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Experimental and modeling studies on the acid-catalyzed conversion of inulin to 5-hydroxymethylfurfural in water

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ABSTRACT

Inulin is considered as an attractive feed for the synthesis of 5-hydroxymethylfurfural (HMF), an important biobased platform chemical with high application potential. We here report a systematic study to optimize the HMF yield from inulin in a batch reactor for reactions in water using sulphuric acid as the catalyst. The latter was selected on the basis of a screening study with seven organic- and inorganic Brønsted acids (H₂SO₄, HNO₃, H₃PO₄, HCl, trifluoroacetic acid, maleic acid and fumaric acid). The effect of process conditions such as temperature (160–184 °C), inulin loading (0.05–0.17 g/mL), sulphuric acid concentration (0.001–0.01 M) and reaction time (0–60 min) on HMF and levulinic acid (LA) yields were determined experimentally and subsequently modeled using non-linear multivariable regression. The highest experimental HMF yield was 39.5 wt% (50.6 mol%) and was obtained at 170 °C, an inulin loading of 0.17 g/mL, a sulphuric acid concentration of 0.006 M and a reaction time of 20 min. Agreement between experiments and model for both HMF and LA yield was very satisfactorily.

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1. Introduction

Biomass is a renewable source for bioenergy, biofuels and biobased chemicals and has attracted high interest in recent years (Hoogwijk et al., 2005; Demirbas, 2009; van Putten et al., 2013; Sheldon, 2014; Delidovich et al., 2014; Agirrezabal-Telleria et al., 2014). For instance, biofuels have been commercialized (bioethanol from sugars, biodiesel from plan oils) and are available on the market. However, substantial research and development activities will be required to develop and commercialize efficient chemical processes for the production of a wide range of biobased chemicals. Bozell and Petersen (2010) compiled a list of 12 biobased chemicals that have highest techno-economical potential (Werpy and Petersen, 2004). The top 12 list includes

5-hydroxymethylfurfural (HMF), which may be converted to versatile building blocks for polymers such as 1,6-hexanediol (Buntara et al., 2012), 2,5-furandicarboxylic acid (Boisen et al., 2009) and fuel-additives such as 2,5-dimethylfuran (Roman-Leshkov et al., 2007).

HMF is typically obtained by reacting C6 sugars in water in the presence of a Brønsted acid (Barrett et al., 2006; Bicker et al., 2003; Huber and Dumesic, 2006; Corma et al., 2007; Hu et al., 2008; Tong et al., 2010; Amiri et al., 2010; van Putten et al., 2013; Choudhary et al., 2013; Agirrezabal-Telleria et al., 2014; Wang et al., 2014). By-products of the reaction are levulinic acid and formic acid (Girisuta et al., 2008) and insolubles known as humins (van Zandvoort et al., 2013). In water, fructose gives a maximum HMF yield of around 55 mol%, whereas the yields for glucose are less than 10 mol%. Higher HMF yields from

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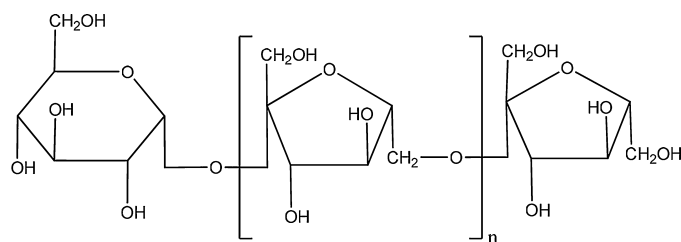


Fig. 1 – Molecular structure of inulin.

fructose (>80 mol%) have been reported in other solvent systems, especially in ionic liquids and aprotic polar solvents such as DMSO (van Putten et al., 2013).

Inulin is a biopolymer consisting of mainly fructose and minor amounts of glucose (Fig. 1) and as such is an attractive biopolymer for the synthesis of HMF (Fleche et al., 1982; Rapp, 1988; Corma et al., 2007). The molecular weight of inulin is by far less than typical biopolymers like cellulose, hemicellulose and starch and degrees of polymerization between 2 and 70 have been reported. Inulin is present in Jerusalem artichoke tubers, Chicory roots, Camas bulbs and Dahlia tubers, with contents of around 20 wt% on fresh weight (Gupta and Kaur, 1997; Franck, 2002; Kays and Nottingham, 2008).

A number of studies have been reported on the synthesis of HMF from inulin in various solvents (van Putten et al., 2013). The most commonly used solvent is water, though organic solvents (including ionic liquids) and biphasic liquid–liquid systems have been explored as well. For instance, Despax et al. reported HMF synthesis from inulin in dimethylsulfoxide (DMSO) without the use of a catalyst and a 47% yield of HMF was reported (Despax et al., 2014). In ionic liquids, HMF yields of up to 59% have been reported when using [HMIM][HSO₄] as the solvent at 80 °C (Qi et al., 2010). Further improvements were possible using a catalyst and for instance Hu et al. (2009) reported yields up to 64% when using ChoCl as the ionic liquid in combination with oxalic acid as the catalyst. However, HMF recovery from these solvents is difficult and cumbersome. Product work-up and yields may be improved considerably by using biphasic liquid–liquid systems. Highest reported HMF yields in such biphasic systems from inulin are up to 87%

using a water-2-butanol system in combination with tantalum catalysts (Yang et al., 2011).

An overview of studies on inulin conversion in water as the solvent, the focus of this research, using both homogeneous and heterogeneous catalysts is given in Table 1.

It can be concluded that only a limited amount of information is available for the conversion of inulin in water using homogeneous Brønsted acids whereas heterogeneous catalysts have been explored in more detail, with HMF yields up to 65 wt%. Also of relevance is a patent of the Süddeutsche Zucker-Aktiengesellschaft who investigated the use of Chicory roots (with about 18% inulin on dry-matter) as a starting material for a potentially commercially attractive HMF production process in water. Starting from 20 kg chicory roots, an HMF yield of 13% was reported. Next to HMF, fructose (30%) and glucose (3.5%) were obtained. The reaction was carried out with sulphuric acid at a pH of 1.8 at 140 °C for 2 h (Rapp, 1988).

