Catalytic inulin conversions to biobased chemicals
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Experimental and modeling studies on the uncatalysed thermal conversion of inulin to 5-hydroxymethylfurfural and levulinic acid

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Abstract

5-Hydroxymethylfurfural (HMF), an important biobased platform chemical, is accessible by the acid catalysed conversion of biopolymers containing hexoses (cellulose, starch, inulin) and monomeric sugars derived thereof. We here report an experimental study on the uncatalysed, thermal conversion of inulin to HMF in aqueous solutions in a batch set-up. The reactions were conducted in a temperature range of 153-187°C, an inulin loading between 0.03 and 0.12 g/mL and batch times between 18 and 74 minutes using a central composite experimental design. The highest experimental HMF yield in the process window was 35 wt% (45 mol%), which is 45% of the theoretical maximum (78 wt%). The HMF yields were modeled using a statistical approach and good agreement between experimental data and model was obtained. The possible autocatalytic role of formic acid (FA) and levulinic acid (LA), two main byproducts, was probed by performing reactions in the presence of these acids and it was shown that particularly FA acts as a catalyst. Inulin is an interesting feed for the synthesis of HMF in water. A catalyst is not required, though autocatalytic effects of FA play a major role and also affect reaction rates and product yields.

Keywords: Inulin, HMF, thermal reaction, autocatalytic effects
3.1 Introduction

Biomass has been identified as an attractive alternative for crude oil, natural gas and coal to produce fuels and chemicals. When considering biobased chemicals, particularly the carbohydrate fraction (cellulose and hemicellulose) of lignocellulosic biomass shows high potential. An example of a biobased chemical is 5-hydroxymethylfurfural (HMF), which has been classified as one of the top 12 biobased chemicals from biomass by the US department of Energy (DOE)[1-2]. HMF is a very versatile building block for biofuels or biofuel additives [3-4], solvents, surface-active agents, fungicides [5] and for interesting monomers for the plastics industry [1], [6-7].

HMF may be produced from a wide range of hexoses by elimination of three water molecules (Scheme 1, example for D-fructose).

\[
\text{Scheme 1 A simplified reaction scheme for HMF formation.}
\]

Conventionally, the reaction is carried out in water using a Brönsted acid with D-fructose as the preferred carbohydrate source [8-20]. Hydrochloric acid and sulfuric acid are the most commonly used Brönsted acids. Kuster (1990) [21], reported that D-fructose is more reactive and selective towards to HMF than D-glucose and a HMF yield from D-fructose of 68% was reported using HCl as the catalyst (C\textsubscript{fruct}= 9 wt%, 1.5 h). Yields in water are less than quantitative due to the formation of insoluble byproducts (humins) and a subsequent reaction of HMF to levulinic acid (LA) and formic acid (FA, Scheme 1). Two main reaction mechanisms have been proposed for the reaction in water, one involving acyclic intermediates and another with cyclic intermediates [22].

Considerable progress has been made to enhance HMF yields, among others by using solvents other than water and the use of advanced catalysts [8]. Typical homogeneous Brönsted catalysts (mineral acids) have the advantage that they are relatively cheap, though recycling is often cumbersome. As such, heterogeneous catalysts could be beneficial and
have been tested in detail. However, catalyst lifetime needs to be established and a major concern is the deposition of humin substances on the heterogeneous catalysts leading to irreversible catalyst deactivation. Examples of solvents other than water tested for the reaction include acetone [17], methanol [17], toluene [23] and dimethyl sulfoxide (DMSO) [24]. Among them, reactions in DMSO give essentially quantitative HMF yields [8], though down-stream processing is considerably more complicated than with water and is a critical issue.

