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The combined hydrolysis and hydrogenation of inulin catalyzed by bifunctional Ru/C

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Abstract

A one-pot process for hydrolysis and hydrogenation of inulin to D-mannitol and D-glucitol over a bifunctional Ru/C catalyst was developed. The hydrolysis is catalyzed by the carbon support, onto which acidity was introduced by pre-oxidation. The effect of different carbon treatments on the hydrolysis of inulin was studied. Oxidation with ammonium peroxydisulfate resulted in a carbon with the highest hydrolysis activity. On this carbon, long chain inulin is hydrolyzed faster than inulin rich in short chains. The application of high pressure (up to 100 bar) increased the hydrolysis rate substantially. The combined process was successfully conducted with a Ru-catalyst supported on this oxidized carbon. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Activated carbon; Heterogeneous catalysis; Mannitol; Glucitol; Fructose

1. Introduction

D-Mannitol is a valuable, non-hygroscopic, low-calorie sweetener. Nowadays, D-mannitol is prepared from mixtures of D-glucose and D-fructose, obtained by hydrolysis of sucrose or by enzymatic isomerization of D-glucose, obtained from starch. D-Mannitol can be isolated from the reaction mixture by crystallization. Inulin, a polysaccharide containing one D-glucose and 10–50 D-fructose units, would be a more attractive feedstock (see Scheme 1), because it has a higher D-fructose content, and, therefore, it may give a higher D-mannitol yield. A combined, one-pot process, using a bifunctional catalyst would be desirable.

For the hydrogenation of carbohydrates, Ru has proved to be the most active metal, although Cu/SiO_2 yields high D-mannitol to D-glucitol ratios in the hydrogenation of D-fructose.[1] A one-pot hydrolysis–hydrogenation can be conducted with a homogeneous catalyst based on $Ru(TPPTS)_3$.[2] However, heterogeneous catalysis would offer the great advantage of easy recovery and re-use of the catalyst. The most common solid acidic catalysts are zeolites[3,4] and ion exchange resins,[5] either used as the catalyst support material or in a mixture with a hydrogenation catalyst like Ru/C.[6]

The benefits of carbon supports are their low costs, high surface area and the easy recovery of the supported precious metal by burning off the carbon. Furthermore, carbon is capable of adsorbing 5-(hydroxymethyl)-furfural (HMF), a possible side product, which is formed by dehydration of D-fructose in acidic environment.[7]

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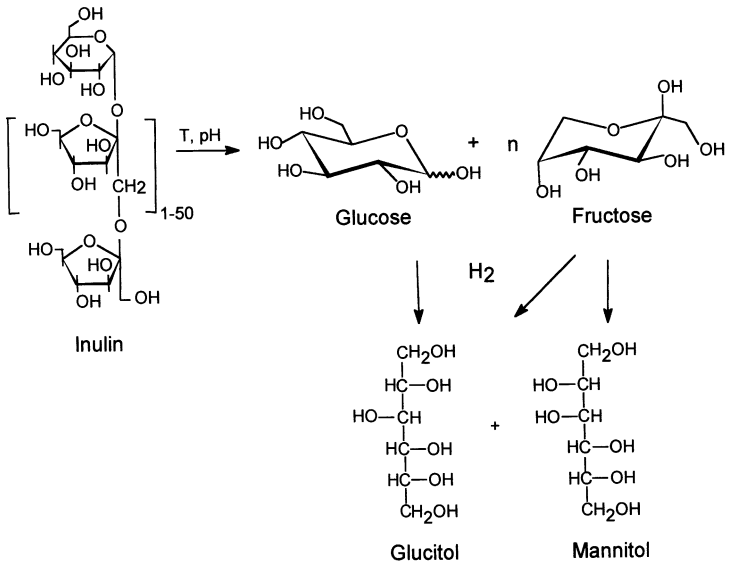


Scheme 1. Simplified scheme of the hydrolysis and hydrogenation of inulin. For the sake of simplicity only pyranose forms of glucose and fructose are depicted. Hydrogenation of inulin fragments, followed by hydrolysis, is also possible.

Here we report on a study of the combined hydrolysis–hydrogenation of inulin, using Ru/C as the catalyst. The carbon support was made acidic by treatment with different oxidizing agents.

2. Results and discussion

Catalyst characterization.—The effect of the carbon treatment on the acidity and the type of surface sites formed was described in a previous paper.[8] It was concluded that mainly carboxylic acid groups are formed during these treatments. Acid sites with different strengths can be distinguished by selective neutralization. Sodium hydroxide neutralizes practically all acidic sites; sodium bicarbonate only the strongest. The amount of carboxylic sites can also be deduced from the infrared spectra, by relating the intensity of the band at 1700 cm^{-1} (carboxylic acids) to that at 1580 cm^{-1} (the carbon skeleton).[8,9] The titration and IR data (see Table 1) lead to the conclusion that oxidation with ammonium persulfate creates the largest amount of acidic surface sites.

The amount of Ru dispersed on carbon SX1GNS (for codes of activated carbon, see footnote of Table 1), as determined with X-ray fluorescence spectroscopy, amounted to 0.89 wt%. Upon impregnation and liquid phase reduction with sodium borohydride, the amount of acid sites as determined by sodium hydroxide neutralization, decreased to 1.3 meq/g. For comparison, reduction in H_2 at 400 °C decreased the sodium hydroxide neutralization capacity to 0.2 meq/g. Liquid phase reduction with sodium borohydride, therefore, is capable of reducing the ruthenium, while keeping most of the oxygen surface sites intact.

