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Hydrothermal formation of 1,2,4-benzenetriol from 5-hydroxymethyl-2-furaldehyde and D-fructose

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ABSTRACT

Thermolysis of 0.05 M aqueous 5-hydroxymethyl-2-furaldehyde (HMF) at 27.5 MPa and 290 to 400°C led to the formation of 1,2,4-benzenetriol in yields of up to 46% at 50% HMF conversion. The reaction temperature and water density have a significant effect on the product composition. Pseudo-first-order reaction rate constants for HMF conversion under these conditions range from 0.107 to 0.308 min^{-1}. For the region 290 to 350°C, the activation energy for HMF conversion was found to be 47.7 kJ.mol^{-1}. When subjecting D-fructose to hydrothermolysis, the main products are HMF, 1,2,4-benzenetriol, and furfural.

INTRODUCTION

The hydrothermal upgrading (HTU) of biomass to liquid fuels has many advantages over other liquefaction processes, such as pyrolysis. HTU involves the conversion of the biomass in liquid water at temperatures of 300 to 350°C, with residence times from 5 to 15 min[1]. In HTU, no drying of the biomass is required, and oxygen is predominantly removed as CO_2, thus producing an oil with a relatively low content of oxygen, which can be easily separated from the water layer. It was found[1] that biomass with a large content of cellulose and hemicellulose gave the best results with respect to decarboxylation and oil formation.

The chemistry of this hydrothermal biomass conversion and especially the formation of oil-like or tarry compounds is, however, very complex and still largely unknown. Model compounds, ranging from simple alcohols[2,3] and aldehydes[4,5] to more complex compounds, such as monosaccharides and derivatives[6,7], have been used to study hydrothermolysis of the carbohydrate fraction of the biomass. The dehydration product of glucose and fructose, 5-hydroxymethyl-2-furaldehyde (**1**, HMF), has also been used as a model compound for studies of hydrothermal

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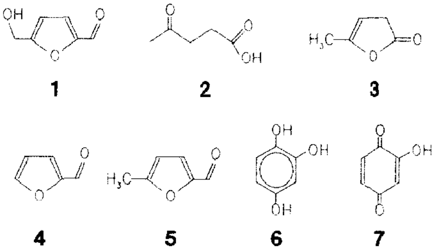

Fig. 1. Some compounds found in HMF (**1**) hydrothermolysis.

biomass liquefaction under various conditions[7,8,9]. HMF is also formed in hydrothermal treatment of carbohydrates[10,11] and could possibly be an important intermediate in hydrothermal biomass upgrading. Depending on the reaction conditions, HMF hydrothermolysis products (cf. Fig. 1), such as 4-oxopentanoic acid (**2**, levulinic acid)[7,8,9] and its lactone (**3**, α-angelicalactone)[8], 2-furaldehyde (**4**, furfural)[8], and 5-methyl-2-furaldehyde[7,8] (**5**), could be detected in the reaction mixture. Temperatures applied in these studies range from 190 to 350°C. We have investigated the hydrothermolysis of HMF at temperatures up to 400°C under a pressure of 27.5 MPa, thus extending the hydrothermolysis area to the supercritical region of water ($T_c = 374.1$°C, $P_c = 22.1$ MPa)[6]. The continuous tubular reactor set-up allowed us to use short reaction times ranging from 1 to 15 min. Under these conditions, we identified 1,2,4-benzenetriol (**6**, hydroxyhydroquinone) as a major product[12].

EXPERIMENTAL

Chemicals.—HMF was kindly provided by Südzucker AG and was dried prior to use. D-Fructose was obtained from Merck, and 1,2,4-benzenetriol was obtained from Aldrich or synthesised from *p*-benzoquinone according to Thiele[13], and Gattermann and Köbner[14]. All other chemicals were purchased from Janssen Chimica.

Reactor set-up.—The reactor set-up (Fig. 2) consists of an open coiled Hastelloy C-276 tube (i.d., 1.43 mm; length, 3.18 m; active reactor volume, 4.8 mL) fed by a Waters 6000A HPLC pump. The reactor is heated in a Perkin–Elmer F11 GC oven with an additional electrical heating at the entrance. The reactor is equipped with tap-water cooling at the entrance and the end of the reactor tube. Pressure is released via a Tradinco dome-loaded back-pressure regulator to which a reference oil pressure is applied with a Barnet deadweight tester.