Despite these improvements, efficient, economically viable routes to produce HMF from D-fructose have not yet been commercialised. Bicker et al., [17] estimated an HMF cost price of 2 €/kg, using the assumption that D-fructose is available at a price of 0.5 €/kg. Torres et al., [25] reported that the manufacturing costs of HMF are between 1.97 $/kg and 2.43 $/kg, depending on the solvent used, based on a D-fructose price of 0.55 $/kg and 7000 ton/year HMF production unit. An HMF price of around 1.00 $/kg is considered a good starting point to allow its use in bulk-scale chemical applications.

The major variable cost item in the economic evaluations for HMF manufacture is the cost of the D-fructose feed. As such, the identification of low priced D-fructose alternatives is of high importance for the development of techno-economically viable routes to HMF. Alternative feeds are biopolymers enriched in D-fructose units, which are likely cheaper than purified D-fructose. An interesting biopolymer is inulin, an oligosaccharide consisting of mainly fructose units, in some cases capped with a glucose unit [6], [15], [26]. Inulin can be extracted from plants, examples are jerusalem artichoke [27-31], chicory [28-31] and dahlia tubers [28-31]. Of particular interest are the Jerusalem artichoke and chicory, which are reported to have a high inulin content of up to 20% on fresh weight [32].

A number of studies have been performed on the catalysed inulin conversion to HMF in water, the solvent of choice in the current investigation (Table 1). Temperatures are typically between 80 and 200°C, reaction times vary between minutes and 3 h, and intakes of inulin are between 5 and 10 wt% on solvent. A range of catalysts has been applied, varying from homogeneous (H$_2$CO$_3$, formed in situ by CO$_2$ addition) to heterogeneous catalysts. Reactions not only have been performed in water but also in water-organic solvent mixtures and ionic liquids. Highest HMF yields (88 mol% on inulin) were reported by Hu et al., using DMSO as the solvent [33].
We here report a study on the conversion of inulin to HMF using water as the solvent in the absence of a catalyst. In this way, catalyst recycle procedures are eliminated and drawbacks of heterogeneous catalysts (among others deactivation by humin deposition) are avoided. Water was selected as the solvent of choice, as it is environmentally benign, is a good solvent for many carbohydrates and it is cheap, nontoxic, and nonflammable [39-42].

A number of studies have been reported on the uncatalysed conversion of D-fructose to HMF (Table 2). For inulin, very limited information is available in the literature. The only paper is by Wu et al., [34] who reported an HMF yield of 48% (200°C, inulin loading of 5 wt% and 1 h reaction time).

Thus, it can be concluded that a detailed study on the effect of process conditions on HMF yields for the thermal decomposition of inulin in water has not been reported to date. We here report a systematic study on the effect of process conditions like reaction time, inulin intake and reaction temperature on the HMF yield. A total of 24 batch experiments were performed using a composite design. The data were analysed statistically and a model was developed to describe the HMF yield versus process conditions. Finally, possible
autocatalytic effects of organic acids (formic acid and levulinic acid) on the rates of reactions and HMF yields were explored.

Table 2 Overview of studies for the uncatalysed reaction of d-fructose and inulin to HMF in water.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Substrate intake, (wt%)</th>
<th>T, (°C)</th>
<th>t</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-Fructose</td>
<td>4.5</td>
<td>175</td>
<td>45 min</td>
<td>56&lt;sup&gt;c&lt;/sup&gt;</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>140</td>
<td>1 h</td>
<td>4 (mol%)</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>200</td>
<td>5 min</td>
<td>41 (mol%)</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>160&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5 min</td>
<td>1 (mol%)</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>190&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5 min</td>
<td>36 (mol%)</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>200&lt;sup&gt;a&lt;/sup&gt;</td>
<td>5 min</td>
<td>13 (mol%)</td>
<td>[44]</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>170</td>
<td>3 h</td>
<td>43 (mol%)</td>
<td>[45]</td>
</tr>
<tr>
<td></td>
<td>0.05&lt;sup&gt;d&lt;/sup&gt;</td>
<td>240</td>
<td>3 min</td>
<td>20&lt;sup&gt;c&lt;/sup&gt;</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>125</td>
<td>5 min</td>
<td>0.8&lt;sup&gt;c&lt;/sup&gt;</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>200</td>
<td>30 min</td>
<td>51&lt;sup&gt;c&lt;/sup&gt;</td>
<td>[48]</td>
</tr>
<tr>
<td>Inulin</td>
<td>5</td>
<td>160</td>
<td>4 h</td>
<td>38&lt;sup&gt;c&lt;/sup&gt;</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>180</td>
<td>2 h</td>
<td>41&lt;sup&gt;c&lt;/sup&gt;</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>200</td>
<td>1 h</td>
<td>48&lt;sup&gt;c&lt;/sup&gt;</td>
<td>[34]</td>
</tr>
</tbody>
</table>

