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# High purity fructose from inulin with heterogeneous catalysis – kinetics and modeling

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## ABSTRACT

**BACKGROUND:** Inulin can be extracted from the non-edible chicory root and high purity fructose can be obtained from hydrolysis of inulin and used as a valuable platform molecule for further valorization. Heterogeneous catalysts are sought after alternatives to mineral acids because of costly separation and severe corrosion problems. In this work, hydrolysis of inulin was performed in a batch reactor with an advanced sulfonic resin (Smopex-101) employing HCl as a reference catalyst, at 75°C - 95°C and pH ranging from 1 to 2.

**RESULTS:** The reaction was shown to proceed predominantly via an end-biting mechanism. The activity of the heterogeneous catalyst was on par with the reference catalyst, with the special advantage that Smopex-101 was more selective towards monomer formation at milder reaction conditions. Mathematical modelling of the kinetics was successfully performed with a recently developed model incorporating a reaction mechanism based on an autocatalytic effect.

1 **CONCLUSIONS:** The current work demonstrates that high purity fructose can be obtained  
2 by hydrolysis of inulin employing a heterogeneous catalyst at ambient pressure. The results  
3 can directly be utilized for optimization and design purposes and they open up novel  
4 possibilities in production and process design, i.e. batch or possibly continuous operation  
5 without the need for costly separation and corrosion problems commonly encountered with  
6 homogeneous catalysts.

7 **Keywords:** Heterogeneous Catalysis, Kinetics, Mathematical Modelling, Biomass, Catalytic  
8 Processes, Green Engineering/Products

## 9 **NOTATION**

10	$k$	Conversion dependent pre-exponential factor ( $\text{L mol}^{-1} \text{min}^{-1}$ )
11	$k_0$	Pre-exponential factor ( $\text{min}^{-1}$ )
12	$\beta$	Ratio between rate constants in Eq. 1
13	$X$	Conversion
14	$\alpha$	Exponential factor in Eq. 1
15	$k_\infty$	Pre-exponential factor at the end of the reaction ( $\text{min}^{-1}$ )
16	$c_F, c_G$	Concentrations of fructose and glucose ( $\text{g/L}$ )
17	$c_{0F}, c_{0G}$	Initial concentrations of fructose and glucose ( $\text{g/L}$ )
18	$c_{\text{mono}}, c_{\text{inu}}$	Concentrations of monomers and inulin ( $\text{g/L}$ )
19	$c_{0\text{mono}}, c_{0\text{inu}}$	Initial concentrations of monomers and inulin ( $\text{g/L}$ )
20	$c_H, c_W$	Concentration of $\text{H}^+$ and water ( $\text{mol/L}$ )

1	$c_{0W}$	Initial concentration of water (mol/L)
2	$V_L$	Volume of the liquid (L)
3	$k_{0I}$	Pre-exponential factor ( $L \text{ mol}^{-1} \text{ min}^{-1}$ )
4	$E_a$	Apparent activation energy (kJ/mol)
5	$R$	Gas constant (J/K mol)
6	$\theta$	Modified temperature
7	$T$	Temperature (K)
8	$T_{\text{mean}}$	Mean temperature (K)
9	$Q$	Sum of residual squares
10	$c_{\text{exp}}$	Concentration measured experimentally (g/L)
11	$c_{\text{est}}$	Concentration estimated by modelling (g/L)
12	$R^2$	Degree of explanation
13	$y_i$	Vector for the values of the desired function
14	$f_i$	Vector with the modelled values
15	Inu	Inulin
16	Fru	Fructose
17	Glu	Glucose
18	Mono	Monomers

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## INTRODUCTION

Inulin is a naturally occurring polysaccharide, which is present as an energy storage carbohydrate in numerous plants and vegetables, such as chicory (*Cichorium intybus*), Jerusalem artichoke (*Helianthus tuberosus*), wheat (*Triticum aestivum*), onion (*Allium cepa*), banana (*Musa acuminata*) and garlic (*Allium sativum*).<sup>1,2</sup> It is a linear polydisperse  $\beta(2\rightarrow1)$  fructan possessing glucose units as the chain-terminating groups. The degree of polymerization (DP) of inulin ranges commonly from 20 to 60, which implies that it is a relatively short chain polysaccharide. Inulin is often extracted and isolated from the non-edible chicory root, which contains in its natural form up to 20% of it.<sup>3-5</sup> The high content of inulin in chicory roots makes it a very attractive source of fructose, which is an interesting molecule not only for the alimentary and beverage industry, but also for the overall carbohydrate industry including many non-food applications.<sup>6</sup> Moreover, inulin has been used in medical applications for renal malfunction diagnosis, drug delivery and anti-tumor activity; it can be fermented by different microorganisms to ethanol, acetone-butanol or 2,3-butanediol, and it can also be chemically derived to various platform chemicals such as glycerol, hydroxymethylfurfural (HMF) or mannitol.<sup>7-10</sup> Carbohydrates represent roughly 75% of the annually growing renewable biomass, being the starting point of an expanding industry, which aims to replace products from petrochemical sources by economically viable transformations of carbohydrates.<sup>11</sup> Fructose is conventionally obtained in the form of high-fructose corn syrup (HFCS) after enzymatic isomerization of glucose produced by starch hydrolysis. Although this process is widely used globally on a million tons scale, it exhibits several disadvantages such as thermodynamic limitations and high-cost separation.<sup>12</sup> Hydrolysis of inulin is an attractive alternative for the synthesis of very high purity fructose, requiring only one reaction step. Inulin can be enzymatically hydrolyzed to produce fructose

1 <sup>13</sup>, however, similar to other processes involving enzymes, this technology is costly and low  
2 yields are achieved.<sup>14</sup>

3 Acid hydrolysis of inulin is a feasible alternative for fructose production and it can be  
4 performed by using mineral acids, such as sulfuric or hydrochloric acids, however, separation  
5 in this process is further complicated by the neutralization step, as it involves downstream salt  
6 separation. Based on the literature, it can be stated that acidity is the main parameter  
7 controlling the reaction rate, while temperature has a strong influence on fructose  
8 degradation.<sup>15</sup> An adequate knowledge of the reaction kinetics is crucial in controlling the  
9 consecutive reactions.<sup>16-18</sup> The ability to employ solid acid catalysts in the hydrolysis of inulin  
10 would resolve the problems related to utilizing mineral acids such as corrosion, reuse of the  
11 catalyst, the need for neutralization and costs related to separation of the catalyst from the  
12 products.<sup>19</sup> The main objective of the current research is to demonstrate the feasibility of  
13 utilizing a selected heterogeneous catalyst for hydrolysis of inulin and to compare its  
14 performance with a homogeneous catalyst under identical experimental conditions.

