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Catalytic dehydration of biomass-derived polyols in sub- and supercritical water

Vanessa Lehr, Michael Sarlea, Lothar Ott, H. Vogel *

Darmstadt University of Technology, Ernst-Berl-Institute of Technical Chemistry and Macromolecular Science,
Petersenstraße 20, D-64287 Darmstadt, Germany

Dedicated to Professor Dr.-Ing. Dr.h.c. Hartmut Fueß on the occasion of his 65th Birthday.

Abstract

The increasing CO_2 content in the atmosphere and the increasing demand for raw materials due to population growth makes the organisation of a post-fossil and sustainable era of energy and material supply, and the development of new chemical processes for intermediates essential. One possibility is to use biomass as a renewable material source. This is the reason why several polyols (→1,2- and 1,3-propanediol; 1,2-butanediol; glycerol and *m*-erythritol), which are easily available from sugars via biochemical conversion or hydrogenolytic cleavage, were dehydrated in sub- and supercritical water (SCW). During the dehydration of polyols in SCW mainly aldehydes or furan derivatives are formed, which are important industrial intermediates. The focus was on the influence of electrolytes versus acids on the reactions.

It could be concluded that converting polyols in sub- and supercritical water with the addition of bivalent transition metal sulphates is a well-promising approach to substitute crude oil based processes for the CO_2-neutral production of intermediates from renewable resources.

Keywords: Dehydration; Biomass-derived polyols; Sub- and supercritical water; Aldehydes; Furan derivatives; Industrial intermediates

1. Introduction

Oil is currently the most important raw material of the chemical industry. Today, mankind annually uses the same amount of oil per year as would be formed in 1 million years; inexpensive oil will only be available to a few generations. The fluctuations in price and availability of oil increase partially due to the unstable political situation in the oil-producing countries of the Middle East. A future strategy of the chemical industry based on the raw material oil becomes ever more precarious, as 10 years pass from the first idea of a new process to its realisation [1].

One solution is to reserve the use of the carbon – that is constantly generated in the form of biomass by photosynthesis – for the syntheses of chemicals, plastics and fuels. Since other forms of energy such as electricity and heat can be provided via non-chemical and therefore CO_2-free paths (e.g. nuclear power, water, wind, solar, photovoltaic and geothermal) biomass must be reserved for material production in order to ensure a sensible coexistence of the various sources of energy and carbon. However, in order to establish renewable resources for material production new processes must first be developed so that they can replace oil.

Annually renewable biomass consists mainly of carbohydrates (ca. 180 billion t/a = 75% of the biomass [2]). This enormous raw material and production potential is currently only used in small proportions. Until recently one saw the chance to use carbohydrates as raw materials where it was possible to preserve their structure and functionality to the furthest possible degree. Since the middle of 2005 against a background of the exploding and strongly fluctuating oil price, the question of using carbohydrates as raw materials for the production of basic products and intermediates has arisen again [2–5]. However, selective synthesis is difficult due to over functionalisation of the carbohydrates with hydroxyl groups of approximately the same reactivity [6]. One starting point for the solution of this problem is the defunctionalisation of the polyol structure via selective dehydration in supercritical fluids.

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* Corresponding author. Tel.: 49 6151 1621 65; fax: 49 6151 1634 65.
E-mail address: vogel@ct.chemie.tu-darmstadt.de (H. Vogel).

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2. Synthesis of polyols from carbohydrates

In general, di- and tri-, as well as polyols are selectively available via chemocatalysis as well as biocatalysis (Table 1).

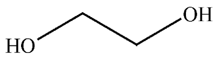
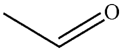
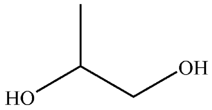
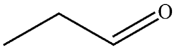
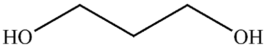
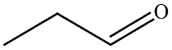
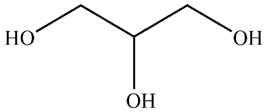
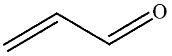
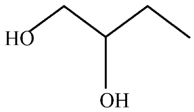
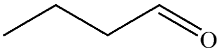
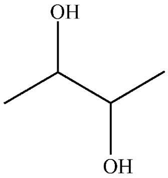
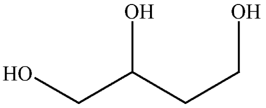
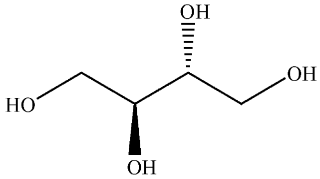
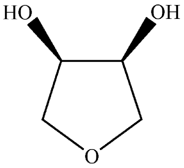
The simplest dioles such as ethanediol and propanediol are directly available from carbohydrates via biocatalytic reactions. 1,2-Propanediol can be extracted from simple sugars such as glucose, fructose or mannose by the application of *Clostridium sphenoides*. The synthesis of 1,3-propanediol from glycerol is achieved via addition of *Klebsiella*, *Clostridium* or *Lactobacillus* bacteria. Glycerol is available in large quantities from the glycerol containing waste water from the biodiesel production and the cleavage of fats [7,8]. *m*-Erythritol, which has broad applications as a sugar substitute, is extracted technically by the fermentation of D-glucose with *Trichosporonoides megachiliensis* or *Moniliella pollinis* [9].