<sup>a</sup>: heating by microwave irradiation  
<sup>b</sup>: wt or mol in brackets after entries  
<sup>c</sup>: wt% or mol% not provided  
<sup>d</sup>: in M

3.2 Experimental section

3.2.1 Chemicals

Inulin from Dahlia tubers was purchased from Acros Organic (Geel, Belgium). D-fructose (99%) and levulinic acid (≥ 97%) were obtained from Acros Organic (Geel, Belgium). Formic acid (≥ 95%) and D-glucose (≥ 99.5%) were purchased from Merck KGaA (Darmstadt, Germany). 5-Hydroxymethylfurfural (HMF) (≥ 99%) was obtained from Sigma Aldrich (Steinheim, Germany). 2,5-Dihydroxybenzoic acid (DHB) (≥ 99%) was purchased from Fluka (Deisenhofen, Germany). All chemicals were used without purification. De-ionized water was used to prepare the solutions.

3.2.2 Experimental procedures

The experimental procedures are based on previous research by our group (Girisuta et al, [19]. In a typical experiment, the pre-determined amount of inulin and de-ionized water (4 mL) were loaded to glass ampoules with an internal diameter of 5 mm, a length of 15 cm and thickness of 1.5 mm. The ampoules were sealed with a torch.

For the exploratory experiments, a series of ampoules was placed in a rack in a heating oven (Heraeus Instruments Type UT6060) at constant temperature. At different reaction times, an
ampoule was taken from the oven and quickly quenched in cold water to stop the reaction. The experiments carried out in the framework of the experimental design were individually performed in an oven (Heraeus Instruments Type UT6060) at the pre-set temperature. For the autocatalytic experiments with LA and FA, a series of ampoules were filled with inulin (0.1 g/ml) and the appropriate amount of each acid (0 or 0.1 M) and placed in an oven (Binder, APT Line™ FD (E2)) at 180 °C for a predetermined reaction time. The experiments were repeated at different reaction times allowing construction of an HMF yield versus time plot for each individual organic acid and the blank experiment. All experiments were conducted in duplicate and the average value is taken. The outcome of the autocatalytic experiments cannot be compared directly with that of the screening and experimental design experiments as the heating up profile (temperature versus time) for both ovens differs.

After reaction, the ampoules were opened and the reaction mixture was taken out, and centrifuged for about 10-30 minutes to remove the solids. The liquid product was diluted with demi water before analysis.

The composition of the inulin sample and particularly the type and amount of C₆-sugars was determined by an acid-catalysed hydrolysis reaction. For this purpose, inulin (2.5 g) was dissolved at 70°C in 150 mL of water under stirring. The pH was adjusted to 1.4-1.6 by adding HCl (12 M). Then, the solution was placed in a water-bath for 30 minutes at 90°C. A liquid sample was taken and analysed by HPLC.

### 3.2.3 Analysis

Matrix assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) on a Voyager-DE PRO was used to determine the molecular weight of the inulin sample. 2,5-Dihydroxybenzoic acid (DHB) was used as the matrix.