15 Commonly applied for hydrolysis of polysaccharides, HCl was chosen as the homogeneous  
16 reference catalyst. The heterogeneous catalyst was selected based on literature, considering a  
17 number of criteria related to physical and chemical properties of the reactants and catalysts as  
18 well as on previous experience with hydrolysis of hemicelluloses.<sup>20-22</sup> Inulin is a fairly large  
19 molecule, which needs to be taken into account when choosing the catalyst, as undesirable  
20 internal mass transfer limitations become inevitable with porous catalysts, especially if the  
21 pore diameter is too small. Given the size of the molecules, a heterogeneous catalyst with a  
22 high external surface area was sought after. Another important factor is the thermal stability,  
23 as temperatures close to 100°C should be employed to ensure a reasonable hydrolysis rate. A  
24 highly acidic catalyst was also desired, as the hydrolysis rate is known to be pH dependent.  
25 Taking into account all the physical and chemical requirements, Smopex-101 was selected as

1 the heterogeneous catalyst for the hydrolysis. The catalyst has also proven to be effective in  
2 the hydrolysis of hemicelluloses such as arabinogalactan, xylan and *o*-  
3 acetylgalactoglucomannan.<sup>20-22</sup>

## 4 **EXPERIMENTAL**

### 5 **Materials**

6 Inulin from chicory (Sigma Aldrich) with an average degree of polymerization of 36 was used  
7 as the reactant. Hydrochloric acid (36-38%) (J.T. Baker) and Smopex-101 (Johnson Matthey)  
8 were used in the experiments as homogeneous and heterogeneous catalysts, respectively.  
9 Smopex-101 has a fibrous morphology and nonporous structure. Fiber dimensions are 40  $\mu\text{m}$   
10 (diameter) 250  $\mu\text{m}$  (length). The functional group is  $\text{SO}_3\text{H}$  with a capacity of 3.6  $\text{mmol}_{\text{eq}}/\text{g}$ . A  
11 SEM image of the catalyst is displayed in Figure. 1.

### 12 **Reactor set-up**

13 An isothermal glass-made batch reactor equipped with intense mechanical agitation (300  
14 rpm), a reflux condenser and a double jacket was used for all experiments. Silicone oil was  
15 heated in a bath (VWR® International) equipped with a thermostat and circulated in the  
16 double jacket to heat the reaction mixture. The temperature of the reaction mixture was  
17 measured using a thermocouple immersed in the solution and regulated by varying  
18 temperature in the oil bath. The temperature was recorded every 30s with the data being  
19 stored on a PC. The thermocouple was Teflon coated to withstand the harsh conditions.

### 20 **Experimental procedure**

21 In order to achieve the desired pH with the solid catalyst, the acid capacity provided by the  
22 manufacturer was taken into account. The dry content was experimentally verified with  
23 gravimetry by drying the catalyst overnight in an oven at 70°C. The inulin solution was

1 prepared in the desired concentration (0.5% wt) by dissolving a pre-determined amount of  
2 inulin in distilled water and heating it under warm water until a clear solution was obtained.  
3 Approximately 150 mL of the inulin solution was introduced into the batch reactor and heated  
4 to the desired reaction temperature. Once the temperature was attained, the catalyst was  
5 introduced with a funnel followed by 50 mL of the solution to avoid loss of catalyst.

6 With the homogeneous catalyst, the inulin solution was first loaded into the reactor and heated  
7 to the desired temperature whereafter the reaction was started by introducing the catalyst. The  
8 temperature in the reactor remained stable throughout the reaction ( $\pm 0.5^{\circ}\text{C}$  of the set point).  
9 The overall reaction time was 3-4 hours. The stirring rate was kept constant (300 rpm) during  
10 the heating and the reaction. Samples were withdrawn using a syringe (10 mL) connected to a  
11 silicone tube, which was immersed in the reactor. Both the solid and liquid phases were  
12 withdrawn during sampling in equal proportions, keeping the solid-liquid ratio constant inside  
13 the reactor. To separate the liquid fraction from the solid catalyst, the samples were filtered  
14 using syringe filters (Acrodisc LC 13 mm with 0.45 $\mu\text{m}$  PVDF membrane). When using HCl  
15 as the catalyst, the sample was cooled down and neutralized with NaOH to pH 4–4.5 and  
16 placed in a freezer.

17 Experiments with the heterogeneous Smopex catalyst were conducted at three different  
18 temperatures, 75 $^{\circ}\text{C}$ , 85 $^{\circ}\text{C}$  and 95 $^{\circ}\text{C}$ , to reveal the temperature dependence of the reaction  
19 rates. The main goal was to conduct hydrolysis at high temperature to achieve reasonable  
20 reaction rates, while still avoiding monomer degradation, ensuring operation at ambient  
21 pressure, as well as, staying below the limits of the catalysts thermal stability.

22 The pH values in the experiments were chosen to determine the inulin hydrolysis kinetics, as  
23 well as, to observe kinetics of fructose degradation. This was done, as the formation of the  
24 degradation products has been one of the limiting factors in the production of fructose by



1 chemical hydrolysis. The reaction should be optimized towards the fructose production, while  
2 still avoiding consecutive low-molecular degradation reactions. Experiments were carried out  
3 at pH values of 1, 1.26 and 2 to study the influence of acidity on the reaction rates. For  
4 practical reasons, it was not possible to reach pH = 0 using Smopex-101, as the solid-liquid  
5 ratio would have been too high. The catalyst amounts used in the experiments were calculated  
6 by taking into account the capacity of the catalyst, provided by the manufacturer and a  
7 volume of 200 mL of inulin solution used in each experiment.

### 8 **Analysis**

9 The HPLC analysis provided, after proper calibration, not only the concentration of the  
10 monomers, fructose and glucose, but also the amount of inulin. An Aminex® HPX-87C, 300  
11 mm x 7.8 mm column optimized for analyzing monosaccharides was used, being also able to  
12 provide class separation of some oligomers. It is typically used for the quantification of  
13 glucose and fructose in high fructose corn syrup and general monosaccharide analysis. For  
14 HPLC a VWR Hitachi Chromaster equipped with a 5450 RI detector, 5310 column oven,  
15 5210 autosampler and 5110 pump was used. Analysis was performed at 85°C and with a  
16 carrier solution (1.2 mM CaSO<sub>4</sub>) flow rate of 0.5 mL/min. The samples did not require any  
17 pretreatment for this analysis.

18 The peak separation for inulin, fructose and glucose in the HPLC analysis was very good.  
19 However, minor leaching of the sulphonic groups from Smopex-101 took place, which was  
20 noticed in the results of the experiments with high catalyst concentrations. The leached  
21 compounds appeared in the chromatogram at the same retention time (RT) as inulin, hence a  
22 calibration for this effect was made with Smopex-101 solutions in water to correct the values  
23 obtained for inulin.

1 In order to determine the amount of sulphonic groups leached from the catalyst, separate  
2 leaching experiments were performed in identical conditions to the hydrolysis experiments.  
3 The quantification was made by placing Smopex-101 (pH=1) in distilled water (95°C) with  
4 agitation for four hours and filtering the solid from the liquid, after which the pH of the  
5 solution was measured. The pH of the liquid phase is directly proportional to the amount of  
6 leached sulphonic groups and the results showed that only about 1% of the sulphonic groups  
7 were leached. This verifies that the leaching does not influence the reaction kinetics in  
8 practice, but it interferes slightly with the analysis. Kusema et al.<sup>23</sup> showed that kinetics of  
9 hydrolysis of hemicellulose such as arabinogalactan over pH=3 were very slow and almost no  
10 reaction takes place.

11 For determining oligomers, the samples were analyzed by gas chromatography (GC). The  
12 analysis of the oligomer content gave the overall fraction of the monomers, dimers, trimers,  
13 tetramers, pentamers and hexamers in the analyzed samples, and the concentrations of each  
14 fraction of oligosaccharides was calculated using the monomer concentrations obtained in the  
15 previous HPLC analysis as a quantitative reference.

16 The GC samples were prepared by freezing them at -18°C and then freeze drying overnight,  
17 since the analysis is sensitive to moisture. In the next step, the samples were derivatized by  
18 adding the silylation reagents (150µL pyridine, 150µL HDMS, 70µL TMCS), shaking in a  
19 vortex and placing for 30 s in an ultrasound bath. The samples were left overnight and  
20 transferred to GC vials and analyzed. The oligosaccharides were determined by GC with a 7  
21 m (L) x 0.53 mm (ID) column (J&W HP-1/SIMDIST) and a flame ionization detector (45  
22 ml/min). The GC was a Perkin-Elmer Autosystem XL instrument using the following  
23 temperature profile: 100°C, ramping rate 12°C/min to 340°C. The carrier gas was H<sub>2</sub> with a  
24 flow rate of 7 mL/min.