Reaction conditions.—The formation of D-fructose and D-glucose during the hydrolysis of inulin with a dp of 10 at 100 °C on different amounts of carbon SX1GN65 is shown in Fig. 1(a). The formation of monosaccharides was taken as a measure of hydrolysis activity.

The rate of formation of monosaccharides increases with the amount of catalyst. An

Table 1
Titration and IR results of the different carbons

Carbon [a]	NaOH (meq/g)	$NaHCO_3$ (meq/g)	$I_{1700/1580}$ (cm^{-1})
SX1G	0.1	0.05	0.0
SX1GOCl	0.4	0.2	0.19
SX1GN65	1.0	0.7	0.38
SX1GNS	1.4	1.2	0.45

[a] SX1G, untreated steam-activated peat-based carbon; SX1GOCl, SX1G oxidized with calcium hypochlorite; SX1GN65, SX1G oxidized with 65% HNO_3; SX1GNS, SX1G oxidized with ammonium persulfate. See also Section 4.

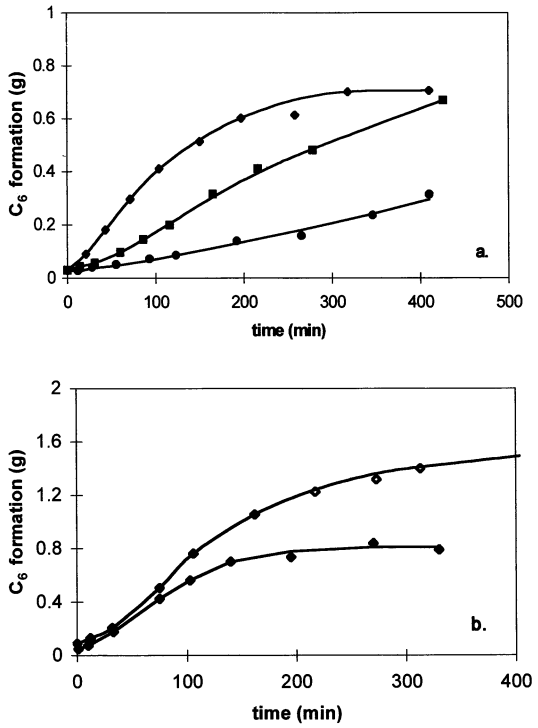


Fig. 1. (a) Hydrolysis of 1 g inulin dp 10 using different amounts of SX1GN65: 0.10 g (●), 0.25 g (■), 0.50 g (◆). (b) Hydrolysis of 1 g (◆) and 2 g (◇) of inulin dp 10 using 0.250 g SX1GNS; 50 mL aqueous solution; 100 °C. The lines are a guide to the eye.

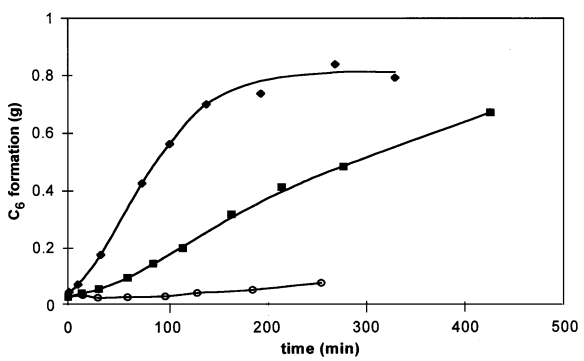


Fig. 2. Hydrolysis of inulin dp 10 with different carbons; SX1GNS (◆), SX1GN65 (■), SX1G (○), 50 mL aqueous solution of 1 g inulin and 0.250 g carbon; 100 °C. The lines are a guide to the eye.

induction period is observed, which may be ascribed to the large amounts of long chains still present at this time, leading to hydrolysis without significant formation of monosaccharides. Upon doubling of the starting concentration of inulin, the induction period and the initial rate remained the same (see Fig. 1(b)), indicating pseudo zero order kinetics. Both Fig. 1(a) and (b) show a decreasing rate of formation of monosaccharides at high conversions.

It may be concluded that the reaction is first order in catalyst and zero order in substrate. This suggests that the reaction occurs at the carbon surface, since the homogeneous reaction is known to be first order both in H^+ and in substrate.[10] The pH of all reaction mixtures was between 4 and 5. Similar experiments with aqueous HCl solutions of pH 4 (in the absence of carbon) gave no hydrolysis. This indicates that the hydrolysis of inulin takes place on the acid sites of the carbon surface.

Inulin was not hydrolyzed fully to the monomers D-glucose and D-fructose (see Fig. 1). Short chain oligomers, mainly unidentified C_{12} compounds, remained after prolonged reaction. Possibly, these products are D-fructose dianhydrides, which are known to be formed as byproducts during acid hydrolysis of inulin.[11] However, 5-(hydroxymethyl)furfural (HMF), was not detected in the products of the carbon catalyzed hydrolyses.

Effect of carbon pretreatment.—As shown in Fig. 2, the activity increases with the carbon acidity, as determined by titration and IR. It can been seen that treatment of the carbon with ammonium persulfate results in the most active catalyst for hydrolysis. Untreated SX1G has almost no activity.

