Sequential and in situ extraction of furfural from reaction mixture and effect of extracting agents on furfural degradation

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Sequential and in Situ Extraction of Furfural from Reaction Mixture and Effect of Extracting Agents on Furfural Degradation

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ABSTRACT: Furfural is a platform chemical that can be obtained from renewable resources. It can be produced by acid-catalyzed dehydration of xylose. Currently, the furfural yield is relatively low due to side reactions (degradation of furfural). The furfural yield can be improved by rapid and continuous removal of the furfural from the reaction mixture (in situ extraction), preventing further furfural degradation. In this work, the (in situ) extraction of furfural from the reaction mixture using different organic solvents and hydrophobic deep eutectic solvents is investigated. First, the distribution coefficients of furfural in various organic solvents were determined. It was found that extracting agents containing phenol groups showed the highest distribution ratios. Thereafter, the acid-catalyzed degradation of furfural in the presence of the different solvents was assessed. Addition of organic solvents or hydrophobic deep eutectic solvents resulted in a significant decrease in furfural degradation compared to the blank and the benchmark. Finally, in situ extraction with the different extracting agents was performed. The xylose conversion was not influenced by solvent addition, whereas the furfural yields were significantly higher compared to the blank experiment, even when low amounts of extracting agents were applied. This was explained by the limited co-extraction of the acid to the organic phase, preventing further contact/reaction between the furfural and the acid. Hence, organic solvents and hydrophobic deep eutectic solvents can be promising in situ extracting agents for the removal of furfural from biorefinery processes.

INTRODUCTION

The development of novel “green” materials, biofuels as well as sustainable chemicals moves toward more ecofriendly and cost-efficient chemical processes and technologies. The main reasons for developing biorefining processes are the depletion of fossil resources and the reduction in the emissions of carbon dioxide and other greenhouse gases. However, the cost of processing renewables to chemicals and fuels is often too high to be economically feasible. This is partly due to the fact that traditional synthesis routes that were developed and optimized for hydrocarbons are not easily adapted for the use of renewables.1 Moreover, biomass is a more complex raw material requiring additional purification and separation steps.

Lignocellulosic biomass is a promising alternative to nonrenewable resources for the sustainable supply of fuels and chemicals in the future.2,3 The hydrolysis of lignocellulose has recently been mentioned to be the most important entry point into a biorefinery.4 Already in 1920, the first acid hydrolysis of lignocellulose was developed.5 Most important products are glucose (by hydrolysis of cellulose), xylose (by hydrolysis of hemicellulose), and phenols (by hydrolysis of lignin).6 These products can be further converted into useful building blocks for the chemical industry, such as furfural, hydroxymethylfurfural, levulinic acid, and glycols.7,8 This work focuses on the production of furfural from lignocellulose.
Furfural is a key derivative used for the production of a wide range of important chemicals, including pharmaceuticals and phenolic resins, as well as an intermediate for lubricants, nylon, adhesives, plastics, and solvents.\(^{12}\) Furfural is mainly obtained by the dehydration of xylose in the presence of an acidic catalyst at high temperatures.\(^{11,13-16}\) However, furfural yields are still relatively low. Subsequent reactions between furfural and its precursors are the primary cause of these low yields.\(^{17-23}\) Higher yields can be achieved by rapid and continuous removal of furfural from the aqueous reaction mixture.

Conventionally, liquid–liquid extraction is used for the recovery of furfural. If this extraction step could be carried out simultaneously with the reaction (i.e., in situ extraction),\(^{17}\) then undesired side reactions (further conversion/degradation of furfural to humins) can be prevented. In that case, the dehydration of xylose to furfural should be carried out in the presence of an immiscible solvent, so that most of the furfural can be transferred from the aqueous (reaction) phase to the solvent (extraction) phase almost immediately after it is formed, preventing any further degradation of the furfural. Thereafter, the furfural can be recovered from the solvent by simple binary distillation.

The suggested process for in situ extraction of furfural from its reaction mixture requires the selection of an appropriate solvent. Suitable solvents should be water-immiscible and thermally and acid stable (dehydration conditions) and show a high furfural distribution coefficient. Very recently, hydrophobic bio-based deep eutectic solvents (DESs) were discovered, which are combinations of two or more solids (e.g., menthol, thymol, or lidocaine), which liquefy at room temperature upon mixing due to attractive interactions.\(^{18}\) These hydrophobic DESs were found to show high distribution coefficients for furfural and very low water solubilities.\(^{17,19}\) Therefore, hydrophobic DESs are expected to be promising solvents for in situ extraction of furfural from its reaction mixture. However, the effect of hydrophobic DESs on the prevention of furfural degradation has never been investigated before.