We here report a screening study on the conversion of inulin in water using a range of Brønsted acids. Such studies have not been reported in the literature and are an absolute novelty of this paper. Water was selected as the solvent as it is environmentally benign and is more easily removed from the products in the work-up section than polar organic solvents like DMSO. One of the best catalyst from this screening study (sulphuric acid) was taken and used for a systematic study to determine the effect of process conditions (temperature, reaction time, inulin intake, catalyst concentration) on the HMF and LA yield with the main objective to optimize HMF yields. The experimental data were modeled using multivariable non-linear regression to quantify the results.

Table 1 – Overview of HMF yield data for the catalyzed conversion of inulin to HMF in water.

C _{inulin} (wt%)	T (°C)	t	Catalyst	Catalyst loading	HMF yield (%) ^a	Ref.
Water/homogeneous catalyst						
5	160	4 min	CO ₂	6 MPa	45 ^b	Wu et al. (2010)
5	160	4 min	CO ₂	9 MPa	42 ^b	Wu et al. (2010)
5	180	2 min	CO ₂	4 MPa	45 ^b	Wu et al. (2010)
5	180	2 min	CO ₂	6 MPa	50 ^b	Wu et al. (2010)
5	180	2 min	CO ₂	11 MPa	52 ^b	Wu et al. (2010)
5	200	45 min	CO ₂	6 MPa	53 ^b	Wu et al. (2010)
5	200	45 min	CO ₂	9 MPa	49 ^b	Wu et al. (2010)
Water/solid catalyst						
6	100	3 h	Niobium phosphate	SCR = 1.6 ^c	31 (mol%)	Carlini et al. (1999)
6	100	0.5 h	Cubic ZrP ₂ O ₇	SCR = 1.8 ^c	26 (wt%)	Benvenuti et al. (2000)
6	100	1 h	Cubic ZrP ₂ O ₇	SCR = 1.8 ^c	35 (wt%)	Benvenuti et al. (2000)
6	100	2 h	Cubic ZrP ₂ O ₇	SCR = 1.8 ^c	36 (wt%)	Benvenuti et al. (2000)
6	100	1 h	Ti(PO ₄)(H ₂ PO ₄)·2H ₂ O	SCR = 1.8 ^c	41 (wt%)	Benvenuti et al. (2000)
6	100	2 h	Ti(PO ₄)(H ₂ PO ₄)·2H ₂ O	SCR = 1.8 ^c	65 (wt%)	Benvenuti et al. (2000)
6	80	2 h	FeVOP	5 wt%	35 (mol%)	Carlini et al. (2004)
10	155	18 min	HNb ₃ O ₈	SCR = 50 ^c	43 (mol%)	Wu et al. (2013)

^a wt or mol in brackets after entries.

^b wt% or mol% not provided.

^c SCR = substrate to catalyst ratio.

2. Experimental

2.1. Chemicals

Inulin from dahlia tubers was purchased from Acros Organic (Geel, Belgium). Sulphuric acid (96–98%) was purchased from Merck KGaA (Darmstadt, Germany). D-fructose (99%) and levulinic acid ($\geq 97\%$) were obtained from Acros Organic (Geel, Belgium). Formic acid ($\geq 95\%$) and D-glucose ($\geq 99.5\%$) were purchased from Merck KGaA (Darmstadt, Germany). Hydroxymethylfurfural ($\geq 99\%$) was obtained from Aldrich (Steinheim, Germany). All chemicals were used without purification and de-ionized water was used to prepare the solutions.

2.2. Experimental procedures

The experiments were performed in small glass ampoules (internal diameter of 5 mm, a length of 15 cm and thickness of 1.5 mm) according to a procedure reported earlier by our group (Girisuta et al., 2006). Different ovens were applied for the catalyst screening study and the optimization studies with sulphuric acid. This may affect the heating profile (temperature versus time) for the ampoules when placed in the oven and this may, particularly for the fast reactions affect the outcome considerably. As such the reported HMF yields for the catalyst screening study and the experimental design study using sulphuric acid are not directly comparable.

2.3. Screening experiments with a range of Brönsted acids

The experiments were carried out using a similar procedure as described above. To reduce experimental error, a series of ampoules was filled with inulin (0.17 g/mL) and the appropriate amount of each Brönsted acids (0.006 M) used in this study. The ampoules were placed in a metal rack and placed in the oven (170 °C). After a pre-determined reaction time, the metal rack was removed and all ampoules were quickly quenched in cold water. Products were taken from the ampoules and centrifuged at 7000 rpm for 10–30 min to separate the solid. Supernatants were taken, diluted with demi water and subsequently the concentration of HMF was determined by HPLC. The experiments were repeated at different reaction batch times allowing construction of an HMF yield versus time plot for each individual acid. All experiments were conducted in duplicate and the average value is taken.

2.4. Typical experiment for the experimental design study using sulphuric acid as the catalyst

Predetermined amounts of inulin and sulphuric acid in water (4 mL) were loaded in the glass ampoules. The ampoules were sealed with a torch. A series of ampoules was placed in a rack in a heating oven at constant temperature. At different reaction times, an ampoule was taken from the oven and quickly quenched in a cold water bath to stop the reaction. The ampoules were opened and the reaction mixture was taken out, and centrifuged for about 10–30 min to remove the solids. The liquid product was diluted and used as such for analyses.

2.5. Analysis

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 Water 410 differential refractive index detector. A very dilute aqueous sulphuric acid solution (5 mM) was used as the eluent with a constant flow rate of about $0.55 \text{ cm}^3 \text{ min}^{-1}$. 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 curve, the unknown concentrations of components in the liquid phase was determined.