No loss of activity was observed upon reuse of the acidic carbons. IR spectra of the carbon before and after catalytic experiments also revealed no loss of carboxylic acid groups. However, after the experiments, the IR spectra showed an increased absorption at 1100 cm^{-1}, which was no longer present after washing with hot water. This adsorption is most probably due to the C–O stretching vibration of adsorbed carbohydrate species.

Region of splitting.—To get more insight into the hydrolysis process, samples taken during the experiments were analyzed with high pressure anion exchange chromatography, coupled with a pulsed amperometric detector (HPAEC–PAD), as described by De Leenheer.[12] In this way, inulin can be separated upon chain length. The eluent is strongly alkaline, converting the hydroxyl groups partly into oxyanions. Therefore, the longer chains exhibit longer elution times.

The chromatogram of inulin with an average dp of 10 is shown in Fig. 3(a). Inulin not only consists of the so called GF_n chains, but also contains small amounts of F_m chains,[12] which do not contain a D-glucose end group. These chains are visible as the small shoulders of the GF_n peaks. The difference in average degree of polymerization between inulin dp 10 and its long chain fraction dp 25, obtained by selective precipitation, is clearly shown in Fig. 3(b).

Fig. 4 presents the chain length distribution of inulin dp 25 at different time intervals during the hydrolysis. The increasing concentration of F_{18}–F_{24} chains indicates that hydrolysis takes place by random-splitting of the chains rather than by sequential hydrolysis of end groups. This is in line with the observed quasi induction time, which would be absent in the latter case. It should be noted that no peaks corresponding to F_{10}–F_{17} are observed in the chromatograms, probably due to overlap with other peaks.

Hydrolysis rate and chain length.—The hydrolysis of inulin with various molecular weight distributions on SX1GNS is shown in Fig. 5(a). Besides inulin dp 10, dp 25 (a long chain fraction of dp 10) and dp 30, a long chain and a short chain fraction of this 'dp 30' were used as substrate. These fractions were obtained by precipitation of the long chains out of an aqueous solution of inulin dp 30 at 4 °C. It is striking that these long chain fractions result in a significantly higher rate of monosaccharide formation than the unfractionated inulin and the short chain fraction.

As shown in Fig. 5(b), the hydrolysis of a 1:1 mixture (on weight base) of inulin dp 10 and dp 25 results only in a small decrease in the rate of monosaccharide formation, compared to 100% for dp 25. A similar effect was observed with a mixture of sucrose (10 wt%) and inulin dp 25. Addition of 0.1 g D-glucose to 0.9 g inulin dp 25 gave the same curve for the monosaccharide formation as a solution of 1 g of this inulin, despite the lower inulin

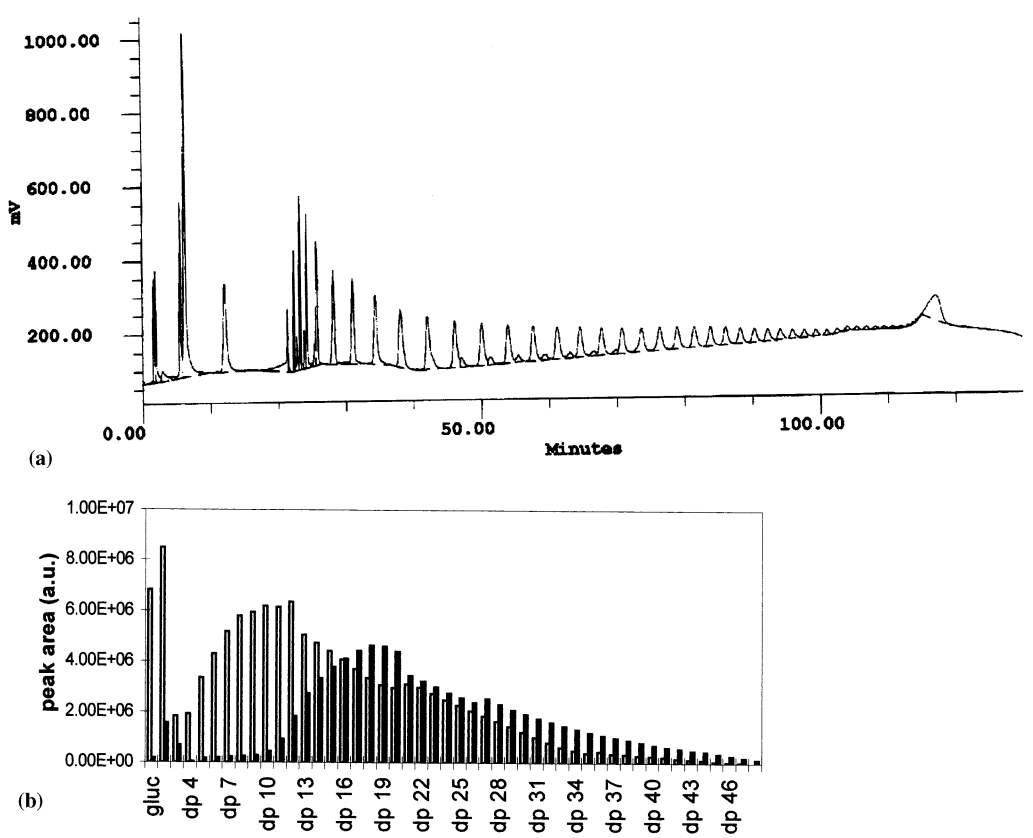


Fig. 3. (a) HPAEC chromatogram of inulin dp 10 and (b) chain length distribution of inulin dp 10 (□) and its long chain fraction with dp 25 (■).