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## **RESULTS AND DISCUSSION**

The reproducibility of the experiments was evaluated by duplicating three experiments at different experimental conditions. The results of the experiments are displayed in Figure S1 in the supporting information. The average standard deviation in the experiments was 2 %, when calculated on the basis of the substrate concentration, which demonstrates that the reproducibility of the experimental procedure and the analysis is very good. The influence of external mass transfer limitations on the reaction rate was evaluated by performing experiments with stirring speeds of 330 rpm and 400 rpm. No increase in the hydrolysis rate was observed at the higher agitation rates, compared to the experiments performed at 300 rpm, which confirms the absence of external mass transfer limitations. The leaching behavior of the catalyst was investigated by analyzing the amount of sulphonic groups in the liquid phase after the experiment performed in the harshest experimental conditions used in this work. It was concluded, that less than 1 % of the sulphonic groups were leached to the liquid phase, which confirms that the hydrolysis is catalyzed by the solid catalyst as the contribution of the liquid phase sulphonic groups to the pH was negligible.

### **Influence of pH and temperature on hydrolysis rate and product distribution**

The pH of the solution affects not only the hydrolysis of inulin to fructose and glucose, but also the degradation of the monomers, especially fructose, as it is in general more prone to degradation. A wide catalyst concentration range was investigated in the experiments to be able to observe both the monomer formation and degradation, as the overall kinetics involved in the hydrolysis process is important for process optimization towards the monomer production.

1 The effect of temperature effect on the hydrolysis was evaluated by comparing the  
2 experimental results obtained at 75°C, 85°C and 95°C. The temperature range was chosen as  
3 high as possible, while still operating at ambient pressure. Previously, the reaction rate has  
4 been observed to be extremely slow with other hemicelluloses at 60°C<sup>23,24</sup>. From the analysis  
5 results, it was noticed that glucose accounts only for a small fraction (<5%) of the total  
6 monomers, according to the structure of inulin. For the sake of simplicity, the monomers are  
7 considered as one product from now on. Concentration profiles of monomers as a function of  
8 time obtained with Smopex-101 at pH between 1 and 2 at 75°C - 95°C are displayed in Figure  
9 2. It can be noticed, that the formation rate of monomers was highly dependent on solution  
10 pH. For the lowest catalyst concentration (pH 2) the reaction proceeded very slowly, not  
11 reaching total conversion during the experiment, while for higher catalyst concentrations (pH  
12 1 and 1.26), the reaction proceeded at faster rates and almost complete conversion of inulin  
13 into monomers was achieved in 250 min.

14 Only minor, almost negligible, amounts of degradation products were observed, mainly at the  
15 lowest pH=1 and at the highest temperature (95°C). At pH=1.26 and 95°C, degradation was  
16 almost non-existent, and a yield of 95% was achieved (Figure 3a).

17 It can be concluded, that considerable differences in the reaction rates were observed under  
18 different experimental conditions. For instance, at 95°C, the reaction proceeded very rapidly  
19 and the maximum yield was obtained within 30 minutes at pH=1, while at 75°C the yield was  
20 ca. 23 % at the same pH (Figure 2e). On the other hand, at pH=2 the yield of monomers  
21 ranged from 12% at 75°C to 86% at 95°C (Figure 2a).

22 The yields of monomers correlated rather well with the inulin conversion, however, oligomers  
23 were also present, as can be seen in Figure 3, where the concentrations of the reactant (inulin),  
24 products (monomers) and intermediates (oligomers) are presented as a function of time.

1 In the harshest conditions, the hydrolysis of inulin to monomers was very rapid and some  
2 oligomers were present only during the first minutes of the reaction. At the lowest  
3 temperature, more oligomers were observed during the reaction, as the overall kinetics was  
4 much slower. Figure 3c displays the concentration of di- to tetramers during the first minutes  
5 of the reaction at pH 1.26 and 95°C. The concentrations of oligomers were so low, that some  
6 fluctuations are present in the results, due to the sensitivity of the analysis.

7 The concentration of the oligomers was low after a prolonged reaction time. In practice, the  
8 concentrations of compounds with DP exceeding 3 were negligible, with dimers being the  
9 most significant fraction among the intermediate products. The same phenomenon was  
10 observed with both catalysts. The obtained results can be rationalized by considering  
11 hydrolysis to proceed, partly via a consecutive reaction pathway where oligomers are the  
12 intermediate species, and partly as inulin direct conversion to monomers.

13 Inulin is first hydrolyzed into oligomers, which are then hydrolyzed rapidly to monomers.  
14 However, hydrolysis of the dimers to fructose requires a longer time and is very pH sensitive,  
15 i.e. the dimers appear to be the most stable intermediates.

16 The yield of monomers at pH between 1 and 2 at different temperatures can be seen in Figure  
17 4. It is evident that the formation of monomers was very rapid at pH=1 and relatively fast  
18 even at pH=2 and 95°C. It can also be noticed, that some degradation occurred at pH=1, since  
19 lower yields are achieved compared to the values obtained at pH 1.26. Moreover, the results  
20 in Figure 4. show that the mass balance obtained in the experiments is very close to 100 %, as  
21 total conversion is obtained at the harsher conditions according to the monomer analysis.

22 As a comparison, the results with HCl at pH=0.5 and 95°C showed that severe degradation  
23 took place, with the yield of fructose being 35% after 250 min. For the experiment carried out  
24 with HCl at pH=1 and 95°C, a high conversion was achieved, however 10% of fructose

1 degraded within 5 hours. The maximum yield obtained at pH=0 with HCl was ca. 74 %. A  
2 comparison between experiments carried out with HCl and Smopex-101 in identical reaction  
3 conditions is displayed in Figure 2e. It can be seen, that the hydrolysis rate with HCl was  
4 faster compared to Smopex-101, however, some degradation occurred already in the early  
5 stages of the experiment. In comparison, the hydrolysis rate compared with Smopex-101 was  
6 also efficient and the degradation was avoided.

### 7 **Kinetic modelling principles**

8 A common approach to describing hydrolysis of polysaccharides is to consider hemicelluloses  
9 as a single unit instead of a mixture of molecules of different sizes, with branching and  
10 folding. Hydrolysis of hemicelluloses, such as xylan, in the presence of a homogeneous  
11 catalyst is often described with a rate changing kinetics, with rapid hydrolysis occurring at the  
12 beginning of the reaction and slower hydrolysis proceeding at the later stage, due to the  
13 assumed existence of two different fractions of hemicelluloses with varying reactivity.<sup>25</sup>  
14 However, this is not necessarily the case in inulin hydrolysis when using a heterogeneous  
15 catalyst, as observed in the current study.