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.

The composition of the inulin sample and particularly the type and amount of C6-sugars was determined by an acid-catalyzed 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 an aqueous HCl solution. Then, the solution was placed in a water-bath for 30 min at 90 °C. A liquid sample was taken and analyzed by HPLC.

2.6. Definitions

The HMF yield (Y_{HMF}) and LA yield (Y_{LA}) are defined on a wt% basis and determined from the concentration of HMF and LA after reaction (HPLC) and the inulin intake, see Eqs. (1) and (2) for details.

$$Y_{\text{HMF}} = \frac{C_{\text{HMF}} \times M_{\text{HMF}} \times V}{W_{\text{In}}} \quad (\text{wt}\%) \quad (1)$$

$$Y_{\text{LA}} = \frac{C_{\text{LA}} \times M_{\text{LA}} \times V}{W_{\text{In}}} \quad (\text{wt}\%) \quad (2)$$

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 consist of linked glucose/fructose units ($\text{C}_6\text{H}_{10}\text{O}_5$) which react to HMF according to the following stoichiometry:



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.

2.7. Statistical modeling

The optimization experiments were modeled using Design-Expert 7 software (Stat-Ease). The yield of HMF was modeled using a standard expression as given in Eq. (4):

$$y_{\text{HMF}} = b_0 + \sum_{i=1}^4 b_i x_i + \sum_{i=1}^4 \sum_{j=1}^4 b_{ij} x_i x_j \quad (4)$$

The independent variables (inulin intake, H_2SO_4 concentration, temperature and reaction time) are represented by the

indices 1–4. The regression coefficients were obtained by statistical analyses of the data. Significance of the factors was determined by their *p*-value in the ANOVA analysis. 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 0.05. Insignificant factors were eliminated using backward elimination, and the significant factors were used to model the data.

3. Result and discussion

3.1. Inulin characterization

The molecular weight distribution of the inulin used in this study, which originates from Dahlia tubers, was determined by MALDI-TOF MS, a technique particularly suited for oligosaccharides and polysaccharides (Harvey, 1996; Kazmaier et al., 1998). The M_n value was 2560, and the M_w was 3680, indicating an average degree of polymerization (DP) of about 16. Roberfroid (2005) reported that the DP of inulin varies according to plant species, weather conditions, and the physiological age of the plant. In chicory, the reported DP range from 2 to 65, but 15 is 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 DP of the Dahlia tuber sample used in this study is within the ranges reported in the literature.

The D-fructose and D-glucose content were determined by a mild hydrolysis of the samples followed by HPLC analyses of the liquid phase (see Section 2.5). The fructose content was 94 mol%, and a fructose to glucose ratio of 15:1 was obtained. Thus, the inulin sample contains mainly fructose, with each oligomer chain on average capped with a D-glucose molecule, in line with literature data (Roberfroid, 2005).

3.2. Brønsted acid catalyst screening

In the first stage of the project, a Brønsted acid screening study was performed using seven organic and inorganic Brønsted acids to identify the best catalyst for the conversion of inulin to HMF. All screening experiments were conducted at 170 °C, an inulin loading of 0.17 g/mL, an acid concentration of 0.006 M and a maximum reaction time 60 min. After reaction, typically a brown solution was obtained accompanied, in some cases, with some dark brown solids (humins). The HMF yield versus the reaction time for the various acids is given in Fig. 2.

As seen in Fig. 2, distinct differences in reaction rates were observed. Highest rates were observed for the strong acids (H_2SO_4 , HCl, HNO_3 , TFA) as is evidenced from the slope of the

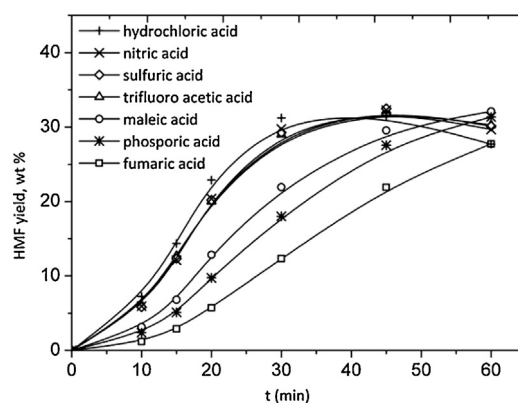


Fig. 2 – HMF yield versus reaction time for various Brønsted acid catalyst (170 °C, inulin loading 0.17 g/mL, acid concentration 0.006 M).

HMF yield versus time curve between 0 and 30 min reaction times. For these acids, an optimum in HMF yield was observed within the timeframe 0–60 min. The maximum HMF yield for these acids was about 32 wt% (41 mol%). The reaction rate for the other weaker acids (maleic, fumaric and phosphoric acid) was considerably lower and the maximum HMF yield was not yet attained within the timeframe of the experiments.

To quantify the data, the HMF yield after 30 min (Table 2) is plotted against the pKa value of the Brønsted acid (Fig. 3, left). Two distinct regimes can be observed: (i) one with an almost constant Y_{HMF} when the pKa of the acid is below 0 (very strong acids) and (ii) a regime with an inverse linear relation between the HMF yield and the pKa of the acids for a pKa between 2 and 3. Thus, strong acids give a higher HMF yield after 30 min than the weaker acids. This indicates that the concentration of H^+ plays a major role regarding the rate of the reactions leading to HMF, see Fig. 3 (right). An almost linear relation between the pH of the solution and the HMF yield is observed, with lower pH values leading to higher rates. This trend may be rationalized by positive effects of protons on both the hydrolysis rate of the inulin ether bonds to fructose and glucose and the subsequent reaction rate of fructose/glucose to HMF.

For all strong acids, a clear maximum of the HMF yield was observed within the timeframe of the experiments. This maximum HMF yield is essentially independent of the acid and about 32 wt%. For the weaker acids, the maximum HMF yield was not yet attained after 60 min reaction time due to the lower reaction rates (vide supra). However, the yields are at least comparable to those for the strong acids (Fig. 2).

