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Hydrothermal upgrading of biomass to biofuel; studies on some monosaccharide model compounds

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Abstract—During the hydrothermal upgrading of biomass, hydrolysis to glucose is an important step. To elucidate some of the reaction pathways that follow this initial hydrolysis, the hydrothermal treatment (340 °C, 27.5 MPa, 25–204 s) of dilute (50 mM) solutions of D-glucose and some other monosaccharides were studied. As a result of the increase of K_w under subcritical conditions, both acid and base catalysed reactions occur. The acid catalysed reactions are mainly dehydrations leading initially to 5-hydroxymethylfurfural. Important base catalysed reactions result in glycolaldehyde and glyceraldehyde. Further fragmentations and dehydrations lead to a variety of low molecular weight compounds such as formic acid, acetic acid, lactic acid, acrylic acid, 2-furaldehyde and 1,2,4-benzenetriol. Important pathways leading to a decrease of the O-content of the liquid reaction products start from the intermediate glyceraldehyde, which forms pyruvaldehyde, which in its turn is converted into formic acid and acetaldehyde. The latter compound can also be formed via isomerisation of glyceraldehyde into lactic acid followed by decarbonylation.

Keywords: Sustainable energy; Renewables; Subcritical reactions; Glucose

1. Introduction

The anticipated depletion of fossil fuels and the concerns about global warming ask for initiatives to search for renewable energy sources. Particularly interesting in this respect are forms of biomass including wood, grass, agricultural waste and domestic waste. Several technologies have been developed to convert biomass into a biofuel with a higher heating value, such as gasification, fast pyrolysis[1] and hydrothermal upgrading (HTU).[2,3] In the latter process, the biomass is treated during 5–20 min with water under subcritical conditions (300–350 °C, 10–18 MPa) to give a heavy organic liquid ('biocrude') with a heating value of 30–35 MJ/kg. During this process, the oxygen content of the organic material is reduced from about 40% to between 10% and 15%. The removed oxygen ends up in CO_2, H_2O and CO. The main components of biomass resources typically are lignin, cellulose, hemicellulose and minerals. Sasaki et al. have studied the decomposition of cellulose in water under subcritical and supercritical conditions.[4] After 1.6 s at 320 °C and 25 MPa, 47% conversion was obtained yielding hydrolysis products (cellobiose, glucose, etc., 44%) and decomposition products of glucose (erythrose, 1,6-anhydroglucose, 5-hydroxymethylfurfural, 3%).[4] Furthermore, it has been shown that cellobiose decomposes via hydrolysis to glucose and via pyrolysis to glycosylerythrose and glycosylglycolaldehyde, which are further hydrolysed into glucose, erythrose and glycolaldehyde.[5]

Therefore, glucose may be a good model compound for studying the reaction paths of the HTU reaction of cellulose in biomass. Various groups have studied

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reactions of glucose in water under HTU conditions.[4–10] Usually, these reactions were performed at short reaction times (0.02–10 s). Remarkably, all studies indicate that the amount of CO or CO_2 that is formed is negligible, under the conditions applied, whereas the reaction products identified usually can be ascribed to fragmentations and dehydrations. Recently, a study of hydrothermal treatment under HTU conditions (310–410 °C, 30–50 MPa, 15 min) of baby food as a model for phytomass (lignin free) was reported.[11] Large amounts of CO_2 were evolved under these conditions. A gap exists between the studies on glucose at very short residence times and the latter study, which is closer to the conditions of the actual HTU process.

Therefore, we report here the results of a systematic study on the hydrothermal reactions of diluted solutions (50 mM) of glucose, fructose, mannose and galactose for longer reaction times (25–200 s). To obtain more insight into the reaction paths, the C_3–C_5 sugars glyceraldehyde, erythrose and arabinose, glycolaldehyde and the identified initial reaction products of these compounds were treated under similar conditions. For comparison, sorbitol was included as substrate. The results are discussed in relation to the HTU process of biomass.

2. Results and discussion

The hydrothermal reactions of the model compounds were performed with 50 mM solutions in water using a continuous flow-type reactor (see Fig. 1). This allowed short residence times (25–204 s) and rapid heating and cooling of the reaction mixture. The reaction temperatures were measured by a thermocouple located inside the reactor.

2.1. D-Glucose (1), D-mannose (2), D-fructose (3), D-galactose (4) and D-sorbitol

Hydrothermal treatment at 340 °C and 27.5 MPa of 50 mM aqueous solutions of these compounds resulted in brown solutions with pH values between 2.5 and 2.8 and small amounts of tar. The amount of tar increased with the residence time (τ). No gases were observed during these reactions. The liquid samples were complex mixtures of low molecular weight compounds, most of which could be identified by HPLC and ^{1}H NMR. The 14 identified compounds are compiled in Table 1. These compounds have also been detected in studies using shorter residence times, reported in the literature.[4–9] The major initial compounds are glycolaldehyde (**10**) and 5-hydroxymethylfurfural (HMF, **7**). These compounds

Table 1. Compounds that have been identified after HTU reactions of monosaccharides

Name	Formula	Concentration (mmol/L)[a]
5-Hydroxymethylfurfural (**7**)	$C_6H_6O_3$	8.0
2-Furaldehyde (**9**)	$C_5H_4O_2$	4.6
Glycolaldehyde (**10**)	$C_2H_4O_2$	15.3
Dihydroxyacetone (**12**)	$C_3H_6O_3$	0.5
Glyceraldehyde (**13**)	$C_3H_6O_3$	<0.1
1,2,4-Benzenetriol (**18**)	$C_6H_6O_3$	2.5
Pyruvaldehyde (**20**)	$C_3H_4O_2$	0.6
Lactic acid (**21**)	$C_3H_6O_3$	1.6
Acrylic acid (**22**)	$C_3H_4O_2$	<0.1
Acetaldehyde (**23**)	C_2H_4O	1.1
Formic acid (**24**)	CH_2O_2	4.3
Acetic acid (**26**)	$C_2H_4O_2$	1.2
Glycolic acid (**28**)	$C_2H_4O_3$	3.1
Acetone (**30**)	C_3H_6O	0.5
Total amount of identified carbon		141.2 mmol C/L
Total organic carbon		234 mmol C/L

[a] In reaction mixture of glucose (50 mM, 340 °C, 27.5 MPa, 120 s).