In this study, 15 hydrophobic volatile organic solvents were evaluated as furfural extracting agents first. The furfural distribution coefficients were experimentally determined, and a relationship between the structure of the solvent and the obtained distribution coefficient was established. Two extracting agents with the highest distribution coefficients (i.e., carvacrol and 2-sec-butylphenol), as well as two solid chemicals that interact with furfural (i.e., thymol and menthol) and a benchmark (i.e., toluene), were selected to determine the behavior of the degradation reaction of furfural to humins at five different acid concentrations (0, 10, 20, 30, and 40 wt %) and at three different temperatures (335, 383, and 413 K). Also, the effect of the acid concentration and temperature on the conversion of xylose (with an initial concentration of 4 wt %) to furfural was experimentally determined. The best reaction conditions were determined and selected (4 wt % xylose, 20 wt % H\textsubscript{2}SO\textsubscript{4}, and 403 K) to investigate the influence of the selected extracting agents on the xylose conversion and the furfural yield. Finally, four hydrophobic DESs (decanoic acid–menthol (1:1), decanoic acid–thymol (1:1), thymol–lidocaine (2:1), and thymol–menthol (1:2)), which were selected on the basis of their molecular structure, viscosity, distribution coefficient for furfural, and selectivity for acid, were tested as in situ extracting agents to reduce the degradation of furfural during the integrated process (combined reaction and in situ extraction).

## EXPERIMENTAL SECTION

### Chemicals

Table 1 the chemicals used in this work, including their purities and sources, are presented. All chemicals were used without further purification.

### Extraction Measurements

The extraction of furfural (FF) with the 15 solvents was measured using a 1 wt % FF (as

Table 1. Chemicals Used, Including Purity, Source, CAS Number, Structure Formula, and Melting Point (\(T_m\)) (As Provided by the Supplier)