16 The observed initial reaction rate was low, but the rate of monomer formation increased with  
17 a decrease in the degree of polymerization (DP), i.e. rate acceleration was noticed. [This is](#)  
18 [clearly visible in Figure 4, especially at the milder experimental conditions, where the rate of](#)  
19 [hydrolysis notably increases during the experiment. Similar behavior was previously observed](#)  
20 [for O-acetyl-galactoglucomannan \(GGM\) hydrolysis by Kusema et al.<sup>21</sup> This phenomenon](#)  
21 [can be explained mechanistically by the decrease of the DP, and consequently, an increase in](#)  
22 [the number of accessible glycosidic bonds at the end of the polymer chains. This reaction](#)  
23 [mechanism was previously described by Salmi et al.<sup>26</sup>, who applied it to the hydrolysis of](#)  
24 [GGM.](#)

1 At the initial stage of the reaction, the inulin molecule in the aqueous solution is rather long  
2 and linear. The reaction occurs when the glycosidic bonds in inulin randomly encounter  
3 protons from the sulphonic groups at the external surface of the polymeric matrix. The bonds  
4 located at the ends of the molecule are more likely to meet the reactive protons, resulting in  
5 the excision of terminating the sugar units. This mechanism of 'end-biting' hydrolysis allows  
6 the molecule to progressively reduce its size directly to more monomers, rather than to  
7 oligomers with high DP. As the reaction progresses, the inulin chain length diminishes and  
8 hence, the probability of encounter of the glycosidic bonds with the catalyst active sites  
9 increases since more smaller molecules are formed, which translates into an increasing  
10 reaction rate. The observed formation of short oligomers also contributes to this phenomenon.  
11 This 'end-biting' mechanism is confirmed by the experimental results. Glucose appears in  
12 inulin as a chain terminating unit. For instance, in an experiment carried out at 85°C and pH 1,  
13 after ca. 30 min of reaction the glucose concentration reaches a stable value and remains  
14 constant until the end of the experiment, unlike fructose, which concentration keeps  
15 increasing until achieving a maximum stable concentration value at around 100 min. This  
16 confirms that the end groups in the molecule are released in the first stages of the reaction.  
17 Similar accelerating kinetics on heterogeneous catalysts was described by Salmi et al.<sup>26</sup>, who  
18 demonstrated that the autocatalytic effect can be accounted for by a two parameter model,

$$19 \quad k = k_0(1 + \beta X^\alpha) \quad (1)$$

20 where  $k_0$  is the pre-exponential factor in the absence of autocatalysis,  $k$  is the conversion  
21 dependent pre-exponential factor and  $X$  is conversion. Parameter  $\beta$  is expressed by

$$22 \quad \beta = \frac{(k_\infty - k_0)}{k_0} \quad (2)$$

1 If  $\beta$  obtains a value of 0, which means that  $k_{\infty}=k_0$ , i.e. the rate constant at the end of the  
 2 experiment is identical to the beginning and thus, no autocatalytic effect is present. If  $\beta$  is  
 3 positive, autocatalysis exists, and the higher the value, the stronger the phenomenon. The  
 4 parameter  $\alpha$  is the exponential factor which influences how the rate constant changes with  
 5 conversion, e.g. if  $\alpha=1$  the relation with  $\beta$  is linear; if it is 0.5 the rate constant changes more  
 6 in the beginning of the reaction which indicates that also oligomers are formed. In a pure  
 7 monomer ‘end-biting’ mechanism, a value of 1 should be obtained for  $\alpha$ , if a linear molecule  
 8 is assumed.

9 Total conversion can be calculated from the monomer products or from the unreacted inulin

$$10 \quad X = \frac{\sum c_j}{\sum c_{0j}} = \frac{c_F + c_G}{c_{0F} + c_{0G}} = \frac{c_{mono}}{c_{0mono}} = 1 - \frac{c_{inu}}{c_{0inu}} \quad (3)$$

11 where the parameters  $c_F$ ,  $c_G$  and  $c_{inu}$  represent the concentrations of fructose, glucose and  
 12 inulin, respectively and  $c_{0F}$ ,  $c_{0G}$  and  $c_{0inu}$  are the initial concentrations at  $t = 0$ .

13 A first order reaction was assumed for inulin hydrolysis based on the reaction mechanism. As  
 14 can be seen from the experimental results the concentration of glucose is rather small in  
 15 comparison to fructose (less than 10% of the total monomer content), therefore for the sake of  
 16 simplicity the sum of both monomers was considered as a single lumped product:



18 For an isothermal batch reactor with a constant volume and in the presence of a heterogeneous  
 19 catalyst, the general balance equations can be written as

$$20 \quad \frac{dc_{inu}}{dt} = -k c_H c_w c_{inu} \quad (5)$$

$$21 \quad \frac{dc_{mono}}{dt} = k c_H c_{inu} c_w \quad (6)$$



1 where  $c_H$  is the concentration of the active sulphonic sites,  $c_w$  is the concentration of water,.

2 The concentration of water can be written as

3 
$$c_w = c_{0w} - c_{mono} \quad (7)$$

4 In the case of dilute solutions ( $c_{0w} \gg c_{mono}$ ) can be considered constant during the reaction

5 ( $c_w = c_{0w}$ ), thus it can be included in the pre-exponential factor.

6 The model takes also into account the influence of temperature. A modified form of the

7 Arrhenius equation was used to take into account the temperature effect on the reaction rate,

8 
$$k_0 = k_{0I} \exp(-Ea/R\theta) \quad (8)$$

9 where  $k_{0I}$  is the pre-exponential factor and  $E_a$  the apparent activation energy. Temperature is

10 expressed as <sup>27</sup>,

11 
$$\frac{1}{\theta} = \frac{1}{T} - \frac{1}{T_{mean}} \quad (9)$$

12 where  $T_{mean}$  is 90°C. Even though temperature was stable during most of the experiments, a

13 variation of several degrees was recorded at the beginning of the reaction during heating.

14 These variations were taken into account in modelling.

15 Inserting eq. (8) in eq. (1), the following equations can be obtained

16 
$$k = k_{0I} \exp(-Ea/R\theta) (1 + \beta X^\alpha) \quad (10)$$

17 
$$k = k_{0I} \exp(-Ea/R\theta) (1 + \beta (c_{mono}/c_{0mono})^\alpha) \quad (11)$$

18 The mass balance becomes

19 
$$\frac{dc_{inu}}{dt} = -k_{0I} \exp(-Ea/R\theta) (1 + \beta (c_{mono}/c_{0mono})^\alpha) c_H c_{inu} \quad (12)$$

1 The ODE-solution and optimization software MODEST<sup>28</sup> was used for the estimation of the  
 2 kinetic parameters by nonlinear regression analysis. The model consists of ordinary  
 3 differential equations (ODEs) which describe the concentrations of reacting species. The  
 4 system of ODEs was solved with the backward difference method implemented in the  
 5 software. All sets of experimental data containing temperature and concentrations of  
 6 components as a function of time were used together in numerical data fitting. The sum of  
 7 residual squares Q was calculated with the following formula,

$$8 \quad Q = \|c_{exp} - c_{est}\|^2 = \sum_{k=1}^{nsets} \sum_{j=1}^{nobs(k)} \sum_{i=1}^{nydata(j,k)} (c_{exp,ijk} - c_{est,ijk})^2 \quad (13)$$

9 The objective function Q was minimized by the simplex-Levenberg-Marquard method where  
 10  $c_{est}$  and  $c_{exp}$  are the values of the estimated and experimental concentrations, respectively.

11 The model gave a very good fit to the experimental data as visible from Figure 5. Parameter  
 12  $R^2$  can be used to assess the degree of explanation of the modelling and is defined as,

$$13 \quad R^2 = 1 - \frac{\sum_i (y_i - f_i)^2}{\sum_i (y_i - \bar{y})^2} \quad (14)$$

14 where  $y_i$  is the vector for the values of the desired function and  $f_i$  is the vector for the  
 15 modelled values. A high degree of explanation ( $R^2=98.6\%$ ) was achieved, which confirms the  
 16 accuracy of the model to the experimental data. A value of 0.89 was found for the parameter  
 17  $\alpha$ , however, an almost equally good fit of the model was obtained by fixing the value to 1,  
 18 meaning that there is a linear dependence of the rate constant increase with the conversion.  
 19 The model could in this way be simplified.