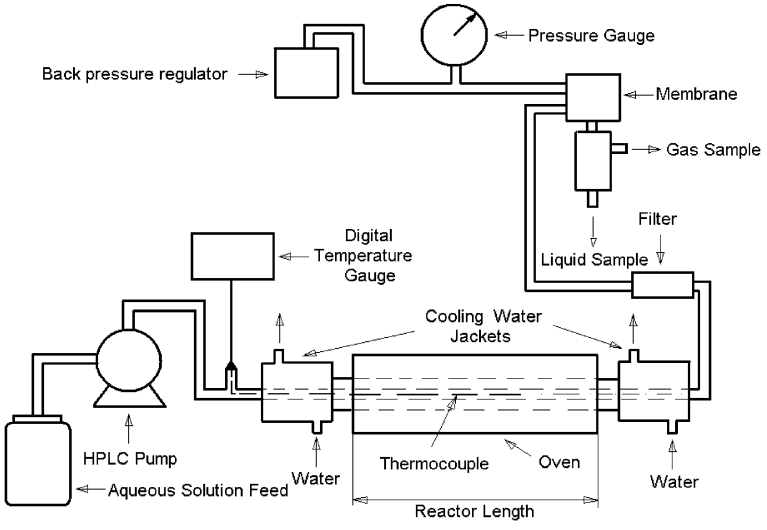


Figure 1. Experimental set-up for hydrothermal reactions.

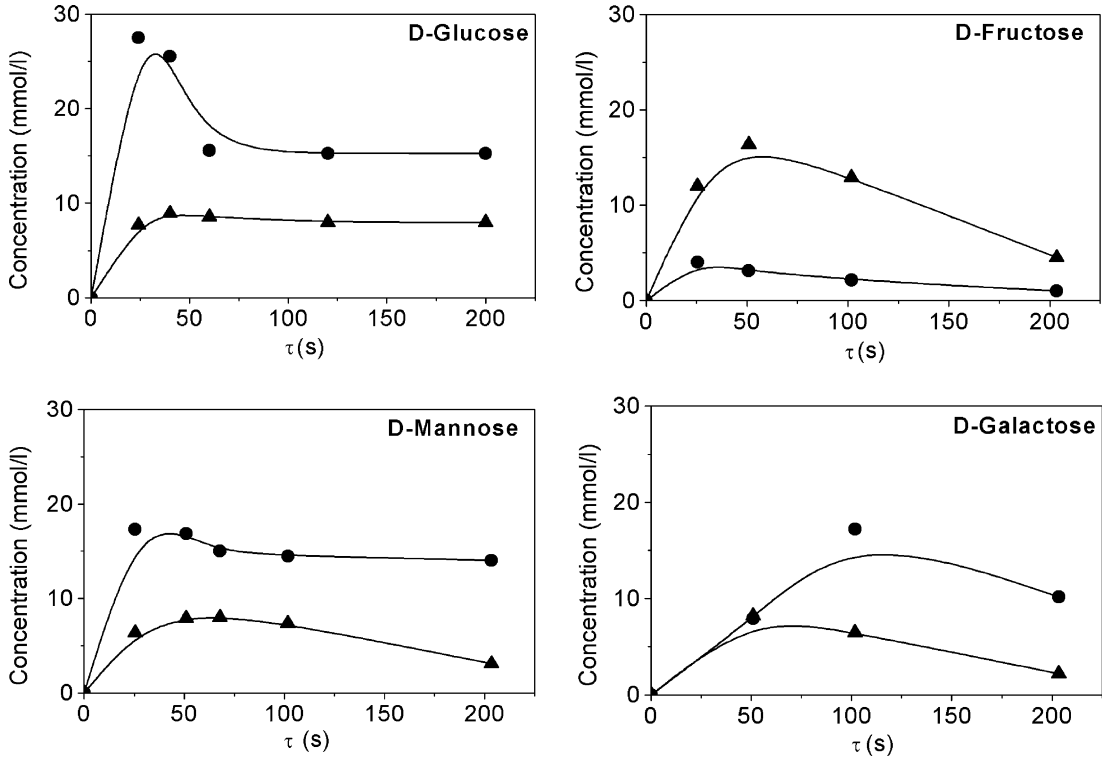


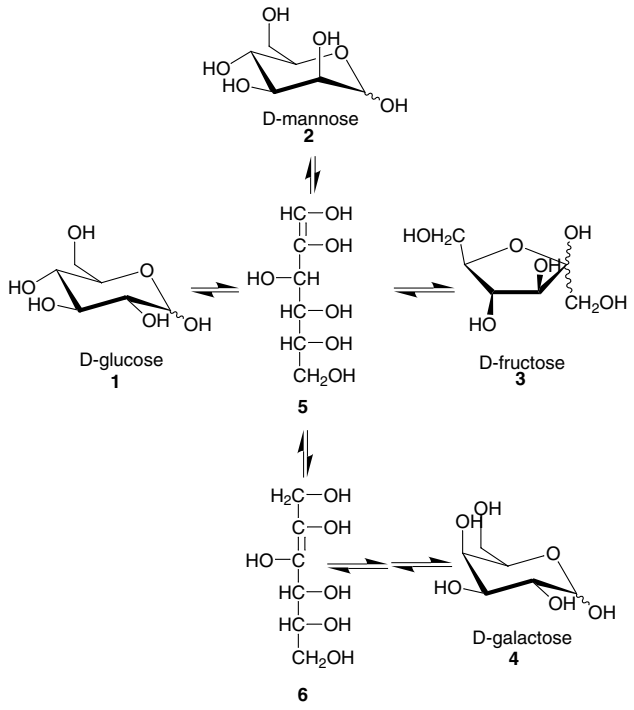
Figure 2. Formation of 5-hydroxymethylfurfural (▲) and glycolaldehyde (●) during the hydrothermal reactions of some monosaccharides (50 mM, 340 °C, 27.5 MPa).

are clearly intermediates, as their concentrations initially increase until they reach a maximum at $\tau = 30$–100 s, after which they decrease (see Fig. 2). The concentration of all other compounds initially steadily increased to an almost constant value at a τ-value of about 100 s.