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Purity (wt %)</th>
<th>Source</th>
<th>CAS Reg. No.</th>
<th>(T_m) (K)</th>
<th>Structure Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decanoic Acid</td>
<td>Deca</td>
<td>&gt;98</td>
<td>Sigma-Aldrich</td>
<td>98-01-1</td>
<td>300–305</td>
<td>CH(_3)(CH(_2))COOH</td>
</tr>
<tr>
<td>Furfural</td>
<td>FF</td>
<td>&gt;99</td>
<td>Sigma-Aldrich</td>
<td>98-01-1</td>
<td>237</td>
<td>C(_5)H(_4)O(_2)</td>
</tr>
<tr>
<td>Thymol</td>
<td>Thy</td>
<td>&gt;99</td>
<td>TCI Chemicals</td>
<td>89-83-8</td>
<td>322–325</td>
<td>[(CH(_3))(_2)CH]C(_6)H(_5)](_2)((\text{CH}_3)\text{OH})(_3)</td>
</tr>
<tr>
<td>Menthol</td>
<td>Men</td>
<td>&gt;99</td>
<td>TCI Chemicals</td>
<td>15356-60-2</td>
<td>304</td>
<td>C(_6)H(_5)O</td>
</tr>
<tr>
<td>Lidocaine</td>
<td>Lid</td>
<td>&gt;99</td>
<td>Sigma-Aldrich</td>
<td>137-58-6</td>
<td>339–342</td>
<td>C(_6)H(_5)N(_2)O</td>
</tr>
<tr>
<td>α-Xylose</td>
<td>Xylose</td>
<td>&gt;98</td>
<td>TCI Chemicals</td>
<td>56-86-6</td>
<td>56-86-6</td>
<td>C(_5)H(_4)O(_3)</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>Sulf</td>
<td>&gt;99</td>
<td>TCI Chemicals</td>
<td>7664-93-9</td>
<td>56-86-6</td>
<td>H(_2)SO(_4)</td>
</tr>
<tr>
<td>Carvacrol</td>
<td>Car</td>
<td>&gt;98</td>
<td>TCI Chemicals</td>
<td>499-75-2</td>
<td>276</td>
<td>(CH(_3))(_2)C(_6)H(_5)(CH(_3))OH</td>
</tr>
<tr>
<td>2-sec-Butylphenol</td>
<td>Sec</td>
<td>&gt;98</td>
<td>TCI Chemicals</td>
<td>89-72-5</td>
<td>263</td>
<td>C(_5)H(_4)CH(CH(_3))C(_2)H(_5)OH</td>
</tr>
<tr>
<td>Toluene</td>
<td>Tol</td>
<td>&gt;99</td>
<td>TCI Chemicals</td>
<td>108-88-3</td>
<td>304</td>
<td>C(_6)H(_5)CH(_3)</td>
</tr>
<tr>
<td>2-Adamantanol</td>
<td>2Ada</td>
<td>&gt;98</td>
<td>TCI Chemicals</td>
<td>700-57-2</td>
<td>304</td>
<td>C(_6)H(_5)O</td>
</tr>
<tr>
<td>Cinnamyl Alcohol</td>
<td>Cim</td>
<td>&gt;98</td>
<td>TCI Chemicals</td>
<td>4407-36-7</td>
<td>306</td>
<td>C(_6)H(_5)CH(_3)CHCH(_3)OH</td>
</tr>
<tr>
<td>Camphor</td>
<td>Cam</td>
<td>&gt;96</td>
<td>Sigma-Aldrich</td>
<td>76-22-2</td>
<td>448</td>
<td>C(_6)H(_5)O</td>
</tr>
<tr>
<td>Citronellol</td>
<td>Cit</td>
<td>&gt;95</td>
<td>TCI Chemicals</td>
<td>7540-51-4</td>
<td>304</td>
<td>(CH(_3))(_2)(CH(_3))(_2)CHCH(_3)OH</td>
</tr>
<tr>
<td>2-Ethylphenol</td>
<td>2Et</td>
<td>99</td>
<td>Sigma-Aldrich</td>
<td>90-00-6</td>
<td>255</td>
<td>C(_6)H(_5)C(_2)H(_5)OH</td>
</tr>
<tr>
<td>2-Propylphenol</td>
<td>2Pro</td>
<td>98</td>
<td>Sigma-Aldrich</td>
<td>644-35-9</td>
<td>255</td>
<td>C(_5)H(_4)CH(CH(_3))C(_2)H(_5)OH</td>
</tr>
<tr>
<td>4-Ethylphenol</td>
<td>4Et</td>
<td>&gt;98</td>
<td>Sigma-Aldrich</td>
<td>123-07-9</td>
<td>313</td>
<td>C(_6)H(_5)C(_2)H(_5)OH</td>
</tr>
<tr>
<td>2,6-Diisoproplyphenol</td>
<td>26Diiso</td>
<td>&gt;97</td>
<td>Sigma-Aldrich</td>
<td>2078-54-8</td>
<td>291</td>
<td>[(CH(_3))(_2)](_2)CH(_3)OH</td>
</tr>
<tr>
<td>4-sec-Butyl-2,6-diisobutylphenol</td>
<td>4s</td>
<td>96</td>
<td>Sigma-Aldrich</td>
<td>17540-75-9</td>
<td>298</td>
<td>C(_5)H(_4)CH(CH(_3))(_2)C(CH(_3))(_3)OH</td>
</tr>
<tr>
<td>2,4-Di-tert-Butylphenol</td>
<td>24Diter</td>
<td>99</td>
<td>Sigma-Aldrich</td>
<td>96-76-4</td>
<td>328</td>
<td>[(CH(_3))(_2)](_2)CH(_3)OH</td>
</tr>
<tr>
<td>2,6-Di-tert-Butylphenol</td>
<td>26Diter</td>
<td>99</td>
<td>Sigma-Aldrich</td>
<td>128-39-2</td>
<td>308</td>
<td>[(CH(_3))(_2)](_2)CH(_3)OH</td>
</tr>
</tbody>
</table>

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starting concentration) solution in water. In a 50 mL centrifuge tube, 10 g of these aqueous solutions and different amounts of solvent (different solvent-to-feed ratios, 10:1, 5:1, 1:1, and 1:2 molar ratio) were added and mixed in a shake machine (IKA KS 4000i) during 2 h at 500 rpm at the selected temperature (i.e., 298 and 323 K). To separate the solvents from the aqueous phase, the tubes were centrifuged (Sigma 2-16KL) for 30 min with a speed of 8000 rpm at a temperature of 298 K. To obtain the concentration of FF, a sample of the aqueous phase was taken (±1 mL) and analyzed using high-performance liquid chromatography (HPLC).