## 20 **Summary of modelling results**

21 The fit of the model to experimental data at different experimental conditions can be seen in  
 22 Figure 5. It can be concluded that the model fits the data very well, despite very large

1 differences in the reaction rates under different experimental conditions. The results also  
2 display that the mass balance in the experiments is complete as the substrate and product  
3 concentrations correlate very well. Moreover, the results confirm the absence of external mass  
4 transfer limitations, as the kinetic model fits very well the experimental data at very differing  
5 reaction rates. The parameter values obtained in the modelling were obtained for  $E_a$  (114  
6 kJ/mol),  $k_{oi}$  ( $0.2054 \text{ L mol}^{-1} \text{ min}^{-1}$ ) and  $\beta$  (4.14) with estimated relative standard errors of  
7 1.5%, 5.4% and 11.6%, respectively. Parameter estimation obtained in the modeling gave a  
8 rather high activation energy for the hydrolysis, 114 kJ/mol. This value is in the same order of  
9 magnitude as the activation energies obtained for the hydrolysis of other hemicelluloses in the  
10 presence of homogeneous catalysts, such as arabinogalactan ( $E_a=126 \text{ kJ/mol}$ ) or *o*-acetyl  
11 galactoglucomannan ( $E_a=150 \text{ kJ/mol}$ )<sup>23,29</sup>. However, activation energy in the current work is  
12 lower in comparison to the above mentioned compounds, which is in line with faster inulin  
13 hydrolysis kinetics in similar conditions.

14 The value found for  $\beta$  was 4.14, meaning that this is the slope of the linear relationship  
15 between the rate constant and the conversion. Mechanistically, it shows that the amount of  
16 ends in the molecule increases, so the statistical probability of new excisions in the molecule  
17 increases. From eq. 2 can be obtained that  $k_{\infty}/k_0 \approx 5$  that is to say, the probability of  
18 producing new excisions is 5 times higher per existing reactant molecule at the end of the  
19 reaction when conversion is close to 1.

20 Sensitivity analysis was performed to check consistency of the parameters obtained with the  
21 nonlinear regression analysis. This was done by fixing two of the parameters at the final  
22 values obtained in data fitting and varying one remaining parameter. The values of the  
23 objective function were then calculated and plotted against the varied parameter. For all three  
24 estimated parameters clear minima were found, meaning that the parameters are well defined.  
25 This is illustrated for the three parameters ( $E_a$ ,  $k_{oi}$  and  $\beta$ ) in Figure 6a. In order to evaluate the

1 correlations of the estimated parameters, a two-dimensional contour plots were calculated  
2 (Figure 6b). The objective function (Q) was investigated as a function of a pair of parameters.  
3 By changing the value of the parameters, non-optimal values of the objective function were  
4 obtained. The ideal case is to obtain a plot with a circular shape, which indicates low or even  
5 negligible correlation between the parameters. The minimum value for the objective function  
6 can be found in the center of the circular plots. No severe correlations of the parameters were  
7 observed in the study, but a slight correlation between  $\beta$  and  $k_{01}$  can be seen from the  
8 elongated contour plot. However, a clearly defined minimum could be found in each case.

## 9 **CONCLUSIONS**

10 The current work demonstrates that high purity fructose can be obtained by hydrolysis of  
11 inulin employing a heterogeneous catalyst at ambient pressure. The reaction kinetics was  
12 investigated and modelled mathematically taking into account the detailed reaction  
13 mechanism including the autocatalytic effect; the results can directly be utilized for  
14 optimization and design purposes. Moreover, the demonstrated results open up novel  
15 possibilities in production and process design, i.e. batch or possibly continuous operation  
16 without the need for costly separation and corrosion problems commonly encountered with  
17 homogeneous catalysts.

## 18 **ACKNOWLEDGEMENTS**

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22 acknowledged.

23

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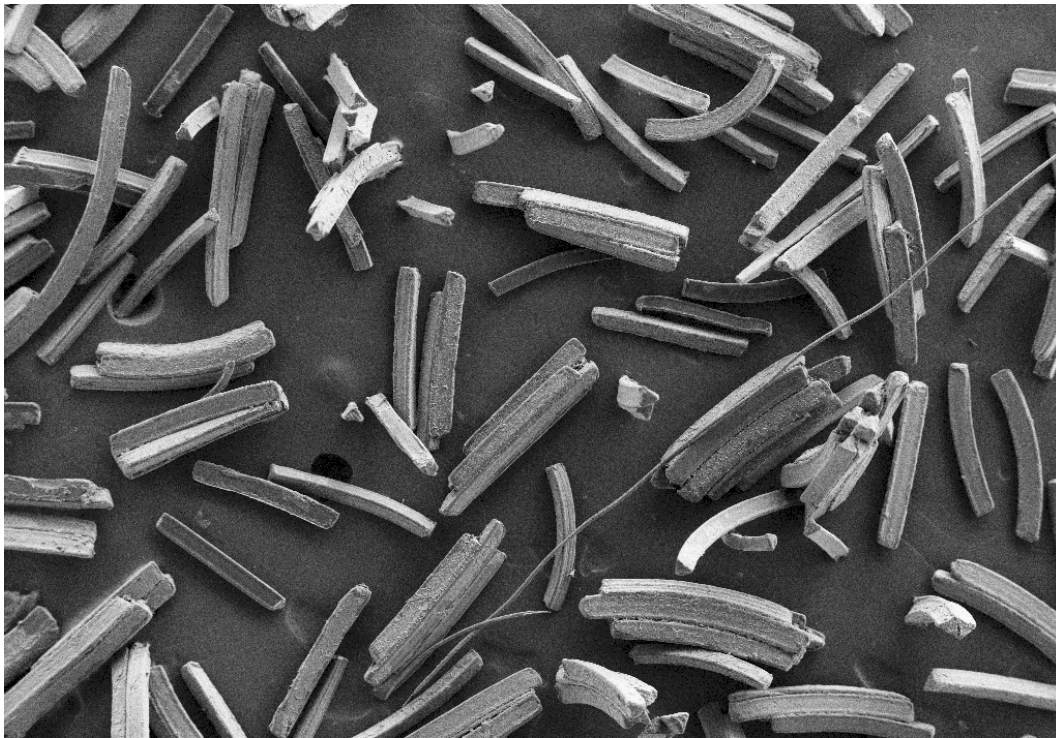
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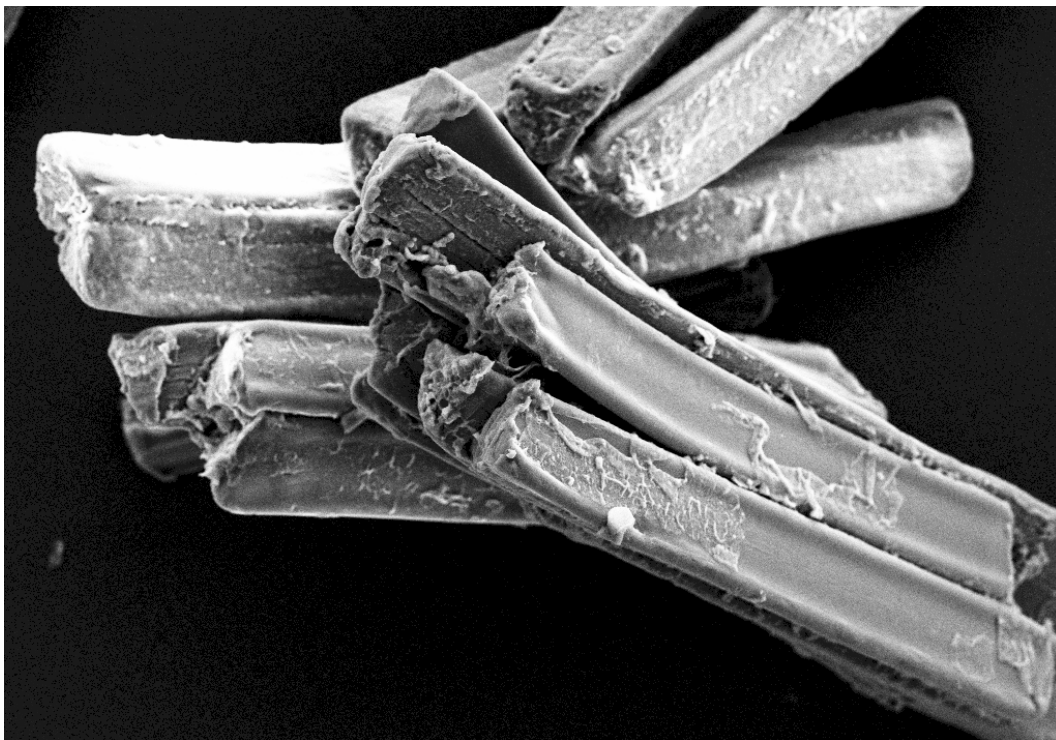