Qualitatively, no differences existed in the products formed from the sugars investigated. However, the amounts of the various compounds and their rates of formation depend strongly on the nature of the starting sugar.

The reaction mixtures obtained from these sugars contain compounds that are characteristic for acid degradation of sugars next to others that are characteristic for basic degradation. For example, HMF (**7**) is a product that typically is formed upon acid degradation of sugars,[12] whereas glycolaldehyde (**10**) has been observed as an important product in alkaline degradation.[13–17] The occurrence of both acidic and base catalysed reactions can be ascribed to the increase of the value of the ion product of water, K_w, near the critical point.[18,19] Under those conditions K_w is about three orders of magnitude higher than under ambient conditions.

The similarity of the hydrothermal reaction products of D-glucose (**1**), D-mannose (**2**), D-fructose (**3**) and D-galactose (**4**) may be explained by the base catalysed Lobry de Bruyn–Alberda van Ekenstein rearrangement, which results in interconversion of glucose (**1**), mannose (**2**) and fructose (**3**) via the 1,2-enediol anion (**5**, see Scheme 1).[20] It should be noted that mannose and fructose have been observed in the reaction mixtures obtained upon hydrothermal treatment of glucose using very short residence times.[9] Possibly, successive



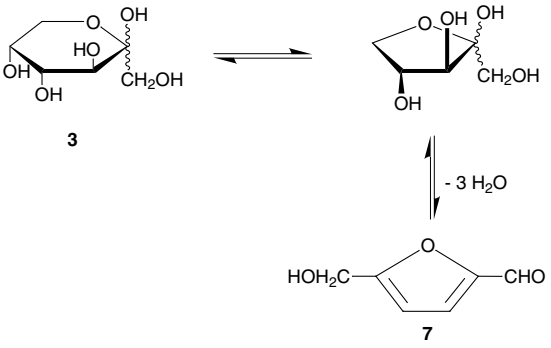
Scheme 1. Rearrangements of monosaccharides via enediol during the hydrothermal reaction.

rearrangements via other enediol anions (e.g., **6**) result in interconversion of all C_6-monosaccharides.

Although the reaction products of the four monosaccharides **1**–**4** are qualitatively similar, a remarkable difference exists between the product distribution from fructose (**3**) and those of the other sugars. For fructose (**3**), HMF (**7**) is the major reaction product and glycolaldehyde (**10**) is much less abundant than with the other sugars. Of the four sugars studied, fructose (**3**) has the energetically most favourable furanose form. Under ambient conditions, 28% of this anomeric form occurs, whereas glucose (**1**), mannose (**2**) and galactose (**4**) occur almost exclusively in pyranose forms. Furthermore, the epimerisation rate of glucose to fructose is much faster than the reverse reaction.[8] This supports the formation of HMF (**7**) via successive acid catalysed dehydrations of fructofuranose (**3**) as proposed by Antal et al. (see Scheme 2).[12]

Glycolaldehyde (**10**) can be formed from glucose in the open form via a retro-aldol reaction (see below, Scheme 4). Formation of large amounts of this compound is remarkable, since Kabyemela et al. have observed glyceraldehyde (**13**) as an important reaction product after extremely short reaction times ($\tau = 0.02$–2 s). Under the conditions that we applied, glyceraldehyde was not observed (**13**); only minor amounts of its isomerisation product dihydroxyacetone (**12**, $\leqslant 1$ mM) were detected. Both the formation of glyceraldehyde (**13**) and its consecutive reactions are very fast,[8,21] and, therefore, possibly only the secondary reaction products are observed at the relative long residence times that we applied (see also below).

During the hydrothermal reactions of the monosaccharides only minor amounts of gases were formed; the amount was negligible for D-glucose (**1**). It should be noted that the solubility of CO_2 in water is about 33 mmol/L. However, a ^{13}C NMR spectrum of a sample taken at $\tau = 400$ s showed that the amount of bicarbonate in the sample is negligible. The molecular formulae of most of the identified compounds can be given as $C_n(H_2O)_m$ (see Table 1). Only some minor compounds had a different H/O ratio (acetaldehyde (**23**), formic acid (**24**), glycolic acid (**28**) and acetone (**30**)). This supports the suggestion that decarboxylation and decarbonylation are relatively unimportant pathways under the conditions applied.



Scheme 2. Formation of furan derivatives during the hydrothermal reactions of monosaccharides. Here the reaction of D-fructose is shown as an example.

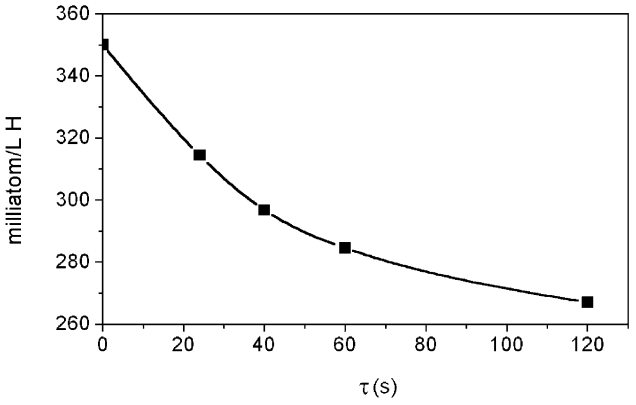


Figure 3. The total amount of nonexchangeable protons of the organic substrate during the hydrothermal reaction of glucose.