**HPLC Analyses.** The concentrations of FF and xylose were measured with an HPLC Agilent Technology 1260 Infinity Series instrument (Agilent Technologies, Santa Clara, CA, USA), which made use of MetaCarb 67C Guard cartridges; a MetaCarb 67C analytical column operating at a temperature of 353 K; a G1311B isocratic pump operating at a pump flow rate of 0.400 mL min$^{-1}$; a G1314A variable wavelength detector (VWD) with a zero offset of 5%, an attenuation of 1000 mA U, and a wavelength of 254 nm; and a G1362A refractive index detector (RID) with a zero offset of 5%, a positive signal polarity, and an operation temperature of 308 K. The sample volume was 1.0 μL, and run time was 50 min per sample. A chromatogram and the calibration curve are plotted in the Supporting Information (Experimental S1).

**Degradation Experiments.** Two extraction solvents with the highest distribution coefficients (car and 2sec), two solid chemicals that have an interaction with furfural (thym and men), and a benchmark (tol) were selected to determine the behavior of the deconstructive reaction of furfural. Samples of 10 g amounts of 1 wt % FF in different acid concentration (0, 10, 20, and 40 wt %; 0.1, 1.8, 3.7, and 7.3 M) solutions were put in 20 mL vials, and different amounts of solvent (different solvent-to-feed ratios) were added. The vials were heated to 335, 383, and 413 K and at different times (0, 10, 15, 30, 45, and 60 min) the vials were cooled to 273 K to stop the degradation. All experiments were done in duplicate. The concentrations of FF and xylose of the sample of the water phase were measured with HPLC, and a sample of the organic phase was measured with GC-MS. All experiments were done in duplicate.

**Yield Predictions.** Yields for FF in the presence of different in situ extracting agents were predicted on the basis of the distribution coefficients obtained from the extraction experiments (without reaction) and the blank reaction experiment (without addition of any extracting agent). A set of modeling equations was derived from the mole balances of the main components (i.e., xylose and FF) and two liquid phases (i.e., water and organic solvent/DES) and solved numerically using MATLAB (see the Supporting Information, Experimental S3). This model assumes an ideally stirred batch reactor, a mass transfer coefficient of 0.1 s$^{-1}$ (a standard value for a well-stirred system$^{25}$), and the kinetic mechanism reported by Weingarten et al.$^{26}$ Note that this kinetic model was obtained by empirical fittings using 0.1 M HCl, i.e., significantly lower acid concentrations than those used in this work (0–40 wt % H$_2$SO$_4$). In the absence of literature data for higher acid concentrations, we have assumed a linear dependence of all reaction rates with respect to the concentration of protons, thus limiting the validity of our predictions to qualitative trends. A quantitative prediction of the system performance lays outside the scope of this work.

**DESS Preparation.** The four different hydrophobic DESs prepared in this work, including their hydrogen bond donors (HBDs), hydrogen bond acceptors (HBAs), and the ratio between the HBD and HBA, are presented in Table 2. In a round-bottom flask, both solids (HBD and HBA) were weighed in the desired molar ratio, stirred, and heated in an oil bath at 313 K for 2 h to obtain an approximate amount of 100 g of a liquid (DES), which stayed liquid after cooling to room temperature.

**RESULTS AND DISCUSSION**

**Extraction of FF Using 15 Organic Solvents.** The distribution coefficient (K) is an important parameter for liquid–liquid extraction.$^{27}$ It is the ratio between the mole
fraction of the solute in the solvent (or extract) phase, $x_E$, and the mole fraction of the solute in the water (raffinate) phase, $x_R$, when in equilibrium:

$$K = \frac{x_R}{x_E}$$ (1)

In this work, the solute concentrations used are low (~1%) and operation takes place at constant solvent-to-feed ratios. Therefore, the solvent and feed streams can be assumed to be constant and identical, and eq 1 can be approximated with (eq 2):