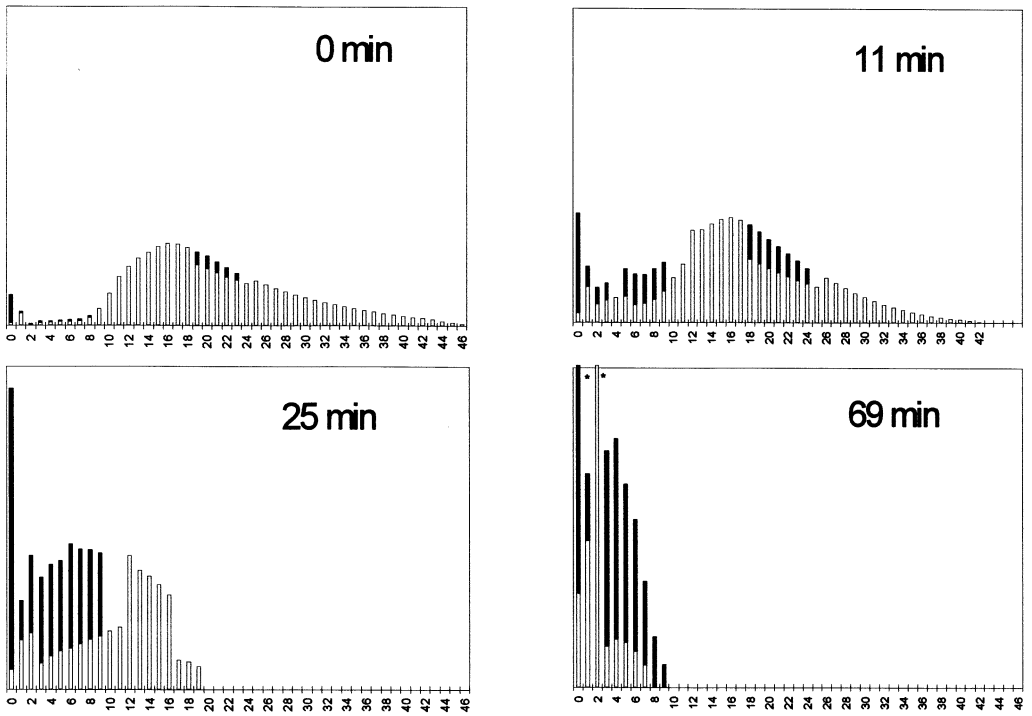


Fig. 4. Chain length distribution of inulin dp 25 during hydrolysis over SX1GN65; GF_n (□) and F_m chains (■); 50 mL aqueous solution of 1 g substrate and 0.250 g catalyst, 100 °C. The peaks corresponding to F_{10}–F_{17} probably overlap with other peaks. The *y*-axis scale (in a.u.) in all figures is equal, so at 69 min some bars* exceed the maximum.

concentration. These experiments prove that short chains do not inhibit the hydrolysis of longer chains.

Two effects will influence the rate of monosaccharide formation. Long chains can be hydrolyzed faster, due to multiside attack and the increase in entropy upon splitting of the chain on one hand and a stronger adsorption on the carbon surface on the other hand. If long and short chains would hydrolyze with equal rates, the rate of production of monosaccharides would be higher with short chains. The faster formation of monosaccharides from long chains may therefore be ascribed to the increasing adsorption strength on carbon with inulin chain length.[13] This also explains the decreasing rate of monosaccharide formation at high conversions, where predominantly short chains remain.

In Fig. 6, the hydrolysis of inulin dp 10 and inulin dp 25 on Amberlyst 15 and zeolite H-Beta is presented. Compared to oxidized carbon SX1GNS (Fig. 5(a)), Amberlyst 15 is slightly more active, whereas H-Beta is less active. Amberlyst 15 is a macroporous, strongly acidic polystyrene resin, functionalized with sulfonic acid groups. All inulin oligomers are assumed to be able to diffuse into the Amberlyst 15 beads. However, on zeolite H-beta, probably only the di- and trisaccharides diffuse into the inner pores with a reasonable rate. The large outer-surface of H-beta may be responsible for the hydrolysis of the longer inulin chains.

On Amberlyst 15, both types of inulin are hydrolyzed with the same rate of monomer production; the same result was obtained using a homogeneous HCl solution of pH 3.0. On zeolite H-beta, the rate of monosaccharide production out of inulin dp 10 is higher than that out of inulin dp 25. Apparently, long chains do not adsorb stronger on the zeolite surface than short chains. This results in a faster monosaccharide production with inulin dp 10. The high acidity of Amberlyst 15 and its large amount of acid sites (4.6 meq/g) probably results in fast hydrolysis of all inulin chains. To obtain insight in the roles of adsorption and diffusion, a more detailed analysis would be required.

