works, formic acid formation from furfural under the tested conditions can be regarded as playing a far less pronounced role than suggested before.

KEYWORDS: furfural, biorefinery, acid catalysis, chemicals from biomass

Introduction

Furfural is nowadays one of the most important biomass derived chemicals having a market of roughly 300 kton/year, Corma et al. [2007], and it has numerous applications in many chemical sectors. Besides being a solvent itself, it is also used as starting material for the production of several furanic compounds like furfuryl alcohol and tetrahydrofuran (THF) among the others, Zeitsch [2000], Gandini and Belgacem [1997]. In a bio-based economy, furfural can also replace or substitute some oil derivatives as platform chemical and be a starting material for liquid fuels production. In fact, furanic biofuels have lately been referred as representing a very interesting option to current biofuels, showing advantageous qualities, Mascal and Nikitin [2008], Kar and Deveci [2006]. This is especially relevant when also considering the increasing concern on the competition of first generation biofuels for feed and food crops. On the other hand, as furfural is derived from C_5 sugars contained in biomass, its integrated production in a modern biorefinery concept might represent a profitable way for valorizing hemicellulose, Kamm and Kamm [2004, 2007]. Despite the relative simplicity of current furfural production processes, Zeitsch [2000], there are still some questions that must be addressed concerning the chemistry of C₅ sugars which might lead to significant improvements of furfural production processes. Although it is well known that C_5 sugars like D-Xylose can be converted quantitatively into furfural under acidic conditions, Dunlop [1948], Garret and Dvorchik [1969], Zeitsch [2000], Root et al. [1959], there are many aspects of the reaction that are not totally clear yet, especially concerning the reaction kinetics of both furfural formation and destruction under the same conditions of pH and temperature. The information available covers a wide range of conditions and shows inconsistencies between different works, Root et al. [1959], Dunlop [1948], Garret and Dvorchik [1969], Antal Jr et al. [1991]. In order to clarify these and other issues related with this process, a new lab-scale titanium reactor was designed and built to enable liquid phase reactions in a relatively broad range of conditions of pressure, temperature and pH. The work reported here concerns the use of this new reactor in the study of furfural destruction under aqueous acidic conditions, where sulphuric acid is used as catalyst.

Materials and methods

Furfural reagent grade (Sigma-Aldrich, 99%) was used as the only model compound in the experiments after distillation under reduced pressure (50 mbar) for further purification. An acidic aqueous solution of furfural was prepared using demineralized water and H_2SO_4 . The acid concentration varied between 145.5 and 36.4 mM, while initial concentration of furfural varied between 60.4 and 72.5 mM. Analysis of the reaction products was carried out by means of an HPLC apparatus equipped with a Resex ROA-Organic acid column, 8% cross linked H^+ , 300×7.80 mm, (Phenomenex Inc., Torrance, CA, USA). A Marathon XT auto-sampler (Separations, Ambacht, NL) was used to enhance reproducibility. Quantification of the components was carried out by means of both Refractive Index detector (Varian Model 350) and UV detector (Varian Model 310 Pro Star) in series.

The mobile phase consisted of a 10 mM sulphuric acid solution in demineralized water, the HPLC was operating at a flow rate of 0.6 ml/min and the column was heated to 80 $^{\circ}$ C.

Experimental setup



Figure 1: Experimental setup

The experimental setup consists of a coiled tube reactor immersed in a thermostatic oil bath. The reactor is made of titanium grade 2 (Merinox, Alblasserdam, NL) to ensure high resistance to corrosion and minimal catalytic effects. The tube reactor has an external diameter of 3.2 mm, internal diameter of 1.7 mm, and a length of 4.40 m. The reactants are fed to the reactor by a Waters HPLC pump,



Figure 2: $E(\vartheta)$ for different flow-rates, at $T = 180^{\circ}C$

while the reaction temperature is precisely controlled and kept constant by the oil bath. The reaction solution is rapidly heated up to the set temperature by an electrical heater consisting of an insulated aluminium block which encloses the tube reactor for a length of approximately 15 cm. Downstream the reactor the solution is cooled down by means of a double pipe heat exchanger fed with tap water, see figure 1.