The exchange of the OH and COOH protons and the water protons is rapid on the ^1H NMR time scale. Consequently only an averaged signal can be observed. For the reaction of glucose, the total integral of the other (nonexchangeable) protons indicated that the amount of this type of protons decreased from 350 to about 267 milliatom/L during the first 120 s of the reaction (see Fig. 3). Similar behaviour was observed for the other sugars. This indicates that about 24 mol% dehydration occurs under these conditions, which corresponds with a decrease of the amount of oxygen with the same percentage.

The total organic carbon number (TOC) of the samples at the longest residence times showed that in the liquid samples between 60% and 96% of the total amount of carbon was recovered. The losses can be ascribed to tar deposited on the wall of the reactor. Upon increase of the concentration of the substrate, the amount of tar increased, which frequently resulted in blocks of the reactor.

Surprisingly, D-sorbitol remained unreacted when it was subjected to similar hydrothermal conditions (50 mM solution, 240 s at 340 °C and 27.5 MPa). This indicates that the hemi-acetal function of the sugars is essential for their conversion. Most likely, the enediol (and/or its anion) is an important intermediate for the basic catalysed pathways, whereas cyclic structures are important in the acid catalysed reactions.

2.2. D-Arabinose (8)

When the C_5 monosaccharide D-arabinose (**8**) was subjected to the hydrothermal treatment, mainly glycolaldehyde (**10**) and 2-furaldehyde (**9**) were obtained.

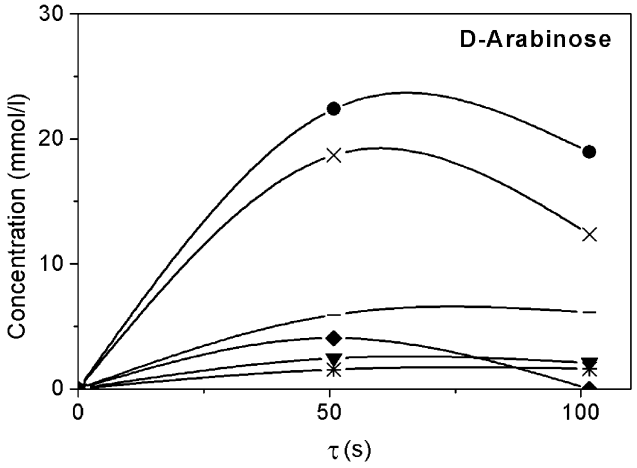


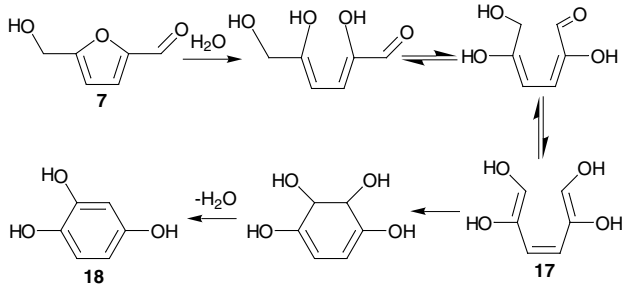
Figure 4. Distribution of the most important species during the hydrothermal treatment of D-arabinose (50 mmol/L, 340 °C, 27.5 MPa). ▲ 5-hydroxymethylfurfural, ■ 1,2,4-benzenetriol, ● glycolaldehyde, ▼ acetone, ♦ glycolic acid, + formic acid, × 2-furaldehyde, ∗ acetic acid, - lactic acid.

Smaller amounts of glycolic acid (**28**), lactic acid (**21**), acetic acid (**26**) and acetaldehyde (**23**) were identified in the reaction mixture (see Fig. 4). Apparently, similar reaction paths occur as with the C_6 monosaccharides. Once again, initially dehydration and retro-aldol condensation seem to be important.

2.3. Reaction pathways via 5-hydroxymethylfurfural (7)

To untangle the reaction pathways of the reaction of D-glucose (**1**), we also performed hydrothermal reactions on compounds that were identified as the initial reaction products of this sugar. HMF (**7**) showed some decomposition; at $\tau = 400$ s, the concentration of HMF (**7**) in the reaction mixture was decreased from 55 to 28 mM. The ^{1}H NMR spectrum showed the presence of several minor reaction products of which 1,2,4-benzenetriol (**18**) was by far the most abundant (1.3 mM at $\tau = 400$ s). This compound was identified before by Luijkx et al.[7] It has been suggested that this compound is formed from HMF (**7**) by hydrolysis of the furan ring followed by a rearrangement to a hexatriene (**17**), electrolytic rearrangement and dehydration (see Scheme 3).[22] 1,2,4-Benzenetriol (**18**) is stable under HTU conditions, so it is one of the end products of this reaction. However, aqueous samples of this compound are not stable in air. They slowly convert into a dimer via an oxidative coupling.