Table 3. Distribution Coefficient of FF Obtained by Extraction with 15 Different Solvents at 298 and 328 K and 1.01 bar from a Starting Solution Consisting of 1 wt % FF at Different Solvent-to-Feed Ratios

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Structure</th>
<th>[298]</th>
<th>[328]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20:1</td>
<td>10:1</td>
<td>2:1</td>
</tr>
<tr>
<td>tol</td>
<td></td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>2sec</td>
<td></td>
<td>44</td>
<td>67</td>
</tr>
<tr>
<td>thy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2pro</td>
<td></td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>2et</td>
<td></td>
<td>30</td>
<td>45</td>
</tr>
<tr>
<td>car</td>
<td></td>
<td>27</td>
<td>46</td>
</tr>
<tr>
<td>26di iso</td>
<td></td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>24 di tert</td>
<td></td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>4sec</td>
<td></td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>cit</td>
<td></td>
<td>37</td>
<td>7</td>
</tr>
<tr>
<td>26 di tert</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cam</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2 ada</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cin</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>men</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

"Standard uncertainties are $u(T) = 1$ K, $u(p) = 0.03$ bar, and $u(K) = 2$."


agent should be in the liquid phase, otherwise one cannot have not been measured. One reason is that the extracting obtained are shown in Table 3. Some distribution coe

hindrance). Also, the e

solvent-to-feed ratio were studied. All distribution coe

values at the 5:1 ratio were too low to be useful as extracting agents.

The extraction of the pure component FF using 15 different extraction solvents was performed in order to study the effect of the chemical structure on the extraction performance. The 15 different extraction solvents were selected on the basis of their chemical structure. The selected solvents either contain OH groups (allowing hydrogen bonding), and/or benzyl groups with different functional side groups (resulting in steric hindrance). Also, the effects of the temperature and the solvent-to-feed ratio were studied. All distribution coefficients obtained are shown in Table 3. Some distribution coefficients have not been measured. One reason is that the extracting agent should be in the liquid phase, otherwise one cannot perform liquid—liquid extraction, but men (melting point is 304 K 25) and thy (melting point is 324 K 25) are solids at 298 K and are therefore not included in Table 3. Also, the distribution coefficients of 26tert, cam, 2ada, and cin were not determined at solvent-to-feed ratios other than 5:1, as their values at the 5:1 ratio were too low to be useful as extracting agents.

From Table 3 the following four observations can be made: (i) an OH group, (ii) a benzyl group, (iii) an OH group on the benzyl group, and (iv) less and smaller side groups lead to higher distribution coefficients. Thus, phenol (containing both an OH group and a benzyl group, and no other side groups) would be the best extracting agent. However, phenol is also a high-risk solvent that should be avoided in “green” processing. Therefore, the best extracting agents have structures comparable to that of phenol, but without the disadvantages. In this study the best performing extracting agents were 2sec, 2et, car, thy, 2pro, and 26diso.

The effect of the temperature on the extraction performance was found to be limited. This is consistent with previous observations showing that the temperature is not a significant factor influencing the FF extraction coefficient. 10 However, the solvent-to-feed ratio does have a significant influence on the obtained extraction coefficients, as different compositions of extract and raffinate phases are achieved when different solvent-to-feed ratios are applied, with the highest values obtained for a ratio of 10:1 (=10 mol car:1 mol FF = 1.5 g car:10 g water/acid/xylose). Thus, the solvent-to-feed mole ratio is a subject of optimization. As expected, higher values result in higher extraction coefficients. The interactions between FF with the organic solvent, i.e., the activity coefficient of FF in the organic solvent (which is most influenced by changing the organic solvent/water ratio) is the most important factor determining the observed distribution ratios.

Degradation of FF. Degradation at Different Reaction Conditions. The concentration of FF in the water phase (without addition of any solvent, a blank experiment) as a function of time has been measured at different temperatures (373, 393, and 413 K) and different acid concentrations (H2SO4, 0, 10, 20, and 40 wt %). The degradation was determined as the ratio of the amount of FF lost/converted over the initial amount of FF. Figure 1 shows the degradation results of FF (a) at one temperature (373 K) and four different acid concentrations and (b) at one acid concentration (20 wt %) and three different temperatures. All other degradation results can be found in the Supporting Information (Figures S1–S5).