The simplest diols such as 1,2-ethanediol and 1,2-propanediol are similarly available chemocatalytically from simple sugars in good yields [10,11]. Thus, via the hydrogenolytic decomposition of sugars on heterogeneous metal catalysts (Co/Cu/Mn) at 250 °C and 30 MPa, the following typical mixture is formed:

60% 1,2-propanediol;
20% 1,2-ethanediol;
5% 1,2-butanediol;
5% 1,2,5,6-hexanetetraol;
10% others + methane (2–3%).

The further refinement of polyols with adjacent hydroxyl groups to the corresponding aldehydes or ketones occurs via pinacol–pinacolone rearrangement. This rearrangement

Table 1
Overview of biomass-derived polyols and their reactions in sub- and supercritical water (SCW)

C-fragment	Polyol	Source	Conversion	… via …
C2	ethanediol 	Carbohydrates, heterogeneous catalyst		Homogeneous catalyst in SCW
C3	1,2-propanediol 	Carbohydrates, heterogeneous catalyst and biocatalyst		Homogeneous catalyst in SCW
	1,3-propanediol 	Glycerol, biocatalyst		Homogeneous catalyst in SCW
	glycerol 	Oils/fats, homogeneous catalyst		Homogeneous catalyst in SCW
C4	1,2-butanediol 	Carbohydrates, biocatalyst		Homogeneous catalyst in SCW
	2,3-butanediol 	Carbohydrates, biocatalyst		
	1,2,4-butanetriol 	Carbohydrates, biocatalyst		
	m-erythritol 	Biocatalyst *Escherichia coli* construct.		Homogeneous catalyst in SCW

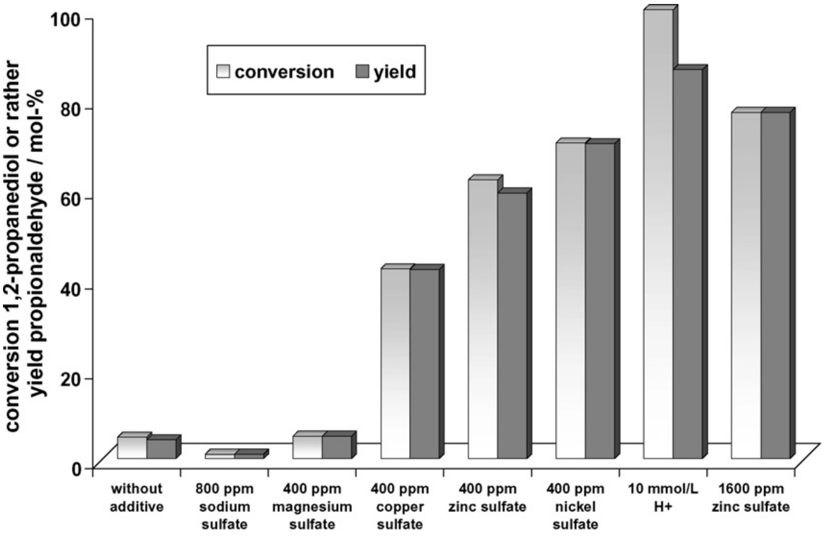


Fig. 1. Influence of electrolytes on the maximum achieved conversion of 1,2-propanediol and the yield of propionaldehyde. Conditions: aqueous 5% (g g^{-1}) 1,2-propanediol solution, 320 °C, 90 s residence time, 34 MPa. The related molecular concentrations at STP are 2.5 mmol L^{-1} copper, zinc and nickel or rather 10 mmol L^{-1} zinc, 3 mmol L^{-1} magnesium and 35 mmol L^{-1} sodium (this experiment was conducted at 360 °C).

occurs during distillation of pinacol in the presence of concentrated sulphuric acid. It is beneficial to use hot high-pressure water for the rearrangement in the approach described here.

Polyols that have two hydroxyl groups in the 1,4-positions can be converted into furan derivatives in hot high-pressure water in the presence of catalytic amounts of zinc sulphate.

3. Experimental

The synthesis examples described in Section 4 were achieved with the help of a continuously driven high-pressure apparatus with a flow tube reactor made of stainless steel [12]. Temperatures up to 500 °C and pressures up to 35 MPa are feasible in this apparatus. The residence time range lies between 10 and 180 s. Quantitative analysis of the reaction products was carried out by GC-FID as well as HPLC with RI detector. A detailed description of the experiments carried out and of the apparatus are mentioned by Ott et al. [12] and Jung [13].

