Furfural production by reactive stripping

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Furfural Production by Reactive Stripping: Process Optimization by a Combined Modeling and Experimental Approach

V. Krzelj, J. van Kampen, J. van der Schaar, and M. F. Neira d’Angelo

Chemical Reactor Engineering Laboratory, Chemical Engineering and Chemistry Department, Eindhoven University of Technology, Eindhoven, The Netherlands

ABSTRACT: In this paper, we describe the continuous production of furfural coupled with in situ stripping using hydrogen gas. With respect to the conventional semibatch process, which requires excessive steam as stripping agent and results in highly diluted furfural, this new process configuration reduces the net energy input, increases the efficiency of the downstream hydrogenation of furfural, and proposes a shift toward a continuous operation. Based on well-established thermodynamic data and previously reported kinetics, we have developed a first-principle reactor model that successfully describes the experimental observations without the use of any fitting parameters. This robust predictive model is used to further optimize the continuous production of furfural via this route.

INTRODUCTION

Following concerns about the environment and the long-term availability of resources, the scientific community is increasingly devoted to ease the transition to a biobased economy.1−4 Biomass, as the only renewable source of carbon, is perceived as the ideal feedstock for the production of chemicals, and biobased furanics are foreseen to play a major role as biobased building blocks. For example, furfural is a key intermediate in the valorization of the hemicellulose fraction of biomass.5−8 Approximately 60−70% of the furfural produced worldwide is further hydrogenated to furfuryl alcohol for the production of sand binders in the foundry industry and the remaining part is used as extractant for aromatics from lubricating oils, purification solvent for C4 and C5 hydrocarbons, reactive solvent, wetting agent, chemical feedstock for other furan derivatives and others.9 Furthermore, furfuryl alcohol offers alternative leads, such as the possibility to convert to levulinate esters or ethylfurfuryl ether.10 Other uses of furfural include its hydrogenation to methylfurfural and methyltetrahydrofuran (i.e., two promising gasoline components) or decarbonylation to furan and subsequently hydrogenation to tetrahydrofuran.8 Recently, it was also shown that furfural can be further hydrogenated to cyclopentanone, which is a potentially attractive monomer in the polymer industry.9,10 Currently, the production of furfural is performed via hemicellulose hydrolysis and dehydration in acid media, usually with sulfuric acid, operated in a semibatch mode.10,11 Corn cobs or bagasse are usually the starting material, because of their high hemicellulose content, while the remaining biomass constituents (i.e., cellulose and lignin) are not being utilized. A large amount of steam is used to strip the furfural produced from the reaction medium, thus minimizing its subsequent degradation via condensation and resinification reactions.10,11 While this process uses an excessive amount of steam, the usual production yield remains rather low. As a consequence, several industrial plants based on this process (e.g., Agirifane, Escher Wyss, Rosenflue) were discontinued because of the high costs,10 while newer pilot processes are being developed with the aim to improve the overall efficiency and yield (e.g., Biofine, Vedernikovs, Suprayield, CIMV, Lignol, MTC).11 In the case of Huaxia/Westpro plants, currently operating in China, 25−35 tons of steam is consumed per ton of furfural at a yield of ~50% of theoretical pentosan content.12 Further increasing furfural stripping renders product dilution, which eventually results in expensive downstream separation. Even more, recycling pure steam back to the reactor without additional purification steps is not possible, since water and furfural form a minimum-boiling-point azeotrope. From this point of view, the use of a "noncondensable" gas (e.g., CO2 or hydrogen) as a stripping agent may be an attractive alternative, because they can be easily separated from furfural by a flash step and subsequently recycled back to the reactor. Agirrezabal and co-workers compared the nitrogen stripping process and stream stripping process, and showed that the former can lead up to 60% reduction in overall utility costs.13 Interestingly, if hydrogen is used as a stripping agent, the mixtures furfural/hydrogen may be directly fed to the downstream hydrogenation reactors with no additional separation steps. Despite the promising results anticipated by Agirrezabal and coauthors, the thermodynamic and kinetic implications of such process configuration during the synthesis of furfural, and, thus, on the overall efficiency of the process, have not been thoroughly investigated.14,15

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Furthermore, a shift from semibatch to a continuous operation mode would be extremely advantageous from an industrial implementation perspective.

This work aims to contribute to the understanding and eventual development of a more efficient and continuous furfural production process using a noncondensable gas (e.g., hydrogen) as a stripping agent. We have performed the synthesis of furfural using xylose as a model compound, representative of other feedstocks, such as hemicellulose hydrolysates, which will become of crucial importance in the future biorefineries, where biomass is fractionated prior to valorization of the individual streams, or even more-complex biomass feeds. Xylose yields similar amounts of furfural as other biomass feedstocks, such as corncob, while it still provides a well-defined reaction system that allowed us to study the effect of thermodynamics and reactor configuration on the overall performance. To this end, a predictive activity-based first-principle reactor model was developed for process optimization purposes. This model considers several thermodynamic and kinetic models and successfully describes the experimental observations from semibatch and continuous reactions using nitrogen as a stripping gas. Furthermore, the model can be extrapolated to other noncondensable gases and is hereby used to evaluate the influence of various process parameters (i.e., stripping gas flow rate, temperature, feed and catalyst concentration) on xylose conversion and selectivity toward furfural.