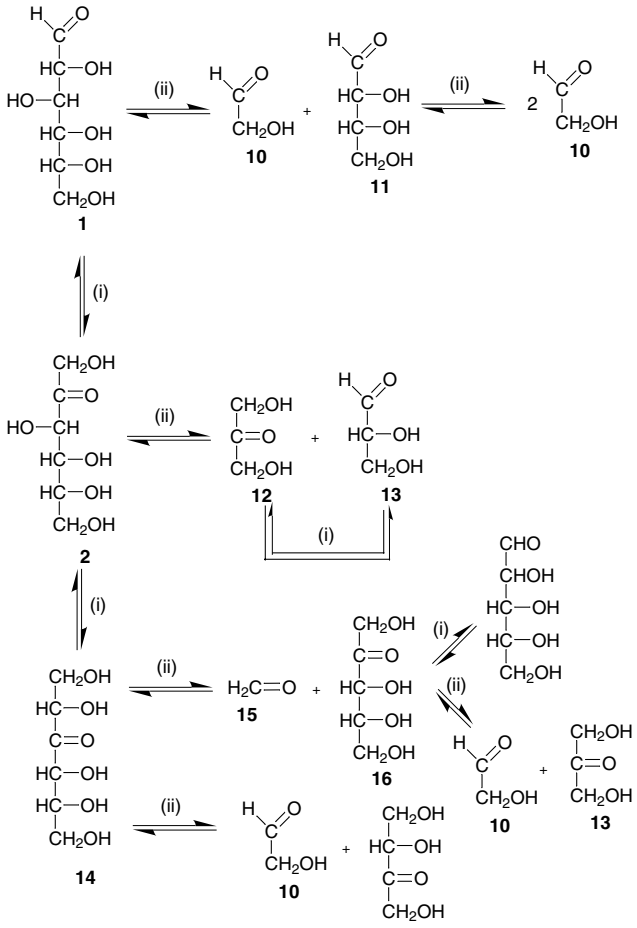
No 2-furaldehyde (**9**) could be detected in the reaction mixtures from the hydrothermal reaction of HMF. This implies that the 2-furaldehyde (**9**) that has been observed in the reaction mixture from the C_6 monosaccharides (see Table 1) has been formed via another pathway, most likely through C_5 ketoses as already proposed previously by Kallury et al.[10] The latter compounds may



Scheme 3. Pathway proposed for the rearrangement of HMF (**7**) to 1,2,4-benzenetriol (**18**).[22]

be formed via several pathways. For example, ketose **14** (see Scheme 4), which can fragment via a retro-aldol reaction into formaldehyde (**15**) and a C_5-monosaccharide (**16**).

Alternatively, the initially formed 1,2-enediol may be converted into the corresponding 1,2-diketone by an α-elimination. Subsequent α-dicarbonyl cleavage results in



Scheme 4. Fragmentation of monosaccharides via (i) Lobry de Bruyn–Alberda van Ekenstein rearrangements and (ii) retro-aldol condensations. For convenience the saccharides are represented in their linear forms.

formic acid (**24**) and the C_5-monosaccharide. The C_5-monosaccharides can then dehydrate to 2-furaldehyde (**9**) as has been demonstrated in the hydrothermal treatment of D-arabinose (**8**, see above). Most likely, first a Lobry de Bruyn–Alberda van Ekenstein rearrangement to ribulose takes place. Then, following the conclusions of the work of Antal et al.,[12] three consecutive dehydration steps may lead to 2-furaldehyde (**9**).

Quantitatively, the compounds identified with NMR and HPLC cannot account for the decrease in the concentration of HMF (**7**) observed during the reaction. We assume that tar deposited on the wall of the reactor tube is responsible for this.

2.4. Reaction pathways via glycolaldehyde (10) and D-erythrose (11)

An important pathway of the hydrothermal reaction of D-glucose and the other C_6 sugars starts with a retro-aldol condensation to form glycolaldehyde (**10**, see Scheme 4). The second product should be a C_4 sugar, such as D-erythrose (**11**), but these sugars could not be identified by ^{1}H NMR because of the presence of many overlapping signals in the region of the spectrum where the resonances of these compounds should be expected. Also in the HPLC chromatogram no C_4 sugars could be identified. To get some insight in possible reactions starting from this type of sugars, we performed an analogous reaction with D-erythrose (**11**). The main reaction product was glycolaldehyde, which can be formed via a retro-aldol reaction.

It should be noted that glycolaldehyde (**10**) cannot be formed directly from a retro-aldol condensation from D-fructose (**3**). This compound should first isomerise to glucose to enable this reaction. This is reflected in the low initial rate of formation of glycolaldehyde from D-fructose.

Glycolaldehyde (**10**), when subjected to the same reaction conditions, converted with small yield into a complex mixture of compounds with NMR resonances at chemical shifts (3–5 ppm) that are characteristic for polyhydroxy compounds (see Fig. 5). Most likely these products are the result of condensation reactions.

2.5. Reaction pathways via glyceraldehyde (13)

Another initial product of the hydrothermal reactions of monosaccharides is, once again as the result of a retro-aldol condensation reaction, glyceraldehyde (**13**, see Scheme 4). This reaction can only occur in 2-ketoses, such as fructose (**3**). Therefore, starting from D-glucose (**1**) a Lobry de Bruyn–Alberda van Ekenstein rearrangement should precede this route. Only minor amounts of glyceraldehyde (**13**) were detected, but up to 1 mM of dihydroxyacetone (**12**) was observed at

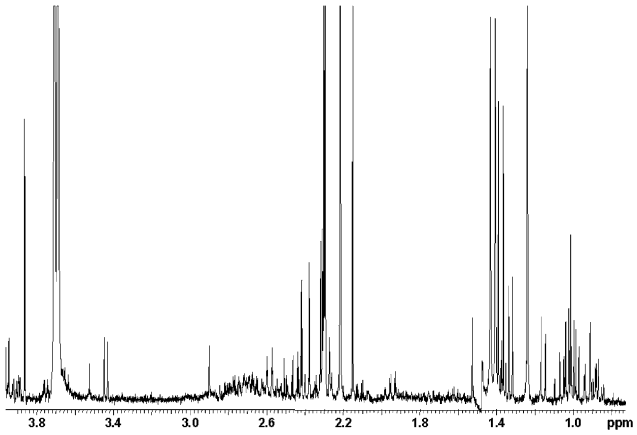


Figure 5. Expanded ^{1}H NMR spectrum of the reaction product of the hydrothermal treatment of glycolaldehyde (**13**), showing the presence of a complex mixture of polyhydroxy compounds.