Table 2 – HMF yield after 30 min batch time for the various acids.

Acid catalyst	Y_{HMF} , wt% ^a	Acidity, pKa ^b	pH ^c	Reference for pKa value
Fumaric acid	12	3.03 (4.44)	2.71	Dawson et al. (1959)
Phosphoric acid	18	2.12 (7.20, 12.31)	2.54	Bjerrum et al. (1957)
Maleic acid	21	1.93 (6.07)	2.35	Dawson et al. (1959)
Trifluoroacetic acid	29	0.23	2.23	Milne and Parker (1981)
Nitric acid	30	–1.3	2.22	Kolthoff and Elving (1959)
Sulphuric acid	29	–3 (1.92)	2.22	March (1985)
Hydrochloric acid	31	–8	2.22	March (1985)

^a T = 170 °C, inulin = 0.17 g/mL, C_{acid} = 0.006 M, 30 min reaction time.

^b pKa of the first proton dissociation is given, values in brackets are the second and third when applicable.

^c Calculated at room temperature, temperature effects on pH calculations are given in the Supplementary information.

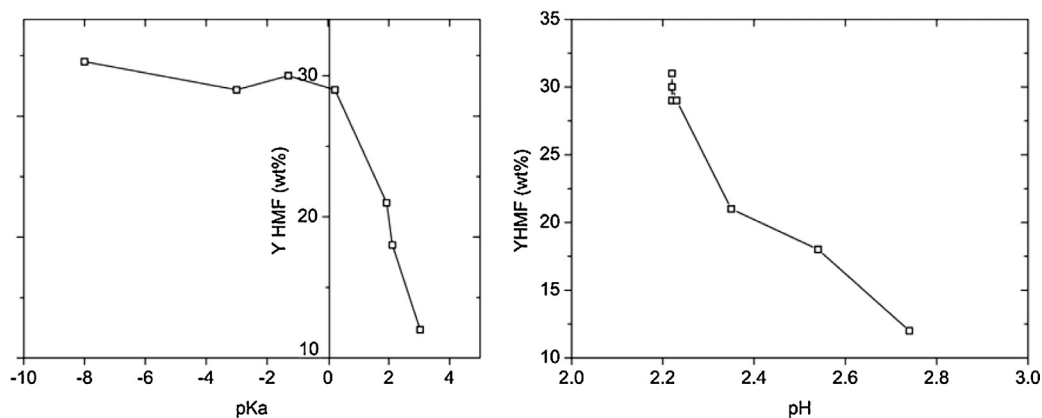


Fig. 3 – HMF yield after 30 min batch time versus the pKa of the acid (left) and the pH of the solution (right).

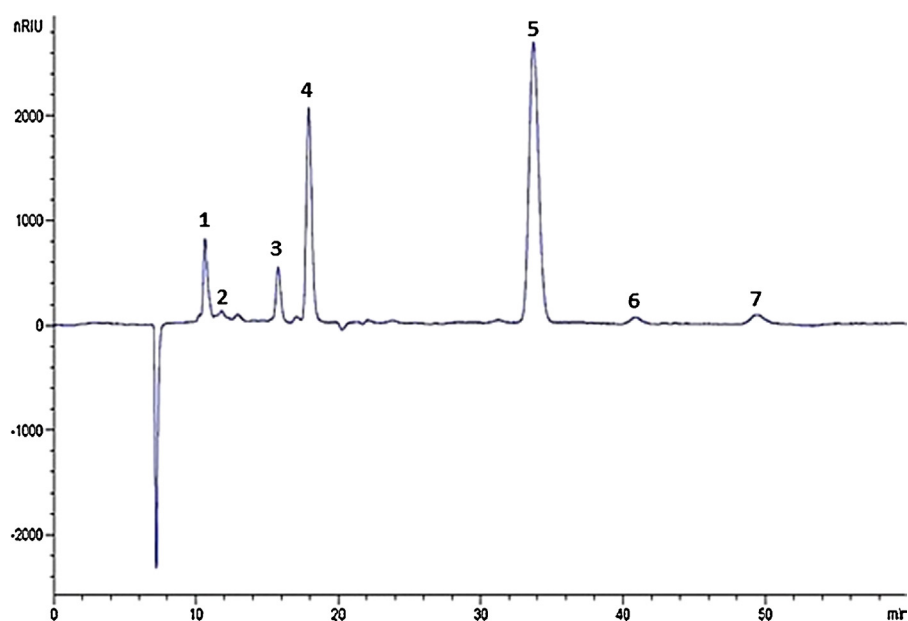


Fig. 4 – HPLC chromatogram for a representative reaction mixture (170 °C, 30 min, $C_{in} = 0.1 \text{ g/mL}$, $C_{H_2SO_4} = 0.005 \text{ M}$). (1) Glucose; (2) fructose; (3) formic acid; (4) LA; (5) HMF; (6) benzenetriol; (7) furfural.

3.3. Product identification

A typical chromatogram of a representative reaction mixture using sulphuric acid as the catalyst is given in Fig. 4 and shows the presence of glucose, levulinic acid, HMF, and a small amount of fructose. Minor amounts of benzenetriol, furfural and acetic acid were also detected (<1%).

A typical concentration profile for the reaction is shown in Fig. 5. Clear intermediates in the reaction are fructose, glucose and HMF, the main final products after prolonged reaction times are LA and formic acid (FA). These findings are consistent with the reaction pathway provided in Scheme 1. In the initial stage, inulin is depolymerized to sugar monomers (mainly fructose and some glucose). In the next step, both fructose and glucose react to HMF by a dehydration reaction. Of interest is the observation that the maximum concentration of fructose is reached at a much shorter reaction time than that of glucose.