As expected, the FF degradation increases with increasing acid concentration and with increasing temperature. However, when no acid is added, two interesting observations can be made: (i) the temperature effect (373, 393, and 413 K) is insignificant, and (ii) the FF degradation is constant at approximately 10% after 5 min (no degradation measured at the starting time). This can only be explained by the occurrence of two different degradation mechanisms. 9,16

Degradation in the Presence of Different Extracting Agents. Two extracting agents with the highest distribution coefficients (i.e., car and 2sec), as well as two solid chemicals that interact with FF (i.e., thy and men) and a benchmark (i.e., tol), were selected to determine the effect of the extracting agent on the FF degradation at different acid concentrations (0, 10, 20, and 40 wt %), different temperatures (335, 383, and 413 K) at a solvent-to-feed ratio of 10:1. It should be noticed that men and thy become liquid upon mixing with FF in certain ratios (i.e., deep eutectic solvent formation). Outside the liquid region, FF concentrations could not be determined and therefore degradation results at these conditions are not included.

\[
K \approx \frac{C_0 - C_R}{C_R} \left( \frac{M_e}{M_f} \right)
\]

where \(C_0\) is the concentration of the solute in the feed stream and \(C_R\) is the concentration of the solute in the raffinate stream, \(M_e\) is the mass of the feed phase, and \(M_f\) is the mass of the solvent phase.

Figure 1. FF degradation (%) in time: (a) at 373 K and different acid concentrations (0, 10, 20, and 40 wt %), (b) at 0 wt % acid concentration and different temperatures (373, 393, and 413 K), and (c) at 20 wt % acid concentration and different temperatures (373, 393, and 413 K).
In Figure 2 the results for the degradation of FF at 393 K and 10 wt % acid are plotted as a function of time. All other graphs (at different acid concentrations and at different temperatures) can be found in the Supporting Information (Figures S6–S30).

From Figure 2 it can be concluded that the degradation of FF in the absence of any extracting agent is increasing in time. This is explained by the fact that the FF is in continuous contact with the acid (catalyst for degradation) in the water phase. However, in the presence of an extracting agent, the degradation of FF does not continuously increase in time but reaches a plateau after about 10 min. This can be explained by the transfer of the FF from the (acidic) water phase to the (non-acidic) organic phase, where the FF is no longer in contact with the acid, and thus the degradation reaction, which is acid-catalyzed, comes to a halt. Furthermore, it can be noticed that the degradation of FF in the presence of car and 2sec is much lower than in the presence of tol and thy. An explanation could be the fact that the acid is co-extracted in the case of tol and thy, while it is not co-extracted when car or 2sec is added as extracting agent. This hypothesis was tested by measuring the pH (pH indicator test strips) of both phases (water phase + organic phase) after extraction of FF at 328 K and a 20 wt % acid concentration using thy, tol, car, and 2sec; see Table 4. Indeed, the pH of the tol (and thy) phase decreased to 4 after contact with the acidic water phase, while the pHs of car and 2sec stayed at 7. Thus, it seems that co-extraction of the acid takes place when tol (and thy) are used as extracting agents, and therefore the FF degradation reaction proceeds in the organic phase. But when car and 2sec are used as extracting agents, the acid is not co-extracted and the FF degradation reaction stops in the organic phase.

**Reaction of Xylose to FF. Determination of Optimum Reaction Conditions.** The effect of the acid concentration and temperature on the conversion and yield of the reaction of xylose to FF has been determined experimentally as a function of reaction time. The conversion of xylose and the yield of FF were obtained at different acid concentrations (1, 5, 10, 20, 30, and 40 wt % H2SO4) and different temperatures (353, 383, 403, and 423 K) at a starting concentration of xylose of 4 wt % in water. It should be noted that not all combinations were measured: (i) at 353 K the conversion and yield at low acid concentrations were too low to be determined (below the detection limit), while (ii) at 403 and 423 K and at high acid concentrations the degradation of FF into humins was too pronounced (forming a black suspension), so that it became impossible to measure conversions and yield.

The conversion of xylose and the yield of FF versus reaction time at different acid concentrations are plotted in Figures 3 and 4 at temperatures of 383 and 403 K, respectively. The conversions and yields at the other investigated temperatures (353 and 423 K) can be found in the Supporting Information, Figures S31–S34.