## METHODS

### Experimental Setup and Procedure.

The experiments were performed in a 300 mL mechanically agitated titanium autoclave reactor, as sketched in Scheme 1. The reactor may be operated in semibatch mode with continuous stripping (see Scheme 2a) or in a continuous/fed-batch mode where both gas and liquid are continuously fed but only gas exits the reactor (see Scheme 2b). Both gas and liquid flow rates are controlled by Bronkhorst mass flow controllers (MFC) and a Gilson HPLC pump, respectively, and the reactor pressure is regulated by a Bronkhorst back pressure regulator (PC) located after a condensing vessel at the reactor outlet. Note that the gas flow rates are reported under normal conditions (i.e., 20 °C and 1 atm).

Two-thirds of the reactor were filled with a solution of sulfuric acid (0.5 wt %) before the start of each experiment. The reactor then was purged, pressurized, and heated up to the desired reaction conditions (i.e., 10 bar, 170 °C). Both the reactor wall and the reactor lid were heated to avoid cold surfaces and reflux of the vapors. Absence of temperature gradients inside the reactor were ensured by checking that the water collected in the condensing vessel perfectly matches the model predictions, assuming isothermal operation. After stable temperature conditions were reached, initial concentration of xylose was achieved by feeding the concentrated xylose solution over a short period of time (1–2 min). The end of this feeding time marks start of the reaction (i.e., t = 0). At this moment, a preheated nitrogen stream was introduced from the bottom of the reactor. Two different modes of operation were tested: (a) semibatch with continuous nitrogen stripping and (b) fed-batch with continuous nitrogen stripping, as sketched in Scheme 2. From this point onward, the semibatch operation will be referred as batch, and the fed-batch will be referred as continuous.

### Product Analysis.

The samples were analyzed by HPLC Shimadzu LC 20AD. The column used was Agilent Metacarb 67C. Xylose was detected with a refractive index detector (RI), while the furfural was detected with a PDA detector. The mobile phase was HPLC grade water with a flow rate of 0.5 mL/min. The column oven was set to a temperature of 85 °C. The conversion of xylose (X$_{xyl}$), total furfural yield (Y$_T$), and furfural yield in condensate (Y$_C$) were calculated using the following equations:

$$X_{xyl} = \frac{[\text{xylose}]}{[\text{xylose}]_0}$$

$$Y_T = \frac{[\text{xylose} + \text{furfural}]_0}{[\text{xylose}]_0}$$

$$Y_C = \frac{[\text{furfural}]_0}{[\text{xylose}]_0}$$
\[ X_{xy} (\%) = \left(1 - \frac{\text{moles of xylose at time } t}{\text{initial moles of xylose + moles of xylose fed}}\right) \times 100 \]  

\[ Y_r = \frac{\text{moles of furfural at time } t \text{ in reactor} + \text{moles of furfural at time } t \text{ in condensate}}{\text{initial moles of xylose + moles of xylose fed}} \times 100 \]  

\[ Y_C = \frac{\text{moles of furfural at time } t \text{ in condensate}}{\text{initial moles of xylose + moles of xylose fed}} \times 100 \]

## MODEL

**Assumptions.** The reactor model developed in this study assumes that the reactor presents and ideally mixed behavior, and that the mass transfer between the phases is sufficiently fast to guarantee equilibrium conditions, which is consistent with the experimental observations. Furthermore, the vapor–liquid equilibrium is described by the modified Raoult’s law, and the gas phase is assumed to obey the ideal gas law. Xylose, sulfuric acid, and side products are considered to be nonvolatile under the reaction conditions. All the relevant equations are presented in the following sections.

**Kinetic Models.** Several kinetic models have been reported for this reaction. The various reaction schemes and kinetic data are listed in Table 1.

As can be seen in Table 1, Model A considers the direct dehydration of xylose to furfural, and two degradation routes: one from xylose and one from furfural. In addition, this model assumes the same temperature dependence for the rate of the two xylose-consuming reactions. On the other hand, model B assumes that there is no direct decomposition of xylose, but together with furfural xylose undergoes condensation reactions to form degradation products. Lastly, model C includes an additional route for furfural formation via the dehydration of xylulose, which is a xylose isomer. In this model, it is assumed that both xylose and xylulose, as well as the product furfural, are susceptible to degradation reactions. In this work, kinetic models A, B, and C have been considered for the prediction of the activity data without using any fitting parameter. Model A includes the dependency of the kinetic constant on the activity of the acid. In this work, the activity coefficient of H\textsubscript{2}SO\textsubscript{4} was obtained from eNRTL Aspen database, and fitted as a function of temperature and acid concentration. Note that the values originally reported for the kinetic constants \((k)\) in models B and C were estimated for a fixed acid concentration. In this work, however, the concentration of acid during the batch mode of operation will not remain constant, because water evaporates together with furfural during the stripping process. To incorporate the effect of increasing acid concentration during the reactive stripping process, a first-order kinetics, with respect to the concentration of protons, has been assumed, and a new kinetic constant \((k^*)\) has been defined accordingly.