When assuming that the rate of the hydrolysis reaction of ether linkages in inulin is equal for a glucose–fructose unit and a fructose–fructose unit, this indicates that the conversion of fructose to HMF is much faster than the reaction of glucose to HMF, in accordance with kinetic studies reported by our group (Girisuta et al., 2006; Fachri et al., 2015a,b). Under the prevailing

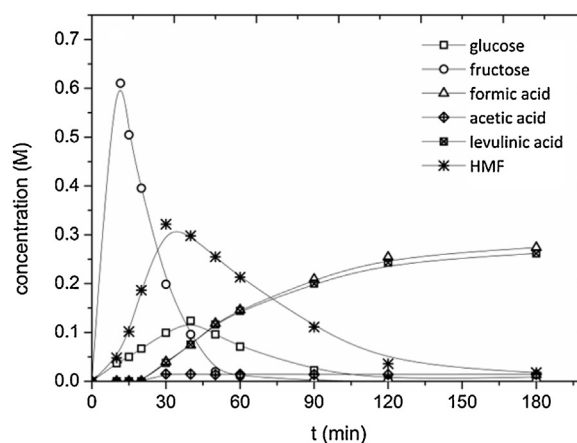
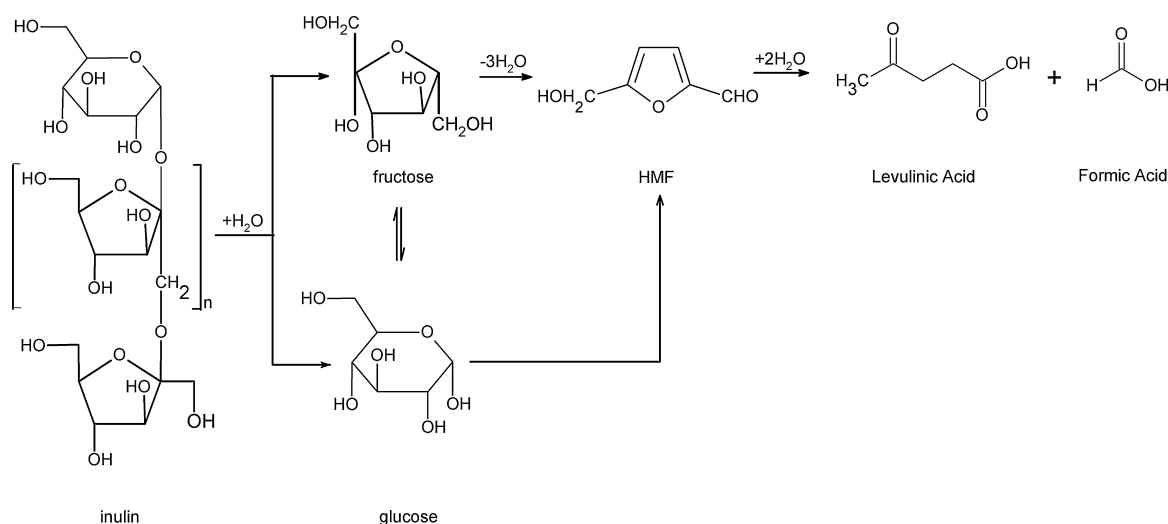


Fig. 5 – Concentration profile for the acid-catalyzed decomposition of inulin ($T = 160 \text{ °C}$, $C_{in} = 0.17 \text{ g/mL}$, $C_{H_2SO_4} = 0.006 \text{ M}$). Lines are for illustrative purposes only.

reaction conditions, HMF is not stable and reacts to LA and the co-product formic acid. Another undesired side reaction that limits the amount of HMF is the formation of insoluble compounds known as humins (Antal and Mok, 1990; Aida et al.,



Scheme 1 – Proposed reaction network for the conversion of inulin to HMF and LA/FA.

2007; Asghari and Yoshida, 2007). The formation pathways for these condensation products are still under debate, though are likely formed from reactions between HMF and sugars (van Zandvoort et al., 2013).

3.4. Systematic investigations for sulphuric acid and statistical modeling

A systematic study on the effect of the main process variables (temperature, inulin intake and acid concentration) on the yield of HMF was performed using sulphuric acid. This acid was selected on the basis of the screening study reported above and earlier studies on our group on the sulphuric acid catalyzed conversions of fructose (Fachri et al., 2015a,b) and

glucose to HMF (Girisuta et al., 2006). A total of 27 experiments were carried out according to an experimental design. The total number of experiments, the setting of the independent variables per experiment and the center point (including the number of replicates) are set by the software package (Design expert, see Section 2.7). The results are given in Table 3.

The center point of the design was measured six times and the HMF yield was found to be on average 34.2 wt% (43.8 mol%) with a standard deviation of 1.5 wt%. Thus, the reproducibility of the experimental procedure appears to be good.

The HMF yield as a function of the process variables was statistically modeled using the Design-Expert 7 software. The best model, shown in Eq. (5), includes quadratic and interaction terms. An extended version with more significant

Table 3 – Overview of experiments for inulin in water using sulphuric acid.