HPLC was used to identify and quantify the liquid product from the reactions. The HPLC system consisted of a Hewlett Packard 1050 pump, a Bio-Rad organic acid column Aminex HPX-87H and a Waters 410 differential refractive index detector. A sulfuric acid solution (5 mM) was used as the eluent with a constant flow rate of about 0.55 ml.min⁻¹. The column was operated at 60 °C. The HPLC was calibrated with solutions of the pure compounds at a range of concentrations. Using the chromatogram peak area and the external calibration curves, the concentrations of components in the liquid phase were determined.
3.2.4 Definitions

The HMF yield \( Y_{HMF} \) is defined according to equation 1 and reported on a weight basis.

\[
Y_{HMF} = \frac{C_{HMF} \times M_{HMF} \times V}{W_{in}} \times 100 \% \quad (\text{wt})
\]  

(1)

\[
Y_{LA} = \frac{C_{LA} \times M_{LA} \times V}{W_{in}} \times 100 \% \quad (\text{wt} \%)
\]  

(2)

Here, the \( C_{HMF} \) and \( C_{LA} \) represents the HMF and LA concentrations (mol L\(^{-1}\)), \( M_{HMF} \) and \( M_{LA} \) the molecular weights of HMF and LA, respectively (g mol\(^{-1}\)), \( V \) the reaction volume (L) and \( W_{in} \) the intake of inulin (g/L).

The yield of HMF was converted from wt\% to mol\% by assuming that inulin consists of linked glucose/fructose units (C\(_{6}\)H\(_{10}\)O\(_{5}\)) which react to HMF according to the following stoichiometry:

\[
\text{C}_{6}\text{H}_{10}\text{O}_{5} \rightarrow \text{C}_{6}\text{H}_{6}\text{O}_{3} + 2 \text{H}_{2}\text{O}
\]  

(3)

As such, the maximum yield of HMF is 78 wt\%. Thus, the yield of HMF in mol\% may be calculated from the yield in wt\% by dividing the latter by 0.78.

3.2.5 Statistical modeling

The optimisation experiments were modeled using Design-Expert 7 software (Stat-Ease). The yield of HMF \( Y_{HMF} \) was modeled using a standard expression as given in equation (4):

\[
Y_{HMF} = b_2 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} \sum_{j=1}^{3} b_{ij} x_i x_j
\]  

(4)

The independent variables (inulin intake, temperature and reaction time) are represented by the indices 1–3. The regression coefficients were obtained by statistical analyses of the data. Significance of factors was determined by their \( p \)-value in the ANOVA analyses. A factor was considered significant if the \( p \)-value was lower than 0.05, meaning that the probability of noise causing the correlation between a factor and the response is lower than 5%.
Insignificant factors were eliminated using backward elimination, and the significant factors were used to model the data.

3.3 Result and Discussion

3.3.1 Inulin characterization

The molecular weight distribution of the inulin used in this study (Dahlia tubers) was determined by MALDI-TOF/MS, a technique particularly suited for molecular weight determinations of oligosaccharides and polysaccharides \[49-50\]. The $\overline{M_n}$ was found to be 2560, the $\overline{M_w}$ 3680, indicating an average degree of polymerisation (DP) of about 16. Roberfroid [31] reported that the DP of inulin varies according to plant species, weather conditions, and the physiological age of the plant. In chicory, DP values range from 2 to 65, with 15 reported as an average. For inulin from onions, the DP is in the range of 2-12, for Jerusalem artichoke the DP is reported to be $< 40$. Thus, the experimentally determined value of the DP of the inulin sample used in this study is within the ranges reported in the literature.

The D-fructose and D-glucose content of the inulin used in this study were determined by a mild hydrolysis of the samples followed by HPLC analyses of the liquid phase. The fructose content was 94 mol%, the remainder being glucose, giving a fructose to glucose ratio of 15 to 1. The fructose content is in close agreement with the literature for Dahlia tubers (94.1 – 96.7 mol%) [51]. Thus, the inulin sample comprises of oligomers with d-fructoside units, with each oligomer chain on average capped with a D-glucose molecule, in line with literature data [31].