$\tau = 400$ s during the hydrothermal treatment of glucose. This compound can be formed from glyceraldehyde (**13**) via another Lobry de Bruyn–Alberda van Ekenstein rearrangement.

When glyceraldehyde (**13**) was applied as the feedstock for the hydrothermal reaction, a rapid conversion into a mixture of compounds was observed that contained most minor compounds observed in the reaction of D-glucose (**1**): dihydroxyacetone (**12**), pyruvaldehyde (**20**), lactic acid (**21**), acetaldehyde **(23)**, formic acid (**24**), acrylic acid (**22**), acetic acid (**26**), glycolic acid (**28**) and acetone (**30**). After 200 s, lactic acid (**21**) was the major component (25 mM, see Fig. 6). The concentrations of pyruvaldehyde (**20**) and acetone (**30**) have maxima after about 50 s, suggesting that these compounds are intermediates. Pyruvaldehyde (**20**) can be formed from

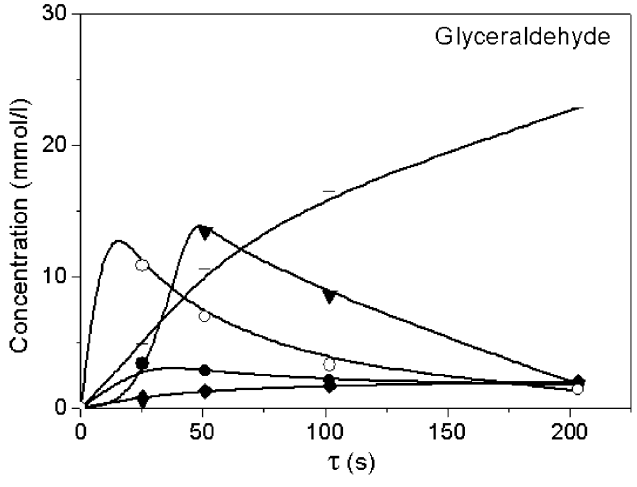
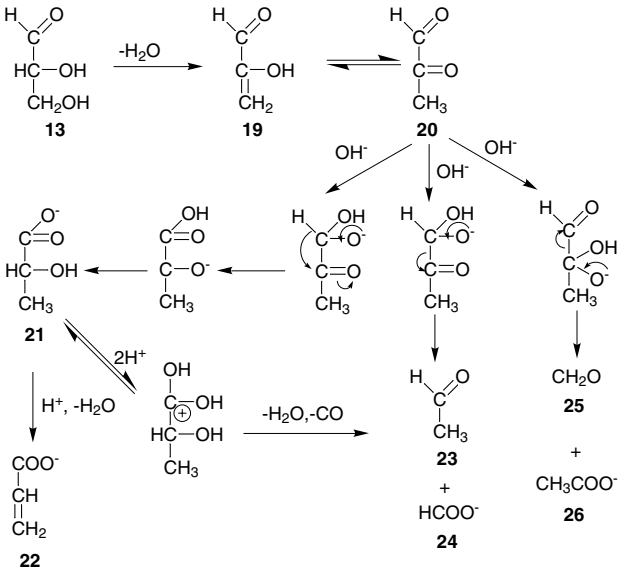


Figure 6. Distribution of the major reaction products during the hydrothermal treatment of glyceraldehyde (**13**). ● glycolaldehyde, ▼ acetone, ♦ glycolic acid, - lactic acid, ○ pyruvaldehyde.



Scheme 5. Possible pathways of the reactions during the hydrothermal treatment of glyceraldehyde (**13**).

glyceraldehyde **(13)** by dehydration to compound **19** (see Scheme 5), followed by a keto-enol rearrangement. Pyruvaldehyde (**20**) in turn can be converted into the isomeric lactic acid (**21**) by means of a benzilic rearrangement. An α-dicarbonyl cleavage can explain the formation of formic acid (**24**) and acetaldehyde **(23)** and of acetic acid (**26**). The latter compound should be accompanied by formaldehyde (**25**), which due to its high reactivity probably has escaped observation. It may be concluded that the pathway glyceraldehyde **(13)** → pyruvaldehyde **(20)** → acetaldehyde **(23)** + formic acid **(24)**, formaldehyde **(25)** + acetic acid **(26)** is an important route to compounds that have a decreased O-content with respect to glucose.

Experimentally, starting from lactic acid as feedstock (**21**), next to acrylic acid (**22**), once again acetaldehyde (**23**) was observed. Both reactions are acid catalysed. Dehydration results in acrylic acid (**22**), whereas an acid catalysed decarbonylation may afford acetaldehyde (see Scheme 5).

2.6. Effects of added acid and base

Since both acid and base catalysed reactions were observed during the hydrothermal reactions of D-glucose, we decided to investigate the effect of added acid and base. In the presence of 6 mM NaOH, the acid catalysed reaction paths via HMF (**7**) and furfural (**9**) appeared to be completely suppressed (see Fig. 7B), neither HMF (**7**), 2-furaldehyde (**9**) nor 1,2,4-benzenetriol (**18**) were observed. The amounts of lactic acid (**21**), acetic acid (**26**) and acetaldehyde (**23**) were considerably higher, indicating that the reaction paths via glyceraldehyde (**10**) are relatively important under basic conditions. Major products were glycolic acid (**28**) and acetone (**30**), which were observed in all other reactions only in minor amounts. Many possible pathways can be envisaged for the formation of glycolic acid (**28**) and acetone (**30**), for example, starting from the 2,3-enediol **6**. An α-elimination followed by enol-keto rearrangement gives diketone **27**, which may give glycolic acid (**28**) and compound **29** after an α-dicarbonyl cleavage (see Scheme 6). The latter could be converted into acetone (**30**) and formic acid (**24**) via dehydration, enol-keto rearrangement followed by a base catalysed fragmentation (see Scheme 6).