Notice that the values of \(k^*\) have been reported in Table 1. Finally, it should also be mentioned that model B has been originally proposed by Weingarten\textsuperscript{17} to describe the dehydration of xylose with HCl instead of H\textsubscript{2}SO\textsubscript{4}, which is a diprotic acid. However, it is well-known that the second dissociation of sulfuric acid is largely dependent on temperature,\textsuperscript{19} and that the bisulfate ion becomes a very weak acid at the temperatures of interest of this work. Therefore, the second dissociation step is neglected.

**Thermodynamic Models.** Several thermodynamic models have been considered for the prediction of activity coefficients. These are listed in Table 2.

**Mole Balances.** The ordinary differential equations (ODEs) that describe the system are derived from the mole balances:

\[
\frac{dN_{xy}}{dt} = F_{xy} - (k_1 + k_2)C_{xy}C_{acid}V_L
\]  

\[
\frac{dN_{fur,L}}{dt} = k_1C_{xy}C_{acid}V_L - k_3C_{fur}C_{acid}V_L - k_4\left(\gamma_{fur}F_{fur}V_L\frac{p_{sat}}{RT} - N_{fur,L}\right)
\]  

\[
\frac{dN_{fur,V}}{dt} = K_4\left(\gamma_{fur}F_{fur}V_L\frac{p_{sat}}{RT} - N_{fur,V}\right) - \frac{F_{fur}V_{fur}}{1 - \gamma_{fur} - \gamma_{water}}
\]  

\[
\frac{dN_{water,L}}{dt} = F_{water} + 3k_3C_{xy}C_{acid}V_L - K_4\left(\gamma_{water}F_{water}V_L\frac{p_{sat}}{RT} - N_{water,L}\right)
\]

### Table 1. Kinetic Models

<table>
<thead>
<tr>
<th>Model</th>
<th>Expression</th>
<th>(A_1) (\text{[min}\textsuperscript{-1}])</th>
<th>(E_a) (\text{[kJ/mol]})</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(X \Rightarrow F + 3H_2O^+) (k^* = \gamma_2[H_2O]_L)</td>
<td>(31.60)</td>
<td>(133.30)</td>
<td>16</td>
</tr>
<tr>
<td>A</td>
<td>(X \Rightarrow DP_1) (k = k^*[H_2O]_L)</td>
<td>(30.39)</td>
<td>(133.30)</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>(F \Rightarrow DP_2)</td>
<td>(26.64)</td>
<td>(123.10)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>(X \Rightarrow F + 3H_2O^+) (k^* = \gamma_2[H_2O]_L)</td>
<td>(28.53)</td>
<td>(123.91)</td>
<td>17</td>
</tr>
<tr>
<td>B</td>
<td>(X + F \Rightarrow DP_1) (k = k^*[H_2O]_L)</td>
<td>(15.78)</td>
<td>(72.47)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>(F \Rightarrow DP_2)</td>
<td>(10.73)</td>
<td>(67.58)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>(Xu \Rightarrow X)</td>
<td>(0.3)</td>
<td>(67.4)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>(Xu \Rightarrow F)</td>
<td>(4.5)</td>
<td>(166.2)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>(Xu \Rightarrow DP_1)</td>
<td>(2.3)</td>
<td>(162.9)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>(Xu \Rightarrow DP_2)</td>
<td>(28)</td>
<td>(134.5)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>(F \Rightarrow DP_3)</td>
<td>(0.2)</td>
<td>(72.0)</td>
<td></td>
</tr>
</tbody>
</table>

\^X\equiv\text{xylose}; \ F\equiv\text{furfural}; \ Xu\equiv\text{xylulose}; \ DP_1, \ DP_2, \ \text{and} \ DP_3 \equiv \text{degradation products.}
Table 2. Thermodynamic Models