Effect of pressure.—As will be shown later, during the combined hydrolysis–hydrogenation of inulin over Ru/C at 100 bar H_2, the hydrolysis rate under those conditions is much higher than during the hydrolysis experiments presented thus far. The hydrolysis rate in the combined process is determined by monitoring the total concentration of the monosaccharides and alditols. As shown in Fig. 7(a),

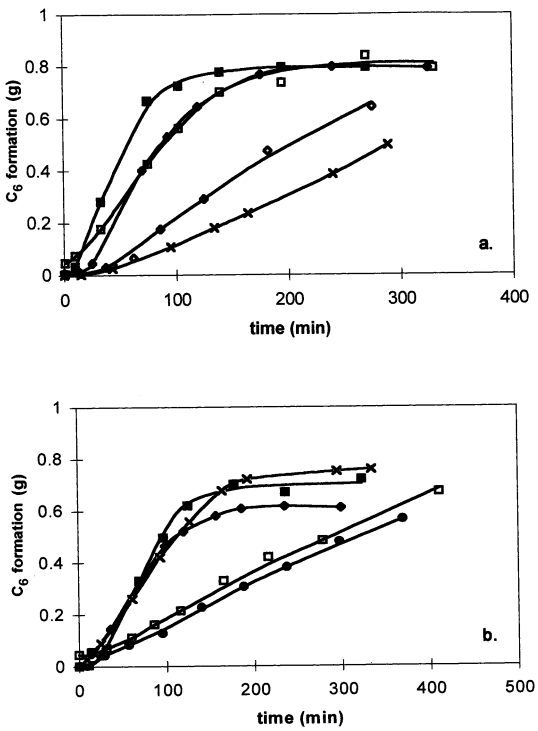


Fig. 5. Hydrolysis of (a) inulin dp 10 (□), dp 25 (■), dp 30 (◇), a long chain fraction of 'dp 30' (◆) and a short chain fraction of 'dp 30' (×) with SX1GNS and (b) sucrose (●), inulin dp 10 (□), dp 25 (■), dp 10 + dp 25 (1:1) (×), dp 25 + sucrose (9:1) (◇) with SX1GN65; 50 mL aqueous solution of 1 g substrate and 0.250 g catalyst; 100 °C. The lines are a guide to the eye.

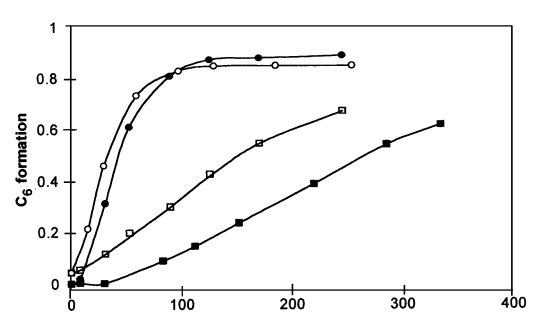


Fig. 6. Hydrolysis of inulin dp 10 (open symbols) and dp 25 (closed symbols) with Amberlyst 15 (○/●) and zeolite H-beta (□/■); 50 mL aqueous solution of 1 g inulin and 0.250 g catalyst; 100 °C. The lines are a guide to the eye.

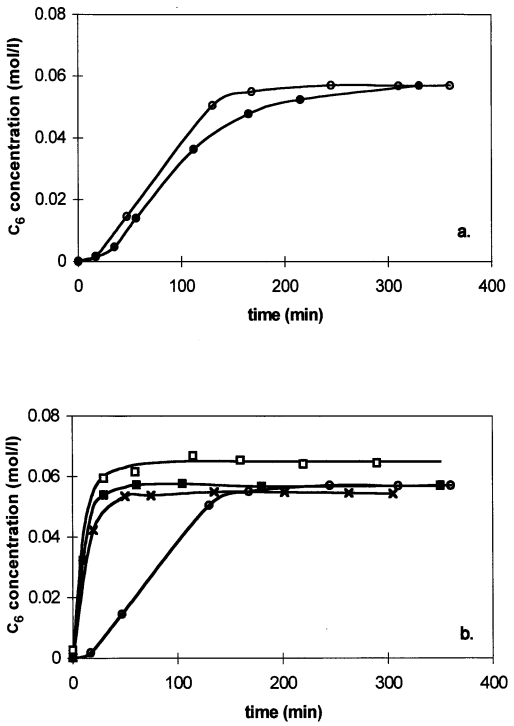


Fig. 7. Hydrolysis of inulin dp 25 (a) in air (1 bar, 100 °C) with 0.1 g SX1GNS (●) and Ru/SX1GNS (○) and (b) at 100 °C, 0.1 g Ru/SX1GNS and 1 bar air (○), 25 bar N_2 (×), 100 bar N_2 (■) and 100 bar H_2 (□). All experiments were carried out in an autoclave, containing 80 mL aqueous solution of 1 g inulin. The lines are a guide to the eye.

hydrolysis of inulin dp 25 on the Ru catalyst is somewhat faster than on the bare carbon. Apparently, Ru introduces extra acidity to the catalyst.

A study on the effect of pressure on the hydrolysis rate led to intriguing results. At nitrogen pressures of 25–100 bar, the hydrolysis rate is much higher than at 1 bar. A similar pressure effect was observed with zeolite H-beta as the catalyst (see Fig. 8(a)). The effect of pressure increased with temperature (90–100 °C; see Fig. 9). The hydrolysis rate in a homogeneous reaction in a HCl solution at pH 3.4 was independent of the pressure.