In the range of process conditions considered, the flow in the tube reactor is within the laminar region as the maximum Reynolds number achieved in this work is around 320. This implies the need of a careful evaluation of the residence time distribution (RTD) along the reactor. To accurately determine the RTD, tests were carried out injecting a small volume of a tracer solution (50% vol formic acid in water) in the proximity of the reactor inlet through an in-line injector, see figure 1, and detecting its concentration distribution in time at the reactor outlet by means of a refractive index detector. This procedure was repeated for various conditions of flow rate and temperature and the detector and the injector were connected to a terminal for data collection and processing.

In figure 2 some experimental RTD curves $E(\vartheta)$ are depicted. All the curves are normalized, ϑ being a dimensionless time scale:

$$\vartheta = \frac{t}{MO_1}$$
 where $MO_1 = \int_0^\infty tE(t)dt$ and $\int_0^\infty E(t)dt = 1$

The quantity MO_1 is the first momentum of the normalized RTD curve E(t), which represents the average residence time of a molecule in the reactor. Normalized variance σ_{ϑ} can be easily calculated by integration of the RTD curves. It is relevant to estimate Péclet (*Pe*) number for all curves using equation (1):

$$\sigma_{\vartheta}^{2} = \frac{2Pe - 2 + 2e^{-Pe}}{Pe^{2}} \quad \Rightarrow \quad Pe \simeq \frac{2}{\sigma_{\vartheta}^{2}} for Pe > 100 \tag{1}$$

as the *Pe* number gives an indication of how axial dispersion counteracts the spreading effect due to the laminar velocity profile. In the cases investigated *Pe* varies from 164 to 775, while MO_1 varies from 2.76 to 37.21 min. A higher *Pe* number means a behavior closer to an ideal plug-flow reactor, as shown in figure 2 where RTD curves present an asymmetrical shape which approaches a sharper Gaussian distribution when the residence time becomes longer and *Pe* higher, Westerterp et al. [1987].

Considering a first order reaction, and knowing E(t), real conversion rates can be calculated by applying equation (2):

$$\frac{C}{C_0} = \int_0^\infty e^{-kt} E(t) dt \tag{2}$$

These values are shown to very closely approach the theoretical conversion rates calculated as $(C/C_0) = e^{-kt^*}$ when $t^* = MO_1$ as shown in figure 3 for a hypothetical case. Thus, when MO_1 is taken into account as the average residence time in the reactor, uncertainties due to the laminar flow spreading effect can be neglected even at higher flow-rates and shorter residence times. In this case the reactor can be considered as an ideal plug-flow reactor.

Main reactor characteristics validation

Since the entire length of the tube is not at reaction temperature and in order to precisely assess the average time of the reactant under actual reaction conditions, the length of the tube at those conditions needed to be estimated. This was done by residence time measurements as described below.

The tube reactor was considered to be the sum of a two portions of tube in series at different temperatures, being the volume V_H at reaction temperature and V_R at room temperature. Temperature transitories were neglected and instantaneous



Figure 3: Theoretical and real conversion rates when $k = 0.1[min^{-1}]$

temperature increments were assumed to occur within the length of the two heat exchangers. For simplicity V_H and V_R are assumed to be constant for all conditions of temperature and flow rates. Thus the total volume between the injector and the detector is $V_{tot} = V_H + V_R$; in the same way the average residence time in the reactor can be considered to be the sum of the average residence time in the high temperature portion of the reactor, which is the one of interest for the reaction, and the average residence time in the rest of the volume, being then $\tau_{tot} = \tau_H + \tau_R$. Considering \dot{m} to be the mass flow rate and ρ the density of the solution, by the mass conservation one derives:

$$\tau_R = \frac{\rho_R V_R}{\dot{m}}; \qquad \tau_H = \frac{\rho_H V_H}{\dot{m}} \tag{3}$$

which results in:

$$\tau_{tot}\dot{m} = V_{tot}\rho_R + V_H\left(\rho_H - \rho_R\right) \tag{4}$$

When the reactor is at room temperature, for every \dot{m} :

$$\dot{m} = \frac{V_{tot}}{\tau_{tot}^0} \rho_R \tag{5}$$

where τ_{tot}^0 is the average residence time in the reactor when the reaction temperature equals the room temperature. τ_{tot}^0 can be measured directly by detecting the tracer