<table>
<thead>
<tr>
<th>model</th>
<th>equations</th>
<th>parameters</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van Laar</td>
<td>[ \ln y_1 = A_{12} \left( \frac{x_2 A_{12}}{x_1 + x_2 A_{12}} \right)^2 ]</td>
<td>[ A_{12} = \frac{205.5}{T_w} + 0.9017 ]</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>[ \ln y_2 = A_{12} \left( \frac{x_1}{A_{12} x_1 + A_{12} x_2} \right)^2 ]</td>
<td>[ A_{12} = \frac{909.1}{T_w} - 0.6089 ]</td>
<td></td>
</tr>
<tr>
<td>NRTL</td>
<td>[ \ln y_1 = x_1 \left( \frac{G_{12}}{x_1 + x_2 G_{12}} \right)^2 + \frac{\tau_{12} G_{12}}{x_1 + x_2 G_{12}} ]</td>
<td>[ \tau_{12} = a_{12} + \frac{b_{12}}{T} ]</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>[ G_{12} = \exp \left( -a_{12} \tau_{12} \right) ]</td>
<td>[ a_{12} = 0.2 ]</td>
<td></td>
</tr>
<tr>
<td>Wilson</td>
<td>[ \ln y_1 = -\ln(x_1 + x_2) + x_1 \left( \frac{\lambda_{12}}{x_1 + x_2 \lambda_{12}} - \frac{\lambda_{21}}{x_1 + x_2 \lambda_{21}} \right) ]</td>
<td>[ \ln \lambda_{12} = a_{12} + \frac{b_{12}}{T} ]</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>[ a_{12} = -2.34 ]</td>
<td>[ a_{21} = 21.10 ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ b_{12} = -346.94 ]</td>
<td>[ b_{21} = -8627.31 ]</td>
<td></td>
</tr>
<tr>
<td>UNIQUAC</td>
<td>[ \ln y_1 = -\ln \left( \Phi \left( x_1 \right) \right) + \frac{Z}{2} q_i \ln \left( \Phi \left( x_1 \right) \right) + \Phi \left( x_1 \right) \ln \left( \frac{\tau_1}{\tau_{12}} \right) - q_i \ln \left( \frac{\tau_1}{\tau_{12}} \right) ]</td>
<td>[ r_{12} = a_{12} + \frac{b_{12}}{T} ]</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>[ \Phi \left( x_1 \right) = \frac{x_{s1}}{x_{s1} + x_{s2}} ]</td>
<td>[ a_{12} = 2.134, a_{21} = 1.143 ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ \theta_i = \frac{x_{s1}}{x_{s1} + x_{s2}} ]</td>
<td>[ b_{12} = 826.83, b_{21} = 244.67 ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ l_1 = \frac{Z}{2} (r_1 - q_i) - (r_1 - 1) ]</td>
<td>[ r_1 = 3.168, r_2 = 0.92 ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ q_i = 2.484, ; q_i = 1.4 ]</td>
<td>[ Z = 5 ]</td>
<td></td>
</tr>
</tbody>
</table>

The system of ODEs was solved numerically by ODE15s in MATLAB.

## RESULTS AND DISCUSSION

### Batch Operation: Experimental Performance

The yield of furfural at different stripping rates is shown in Figure 1. Furfural was the only product detected in the condensate samples.

The batchwise dehydration of xylose without in situ stripping gives ~30% of furfural yield under the explored conditions. Introducing a continuous gas stream at a flow rate of 150 NmL/min renders a sharp increase in the furfural yield up to 70%. Rapid removal of furfural from the reaction medium hinders its consequent degradation, thus increasing the final furfural selectivity. Yet, under these conditions, ~30% of the furfural produced remains in the reaction medium, which indicates that the rate of furfural stripping is still lower than that of its production. Ideally, one would aim at these two
processes (i.e., furfural production and stripping) to occur at the same rate in order to achieve 100% furfural selectivity. However, while the amount of furfural stripped out of the reactor increases upon increasing the gas flow rate, the total furfural yield remains almost unaffected. Even worse, further increasing the gas flow has a negative effect on the final furfural yield. This can be attributed to the unavoidable evaporation of water under these reaction conditions and the consequent increase in the concentration of all soluble species (e.g., xylose, sulfuric acid, furfural), which leads to intensive furfural degradation. Hence, excessive stripping has a negative impact on the furfural yield.

Figure 3 displays the effect of the nitrogen volumetric flow rate on the experimental and predicted mass balance of xylose and furfural (distributed between reactor and condensate), as a function of time. Accordingly, the temporal evolution of the xylose conversion and furfural yields under those conditions are calculated and reported in Figure 2. Note that the model predictions presented in these figures make use of the best fitting kinetics and thermodynamic models, which will be discussed in the following section. As expected, these trends describe the typical profile of reactions in series, which, in this case, is the conversion of xylose to furfural in the reactor, followed by the transfer of furfural in the reaction solution to the stripping stream, which is eventually recovered in the condenser. In this study, we report both the yield of furfural recovered in the condenser and the total yield, including the remaining furfural in the reactor. Consistent with previous observations, the experimental results plotted in Figure 3 reveal that the amount of furfural stripped out of the reactor increases as the nitrogen flow rate increases. Nevertheless, the beneficial effect of the stripping on the final furfural yield diminishes at very large gas flow rates (i.e., 500 NmL/min in this study), because of excessive water coevaporation and a visible increase in the extent of degradation reactions. These results also show that xylose conversion is almost unaffected by the nitrogen flow rate, and, thus, by the furfural stripping rate. To a certain extent, it is not surprising that the changes in furfural concentration caused by in situ removal will not affect the rate of xylose consumption. Nevertheless, the largest gas flow rate explored in this study leads to a noticeable increase in the xylose conversion. Significant water evaporation under such conditions results in an increase of the concentration of all soluble species, including that of sulfuric acid, which will certainly affect the rate of xylose conversion to furfural. Furthermore, the direct consumption of xylose in the degradation reactions with other soluble humin precursors, might be accelerated under such conditions.