From Figures 3 and 4, it can be concluded that the highest conversions and yields are obtained at 383 K and 40 wt % acid. However, at these conditions we already noticed some humin formation (formation of black particles). The next best conversion and yield were obtained at 403 K and 20 wt %, where humin formation was not prevailing. The yield and conversion could be increased with longer reaction times, but also the degradation will be increased. It is also more advantageous to work at 403 K and 20 wt % over working at 383 K and 40 wt % because of the lower sulfuric acid requirement. This will save on material cost and is more environmentally benign, although the energy cost will be slightly higher. Despite that, the acid is used as a catalyst and the recovery and reusability are important. Thus, the optimized reaction conditions for the reaction of xylose to FF were found to be 4 wt % xylose, 20 wt % H2SO4, and 403 K. These conditions were used in the subsequent in situ extraction experiments.

**In Situ Extraction of FF with Organic Extracting Agents.**

The solvents selected for the degradation experiments (car, 2sec, men, thy, and tol) were also applied as in situ extracting agents for the removal of FF during xylose conversion at the optimized reaction conditions (4 wt % xylose, 20 wt % H2SO4, and 403 K). Again, the conversion of xylose and the yield of FF were determined during in situ extraction at a solvent-to-feed molar ratio of 10:1 (see Extraction of FF Using 15 Organic Solvents).

The conversion of xylose and the yield of FF versus reaction time in the presence of different in situ extracting agents are presented in Figure 5a,b, respectively. Figure 5a shows that the conversion of xylose is not significantly affected by the addition of the in situ extracting agent. Apparently, the xylose stays in the water phase, where the reaction occurs, and is not extracted to the organic phase. This is consistent with previous observations that sugars (including xylose) do not dissolve in these organic extracting agents.

On the contrary, the yield to FF is strongly dependent on the addition of the in situ extracting agent (see Figure 5b): high FF yields are obtained in the presence of 2sec, car, and thy, while low FF yields are obtained in the presence of men.
and tol. This is the same trend as observed in Table 3. The high yields for 2sec, car, and thy can be explained by the fact that FF will dissolve in these extracting agents and is removed from the reaction mixture. Because the acid stays in the water phase, the FF is no longer in contact with the acid. Therefore, further degradation of the FF is prevented and much higher yields can be obtained compared to the blank experiment (without the presence of any extracting agent).

In the cases in which men or tol are used as in situ extracting agent, the acid is co-extracted together with FF to the organic phase. Thus, FF stays in contact with the acid, and can be further degraded, so the yield is lower (comparable to the blank experiment where FF and acid stay together in the water phase). This is consistent with the results obtained in the section on the degradation of FF in the presence of different extracting agents, where the pH of the organic phase was found to decrease for tol (benchmark). No other product could be detected with the GC-MS.

The yield obtained for the benchmark tol in our work is much lower than the value reported in the literature (~50%).27 However, we used a much lower solvent-to-feed ratio (molar ratio of 10:1 = volumetric ratio of 1.5:10 = 1:6.7) as compared to the literature, where a volumetric solvent-to-feed ratio of 2:1 was used, which could explain this difference. This indicates that our results for FF yields in the presence of 2sec, car, and thy are remarkably high (three times higher yield compared to the blank and the benchmark) considering the low solvent-to-feed ratios applied.

To validate the results for the yield of FF in the presence of in situ extracting agents, these values were also predicted on the basis of the distribution coefficients obtained in the extraction experiment (without reaction) and the blank reaction experiment (without addition of any extracting agent). The results (both with/without modeling of acid diffusion to the organic phase) are shown in Figure 6A, and in Figure 6B the experimental data are included. It can be concluded that the results obtained in the in situ experiments are consistent with the extraction experiments, as the predictions are qualitatively correct. Thus, an FF yield of around 20% can indeed be expected when a volumetric solvent-to-feed ratio of only 1.5:10 is used, and FF yields in the presence of 2sec, car, and thy are indeed very high at the low solvent-to-feed ratios applied in this work.

Figure 3. (a) Conversion of xylose and (b) yield of FF as a function of reaction time at 383 K and six different acid concentrations (1, 5, 10, 20, 30, and 40 wt %).