In the presence of added HCl (6 mM), initially HMF (**7**) is formed (see Fig. 7C). However, it rapidly decomposes to unidentified products. Most likely tars are being formed. After the reaction a large amount of deposited tar was observed in the reactor. The base catalysed reactions are not fully suppressed, glycolaldehyde (**10**) is still present in considerable amounts. The most abundant products of the reaction in the presence of HCl are acetaldehyde (**23**) and formic acid (**24**), which may be explained by reaction pathways starting from initially formed glyceraldehyde (**13**, see Scheme 5).

3. Conclusions

During the initial stages of the hydrothermal treatment (340 °C, 27.5 MPa) of a low concentration of C_6 monosaccharides (50 mM) both acid and base catalysed reactions play a role. The acid catalysed reactions are mainly dehydrations with HMF as a major intermediate. Several base catalysed reactions lead to fragmentations via, for example, retro-aldol condensation and beta elimination. Decarbonylation and decarboxylation reactions play a minor role at the high dilution of the feedstocks used in this research. Some highly reactive compounds, including glycolaldehyde (**10**) and glyceraldehyde (**13**) are key intermediates in the pathways that were observed in this investigation. It may be expected that, at higher concentrations, condensation reactions may occur similar to those observed for the alkaline degradation of sugars at lower temperature.[12–15] The occurrence of condensation reactions was already observed during the reaction of glycolaldehyde (**10**), which resulted in significant amounts of condensation products. Therefore, at the higher concentrations that are applied for the HTU reaction of biomass it may be expected that fragments formed subsequently enter in condensation reactions with other fragments to afford a complex mixture of compounds. In this dynamic system irreversible reactions similar to those observed in this study may occur, including the formation of 1,2,4-benzenetriol (**18**). Reactions similar to that of the pathway

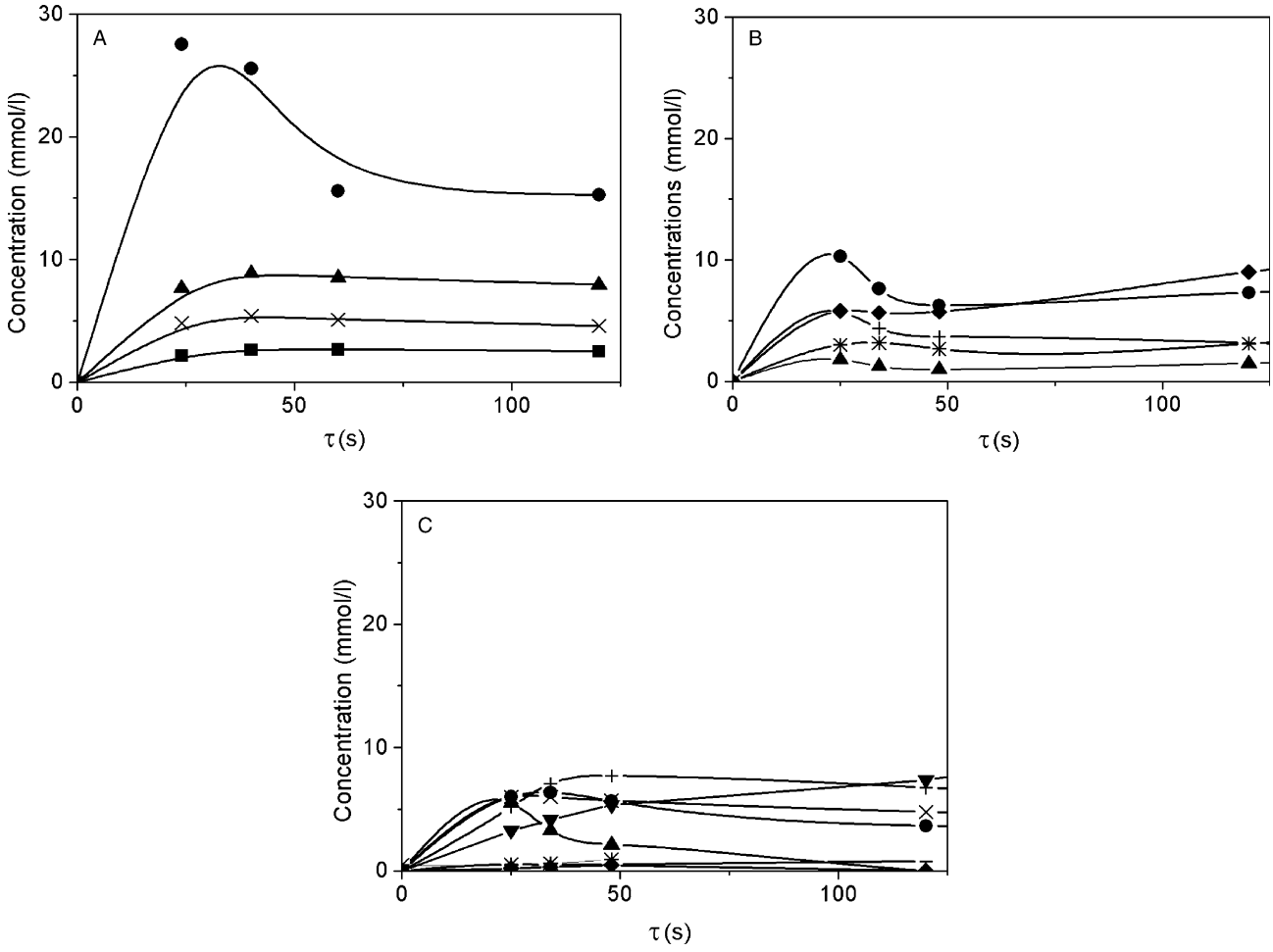
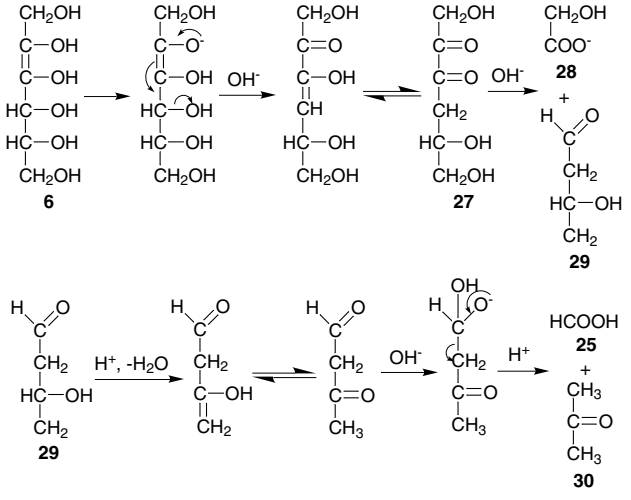