Figure 1. Maximum yield of furfural for different stripping flows. Conditions: \( T = 170 \, ^\circ\text{C}, \, p = 10 \, \text{bar}, \, C_{xylo} = 1 \, \text{wt \%}, \, C_{H_2SO_4} = 0.5 \, \text{wt \%}. \)

Figure 2. Experimental data and model predictions of conversion, total yield of furfural and yield of furfural in condensate. Conditions: \( T = 170 \, ^\circ\text{C}, \, p = 10 \, \text{bar}, \, C_{xylo} = 1 \, \text{wt \%}, \, C_{H_2SO_4} = 0.5 \, \text{wt \%}. \) Kinetic model A; Thermodynamic model NRTL ASPEN: (a) \( F_{N_2} = 150 \, \text{NmL/min}, \) (b) \( F_{N_2} = 300 \, \text{NmL/min}, \) (c) \( F_{N_2} = 500 \, \text{NmL/min}. \)
In view of process profitability, besides increasing the total product yield, achieving high furfural concentrations in the condenser is also desired. Figure 4 shows the experimental and predicted concentration of furfural in the condensate, as a function of residence time and gas flow rate. Regardless of the gas flow rate, the temporal evolution of furfural concentration follows a volcano curve, with a maximum that shifts to lower residence times for the larger gas flow rates. The concentration of furfural in the condensate is determined by the furfural water stripped out of the reaction mixture. On the one hand, the molar flow of water evaporation for a given inlet gas flow rate remains constant throughout the process, assuming thermodynamic equilibrium and a negligible change in the concentration of water in the reactor. Logically, water evaporation increases with the nitrogen flow rate. On the other hand, the extent of furfural evaporation is dependent on its concentration in the reaction mixture, which is a function of the residence time. At the start of the reaction, the total stripping rate exceeds that of the furfural production, which results in a large water-to-furfural ratio in the outlet gas stream. As the reaction proceeds, the furfural production peaks and furfural is stripped out in high concentrations. Note that the peak in furfural production rate is achieved at earlier residence times when operating under fast stripping rates. This is attributed to an increase in acid concentration under these conditions. At high xylose conversion, furfural production rates begin to fade while the rate of water stripping remains constant. Accordingly, the processes can be further optimized by operating the reactor at maximum furfural concentration. For example, a well-mixed continuous system may be suitable for this purpose.

Despite the undesired coevaporation of water, the thermodynamic equilibrium of furfural—water mixtures favors furfural evaporation over that of water (Figure 5). The model predictions of vapor liquid equilibrium (VLE) shown in Figure 5 are in good agreement with the experimental data found in the literature.\textsuperscript{23} Note that the concentration of furfural in the condenser reaches higher values than the initial xylose concentration (i.e., 1 wt %). Thus, besides preventing furfural degradation by in situ product removal, this process configuration manages to reduce the energy demand in the downstream processing of furfural, which is produced, isolated, and concentrated in one single step. Nevertheless, operating at very high gas flow rates leads to unnecessary large amounts of water evaporation (i.e., to low furfural concentrations in the condensate, as shown in Figure 4), and to limited or no benefits, in terms of furfural yield. Thus, the optimum flow rate...
of the stripping gas can be determined, for example, from an economic evaluation that takes into account the gains in product yield and the losses in water evaporation and product dilution. Process optimization may be attained by tuning the VLE of this system. For example, the addition of salts such as sodium sulfate can minimize the evaporation of water by increasing its boiling point. In light of these findings, low temperature operations may also become attractive, although an obvious sacrifice in terms of reaction rate is envisioned.

**Batch Operation: Model Predictions.** Figures 2 and 3 show that the model is able to accurately predict the experimental data obtained at lower stripping rates when using NRTL and kinetic model A to describe the thermodynamic equilibrium and the reaction mechanism, respectively. However, at higher stripping rates (i.e., 500 NmL/min), this model overestimates the amount of xylose in the reactor and that of furfural in the condensate at longer residence times. In other words, the extent of degradation reactions involving the consumption of furfural, and likely xylose, is greater than the model predicts under these experimental conditions. Note that the effect of water evaporation on the concentration of xylose and sulfuric acid, and the impact of these on the xylose consumption rate, are taken into consideration in this model.

Figure 4 also indicates that the model successfully predicts the concentration of furfural in the condensate at lower stripping rates, strongly suggesting that, indeed, the NRTL thermodynamic model is suitable to describe the system under consideration. Thus, the discrepancies between the experiments and the model predictions at large gas flow rates are attributed to an oversimplification of the degradation reactions in the kinetic model A. In particular, the participation in degradation reactions of furfural, and perhaps xylose and other soluble species (i.e., intermediates or soluble degradation products), under increasingly acidic conditions, is insufficiently described. In addition, the reversible oligomerization of xylose under acid conditions is plausible, and it may potentially explain the observed increase in xylose conversion at high stripping rates. Figure 6 shows the increase of sulfuric acid concentration for each of the stripping rates. Further investigation on the reaction mechanism is needed for an accurate description of the system at high acid concentration.

**Figure 5.** Furfural–water VLE at 7.7 bar. Experimental data reproduced from Curtis et al. with permission from CSIRO Publishing and predictions from NRTL ASPEN model.

**Figure 6.** Experimental data and model predictions of sulfuric acid concentration. Conditions: $T = 170 ^\circ C$, $p = 10$ bar, $C_{xylo} = 1$ wt %, $C_{H_2SO_4} = 0.5$ wt %. Kinetic model A; Thermodynamic model NRTL ASPEN.
temperatures (i.e., with a large activation energy), although no kinetic fitting was reported for this specific reaction.

Finally, Ershova proposed that not only xylose and furfural are subject to independent degradation reactions, but also a reaction intermediate (i.e., xylulose) is converted to degradation products (i.e., kinetic model C). This model fails to predict the experimental trends recorded in the present study.