3.3.2 HMF synthesis from inulin in the absence of a catalyst

Exploratory experiments on the thermal conversion of inulin were performed at 170°C, using an inulin intake of 0.1 g/mL. A typical concentration profile is given in Figure 1. Six water soluble components were identified in the reaction mixtures (HPLC). Three show a clear maximum in the course of the reaction, viz. D-fructose, D-glucose and HMF, and are as such intermediates in the reaction sequence. The final products are LA, formic acid (FA) and acetic acid (AA). In addition, some brown-black insolubles were observed, known as humins, which are always formed during the acid catalysed conversions of carbohydrates in water, either in monomeric or polymeric form [8].
Fig. 1 Concentration-time profiles for various compounds during the thermal conversion of inulin in water (170°C, C_in = 0.1 g/mL).

The product composition versus time is in agreement with the reaction network provided in Scheme 2. It involves the saccharification of inulin to the monomeric building blocks (D-fructose and some D-glucose), followed by the reaction of these C6 sugars to HMF. The latter is not inert under reaction conditions and reacts further to LA and FA [18-19], [52-55].

Scheme 2 A simplified reaction scheme for the conversion of inulin to HMF.
Besides these products, acetic acid was detected in small amounts, though not quantified. Acetic acid is likely formed by hydrolysis of acetyl side groups in the inulin [56] or alternatively, from further degradation reactions of the intermediates. For instance, Asghari et al. [46] reported the formation of acetic acid (5 mol%) from fructose in subcritical water (200-320°C, residence time of 120 s, Cfruct of 0.05 M, no catalyst).

3.3.3 Effect of process conditions of the uncatalysed conversion of inulin to HMF

To determine and quantify the effect of process variables on the conversion of HMF, 24 experiments were conducted in a batch reactor set up (glass ampoules) using a central composite design. Three independent variables, the temperature (153-187°C), inulin intake (0.03-0.12 g/mL) and reaction time (18-74 min), were explored and the yields of HMF and LA were taken as the dependent variables. The results are provided in Table 3.

<table>
<thead>
<tr>
<th>Run</th>
<th>Cin, g/mL</th>
<th>Treaction, °C</th>
<th>t, min</th>
<th>YHMF, wt %</th>
<th>YLA, wt %</th>
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<tr>
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<td>170</td>
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<td>22.8</td>
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<td>18</td>
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<td>74</td>
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<td>12.4</td>
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</table>

a The yield of HMF is defined in equation 1; b The yield of LA is defined in equation 2
The center point of the central composite design was measured six times and the HMF yield was found to be on average 21.4 wt% with a standard deviation of 2.9 wt%. Thus, the reproducibility of the experimental procedure appears to be good. The highest experimental HMF yield was about 35 wt% (45 mol%, entry 6 in Table 3) and was achieved at 180 °C, an inulin intake of 0.05 g/mL and a reaction time of 18 min. Wu et al., [34] reported an HMF yield of 41% at 180°C, an inulin intake of 0.05 g/mL and a reaction time of 2 h. Comparison is cumbersome as conditions are not exactly similar and different starting materials were used (among others, inulin source and related properties like DP).

It is also of interest to compare the results with those obtained for inulin in water with sulphuric acid as the catalyst [57]. In the latter case, the highest experimental yield of HMF was 39.5 wt% (50.6 mol%), obtained at 170 °C, 0.17 g/mL inulin intake and an acid concentration of 0.006 M and 20 min reaction time. Thus, the maximum HMF yield for the uncatalysed, thermal reaction within the window of process conditions is only slightly lower than when using a Brönsted acid. The reaction time is in general much longer for the thermal reaction than for the sulphuric acid catalysed reaction. As such, the use of a Brönsted acid catalyst has advantages in terms of reaction rates and as such a smaller reactor will be needed to achieve a certain production rate (kg/h). However, sulphuric acid recycle, complicating the work-up section, is not required for the uncatalysed reaction. Detailed process design studies will be required for both options to evaluate the best approach and these are beyond the scope of the current study.