Gas formed during the reaction is collected in an exchangeable glass sample tube filled with He. This sample tube is connected to an automatic gas burette in order to register gas formation and to keep the pressure constant at 1 atm.

Hydrothermolysis.—The 0.05 M HMF solution was filtered over a P4 glass filter and sparged with He during 20 min to remove the O_2. The preheated reactor,

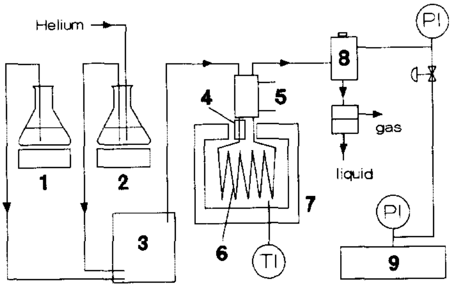

Fig. 2. Reactor set-up for hydrothermal conversions: **1**, water; **2**, reactant solution; **3**, Waters 6000A HPLC pump; **4**, electrical heating; **5**, cooling jacket; **6**, Hastelloy C-276 reactor tube (length, 3.18 m; i.d., 1.4 mm); **7**, Perkin–Elmer F11 GC oven; **8**, Tradinco dome-loaded back-pressure regulator; **9**, Barnet dead-weight tester; PI, pressure indicator; TI, temperature indicator.

which was fed with deaerated water, was switched to the HMF solution until at least 5 to 10 reactor volumes (25 to 50 mL) had been pumped through to reach a steady state. A sample was collected and a second one was collected when another 2 reactor volumes had been pumped through. Kinetic data were based on measurements at 5 to 7 different residence times for each temperature. For the carbon balance measurements, the reactor effluent was collected during a 5- to 6-h run. The tarry product fraction was separated from the water layer by centrifugation. A small amount of tarry material that remained in the reactor tube was dissolved in acetone and added to the tar fraction.

Analyses.—Gas, if formed, was analysed off-line by GC (CarboPLOT column, 12.5 m; i.d., 0.53 mm; TCD detection; carrier gas, H_2) for determination of CO, CO_2, and CH_4.

The tar fraction was subjected to elemental analysis by pyrolysis combustion mass spectrometric element analysis (PCME[15]) for determination of C and H content, and was further analysed by GPC (columns: Waters μStyragel 500 Å and μStyragel 100 Å in series; eluent tetrahydrofuran, at 1 mL/min) for estimation of the molecular weight.

The pH of the water layer was measured directly after the reaction. The water layer was quantitatively analysed by HPLC (Bio-Rad HPX87H column, 60°C, eluent 0.01 M aq CF_3CO_2H, at 0.6 mL/min; or Nucleosil C-18 column, eluent 15:85:0.1 $MeOH–H_2O–CF_3CO_2H$). For identification of the products, HPLC was coupled to a mass spectrometer (VG 70-Se mass spectrometer operating in the plasma spray mode). An extract of the water layer was prepared as described previously[12] and was analysed by ^1H NMR, ^{13}C NMR, and GC–MS after trimethylsilylation. NMR spectra were recorded with a Nicolet NT-200 WB or a Varian VXR-400S spectrometer. 1,2,4-Benzenetriol was identified by comparison of the ^1H and ^{13}C NMR spectra of the water-layer extract with an authentic sample {^{13}C NMR data [$(CD_3)_2CO$]: δ 104.03, 106.54, 116.38 (C-3,5,6), 138.63, 146.52, and 151.75 (C-1,2,4)}.

RESULTS AND DISCUSSION

Product formation.—The composition of the reaction mixture in our experiments differed substantially from earlier findings. Important products such as **5**, found by Kallury et al.[8] at 295–300°C and residence times of 1–2.5 min, could only be detected in small amounts in our experiments. Surprisingly, 1,2,4-benzenetriol could be identified as the major product. Concentrations of HMF and 1,2,4-benzenetriol versus residence time at some selected temperatures are presented in Fig. 3. At temperatures up to 350°C, 1,2,4-benzenetriol formation is directly related to HMF conversion; at higher temperatures, 1,2,4-benzenetriol itself is subject to decomposition. Selectivities for 1,2,4-benzenetriol formation range from 10 to 46% at 50% HMF conversion, depending on the reaction temperature (Fig. 4).