Figure 7. Experimental data and model predictions of the amounts of furfural in reactor and condensate for various thermodynamic models. Conditions: $T = 170 \degree C$, $p = 10$ bar, $C_{\text{xylin}} = 1$ wt %, $C_{\text{H}_2\text{SO}_4} = 0.5$ wt %. Kinetic model A: (a) $F_{N_1} = 150 \text{ NmL/min}$, (b) $F_{N_1} = 300 \text{ NmL/min}$, and (c) $F_{N_1} = 500 \text{ NmL/min}$.

Figure 8. Experimental data and model predictions of the xylose conversion and furfural yield in reactor and condensate for various kinetic models. Conditions: $T = 170 \degree C$, $p = 10$ bar, $C_{\text{xylin}} = 1$ wt %, $C_{\text{H}_2\text{SO}_4} = 0.5$ wt %. Thermodynamic model NRTL ASPEN: (a) $F_{N_1} = 150 \text{ NmL/min}$, (b) $F_{N_1} = 300 \text{ NmL/min}$, and (c) $F_{N_1} = 500 \text{ NmL/min}$. Reaction intermediate (i.e., xylulose) is converted to degradation products (i.e., kinetic model C). This model fails to predict the experimental trends recorded in the present study. More precisely, while the consumption of xylose is described accurately by the model, the formation of furfural is...
underpredicted. In fact, the presence of xylulose in the reaction mixture was not confirmed in the current study. These findings suggest that indeed the formation of xylulose and its further degradation is not a significant reaction path under these experimental conditions. This is consistent with the current understanding that the isomerization of xylose to xylulose is not significant in the presence of Brønsted acids at \( \sim 180-220 \degree C \).\(^{18,24}\)

**Continuous Operation: Model Predictions and Experimental Validation.** Figure 9a shows the observed and predicted values of xylose conversion and furfural yield, as a function of time on stream for a continuous operation. Unlike in the previous sections, we now incorporate a continuous liquid feed of xylose in water. The concentration and flow of this stream is adjusted to compensate for water evaporation and to match reaction rate of xylose at those conditions. As observed in Figure 9a, the model successfully predicts the experimental results, even with the largest flow rate of stripping gas. This proves that, indeed, the excessive evaporation of water and the consequent increase in the concentration of soluble species caused the discrepancies between model and experiments during the batch operation under high stripping rates.

As observed in Figure 9a, the system did not reach steady-state conditions during the initial 150 min tested in the experiments. Since there is no liquid outlet, note that the only possible steady-state conversion is 100%. Nevertheless, with the experimental conditions tested in this study (e.g., inlet flow rate and concentrations), such a degree of conversion would only be reached with a reaction volume greater that that of the reactor used herein. Thus, it was essentially impossible to reach steady-state conditions under the experimental conditions under evaluation. Prior to the steady-state conditions, the unreacted xylose and nonevaporated water accumulate in the reactor, leading to an obvious volume increase, as shown in Figure 9b. Notably, the model was able to successfully predict the overall mass balance of the reactor and condensate in the transient state, and is therefore considered reliable to predict the final steady state.

Figure 10 shows the model predictions at 170 \degree C for different nitrogen flows. Under these reaction conditions, \( \sim 100, 200, \) and 400 min are required to reach steady state for nitrogen flow rates of 150, 300, and 500 NmL/min, respectively (see Figure 10b). As shown in Figure 10a, the steady-state conversion of xylose indeed reaches 100% in all cases, whereas the yield of furfural is \( \sim 70\% \), with a slight positive effect of stripping rate on the final yield. Here, we can observe that most of the furfural is collected in the condensate, particularly when the stripping rate increases, although an important dilution of the collected furfural is observed for the highest furfural stripping rate. An important technical challenge of the continuous system operated as a fed-batch (i.e., without a liquid outlet) is the long-term accumulation of degradation products (i.e., humins) inside the reactor. A possible solution would be to introduce a liquid outlet and recirculate the stream after filtration of the reaction mixture externally.

Table 3 presents the differences in furfural production rate, furfural concentration in the condensate, and furfural yield for continuous and batch modes of operation. For the batch system, the residence time considered to calculate the production rate was the moment when 99% of the furfural was in the condensate. A remarkable 4–6-fold increase in the furfural production rate is obtained in the continuous reactor, with respect to the batch system. This result may sound counterintuitive as it is well-known that a CSTR (i.e., similar to
the continuous reactor (in this study) operates at lower reactant concentrations, and therefore lower reaction rates, than a batch reactor operated under similar conditions (e.g., same starting concentrations and residence time). In this case, however, the continuous reactor is, in fact, a fed-batch reactor (i.e., with no liquid outlet) where the concentration of xylose is maintained under initial conditions (i.e., 1 wt %) by constantly feeding a xylose solution with the exact concentration to balance the rates of xylose conversion and that of water evaporation. On the other hand, the concentration of xylose in the batch reactor decreases over time, thus leading to a lower overall reaction rate.

As shown in Table 3, it is possible to increase the furfural productivity and the furfural concentration in the condensate when the reactor is operated continuously, with respect to the reference batch process. Increasing the nitrogen flow rate in the continuous system leads to a slightly better yield, but at the expense of a more diluted product in the condensate.