Bubbling air through the reaction mixture by means of a sintered glass tube (at 1 bar) did not increase the rate of hydrolysis. Moreover, lower stirring rates, which would increase agglomeration, did not lower the hydrolysis rate, neither at 1 bar, nor at 100 bar N_2. Therefore, it seems unlikely that the pressure effect is related to decreased catalyst agglomeration at higher pressures. Furthermore, it appeared that at 100 bar argon, inulin

hydrolyzed with the same rate as when using 100 bar nitrogen or hydrogen. Since the solubility of argon in water is about three times higher than the solubility of nitrogen and hydrogen,[14] it is, therefore, unlikely that the increase of the hydrolysis rate at high pressure is due to the influence of the solvated gas. Impeding the carbon pores by air, which may be pressed out by applying pressure, was ruled out as an explanation by means of hydrolysis reactions on degassed carbon, both at 1 and at 100 bar. Again, no change in activity was observed, compared to the standard experiments.

Most likely, the rate enhancement upon increase of the pressure is the result of deeper penetration of the inulin chains into the pore system at higher pressures. According to the Washburn equation (Eq. (1)), a liquid is pressed into smaller pores (with radius r) by increasing the pressure P:

$$r = -2\gamma \cos\theta / P \quad (1)$$

Since the surface tension γ decreases with increasing temperature, the pressure effect will be more pronounced at higher temperatures,

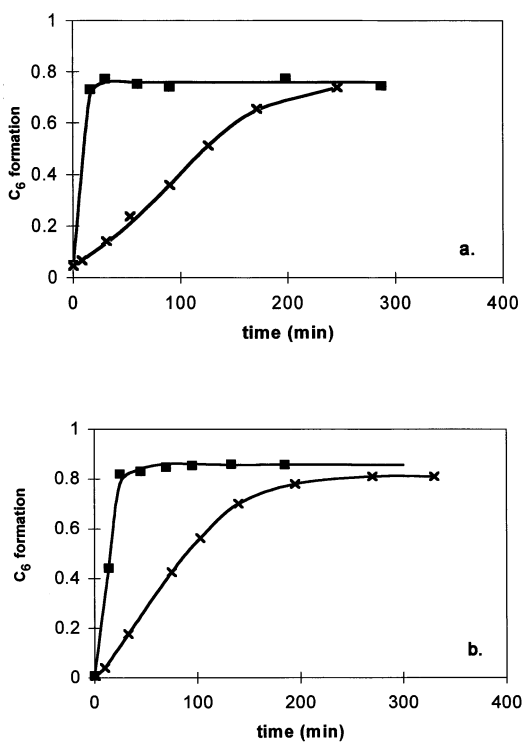


Fig. 8. (a) Hydrolysis of inulin dp 10 on zeolite H-beta at 1 bar (×) and 100 bar N_2 (■); (b) hydrolysis of sucrose on SX1GNS at 1 bar (×) and 100 bar N_2 (■).

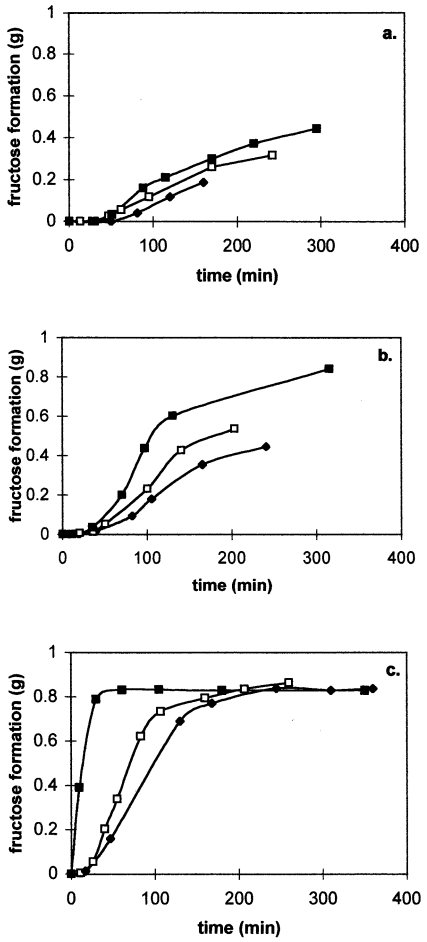


Fig. 9. Hydrolysis of inulin dp 25 on SX1GNS at (a) 90 °C; (b) 95 °C and (c) 100 °C and at different N_2 pressures: (◆) 1 bar; (□) 10 bar and (■) 100 bar. All experiments were carried out in an autoclave, containing 80 mL aqueous solution of 1 g substrate and 0.100 g catalyst. The lines are a guide to the eye.

which is in line with the results presented in Fig. 9. However, for the Washburn equation to be valid, the contact angle θ must larger than 90°. For the system water–graphite $\theta = 86°$,[15] so the role of this effect in the present system will depend on the value of θ for the system inulin solution–activated carbon.