### 3.3.4 Statistical modeling

The HMF yield ($Y_{HMF}$) as a function of the independent variables was statistically modeled using the Design-Expert 7 software package. All independent variables (temperature $T$, intake inulin $C_{in}$ and reaction time $t$) were shown to be statistically significant and to have an effect on the HMF yield. The best model for HMF yield is given in equation 5 and includes both quadratic and interaction terms. An extended version with more significant numbers for the coefficients to be used for among others reactor engineering studies is given in the supplementary information. The R-squared of the model is 0.9664, an indication that the model fits the experimental data well.
\[ Y_{\text{HMF}} = (1466.7)C_{\text{in}} + (11.8)T + (9.3)t - (9.2)C_{\text{in}}T - (0.05)tT - (0.03)T^2 - (0.009)t^2 - 1223.9 \]

(5)

Analysis of the model variance is given in Table 4. A good agreement between the model and the experimental data was observed, as is shown in the parity plot provided in Figure 2.

**Table 4** Analysis of variance of the HMF model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean square</th>
<th>F-value</th>
<th>p-value Prob &gt; F</th>
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<td>&lt; 0.0001</td>
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<tr>
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<td>20.85</td>
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<td>1</td>
<td>50.63</td>
<td>12.39</td>
<td>0.0028</td>
</tr>
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<td>t (C)</td>
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<td>1</td>
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<td>0.56</td>
<td>0.4665</td>
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<td>55.60</td>
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</tr>
<tr>
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</tr>
<tr>
<td>$B^2$</td>
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<td>107.51</td>
<td>26.31</td>
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</tr>
<tr>
<td>$C^2$</td>
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<td>159.51</td>
<td>39.04</td>
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</tr>
<tr>
<td>Residual</td>
<td>65.38</td>
<td>16</td>
<td></td>
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</tr>
</tbody>
</table>

**Fig. 2** Parity plot between the experimental and modelled HMF yields.

With the statistical model available, it is possible to determine the effects of the process conditions on the HMF yield within the design window. To illustrate this, the model
predictions for HMF yield for batch times of 30 min (Figure 3, left) and 40 minutes (Figure 3, right) are given versus the temperature and inulin intake. The yield of HMF is a complex function of the independent variables and it is difficult to draw general conclusions. Though, as expected, the HMF yields after 40 min are lower than for 30 minutes. This is due to the subsequent reaction of HMF to LA and FA (Scheme 2), leading to a lowering in the HMF yield. The effect of the inulin intake on the HMF yield is also complex in nature and temperature depending. At low temperatures, the HMF yield is slightly higher at higher inulin intakes, whereas the opposite trend is observed at higher temperatures, where a lower inulin intake is favoured.

![Fig. 3 Modeled HMF yield versus temperature and inulin intake for two batch times (left: 30 min; right: 40 min).](image)

The occurrence and importance of the consecutive reaction of HMF to LA was also confirmed by considering the LA yield ($y_{LA}$) versus the process conditions (Table 3). The LA yield was modeled and the results are given in Figure 4 and Table 5. The model equation with an R square of 0.9464 is given in equation 6. An extended version with more significant numbers for the coefficients to be used for among others reactor engineering studies is given in the supplementary information. The parity plot (Figure 5) reveals good agreement between the model and the experimental data.
\[ Y_{LA} = 437.51 + (0.09)t + (0.17)C_{in}t + (5.88 \times 10^{-4})Tt + (1422.29)C_{in}^2 + (0.02)T^2 - (188.89)C_{in} - (5.41)T - (0.12)C_{in}T - (1.69 \times 10^{-3})t^2 \] (6)