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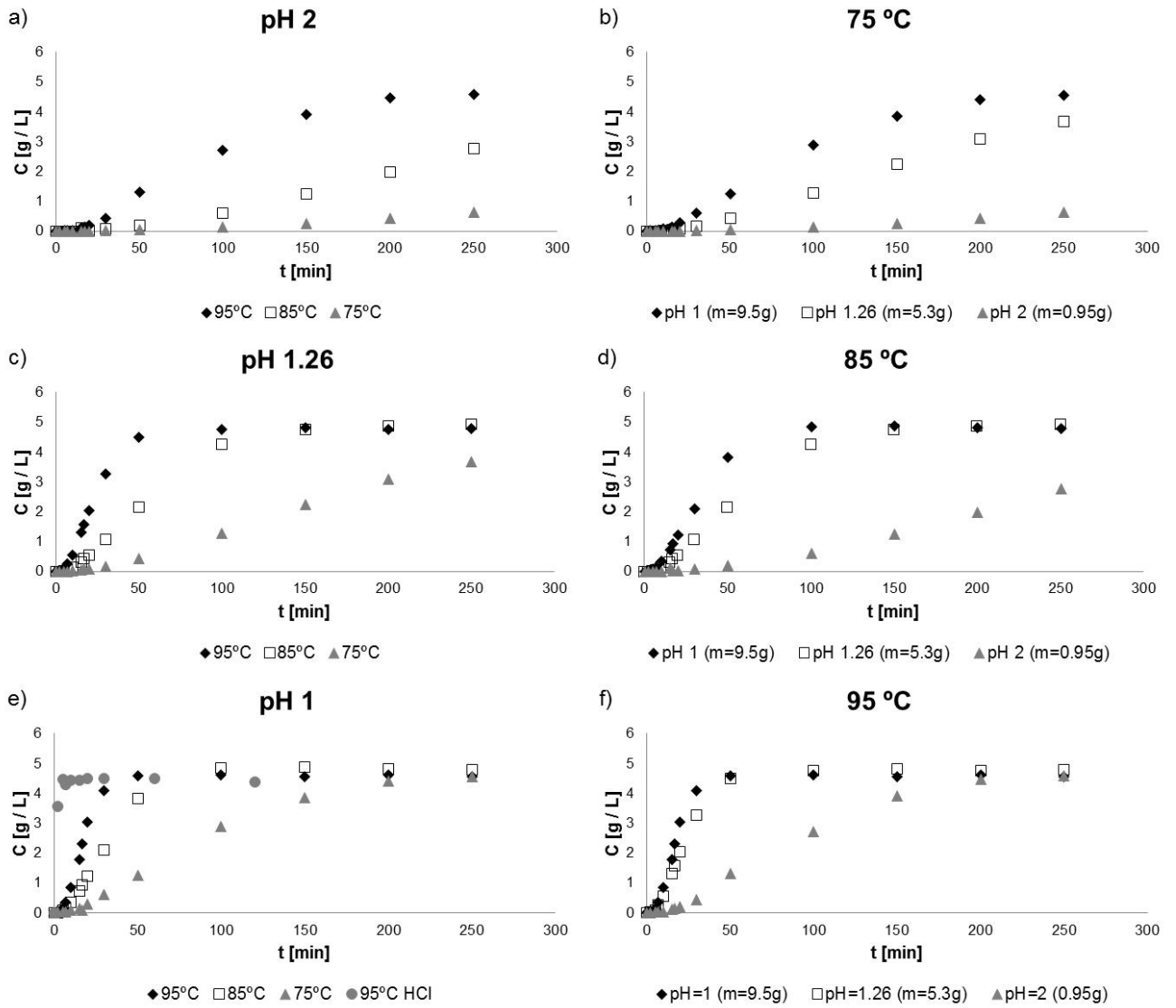
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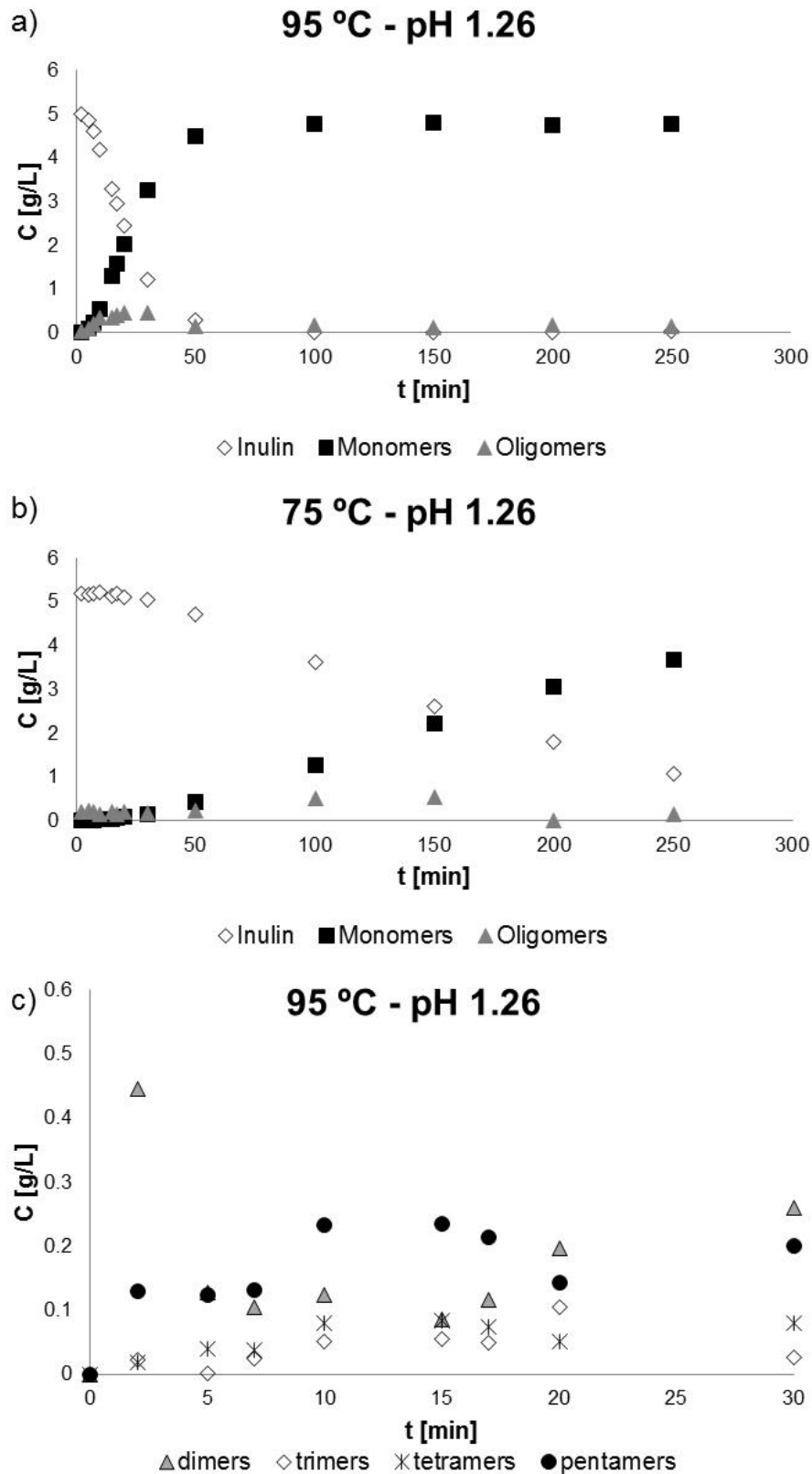
3 Figure1. SEM-Images of Smopex-101.