Figure 4: Apparent reactor volume V^* against solution density ρ_H . (*) Averaged measured values at constant T; (···) measurement dispersion; (-) model used in this work

solution at the outlet of the reactor. Combining equations (4) and (5) results in the following equation:

$$V^* = \frac{\tau_{tot}}{\tau_{tot}^0} V_{tot} = V_R + V_H \frac{\rho_H}{\rho_R}$$
(6)

The volume V^* in equation (6) represents the total apparent volume of the reactor which decreases as the solution density ρ_H decreases with increasing reaction temperature. Experimental assessment of V^* variation with ρ_H allows the estimation of V_H and V_R . In this way the average residence time τ_H can be calculated by equation (3) for every \dot{m} and temperature. Operating with very diluted solutions, density ρ_H was assumed to closely approach that of water and it was computed, given pressure and temperature, using the highly accurate thermodynamic model for water included in the RefProp package by NIST, Lemmon et al. [2002], where the FluidProp package was used as interface, Colonna and Van der Stelt [2005]. Experimental results are shown in figure 4 where V^* is plotted against ρ_H . The solid line in the figure 4 was drawn given V_H , which was derived by estimating the temperature profile along the tube, and deriving V_R by least square fitting. As shown in figure 4 the average error introduced by using the calculated reaction residence time is always less than 3%, and can be mostly regarded as the result of the pump flow rate variation.

Operations

After achieving the desired temperature in the oil bath and pre-heater, the flow-rate \dot{m} was set in order to get the desired τ_H . The operating pressure was kept always around 60 bar by means of a back-pressure regulator, which is higher than the saturated pressure of water in the temperature range considered to ensure entirely liquid phase operation in the reactor. For each set of temperature and flow rate \dot{m} conditions the system was run for a time longer than the corresponding $\vartheta = 1$ (see figure 2) to ensure that steady state was achieved and then a sample was recovered in a vial at the reactor outlet and analyzed. The operation was carried out for every desired τ_H , and every set of temperature and initial pH.

Results and discussion

The aim of this work is to assess the furfural rate of destruction in the particular case of low concentrations of both the acid and furfural itself. The reason for this choice is to resemble reaction conditions when furfural concentration is likely to be kept low by continuously separating it from the reactor mixture to avoid its destruction, and acid concentration is not very high.

Reaction conditions varied between 150 and 200 °C and H_2SO_4 concentration between 145.5 and 36.4 mM (pH between 0.81 and 1.36 at 298 K). Furfural is a very reactive compound and is known to easily polymerize in both acid and basic environment following various routes, moreover, in aqueous acidic media, the furan heterocycle is reported to undergo ring opening resulting in aliphatic openchain products, Gandini and Belgacem [1997]. Under the conditions considered in this work the reaction rate presents a behavior similar to a first order reaction with respect to furfural concentration, hence furfural-furfural polymerization reactions leading to resins seem unlikely to take place, in agreement with earlier works, Williams and Dunlop [1948], Dunlop [1948].

The model proposed takes here into account the protonation of the furfural molecule which is readily transformed, resulting in :

$$\frac{dC_F}{dt} = -k^* C_F \tag{7}$$

The kinetic parameter^{*} k was estimated by least square fitting starting from experimental results. The k^* values showed an evident dependence on temperature as well as on H₂SO₄ initial concentration, and thus an acid catalysis correlation, taking into account the H₃O⁺ influence on the reaction, needed to be formulated. It is known from literature that the second dissociation constant of sulphuric acid

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Figure 5: Arrhenius plot of $k = \frac{k^*}{a_{H_2O^+}} [s^{-1}]$ for the temperature range 150-200 °C

varies significantly with temperature and with the ionic strength of the solution, Dickinson et al. [1990], Marshall and Jones [1966], Quist et al. [1965], and it is important to take into account those temperature effects in the kinetic formulation as observed by many authors, Antal Jr et al. [1991], Zeitsch [2000]. Within the range of conditions of interest for this work, aqueous sulphuric acid can be considered with good approximation to be present as H_3O^+ and HSO_4^- . The bi-sulfate ion at those P,T conditions is only a very weak acid ($pKa_2 \simeq 4$), Dickinson et al. [1990]. Thus H_3O^+ concentration can be assumed to equal the initial acid concentration (Table 1). Nevertheless the formulation $k^* = k[H_3O^+]$ is not satisfactory, showing, at constant temperature, a less than linear dependence on $[H_3O^+]$, and a temperature dependence at constant $[H_3O^+]$ somewhat deviating from Arrhenius formulation.