**Comparison of the Industrial Process and the Proposed Process.** A comparison between the industrial process (i.e., using steam stripping) and the process under investigation (i.e., using noncondensable gases such as H₂ as a stripping agent), on the basis of the net energy consumption, is shown in Table 4. The benchmark industrial process is based on the batch HUAXEI plant.¹² The latter is described by the model predictions of the batch operation under optimized conditions. An important difference between these two examples is the feed used. While the industrial process uses biomass (e.g., corn cob or bagasse) as a starting material, our results are obtained using xylose as model compound. One

![Figure 10](image.png)

**Figure 10.** Model predictions of (a) the conversion and yield for the continuous system and (b) the xylose and furfural concentrations in the reactor, and (c) weight percentage of furfural in the condensate. Conditions: $T = 170$ °C, $p = 10$ bar, $C_{xylo} = 1$ wt %, $C_{H₂SO₄} = 0.5$ wt %. $F_{H₂O} = 0.4 \times 10^{-3}$, $0.81 \times 10^{-3}$, and $1.35 \times 10^{-3}$ mol/s; $F_{xylo} = 6.47 \times 10^{-6}$ mol/s, and $F_{N₂} = 150, 300, and 500$ NmL/min. Kinetic model A; thermodynamic model NRTL ASPEN.

### Table 3. Comparison of Batch and Continuous Operation

<table>
<thead>
<tr>
<th>$N₂$ flow [NmL/min]</th>
<th>$Y_C$ [%]</th>
<th>production rate [g/h]</th>
<th>$FUR_C$ [wt %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>68.19</td>
<td>0.258</td>
<td>0.527</td>
</tr>
<tr>
<td>300</td>
<td>72.24</td>
<td>0.364</td>
<td>0.686</td>
</tr>
<tr>
<td>500</td>
<td>74.45 $(56.64^{a})$</td>
<td>0.524 $(0.423^{a})$</td>
<td>0.966 $(0.760^{a})$</td>
</tr>
</tbody>
</table>

**Continuous Mode**

<table>
<thead>
<tr>
<th>$N₂$ flow [NmL/min]</th>
<th>$Y_C$ [%]</th>
<th>production rate [g/h]</th>
<th>$FUR_C$ [wt %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>68.78</td>
<td>1.537</td>
<td>5.366</td>
</tr>
<tr>
<td>300</td>
<td>72.64</td>
<td>1.625</td>
<td>2.950</td>
</tr>
<tr>
<td>500</td>
<td>74.30</td>
<td>1.663</td>
<td>1.844</td>
</tr>
</tbody>
</table>

¹Experimental values are displayed in brackets for reference. Notice that, in the specific case of large stripping rates, the model predictions differ significantly from the experimental values obtained during batch operation.

### Table 4. Comparison of the Industrial Process and the Proposed Process

<table>
<thead>
<tr>
<th></th>
<th>Huaxei plant</th>
<th>Scenario 1 Stripping</th>
<th>Scenario 2 Stripping</th>
</tr>
</thead>
<tbody>
<tr>
<td>yield in condensate [%]</td>
<td>50</td>
<td>50</td>
<td>72.2</td>
</tr>
<tr>
<td>xylose feed [wt%]</td>
<td>4.2</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>steam feed [ton/ton fur]</td>
<td>25–35</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>$H₂$ feed [ton/ton fur]</td>
<td>n/a</td>
<td>0.68</td>
<td>0.97</td>
</tr>
<tr>
<td>energy for steam generation [GJ/ton fur]</td>
<td>82.7–115.8</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>energy for preheating $H₂$ feed [GJ/ton fur]</td>
<td>n/a</td>
<td>1.4</td>
<td>2.0</td>
</tr>
<tr>
<td>energy for in situ steam generation [GJ/ton fur]</td>
<td>n/a</td>
<td>65.7</td>
<td>93.9</td>
</tr>
<tr>
<td>energy for preheating reaction mixture [GJ/ton fur]</td>
<td>40.9</td>
<td>40.9</td>
<td>40.9</td>
</tr>
<tr>
<td>sum [GJ/ton fur]</td>
<td>123.6–156.7</td>
<td>108.1</td>
<td>136.8</td>
</tr>
</tbody>
</table>

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may argue that, with respect to the conversion of xylose, processing biomass would lead to additional degradation reactions and thus lower furfural yield. However, as shown by Agirrezabal-Telleira et al., processing corn cobs and xylose actually yield similar amounts of furfural when using nitrogen as a stripping agent. This may be well-understood by the fact that the most critical part of the conversion of biomass to furfural, both in terms of reaction rate and selectivity, concerns the dehydration of sugars, while the initial hydrolysis step is faster and does not present major selectivity issues. Thus, for the sake of this study, we trust that (i) this is a valid comparison and (ii) the conclusions derived from it, with respect to energy savings, will remain applicable when using more-complex feedstocks such as hemicellulose or biomass. In our analysis, two specific scenarios have been taken into account: (1) a scenario in which the batch reactor is optimized to reach a yield of 50% of furfural, similar to the benchmark case; and (2) a scenario in which the furfural yield is maximized. In all cases, the xylose concentration equals to that in the Huaxei plant (i.e., feed of 12 wt % corn cobs with 35% pentose content).