Figure 4. (a) Conversion of xylose and (b) yield of FF as a function of reaction time at 403 K and four different acid concentrations (1, 5, 10, and 20 wt %).
Degradation of FF and in Situ Extraction of FF with Hydrophobic DESs. Four different hydrophobic DESs (i.e., deca-men, deca-thy, thy-lid, and thy-men) were selected as promising bio-based in situ extraction agents on the basis of their viscosity, density, and interaction with FF.\textsuperscript{28,29} First, the effect of the addition of these hydrophobic DESs on the FF degradation was studied by measuring the total concentration of FF in both phases over time and determining the ratio of the amount of FF lost over the initial amount of FF. The results for the degradation of FF in the presence of hydrophobic DESs at a starting concentration of 1 wt % FF, 20 wt % acid, and a temperature of 403 K are plotted in Figure 7. In this figure, also the results for the FF degradation in the presence of the organic solvents car and thy at the same conditions are added for comparative reasons.

From Figure 7 it can be concluded that all hydrophobic DESs decrease the degradation of FF in comparison to the blank experiment (without addition of any extracting agent) and the benchmark (toluene, which shows even higher degradation).
degradation than the blank; see Figure 2). This means that all hydrophobic DESs are able to selectively extract FF from the aqueous phase without co-extraction of the acid, so that the FF is shielded from acid-catalyzed degradation. Thus, all DESs show a similar effect on the FF degradation to the organic solvents car and thy. The best performing DES is thy-men. This hydrophobic DES shows remarkably low FF degradation, comparable to the values observed in systems without any acid present.

Next, the hydrophobic DESs were applied as in situ extracting agents for the removal of FF during xylose conversion at the optimized reaction conditions (4 wt % xylose, 20 wt % H₂SO₄, and 403 K), because of the remarkably low degradation of FF and the high distribution coefficients. The conversion of xylose and the yield of FF were determined during in situ extraction at a solvent-to-feed molar ratio of 10:1 and are graphically depicted in Figure 8a,b, respectively. Again, results for in situ extraction with the organic solvents car and thy are added for comparative purposes.

First of all, it can be observed that the solvent has almost no influence on the conversion of xylose, which is in agreement with the results shown in Figure 5a. Thus, in all cases, xylose is not extracted to the organic phase but stays in the water phase, where the reaction takes place. Furthermore, it can be noticed that the FF yield (especially in the first 30 min) in the presence of hydrophobic DESs is higher than the blank experiment and comparable to the values obtained in the presence of organic solvents. The reason is that the acid is not co-extracted (see Figure 7), preventing further contact between the FF and the acid. However, after 30 min the FF yields obtained are not further increasing in the presence of hydrophobic DESs. This cannot be explained by the acid, as it is not co-extracted (see Figure 7). Instead, it may be due to the presence of xylose in the reaction mixture. Xylose can also react with FF and lead to the formation of other side products. However, this is not proven and needs to be further investigated. Still, it should be remarked that it is possible to reach high FF yields (two times higher than the blank experiment) when the hydrophobic DESs deca-men and thy-men are used as in situ extracting agents when the reaction time is limited to 30 min. Thus, hydrophobic DESs are promising in situ extracting agents for the removal of FF from biorefinery processes.

**CONCLUSIONS**

The extraction of FF from water and the in situ extraction of FF from its reaction mixture with xylose using different organic solvents and hydrophobic DESs as extracting agents were investigated, as well as the effect of the extracting agent on the FF degradation. The highest distribution ratios of FF were obtained for extracting agents containing a phenol group. Acid-catalyzed FF degradation was decreased when extracting agents were added (as compared to the blank and the benchmark), because all extracting agents showed limited co-extraction of the acid, preventing further contact/reaction between the FF and the acid. The conversion of xylose to FF optimally (highest yield) took place at a starting concentration of 4 wt % xylose, the addition of 20 wt % H₂SO₄ and a temperature of 403 K. In situ extraction at the optimized reaction conditions using organic solvents and hydrophobic DESs (at a solvent-to-feed molar ratio of 10:1) resulted in comparable xylose conversions but much higher FF yields, compared to the blank experiment. Thus, organic solvents and hydrophobic DESs (especially at short reaction times < 30 min) are promising in situ extracting agents for the removal of FF from biorefinery processes.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b00694.

Modeling equations used; HPLC and GC chromatograms, calibration curves, and the degradation of FF in time at different acid concentrations, different temperatures, and different extracting agents; yield of FF and conversion of xylose in time at different acid concentrations (PDF)

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