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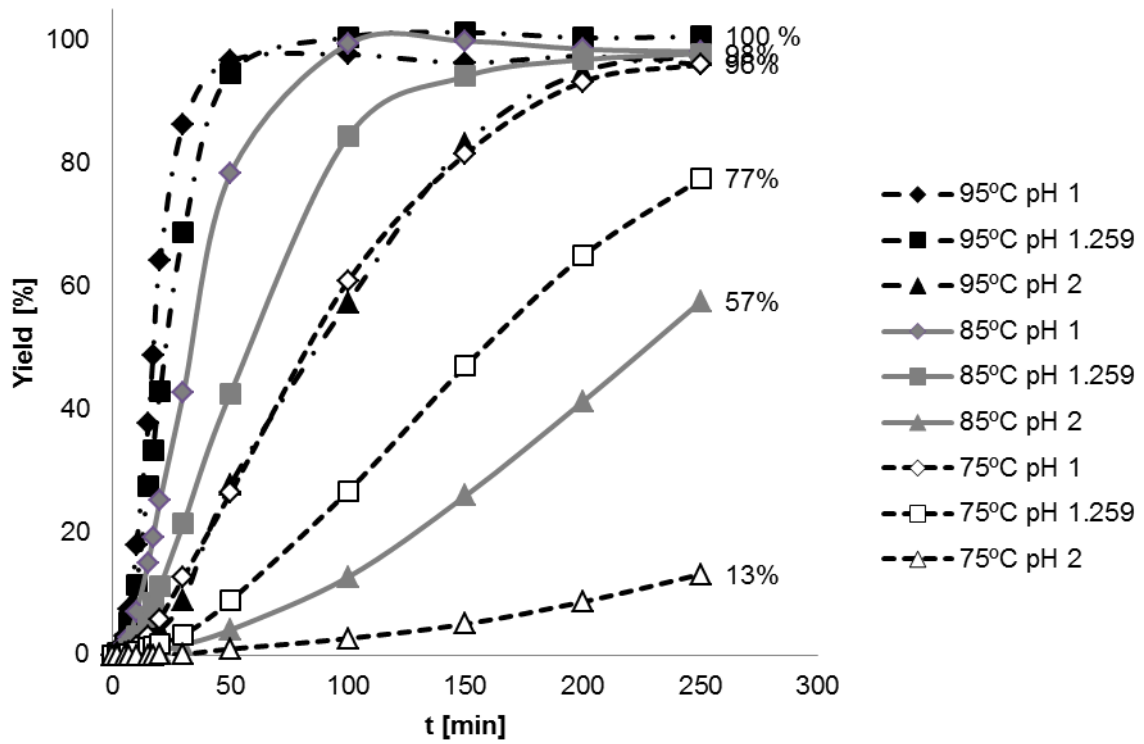
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 2 Figure 2. The concentration of monomers as a function of time at different temperatures with  
 3 Smopex-101: a) at pH 2 c) at pH 1.26 e) at pH 1 with Smopex-101 and HCl. The  
 4 concentration of monomers as a function of time at different values of pH with Smopex-101:  
 5 b) at 75°C d) at 85°C f) at 95°C.

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 2 Figure 3. Concentration profiles of inulin, monomers and oligomers as a function of time at  
 3 different reaction conditions (a) and (b). Concentration profiles of dimers to pentamers in the  
 4 initial stages of the reaction at pH 1.26 and 95°C with Smopex-101 (c).

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3 Figure 4. The yield of monomeric sugars as a function of time under different experimental  
4 conditions.

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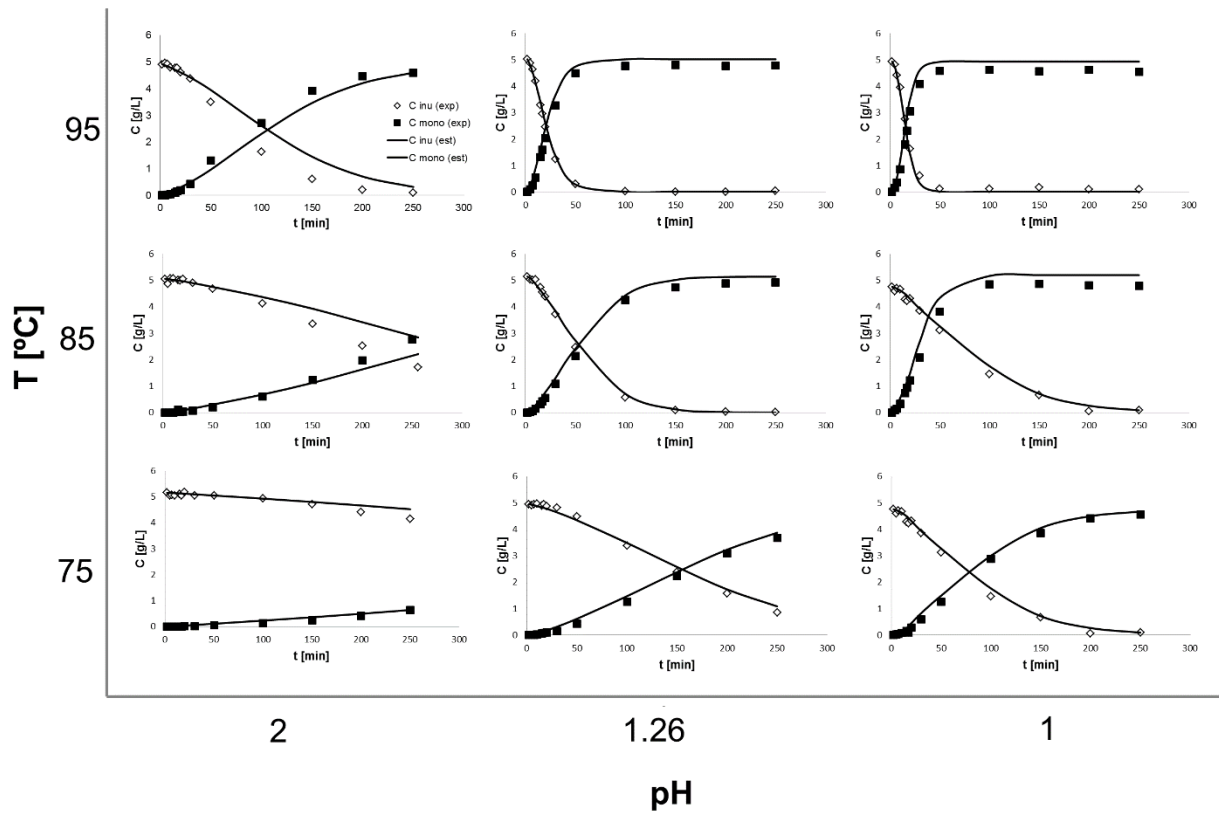
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2 Figure 5. The fit of the model to the experimental data for the inulin and monomer  
 3 concentrations at different values of pH and temperature. The open and closed symbols  
 4 represent the experimental inulin and monomer concentrations, respectively, and the lines  
 5 represent the model.