For acid catalyzed reactions a common approach is to make use of the acidity function H_{\circ} proposed by Hammett and Paul [1934], which takes into account the equilibrium between a weak base and a its protonated form in an acidic solutions. For this work a more general formulation was preferred, which can be used more easily for the considered range of conditions of temperature, pressure and ionic strength. Moreover the Hammett acidity function for low acid concentration approaches the $pH = -Log(a_{H_3O^+})$, Arnaut et al. [2007].

Based on these considerations the ion activity $a_{H O^+} = \gamma_{H O^+} [H_3 O^+]$ was considered instead of the simple ion molar concentration $[H_3 O^+]$, which possibly accounts for the lower "availability" of the ions with increasing ionic strength as well as for the changing dielectric characteristics of the solvent induced by temperature,

Initial H ₂ SO ₄ molar concentration				
	0.145 M	0.109 M	0.073 M	0.036 M
T [^o C]	$\left[H_{3}O^{+} ight](\gamma_{H_{3}O^{+}})$	$\left[H_{3}O^{+}\right]\left(\gamma_{H_{3}O^{+}}\right)$	$\left[H_{3}O^{+} ight](\gamma_{H_{3}O^{+}})$	$\left[H_{3}O^{+}\right]\left(\gamma_{H_{3}O^{+}}\right)$
190	0.146 (0.566)	0.109 (0.607)	0.073 (0.660)	0.036 (0.739)
180	0.146 (0.573)	0.110 (0.614)	0.073 (0.667)	0.036 (0.744)
170	0.146 (0.578)	0.110 (0.620)	0.073 (0.673)	0.036 (0.750)
160	0.147 (0.583)	0.110 (0.625)	0.073 (0.678)	0.036 (0.754)

Table 1: H_3O^+ molar concentration $[H_3O^+]$ and relative activity coefficient $\gamma_{H_3O^+}$ at various temperature and initial acid concentration as estimated by the eNRTL model

Arnaut et al. [2007], Moore [1974]. Using the formulation $k^* = k a_{H_3O^+}$, the resulting rate constant k showed a clear Arrhenius dependence on temperature in the range of conditions considered as depicted in figure 5. Deviation of two measurements at lower temperature can be explained by the amplification of measurement errors in a range of conditions where furfural concentration decay is more difficult to quantify. In this temperature range the reaction is very slow and thus k^* values rather small ($\sim 10^{-5}$).

Sulphuric acid thermodynamics at various pressure and temperature conditions have been thouroughly studied by many authors, Dickinson et al. [1990], Quist et al. [1965], Marshall and Jones [1966]. Nevertheless, an explicit correlation for individual ion activity coefficients depending on temperature, pressure and ionic strength has not yet been formulated. Alternatively some authors have made use of either the Pitzer model, Dickinson et al. [1990], Haubrock et al. [2005], or the electrolytes NRTL (eNRTL) model, Haghtalab et al. [2004]. For simplicity in this work the latter model was chosen and Aspen PlusTM was used for estimating individual ion activity coefficients under actual reaction conditions, see table 1.

The solid line in figure 5, was drawn by least square fitting of the experimental measurements and it refers to the Arrhenius formulation $k = Aexp(-\frac{E_a}{RT})$ where $ln(A) = 26.64[s^{-1}]$ and the activation energy $E_a = 125.1[kJ/mol]$. From these kinetic parameters enthalpy and entropy of activation could easily be derived, resulting in $\Delta H^{\ddagger} = 121.2 [kJ/mol]$ and $\Delta S^{\ddagger} = -35.6 [J/molK]$ at 473K. The negative value for the activation entropy shows a decrease in entropy passing through the activate state, which in this case could mean the association of the furfural molecule with the proton, [Moore, 1974].