Combined hydrolysis–hydrogenation of inulin.—The formation of D-fructose, D-glucose, D-mannitol and D-glucitol during the one-pot hydrolysis and hydrogenation of inulin dp 10 over 1% Ru/SX1GNS at 100°C and 100 bar hydrogen is shown in Fig. 10(a). The D-fructose and D-glucose concentrations rise to a maximum value after about 150 min. Lower pressures (25 and 50 bar) show comparable curves, as is expected from the low order in H_2 reported earlier.[16] The faster hy-

drogenation of D-fructose, compared to D-glucose, is also in line with this study.

Two routes may be faced for this combi-process: (i) hydrolysis followed by hydrogenation of the monosaccharides; and (ii) simultaneous hydrogenation and hydrolysis of inulin fragments. Upon non end-on hydrolysis, F_m and GF_n chains are formed (Scheme 2). The GF_n chains do not contain a reducible group. However, the fructose end-group of the F_m fragments are reducible and can be hydrogenated, releasing D-mannitol and D-glucitol after hydrolysis. Hydrogenolysis of inulin fragments is not likely, because both sucrose and inulin do not react in the presence of a non-acidic Ru/C catalyst.

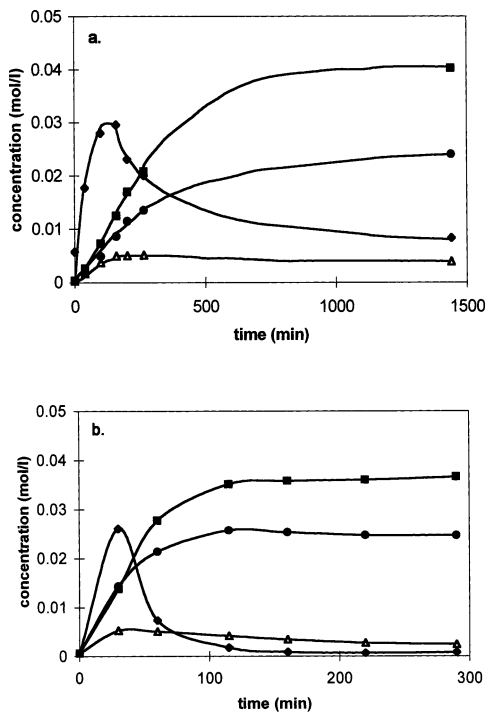
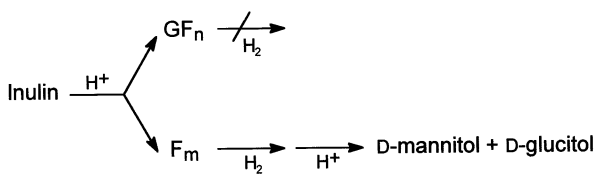


Fig. 10. Concentrations of D-glucose (△), D-fructose (◆), D-mannitol (●) and D-glucitol (■) formed in the hydrogenation of (a) inulin dp 10 and (b) inulin dp 25; 80 mL aqueous solution of 1 g inulin and 0.100 g 1% Ru/SX1GNS, 100 °C, 100 bar H_2. The lines are a guide to the eye.



Scheme 2. Hydrogenation of inulin GF_n chains is not possible; the fructose end-group of F_m chains can possibly be hydrogenated, before hydrolysis to smaller fragments.

In this one-pot process, there is, similar to the hydrolysis reaction (see above), a large influence of the chain length on the D-mannitol and D-glucitol formation (Fig. 10(b)). The initial rates of total D-mannitol–D-glucitol production are 0.112 and 0.013 mol/L/h for inulin dp 25 and dp 10, respectively. With inulin dp 25, the reaction essentially reaches completion in 150 min.

With inulin dp 10, the selectivity to D-mannitol, defined as the concentration of this compound relative to the concentrations D-mannitol and D-glucitol, amounted to 37%. With inulin dp 25, this value was slightly higher (40%), due to the higher D-fructose to D-glucose ratio resulting from long chain inulins. These values are comparable with the hydrogenation of D-fructose over Ru/C catalysts.[16]

3. Conclusions

Our results show that Ru on activated carbon oxidized with ammonium persulfate is a good catalyst for a one-pot process for D-mannitol production from inulin. No byproduct like HMF is formed, however some short chain oligomers remain after completion of the reaction. The hydrolysis of long chains is faster than the hydrolysis of short chains, due to multiside attack and a stronger adsorption of long chains on the carbon surface. The hydrolysis rate can be increased dramatically by applying pressure (25–100 bar).

4. Experimental

Materials.—The activated carbon used in this study (Norit SX1G) was donated by Norit NV (Amersfoort, The Netherlands). Inulin, with an average dp of 10 was a gift from Sensus (Coöperatie Cosun U.A., Roosendaal, The Netherlands). From this inulin, a fraction with an average dp of 25 was obtained by selective precipitation. Ammonium persulfate, $(NH_4)_2S_2O_8$, and inulin dp 30 were obtained from E. Merck KGaA (Darmstadt, Germany). $RuCl_3 \cdot x\ H_2O$ (40 wt% Ru) was a gift from Johnson Matthey (Hertfordshire, UK),

$NaBH_4$ was obtained from Fluka Chemie AG (Buchs, Switzerland), $Ca(ClO)_2$ form Acros Chimica NV (Geel, Belgium) and sucrose from J.T. Baker Chemicals BV (Deventer, The Netherlands). Amberlyst 15 was obtained from Sigma–Aldrich Chemie BV (Zwijndrecht, The Netherlands), zeolite H-Beta (Si/Al = 50) from Süd-Chemie AG (München, Germany).