In an experiment using D-fructose instead of HMF, at 330°C, we were also able to detect 1,2,4-benzenetriol as a major product in the reaction mixture, together

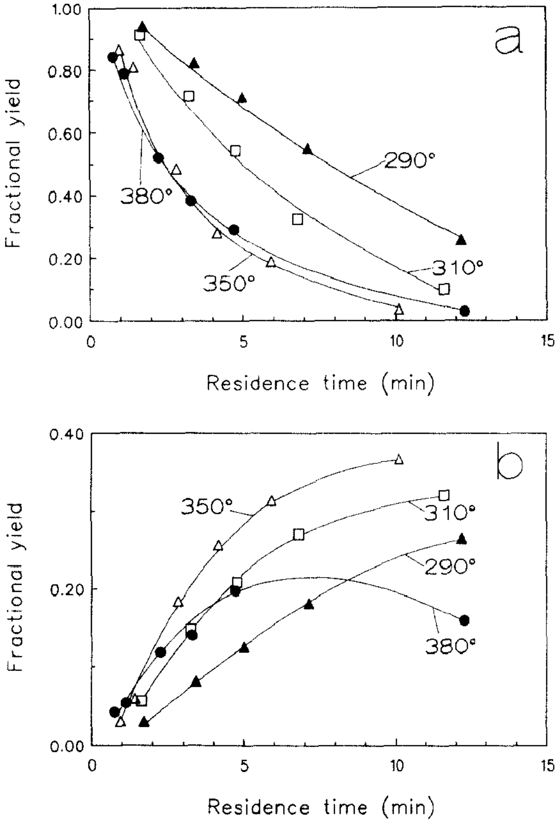

Fig. 3. Fractional yields of HMF (a) and 1,2,4-benzenetriol (b) from 0.05 M HMF in water as a function of the residence time for selected temperatures.

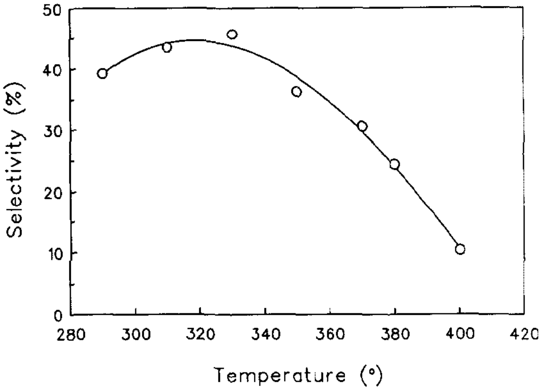

Fig. 4. Selectivity of 1,2,4-benzenetriol formation from HMF at 50% HMF conversion.

with HMF and 2-furaldehyde (Fig. 5). While the concentration of the initially formed HMF decreases with increasing reaction time, 1,2,4-benzenetriol concentration increases. Formation of small amounts of hydroxylated aromatics from carbohydrates and derivatives has been reported previously, for aqueous solutions[16,17,18] as well as under vacuum pyrolysis conditions[19,20]; their source has not been determined. From our results, we conclude that 1,2,4-benzenetriol is formed from HMF, which is a well-known degradation product of sugars.

A possible reaction pathway from HMF to 1,2,4-benzenetriol is presented in Fig. 6. The reaction is thought to be initiated by hydrolysis of the furan ring. The proposed intermediate tetrahydroxycyclohexadiene could result from an aldol-type reaction, or from a hexatriene molecule by electrocyclic rearrangement. 1,2,4-Benzenetriol is finally produced by dehydration of the cyclohexadiene derivative.

Other compounds formed during HMF conversion were 4-oxopentanoic acid (levulinic acid, 2), which is the main degradation product when subjecting HMF to

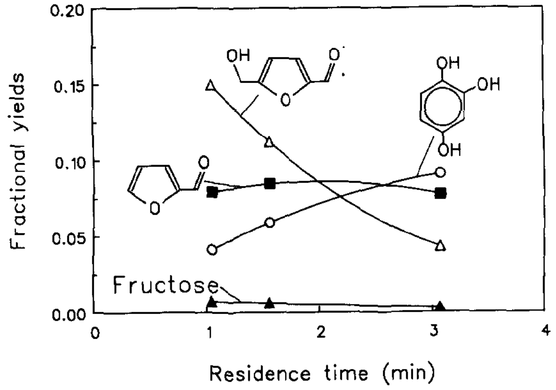

Fig. 5. Fractional yields of compounds formed by hydrothermolysis of 0.05 M D-fructose as a function of the residence time.