Such results are not in agreement with the results reported by Williams and Dunlop [1948] who reports the activation energy for this reaction to be 20 kcal/mol (83.7 kJ/mol). Major differences can be due to the fact that in that study non-ideality of the acid solution as well as the sulphuric acid second dissociation constant varia-

tion with temperature were not taken into account. As shown in table 1, ion activity decreases with temperature and, by taking that effect into account, the variation of k with temperature results to be more pronounced, i.e. the activation energy results to be higher. On the other hand a better agreement is observed when comparing the experimental results reported in the same work with those predicted by using the model proposed here under the same conditions (0.1 N H₂SO₄ at 160°C for 180 min), in this case the deviation in terms of furfural concentration is always lower than 7%.

With respect to the furfural destruction reaction products, in the same work by Williams and Dunlop [1948], it was claimed that formic acid had been identified, which was suggested to result from the hydrolytic fission of the furfural aldehyde group. In this work formic acid couldn't be clearly identified and quantified, and by a qualitative analysis of the HPLC-UV chromatograms, its presence, if it can't be excluded, can be regarded as marginal under the tested conditions, see figure 6. Formic acid detected during furfural production from pentosans might rather be considered as the result of parallel sugar reactions, as noticed by Antal Jr et al. [1991], while a stronger evidence of rehydration of the furfural molecule to components like reductic acid has been shown by Feather [1969].

Preliminary subsequent studies using HCl as acid catalyst instead of H_2SO_4 , have shown some inconsistencies namely in the rate of furfural destruction, which appears to be faster than what could be expected by using the reaction kinetics proposed in this work. Nevertheless a similar dependence on temperature was evidenced. Such results suggest a more complex mechanism involving not only the H_3O^+ ion but also the anions HSO_4^- and Cl^- , which might play a role in the catalysis of the reaction. Further studies are needed in this direction.

Conclusions

This work reports the study of furfural destruction reaction kinetics in the temperature range $150 - 200^{\circ}$ C and H₂SO₄ concentration between 36 and 145 mM. The reaction rate presented a good agreement with the kinetic model proposed in which a first order dependence on furfural concentration was assumed. The rate constant for this reaction was expressed as $k^* = k a_{H_3O^+}$ where the ion activity $(a_{H_3O^+})$ was estimated by means of the eNRTL model. The influence of temperature on the rate constant k showed a clear agreement with the Arrhenius law, being the activation energy for this reaction reported to be 125.1 kJ/mol and the pre-exponential factor $3.71 \cdot 10^{11}$ [s⁻¹]. Furthermore, in qualitative terms, no evidence of prevailing formic acid formation from furfural was observed under the tested conditions.



Figure 6: Qualitative comparison of HPLC-UV chromatograms relative to furfural destruction reaction products and a standard solution of formic acid in water

Preliminary studies showed discrepancies regarding the rate of reaction when using HCl as a catalyst instead of H_2SO_4 , indicating that the anions resulting from the acid dissociation might also significantly influence the reaction mechanism. Thus the results achieved in this work can not be extrapolated as such for different homogeneous acid catalysts. Future work has been planned to elucidate the influence of the anion which might help clarifying the reaction mechanism.

Nomenclature

mM	millimolar [mmol/liter]
eNRTL	electrolyte Non-Random Two-Liquid
HPLC	High Performance Liquid Chromatography
RTD	Residence Time Distribution
t	Time [min]
θ	Dimensionless time [-]
MO_1	First momentum of the distribution curve $E(t)$ [min]
$\sigma_artheta$	Variance of the distribution curve $E(\vartheta)$ [-]
Pe	Péclet number [-]
С	Concentration [mol/liter]
k	Reaction rate constant $[t^{-1}]$
V	Volume [1]
τ	Average residence time [min]
ṁ	Mass flow-rate [g/min]
ρ	Density [g/l]
a	Ion activity in aqueous solution [-]
pK_a	Sulphuric acid second dissociation constant [-]

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