Run	Temperature (T), °C	Inulin intake (C _{in}), g/mL	Sulphuric acid concentration, M	Reaction time (t), min	Y _{HMF} , wt%	Y _{LA} , wt%
1	170	0.10	0.006	60	13.3	13.2
2	180	0.05	0.010	10	4.7	0.6
3 ^a	170	0.10	0.006	20	31.1	2.7
4	180	0.15	0.001	60	1.7	10.1
5	180	0.05	0.001	10	5.3	0.1
6	160	0.05	0.010	10	7.6	0.04
7	160	0.05	0.010	10	7.1	0.06
8	160	0.15	0.010	60	10.1	18.0
9	160	0.15	0.010	60	11.7	16.2
10	156	0.10	0.006	20	21.7	3.5
11	180	0.15	0.010	10	7.0	0.01
12	180	0.05	0.001	60	13.2	10.0
13	170	0.10	0.012	20	25.7	7.1
14 ^a	170	0.10	0.006	20	34.5	3.0
15	170	0.17	0.006	20	39.5	2.0
16	170	0.10	0.006	10	10.6	0.06
17	160	0.15	0.010	10	6.5	0.03
18 ^a	170	0.10	0.006	20	35.1	2.1
19	160	0.05	0.001	60	33.7	2.4
20	160	0.05	0.001	60	30.1	1.9
21 ^a	170	0.10	0.006	20	34.9	3.1
22	160	0.15	0.001	60	24.4	6.8
23 ^a	170	0.10	0.006	20	35.1	2.1
24	180	0.15	0.001	10	11.7	0.01
25	184	0.10	0.006	20	34.3	5.6
26 ^a	170	0.10	0.006	20	34.8	2.1
27	160	0.05	0.010	60	18.0	13.9

^a Center point experiments.

Table 4 – Analysis of variance for the best model for the yield of HMF.

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F	
Model	3954.59	11	359.51	67.02	<0.0001	Significant
A-T	295.66	1	295.66	55.12	<0.0001	
B-C _{load}	25.33	1	25.33	4.72	0.0462	
C-C _{cat}	130.64	1	130.64	24.36	0.0002	
D-t	47.93	1	47.93	8.94	0.0092	
AC	129.80	1	129.80	24.20	0.0002	
AD	294.38	1	294.38	54.88	<0.0001	
BD	124.71	1	124.71	23.25	0.0002	
CD	203.95	1	203.95	38.02	<0.0001	
A ²	115.41	1	115.41	21.52	0.0003	
C ²	146.39	1	146.39	27.29	0.0001	
D ²	1660.30	1	1660.30	309.53	<0.0001	
Residual	80.46	15	5.36			

numbers for the coefficients to be used for among others reactor engineering studies is given in the supplementary information. The R square of 0.9801 indicates that the model fits the experimental data well

$$Y_{\text{HMF}} = (17)T + (56.5)C_{\text{load}} + (50700.9)C_{\text{cat}} + (16.3)t - (249.9)TC_{\text{cat}} - (0.06)Tt - (2.3)C_{\text{load}}t - (125.2)C_{\text{cat}}t - (0.04)T^2 - 4.2 \times 10^5 C_{\text{cat}}^2 - (0.06)t^2 - 1782.5 \quad (5)$$

Analysis of variance of the model is given in Table 4. A good agreement between the empirical model and the experimental data was observed as shown in the parity plot provided in Fig. 6.

The highest experimental HMF yield is 39.5 wt% (50.6 mol%) and was obtained at 170 °C, $C_{\text{in}} = 0.17$ g/mL, $C_{\text{H}_2\text{SO}_4} = 0.006$ M and a reaction time of 20 min. This value is slightly lower than reported by Wu et al. (2010) for the reaction in water under a CO₂ atmosphere. Here, in situ formed carbonic acid catalyses the reaction and a HMF yield of 53 mol% were reported (200 °C, CO₂ pressure of 6 MPa, inulin intake of 5 wt% and a reaction time of 45 min).

The modeled HMF yield versus the temperature and catalyst concentration at different batch times (25–50 min) is given in Fig. 7. Highest HMF yield according to the model was 36.1 wt% (39.5 wt% experimental) obtained at 170 °C, $C_{\text{inulin}} = 0.17$ g/mL, $C_{\text{H}_2\text{SO}_4} = 0.006$ M; and 20 min batchtime. As

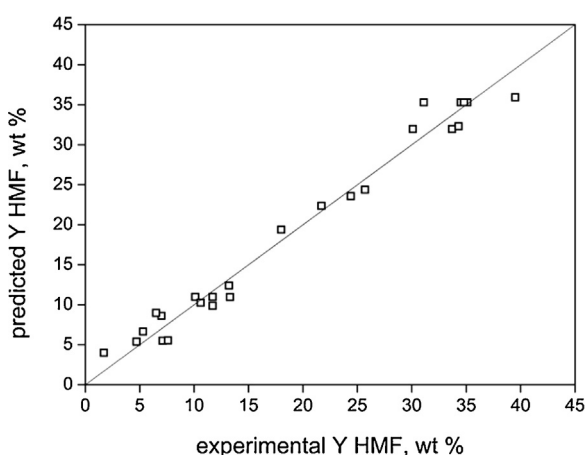


Fig. 6 – Parity plot between the experimental predicted data from the empirical model.

expected based on the reaction network for HMF formation involving multiple consecutive reactions (Scheme 1), the batchtime is an important optimization parameter. Clearly, batchtimes above 40 min lead to a reduction of the HMF yield in the process window due to the subsequent reaction of HMF to LA and FA (vide infra). For a certain batchtime, a broad optimum is observed for the HMF yield as a function of the temperature and catalyst concentration. Highest HMF yields were obtained for a combination of a high temperature–low acid concentration or low temperature–high acid concentration. This is rationalized by considering that at low temperature and low acid concentrations, the rate of HMF formation from fructose is still limited whereas at the high-temperature–high acid concentration, the subsequent reaction to LA is already occurring to a large extent and yield of HMF is already lower than the maximum.

For all reactions performed within this study (Table 3), the yield of LA was also determined experimentally. The LA yield as a function of process variables was quantified using a statistical model (Eq. (6)) and the results are given in Table 5. 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. A good fit between experiments and model was obtained as is evident from the R-squared value of 0.9873 and a parity plot of the experimental versus the modeled LA yields (Fig. 8).

$$ptY_{\text{LA}} = 184.2 + (270.3)C_{\text{in}} - (2.3)T - (616.8)C_{\text{H}_2\text{SO}_4} - (0.9)t - C_{\text{in}}T + (5.8 \times 10^3)Tt + (0.4)C_{\text{in}}t + (24.1)C_{\text{H}_2\text{SO}_4}t + (6.8 \times 10^{-3})T^2 - (468.2)C_{\text{in}}^2 + (39425.7)(C_{\text{H}_2\text{SO}_4})^2 \quad (6)$$

As expected, the LA yield is also a clear function of the reaction time, with higher reaction times leading to the highest yield within the experimental window (Fig. 9). This finding is in line with the proposed reaction pathway in Scheme 1, where LA is the final product within the reaction scheme, which is inert under the prevailing conditions. Higher temperature, particularly at longer reaction times, also leads to higher LA yields, in agreement with the previous statement.