**Fig. 4** Modeled LA yield versus temperature and reaction time at a fixed inulin intake of 0.09 g/mol.

**Table 5** Analysis of variance of the LA model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>df</th>
<th>Mean square</th>
<th>F-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>273.91</td>
<td>9</td>
<td>30.43</td>
<td>27.44</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>C_{in} (A)</td>
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<td>1</td>
<td>1.29</td>
<td>1.16</td>
<td>0.2989</td>
</tr>
<tr>
<td>T (B)</td>
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<td>1</td>
<td>157.95</td>
<td>142.42</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>t (C)</td>
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<td>25.28</td>
<td>22.79</td>
<td>0.0003</td>
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<tr>
<td>AB</td>
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<td>1</td>
<td>$8.95 \times 10^{-3}$</td>
<td>$8.07 \times 10^{-3}$</td>
<td>0.9297</td>
</tr>
<tr>
<td>AC</td>
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<td>1</td>
<td>0.09</td>
<td>0.079</td>
<td>0.7829</td>
</tr>
<tr>
<td>BC</td>
<td>0.15</td>
<td>1</td>
<td>0.15</td>
<td>0.14</td>
<td>0.7151</td>
</tr>
<tr>
<td>A^2</td>
<td>14.29</td>
<td>1</td>
<td>14.29</td>
<td>12.88</td>
<td>0.0030</td>
</tr>
<tr>
<td>B^2</td>
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<td>43.84</td>
<td>39.53</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>C^2</td>
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<td>4.97</td>
<td>4.48</td>
<td>0.0527</td>
</tr>
<tr>
<td>Residual</td>
<td>15.53</td>
<td>14</td>
<td>1.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As expected on the basis of the reaction network proposed in Scheme 2, the LA yield is higher when using a longer batch time and higher temperatures, see Figure 4 for details.
3.3.5 Possible role of acid formation on HMF yields: autocatalytic effects

During the course of the reactions, organic acids such LA and FA are formed. These acids may act as catalysts for all reactions in the proposed reaction network (Scheme 2). To gain insight in the effect of these organic acids on the reaction rates and product distributions, a number of additional batch experiment was performed using inulin as the starting material and with one of the individual acids (LA or FA) and a combination of LA and FA present at the start of the reaction. The experiments were carried out at a temperature of 180 °C, an acid concentration of 0.1 M, and an inulin loading of 0.1 g/mL. The results are given in Figure 6.

When considering the fructose concentration versus time profiles, it is evident that the presence of particularly formic acid has a positive effect on the rate of reaction of fructose and all fructose reacts away considerably faster when compared to the uncatalysed reaction and the reaction in the presence of LA. A similar trend was found for the HMF concentration versus time profiles. Here the presence of FA also leads to a reduction of the time required to reach the maximum HMF concentration. The autocatalytic effect of LA is by far less pronounced than for FA and the profiles are essentially similar to the uncatalysed reaction. This, we may conclude that particularly FA has a positive effect on the reaction rates. These findings may be explained by considering the pKA values of both acids, 3.75 for FA and 4.6 for LA, indicating that a stronger Brønsted acid leads to higher reaction rates due to a higher Brønsted acidity of the solution. Thus, the formation of D-fructose and HMF is mainly due to

![Fig. 5 Parity plot between the experimental and modeled LA yield.](image)
autocatalytic effects of FA. These findings are in line with studies reported in the literature using fructose as the substrate (Table 2). For instance Ranoux et. al.,[45] showed that the reaction of fructose to HMF is autocatalysed by formic acid and that the role of LA is by far less pronounced.

Fig. 6 Autocatalytic effect of LA and formic acid on the concentration time profiles for fructose and HMF (180°C, an acid concentration of 0.1 M, and an inulin loading of 0.1 g/mL).