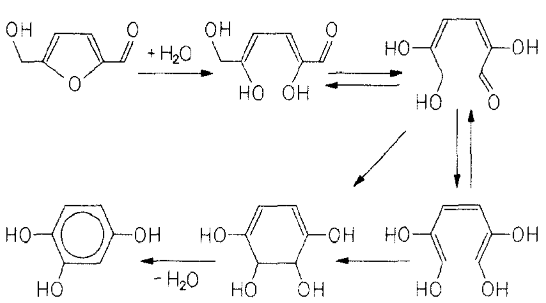

Fig. 6. Tentative reaction pathway for hydrothermal 1,2,4-benzenetriol formation from HMF.

water and acid; hydroxy-1,4-benzoquinone (**7**), the oxidation product of 1,2,4-benzenetriol; and, in smaller amounts, 1,4-benzenediol (hydroquinone), 1,2,3-benzenetriol, and acetone. Formic acid, which is a co-product of **2** and **3**, was not detected. At higher temperatures (> 380°C), 2-furaldehyde (furfural, **4**) and 5-methyl-2-furaldehyde (**5**) could also be detected in the reaction mixture. Typical compositions of the reaction mixture are presented in Table I. The quantified species make up almost 90% of the total amount of carbon. Calculations indicate that dissolved CO_2 would contribute 2–4% to the carbon balance; the remaining deficit is made up of other compounds that were not quantified.

At lower temperatures (290–350°C), hydrolytic opening accounts for more than 90% of the reaction products in the water layer. At higher temperatures, however, typical pyrolysis reactions of HMF[21] are becoming more significant, resulting in the formation of **4** and **5**. These pyrolytic reactions are favoured by the drastic change in water properties at these temperatures, such as a drop of the dielectric constant ϵ, from 10.2 at 380°C to 3.5 at 400°C (Table II).

Thermolysis of 0.05 M HMF in phosphate buffer solutions of pH 6.5 and pH 11.5 at 330°C resulted in heavy tar formation even at very short residence times. In the water layer, no HMF or 1,2,4-benzenetriol could be detected. At pH 6.5, the only compound in the water layer which could be identified was **7**.

The addition of hydrochloric acid (0.01 M) also resulted in complete HMF conversion at 330°C with residence times ranging from 1–5 min. Under these conditions, the normal product of acid-catalysed HMF degradation, 4-oxopentanoic acid (**2**), predominates but formation of 1,2,4-benzenetriol is still substantial. After

TABLE I

Carbon balance in percentages for different conversion temperatures at 27.5 MPa

T (°C)	Time (s)	Liquid phase compounds						Gases			Tar	Total
		1	**2**	**4**	**5**	**6**	**7**	CO	CO_2	CH_4		
310	178	73.8	0.8	0	0	9.0	0.4	0.03	0.05	0	3.71	87.8
350	171	46.0	1.2	0	0	21.2	2.0	0.19	0.23	0	4.18	75.0
400	160	50.8	2.3	0.5	2.4	2.4	18.5	1.56	1.99	0.05	6.72	87.2

TABLE II

Pseudo-first-order reaction rate constants for HMF conversion and their 95% confidence regions at 290–400°C, 27.5 MPa [a]

Temperature (°C)	k_{HMF} (min^{-1})	Water density (kg/m^3)	pK_w	ϵ
290	0.107 ± 0.013	764	11.06	23.0
310	0.170 ± 0.010	729	11.17	20.5
330	0.240 ± 0.017	687	11.37	18.0
350	0.301 ± 0.019	635	11.69	15.3
370	0.308 ± 0.022	562	12.28	12.3
380	0.292 ± 0.012	504	12.86	10.2
400	0.214 ± 0.018	238	17.27	3.5

[a] Water densities in the table are values obtained by interpolating data from Schmidt[22]; pK_w was calculated according to Marshall and Franck[23]; and the static dielectric constant ϵ was calculated according to Uematsu and Franck[24].

initial formation of levulinic acid (32–35%), 1,2,4-benzenetriol (15–19%), and some other products, the composition of the reaction mixture hardly changes with increasing residence time under these conditions.