3.5. Comparison between thermal and acid-catalyzed reaction of inulin to HMF

In a previous study, we have investigated the non-catalyzed, thermal reaction of inulin to HMF (Fachri et al., 2015b). As

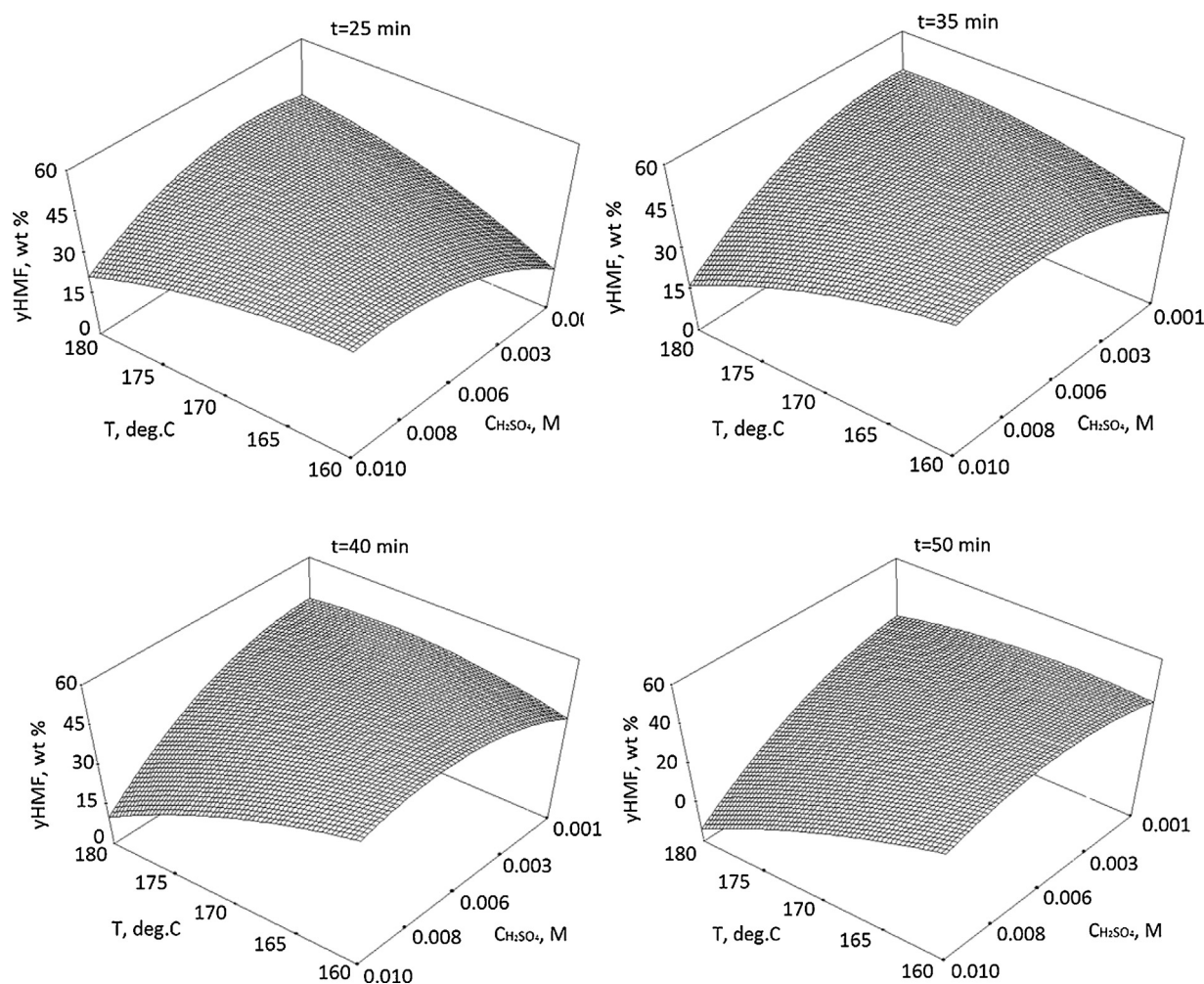


Fig. 7 – Effect of process conditions on HMF yield according to the statistical model given in Eq. (5).

Table 5 – Analysis of variance of the preferred model of LA.

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F	
Model	744.84	11	67.71	106.31	<0.0001	Significant
A-T	31.26	1	31.26	49.08	<0.0001	
B-C _{load}	7.38	1	7.38	11.59	0.0039	
C-C _{cat}	94.75	1	94.75	148.76	<0.0001	
D-t	491.77	1	491.77	772.10	<0.0001	
AB	3.34	1	3.34	5.24	0.0370	
AD	22.17	1	22.17	34.81	<0.0001	
BD	3.35	1	3.35	5.27	0.0366	
CD	70.21	1	70.21	110.23	<0.0001	
A ²	3.59	1	3.59	5.64	0.0314	
B ²	7.00	1	7.00	10.99	0.0047	
C ²	2.91	1	2.91	4.58	0.0493	
Residual	9.55	15	0.64			

such it is of interest to compare the performance of a reaction with a catalyst in the form of sulphuric acid with a non-catalyzed reaction. The HMF yield versus the batchtime for a catalyzed and uncatalyzed reaction at otherwise similar conditions (170 °C, $C_{\text{inulin}} = 0.17 \text{ g/mL}$) is given in Fig. 10. The maximum HMF yield for the catalyzed reaction is occurring at a lower batchtime, indicating that the rate of the various reactions is higher for the catalyzed than the uncatalyzed version. For this particular experiment, the maximum HMF yield for

the catalyzed reaction (40 wt%, 51 mol%) was also considerably higher than for the non-catalyzed version (27 wt%, 35 mol%).