An interesting observation is that the maximum HMF concentration in the concentration-time profile is only slightly dependent on the presence of the organic acids, though evidently the reaction rates are affected. This also seems to be the case for D-fructose, though this is less clear as the fructose concentration may already have reached a maximum before the first sampling point (15 min). Both fructose and HMF are intermediates in the reaction network as given in Scheme 2. The near time independency of the maximum HMF yields as given in Figure 6 (right) suggests that both the rates of inulin hydrolysis to fructose (with oligomeric intermediates), the subsequent formation of HMF and the subsequent reaction to LA and FA are equally affected by the presence of FA, implying a similar reaction order in H⁺ (likely close to 1) [57].

However, without detailed kinetic studies (including determination of the amount of oligomeric sugars during reaction) it is not possible to draw definite conclusions about the exact mode of action of the organic acids and the way they influence reaction rates and thus the product yields. In addition, also for the thermal reaction, organic acids are formed in the course of the reaction, resulting in autocatalytic effects that substantially complicate a detailed kinetic analysis.
3.4 Conclusions

The uncatalysed, thermal conversion of inulin to HMF in water was studied for a wide range of reaction conditions, including variations in temperature (153-187°C), inulin intake (0.03-0.12 g/mL) and reaction time (18-74 min). The highest HMF yield was 35 wt%, corresponding to a 45% yield on a molar basis (180 °C, inulin intake of 0.05 g/mL and a reaction time of 18 min). The experimental data were modelled using a statistical approach. The model shows a good fit with the experimental data and allows estimation of the HMF yield as a function of temperature, inulin intake and reaction time. This model may be used for reactor engineering purposes, for instance to optimise the HMF yield in continuous reactors with different degrees of mixing.

Autocatalysis of reaction products (FA and LA) and particularly by FA, the strongest acid, occurs to a significant extent as was shown by separate experiments with inulin in the presence of organic acids. These findings indicate that it may be advantageous regarding HMF yield to perform the reaction in a buffer solution at neutral pH values. These experiments are in progress and will be reported in due course.

Supplementary information.

Supplementary information is provided in the next paragraph

3.5 Nomenclature

\[ C_{\text{HMF}} \]: concentration of HMF (mol L\(^{-1}\))
\[ C_{\text{LA}} \]: concentration of levulinic acid (mol L\(^{-1}\))
\[ M_{\text{HMF}} \]: molecular weight of HMF (g mol\(^{-1}\))
\[ M_{\text{LA}} \]: molecular weight of LA (g mol\(^{-1}\))
\[ t \]: time (min)
\[ T \]: temperature (°C)
\[ V \]: volume of reaction (L)
\[ W_{\text{in}} \]: intake of inulin (g L\(^{-1}\))
\[ Y_{\text{HMF}} \]: yield of HMF (wt%) 
\[ Y_{\text{LA}} \]: yield of LA (wt%)
3.6 References


3.7 Supplementary Material

Experimental and modeling studies on the uncatalysed thermal conversion of inulin to 5-hydroxymethylfurfural and levulinic acid

\[
\text{HMF yield} = -1223.87339 \\
1466.69731 \times \text{inulin intake} \\
11.75492 \times T \\
9.35425 \times \text{time} \\
-9.19413 \times \text{inulin intake} \times T \\
-0.05071 \times T \times \text{time} \\
-0.02628 \times T^2 \\
-0.00945 \times \text{time}^2
\]

\[
\text{LA yield} = +437.51303 \\
-188.89308 \times \text{inulin intake} \\
-5.41277 \times T \\
+0.092913 \times \text{time} \\
-0.11725 \times \text{inulin intake} \times T \\
+0.17390 \times \text{inulin intake} \times \text{time} \\
+5.88156E-004 \times T \times \text{time} \\
+1422.29493 \times \text{inulin intake}^2 \\
+0.016862 \times T^2 \\
-1.69004E-003 \times \text{time}^2
\]