Tar formation.—Only small amounts of tar were formed during the reaction, accounting for only up to 7% of the initial carbon content. The elemental composition of the tar (Table III) does not differ very much from the elemental composition of HMF itself (C, 57.14; H, 4.80; O, 38.06%). The high content of oxygen indicates that tar formation from HMF is not desirable with respect to oil production via hydrothermal upgrading of biomass. The carbon content of the tar fraction is in good agreement with the carbon content of "humic solids" (58%) found by Baugh and McCarty[9] in HMF decomposition at 190°C. The molecular weights of the compounds in the tar fraction found by GPC range from only ~ 260 to 540 $g.mol^{-1}$. After storing the tar for one month at −4°C, a maximum molecular weight of 2100 $g.mol^{-1}$ was found, indicating that the tar is rather unstable and subject to polymerisation.

HMF conversion.—The conversion of HMF under hydrothermal conditions could be described as a pseudo-first-order reaction. The reaction rate constants (k_{HMF}, Table II) in the region of 290 to 350°C, when plotted as an Arrhenius plot (Fig. 7), generate a straight line. The activation energy for HMF conversion in this reaction is 47.7 ± 4.9 $kJ.mol^{-1}$, which is in agreement with the value of 55.9

TABLE III

Elemental composition of the tar fractions

T (°C)	Reaction time (s)	C (%)	H (%)	O (% by difference)
310	178	56.61	5.458	37.93
350	171	61.84	4.952	33.21
400	160	61.96	4.954	33.09

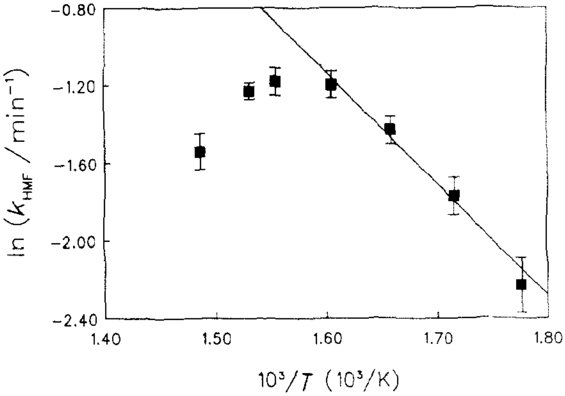

Fig. 7. Arrhenius plot for hydrothermal HMF conversion and fitted line for 290–350°C.

kJ.mol^{-1} found by Baugh and McCarty[9] (190 to 230°C in water). The pre-exponetial factor ($k_{HMF,0}$) could not be determined with great accuracy from our measurements: $\ln[k_{HMF,0}] = 8.1 \pm 1.0$. The pre-exponential factor determined by Baugh and McCarty, which is a function of the pH of the reactant solution at room temperature, is $1300 + 4.1 \times 10^6 \times (10^{-pH})$. Substituting the pH of the reaction mixtures (pH 3.0 to 3.3) in this equation gives values for $\ln[k_{HMF,0}]$ of 8.6 to 8.1.

At temperatures of 370°C and higher, the reaction rate constant of HMF conversion no longer increases with increasing temperature, which is an effect of the decreasing water density and the ionic properties (Table II) of the water phase in this region, resulting in competition between the hydrolysis and pyrolysis reactions.

CONCLUSIONS

Our results show that HMF is a precursor of 1,2,4-benzenetriol formed by hydrothermal and thermal treatment of carbohydrates. This result is very interesting with respect to tracing the origin of hydroxylated aromatics in hydrothermolysis and thermolysis mixtures of carbohydrates.

HMF conversion under hydrothermal conditions appears to be a pseudo-first-order reaction with relatively high reaction rate constants of up to 0.3 min^{-1}. In the subcritical region of water (290–350°C), an activation energy for this conversion could be determined at 47.7 ± 4.9 kJ.mol^{-1}.

The high oxygen content of the tar formed during the reaction and the low decarboxylation rate indicate that HMF is not a suitable model compound for simulation of hydrothermal upgrading of carbohydrates. In the supercritical region of water, competition between hydrolysis and pyrolysis type reactions occurred, as a result of the change of the water properties under these conditions.

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