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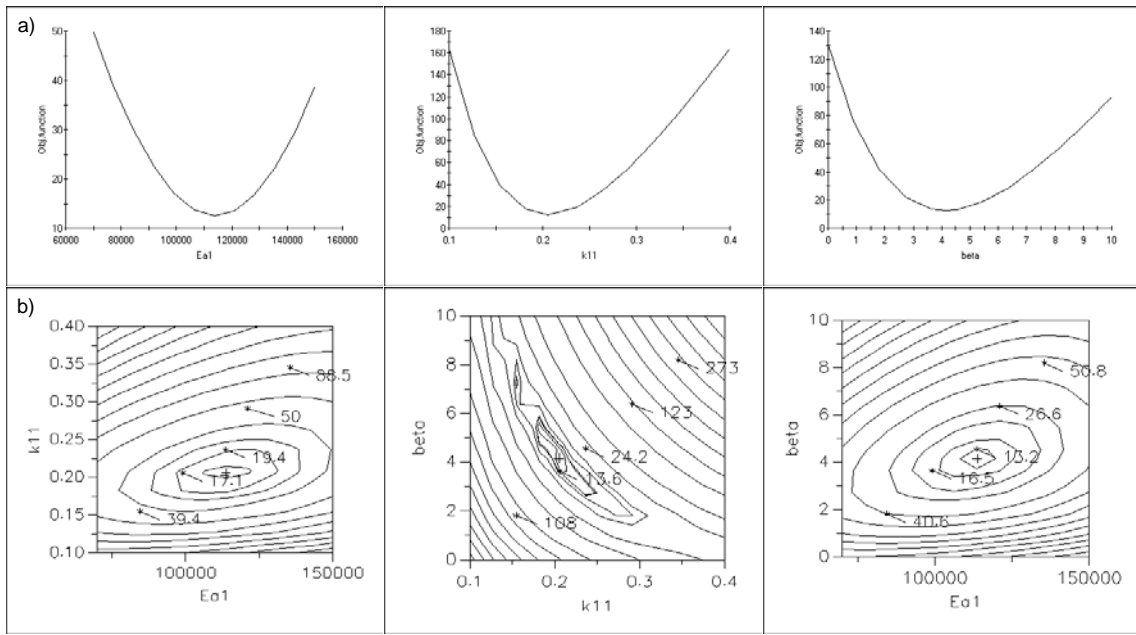
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3 Figure 6. Sensitivity analysis of parameters  $Ea$ ,  $k_{0I}$  and  $\beta$  (a). Contour plots of the parameters

4  $Ea$ ,  $k_{0I}$  and  $\beta$  (b).

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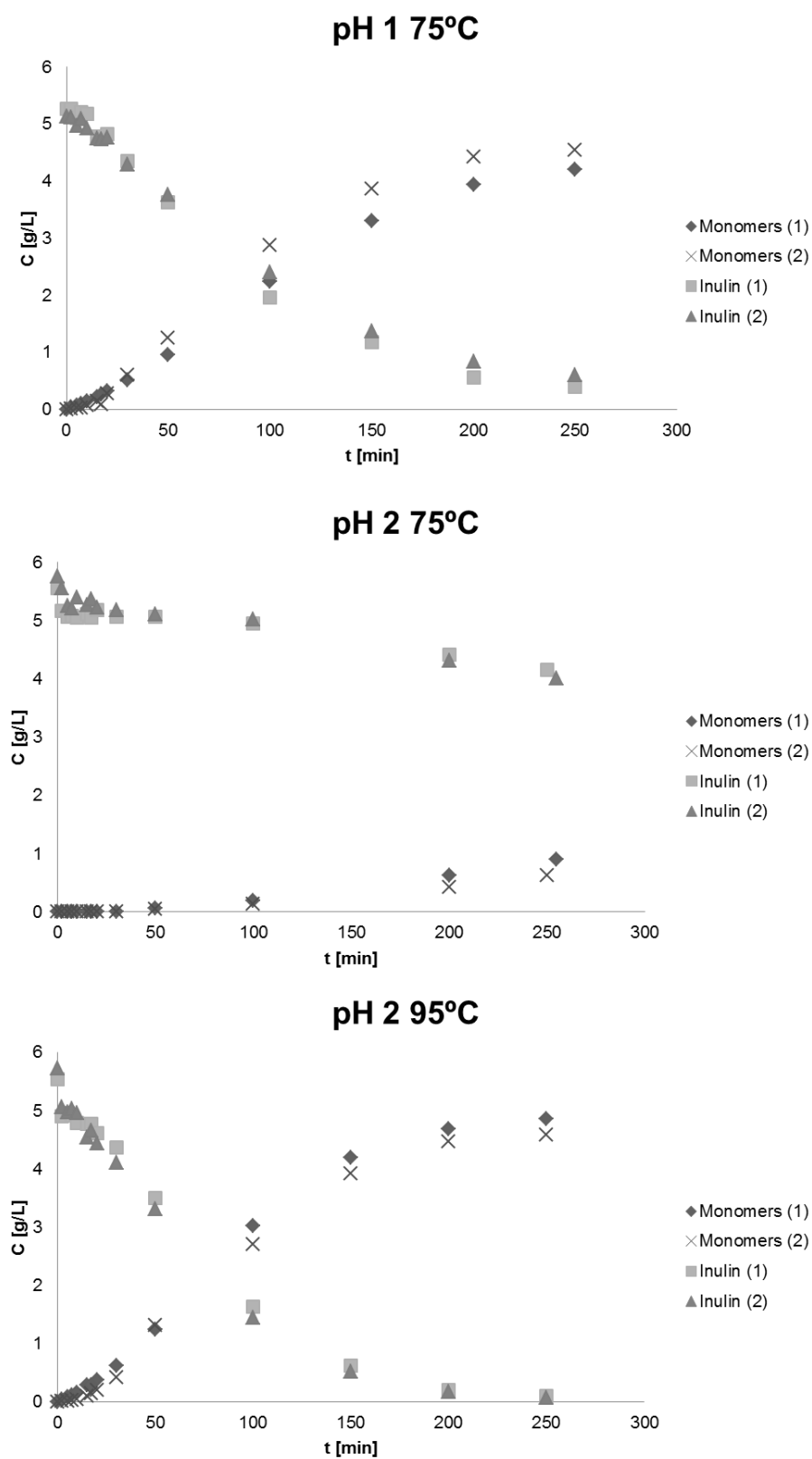
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# 1 SUPPORTING INFORMATION



2

3 Figure S1. The concentration of inulin and monomers as a function of time for three repeated  
4 experiments.