Figure 7. Distribution of the most important products during the hydrothermal reaction of D-glucose (50 mM, 340 °C, 27.5 MPa), (A) without addition of acid or base, (B) in the presence of 6 mM NaOH, (C) in the presence of 6 mM HCL. ▲ 5-hydroxymethylfurfural, ■ 1,2,4-benzenetriol, ● glycolaldehyde, ▼ acetone, ♦ glycolic acid, + formic acid, × 2-furaldehyde, ∗ acetic acid, - lactic acid.



Scheme 6. Possible pathways during the hydrothermal treatment of glucose in the presence of base.

glucose (**1**) → glyceraldehyde (**13**) → pyruvaldehyde (**20**) → acetaldehyde (**23**) + CO/formaldehyde (**25**) + acetic acid (**26**) may ultimately lead to the desired reduction of the O-content of the liquid reaction products. These pathways seem to be favoured under more acidic conditions, whereas under more basic conditions pathways similar to those observed for basic degradation of sugars seem to be dominant. Then, routes via diketones to glycolic acid (**28**) and acetone (**30**) seem to be of special interest with regard to the reduction of the O-content during the HTU reaction. Furthermore, it may be expected that condensation reactions of the initially formed products may afford new compounds and maybe also new pathways may become operative. This might include pathways that result in formation of CO_2.

Another important conclusion of this research is that the HTU reaction mixture of biomass may contain considerable amounts of highly reactive aldehydes, which will have a bad influence on the stability of the biocrude. Further upgrading, for example by hydrodeoxygenation may be required to obtain a more stable fuel.

4. Experimental

4.1. Chemicals

All chemicals used were obtained from Aldrich. A 50 mM solution of glycolaldehyde in water was heated for 10 min at 60 °C to hydrolyse any oligomers present just prior to the hydrothermal reaction. All other substrates were used without further purification. The water used was demineralised and had a conductivity of 18.2 mΩ cm.

4.2. Apparatus and method

The home-built apparatus used for the HTU reactions is schematically depicted in Figure 1. A continuous flow-type reactor (made of stainless steel 316, length 35 mm, internal diameter 4 mm) allowed the short residence times required to study the initial products. A solid cylinder of aluminium with an outer diameter of 25 mm surrounded the reactor. The reactor and the aluminium housing were heated in an oven. The temperature was measured by a chromel–alumel thermocouple located inside the reactor. The inlet and outlet of the reactor were cooled by a cooling water jackets, which decreased the temperature to less than 30 °C. The feedstock had a concentration of 50 mmol/L of the component under study, unless stated otherwise, and was fed to the reactor using an HPLC pump at a rate of 1.0–9.9 mL/min depending on the residence time required. The flow rate was frequently tested by measuring the volume of the water pumped through the reactor as a function of the setting of the flow rate of the HPLC pump. From the flow rates of the feed solutions, the residence time of the solutions in the reactor were calculated. The pressure in the reactor was controlled by a Tradinco dome-loaded backpressure regulator with a Teflon membrane to which a hydraulic reference oil pressure was applied with a Barnet dead-weight tester (maximum pressure 70 MPa). The pressure regulator is designed to allow smooth pressure release for liquids as well as liquid/gas mixtures. No pressure fluctuations could be observed as long as the membrane was clean. All experiments were carried out with a reactor temperature of 340 °C and a pressure of 27.5 MPa.

Reactor shut-down was performed by flushing with water during cooling-down, and if tar had been deposited in the reactor, it was dissolved by pumping acetone through the reactor after cooling down to room temperature. Tar is defined here as any black material that is insoluble in water but soluble in acetone.

4.3. Analyses

At each residence time, three samples of 10 mL were taken. Any solid particles formed were centrifuged or filtered off and the clear solutions were analysed by HPLC and ^{1}H NMR. Assignments of peaks were made by comparison of chromatograms and spectra with those of authentic samples. The quantitative results of the HPLC and ^{1}H NMR analyses agreed with each other within the experimental error (ca. 5%). Some of the samples were also analysed for total organic carbon (TOC).

The HPLC analyses were carried out with a Millipore-Waters 590 pump and Phenomenex Rezex organic acid column at 60 °C. The eluent was 0.01 M aq trifluoroacetic acid and the flow rate 0.5 mL/min. A refractive index (RI) (Shodex model SE-51) detector and an ultraviolet (UV) (Shimadzu spectrometric detector model SPD-6A) at 215 nm were used. The peak areas were determined using an integrator (Kipp & Zonen). HPLC quantitation was achieved using THF as an internal standard.

^{1}H NMR spectra were measured on a Varian Unity INOVA-300 spectrometer at 300 MHz). A weighed amount of *tert*-butanol in D_2O was added to the samples to lock and as an internal standard. The chemical shifts are reported with respect to the CH_3 signal of *tert*-butanol, which was set at 1.20 ppm. The water resonance was suppressed using presaturation with the transmitter. The peak areas were determinded by deconvolution of the spectrum with lorentzian peaks.

Total organic carbon analyses were performed using a Shimadzu T.O.C. 5050A instrument.

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