Carbon treatments.—The activated carbon SX1G is a steam-activated peat-based carbon. This carbon was treated in several ways: (i) oxidation with nitric acid. Carbon (10 g) was refluxed in conc HNO_3 (65%, 200 mL) for 3 h. Then, the carbon was filtered off, washed with water until the pH of the filtrate reached a value of 5.5, dried overnight at ambient conditions, and finally dried for 3 h at 80 °C. The carbon treated in this way is denoted as SX1GN65. (ii) Oxidation with calcium hypochlorite. The oxidation with $Ca(ClO)_2$ was performed at a constant pH of 4.2, at rt. Vinke et al.[17] showed this to be the optimal pH for oxidizing physically activated carbon. SX1G (10 g) was added to 250 mL of aqueous 0.25 M $Ca(ClO)_2$. During the reaction, the pH was adjusted to 4.2 with HCl (0.1 M) and the suspension was maintained at this pH using KOH (2 M). After 3 h of reaction, the carbon was washed and dried as described above. X-ray fluorescence spectroscopy, XRF (Philips PW1480), showed that calcium and potassium were completely removed from the carbon. The carbon treated in this way is coded as SX1GOCl. (iii) Oxidation with $(NH_4)_2S_2O_8$. Carbon (10 g) was added to a satd solution of $(NH_4)_2S_2O_8$ in 1 M H_2SO_4 (175 mL). After 22 h of reaction at rt, the carbon was filtered off, washed and dried as described above. The filtrates were checked for sulfate with $BaCl_2$. The carbon treated in this way is denoted as SX1GNS.

Carbon characterization.—The amount of acid sites on the carbon surface was determined by selective neutralization with NaOH, according to the method of Boehm.[18] To 100 mg of carbon, 0.05 M NaOH (10 mL) was added. After shaking the suspension for 4 days, the carbon was centrifuged, washed and filtered over a 0.45 μm filter (Chromofil) and titrated with 0.05 M HCl.

An indication of the amount of carboxylic acid sites was obtained by infrared spectroscopy. Infrared spectra were recorded with a Perkin–Elmer spectrum 1000 FT-IR spectrometer. KBr tablets were used, containing 2 mg of carbon in 250 mg KBr. The spectra were obtained by co-adding 20 spectra with a resolution of 4 cm^{-1}. The original spectra were corrected for a curved baseline.

Catalyst preparation.—A 1% Ru/C catalyst was prepared by incipient wetness impregnation (i.e. filling of the support with the precursor solution in an amount equal to its pore volume) of SX1GNS (1 g) with a solution of $RuCl_3 \cdot 2.5\ H_2O$ (28 mg) in 2.0 mL acetone. The catalyst was dried overnight under ambient conditions and for 3 h at 80 °C. Reduction with hydrogen at 400 °C resulted in a major loss of carboxylic acid sites, essential for the inulin hydrolysis. Therefore, the precursor was reduced with $NaBH_4$. To this end, aq 1.5 M $NaBH_4$ (20 mL) was slowly added to a suspension of the catalyst in water (20 mL). After 2 h, the unreduced $NaBH_4$ was destroyed by addition of HCl (15 mL, 2.5 M). The suspension was centrifuged and washed twice with MeOH. The MeOH was evaporated under reduced pressure and the catalyst support was protonated with aq HCl (0.1 M).

The metal loadings on the support were measured using X-ray fluorescence spectroscopy, XRF (Philips PW1480).

Hydrolysis experiments.—The carbon was suspended in water (40 mL) and heated to the desired temperature. The experiment was started by introducing an aq solution of the substrate (10 mL). After reaction, the carbon was centrifuged and washed four times with water before re-use. Unless otherwise stated, the experiments were performed at 100 °C, using 50 mL solutions containing 1 g of substrate and 0.25 g of carbon.

Hydrogenation experiments.—The hydrogenation experiments were performed in a Parr 4842 autoclave, made of Hastelloy C276. A suspension of the catalyst (100 mg) in water (50 mL) was introduced into the autoclave. The system was flushed with N_2 and H_2 and heated to the desired temperature under 10 bar H_2 (strirring rate 1000 rpm). After that, 30 mL of an aq solution of the substrate (1 g) in

water was introduced in the system and the H_2 pressure was adjusted to the desired value. Unless stated otherwise, the temperature and H_2 pressure amounted to 100 °C and 100 bar, respectively.

Product analysis.—Samples were taken during the hydrolysis and hydrolysis–hydrogenation experiments. To measure the D-fructose, D-mannitol and D-glucitol concentrations, the samples were filtered and analyzed by HPLC, using a Millipore-Waters 590 pump and a 300×7.8 mm cation exchange column in the Pb^{2+} form (Phenomenex), connected to a refractive index detector (Shodex RI SE-51). The samples were eluted with degassed water at a flow rate of 0.6 mL/min and a column temperature of 60 °C.

The different chain lengths of inulin were separated with high pressure anion exchange chromatography, coupled with a pulsed amperometric detector (HPAEC–PAD). A Waters 625 LC pump was connected to a Dionex CarboPac column and a Dionex PAD detector. The samples were eluted (1 mL/min) with a degassed and carbonate-free solution of 0.1 M NaOH, with a gradually increasing concentration of NaOAc, up to 0.5 M.

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