As shown in Table 4, the use of noncondensable gases leads to an important reduction (ca. 30%) in the energy usage when the process is optimized to reach 50% furfural yield. Greater energy savings may be achieved if the hot furfural/H₂ outlet stream is directly fed to the downstream hydrogenation unit (e.g., for cyclopentatone synthesis), and later on, the remaining unreacted H₂ is recirculated back to the dehydration reactor. This strategy would eliminate the need to preheat H₂ before the hydrogenation unit, and would further reduce the energy requirements of the hydrogenation unit. The comparison shown in Table 4 also reveals that further increasing the furfural yields from 50% to over 72% (i.e., by extending the residence time and therefore increasing the amount of both furfural and water stripping) has an energy penalty, because of excessive water evaporation. Note that, in Scenario 2, the energy costs are 26% higher, since, under these conditions, the rate of water evaporation exceeds that of furfural formation. Hence, process optimization may be accomplished by trading-off the feed and energy costs. Inexpensive biomass is obviously an attractive feedstock that can make this process feasible even when a large part of the feed (e.g., cellulose and lignin) is mis-utilized and furfural yields are relatively low, with respect to the theoretical maximum, as long as the energy demands are maintained low. Although the exact threshold will be dependent on energy prices, we envision that the energy savings achieved by the proposed process, particularly in Scenario 1, will be instrumental in thevalorization of low cost biomass feeds. On the other hand, processing more expensive hemicellulose or even sugar-rich hydrolyzate streams will become of increased relevance in the context of future biorefineries, where raw biomass is first fractionated prior to valorization of the individual fractions to valuable chemicals. Since hemicellulose hydrolysis and sugar dehydration happen under similar conditions, decoupling the processes in different steps does not make a significant difference, in terms of energy demands. However, the pressure on product yield will become more important to compensate for the additional biomass processing costs. Thus, the proposed process, particularly in Scenario 2, is expected to play an important role when processing more costly feedstocks. Here, additional revenues from the valorization of other stream (e.g., cellulose and lignin) also should be taken into account.

## CONCLUSIONS

In this paper, we demonstrate by experiments and first-principle modeling that using noncondensable gases instead of steam as a stripping agent results in important energy savings in the furfural production process. We further suggest that using hydrogen can lead to additional energy integration routes and, thus, greater energy savings, if furfural is later hydrogenated to added value chemicals. Using batch experiments with continuous nitrogen stripping, we show that there is an optimal stripping flow rate that results in a maximum furfural yield of ~72%. Larger stripping flow rates render excessive water evaporation, leading to increased furfural degradation rates. Furthermore, the continuous synthesis of furfural was demonstrated experimentally by coupling the batch process with a continuous feed of xylose in water. Simultaneously with the experimental study, a first-principle reactor model was developed using various thermodynamic and kinetic models available in the literature. This model successfully predicted the experimental observations of the batch and continuous operations in a large range of experimental conditions without the use of any fitting parameters. The kinetics by Marcotullio et al. and the NRTL thermodynamic model (using Aspen database) gave the most accurate prediction of the experimental results. Yet, significant discrepancies between the model predictions and the experiments were observed when using the highest stripping flow rate (i.e., 500 NmL/min) under batch conditions. This was attributed to the limitations of the kinetic model, with respect to side and degradation reactions under highly acidic conditions resulting from the excessive evaporation of water under such conditions. Hence, this work highlighted the need to further investigate the kinetic mechanism of this reaction.

## AUTHOR INFORMATION

**Corresponding Author**

*E-mail: m.f.neira.dangelo@tue.nl.*

**ORCID**

J. van der Schaaf: 0000-0002-2856-8592

M. F. Neira d’Angelo: 0000-0001-8599-2800

**Notes**

The authors declare no competing financial interest.

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## NOMENCLATURE

**Latin Symbols**

- A = pre-exponential factor [s⁻¹]
- C = concentration [mol/L]
- Eₐ = activation energy [J/mol]
- F = flow [mol/s]
- G = NRTL parameter
- k = kinetic constant [s⁻¹]
- Kₒₓ = overall mass transfer [s⁻¹]
- N = number of moles
- p = pressure [Pa]
- p.sat = saturation pressure [Pa]

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$R =$ gas constant $[J/(K\cdot mol)]$

$T =$ temperature $[K]$

$T_{sat} =$ saturation temperature $[K]$

$t =$ time $[s]$

$V =$ volume $[L]$

$X =$ conversion $[%]$

$Y =$ yield $[\%]$

$y =$ molar fraction vapor $[\text{mol} \%]$

Greek Symbols

$\alpha =$ nonrandomness factor in the NRTL model

$\gamma =$ activity coefficient

$\lambda =$ Wilson model parameter

$\tau =$ parameter for interaction energy in the NRTL model

$\chi =$ molar fraction in the liquid phase $[\text{mol} \%]$

Subscripts

acid = sulfuric acid

$C =$ condensate

$D_1 =$ degradation product 1

$D_2 =$ degradation product 2

fur = furfural

$L =$ liquid

$N_2 =$ nitrogen

$V =$ vapor

$xyl =$ xylose

### REFERENCES