The HMF yield for the thermal reaction was determined for a range of process conditions (153–187 °C, an inulin loading between 0.03 and 0.12 g/mL and batch times between 18 and 74 min using a central composite experimental design) (Fachri et al., 2015a,b) and the highest HMF yield was 35 wt% (45 mol%) at 180 °C, inulin intake of 0.05 g/mL and a reaction time of 18 min. A comparison with the maximum HMF yield obtained

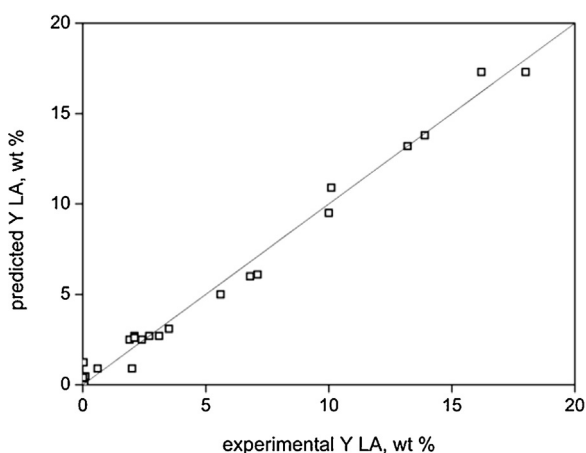


Fig. 8 – Parity plot between the experimental predicted data from the empirical model.

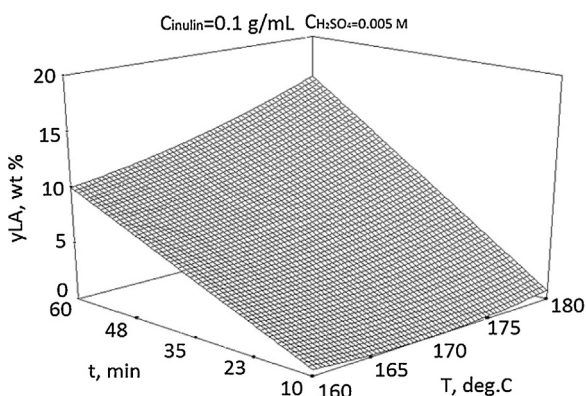


Fig. 9 – Modeled LA yield versus temperature and reaction time at a selected inulin intake.

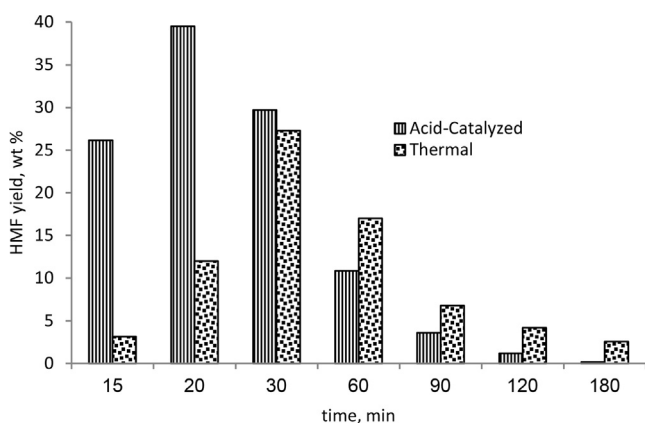


Fig. 10 – HMF yield versus reaction time for the thermal and acid-catalyzed conversion of inulin to HMF ($T = 170^{\circ}\text{C}$, $C_{\text{in}} = 0.17 \text{ g/mL}$, $C_{\text{H}_2\text{SO}_4} = 0.006 \text{ M}$).

in this study, viz. 39.5 wt% (51 mol%, 170°C , inulin intake of 0.17 g/mL, sulphuric acid concentration of 0.006 M and reaction time of 20 min) reveals that the catalyzed reaction leads to a higher HMF yield (about 5 wt%). Combined with the fact that the reaction rates are higher for the acid catalyzed version, the space time yields for HMF ($\text{kg HMF/m}^3 \text{ reactor h}$) are also higher for the catalyzed reaction. However, downstream processing for the uncatalysed version is less complicated

than for the catalyzed version as catalyst recycle is not required.

4. Conclusions

An in-depth experimental and statistical modeling study on the acid-catalyzed reaction of inulin in water to HMF in a batch reactor is reported. Acid screening studies show that strong acids like H_2SO_4 are the best regarding reaction rates. With this particular acid, the effects of process variables such as inulin intake (0.05–0.17 g/mL), temperature ($160\text{--}180^{\circ}\text{C}$), sulphuric acid concentration (0.001–0.01 M) and reaction time (0–60 min) on the HMF yields were determined. The highest experimental HMF yield (39.5 wt%, 51 mol%) was obtained at 170°C , an inulin intake of 0.17 g/mL, a sulphuric acid concentration of 0.006 M and a reaction time of 20 min. The data were modeled using a statistical approach and good agreement between experiments and model were obtained. The maximum HMF yields (39.5 wt%) as well as the reaction rates for the sulphuric catalyzed reactions was shown to be higher than for the uncatalysed version (35 wt% HMF yield). As such, the catalyzed version seems preferred. However, further process studies are required to draw definite conclusions as down-stream processing aspects should be considered. For instance, catalyst recycle is not required for the uncatalysed version and this may have a positive effect on the process economics.

Conflict of interest

The authors declare that they have no competing interests or conflict of interests.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cherd.2016.01.002](https://doi.org/10.1016/j.cherd.2016.01.002).

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