4. Examples for the dehydration of polyols in sub- and supercritical water

The dehydration of the polyols accessible from biomass, 1,2- and 1,3-propanediol, 1,2-butanediol, glycerol and *m*-erythritol were examined with supplement addition of various homogeneous catalysts. The following parameters were varied:

- temperature (280–400 °C);
- pressure (25–34 MPa);
- type and concentration of catalyst (metal sulphates from 0 to 4000 ppm (g g^{-1}), H_2SO_4 from 5 to 20 mmol L^{-1});
- polyol concentration (0.5–10% (g g^{-1}));
- residence time (10–180 s).

4.1. 1,2-Propanediol

The conversion of 1,2-propanediol in high-temperature water at 380 °C, 25 MPa selectively yields propionaldehyde. Catalytic amount of H_2SO_4 (10 mmol L^{-1}) accelerates the reaction at the expense of selectivity. An increase in conversion without the loss of selectivity is attained by the addition of catalytic amounts of bivalent transition metal sulphates (Fig. 1). Also the addition of 10% (g g^{-1}) acetic acid improves conversion and selectivity [13]. The addition of Na_2SO_4 practically causes conversion to cease [14].

The yield of propionaldehyde reaches its maximum at subcritical conditions (ca. 360–380 °C) (Fig. 2). Already without additive a maximum yield of over 50 mol% at 380 °C can be obtained; the addition of $ZnSO_4$ increases this value to almost 80 mol% at 360 °C.

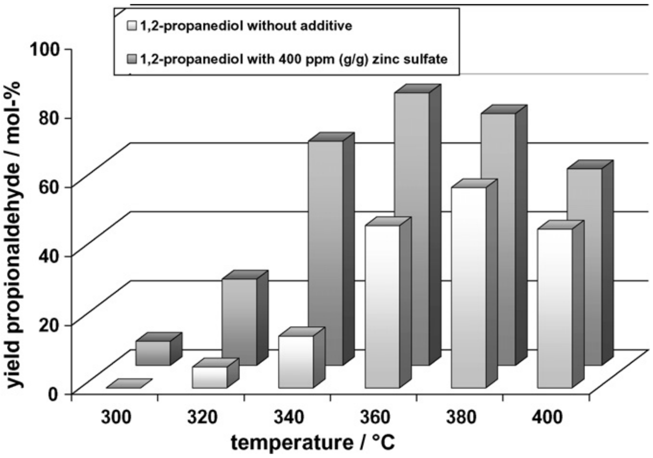


Fig. 2. Influence of temperature on the yield of propionaldehyde for the dehydration of an aqueous 5% (g g^{-1}) 1,2-propanediol solution at 34 MPa, 120 s residence time, without and with 400 ppm (g g^{-1}) $ZnSO_4$.

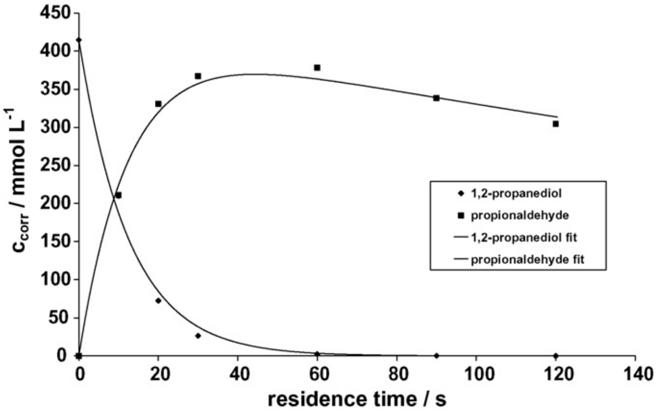


Fig. 3. Kinetics of the dehydration of 1,2-propanediol at 360 °C, 34 MPa with 400 ppm (g g^{-1}) $ZnSO_4$.

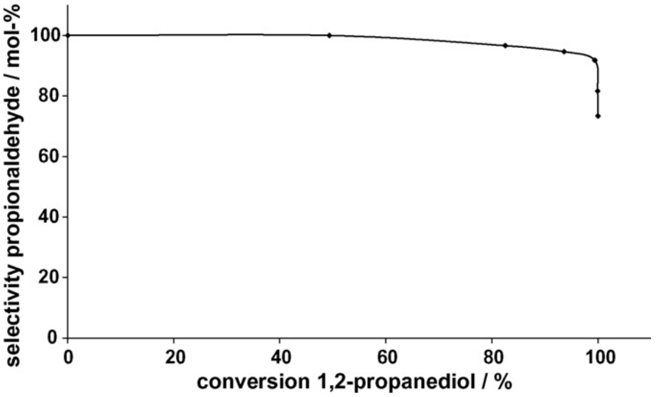


Fig. 4. *S*/*X*-diagram of the dehydration of 1,2-propanediol at 360 °C, 34 MPa with 400 ppm (g g^{-1}) $ZnSO_4$.

The kinetic analyses of the concentration/residence time-plot (Fig. 3) and of the selectivity/conversion (*S*/*X*) behaviour (Fig. 4) at 360 °C suggests a consecutive reaction in which propionaldehyde arises as an intermediate. A parallel reaction can be excluded.

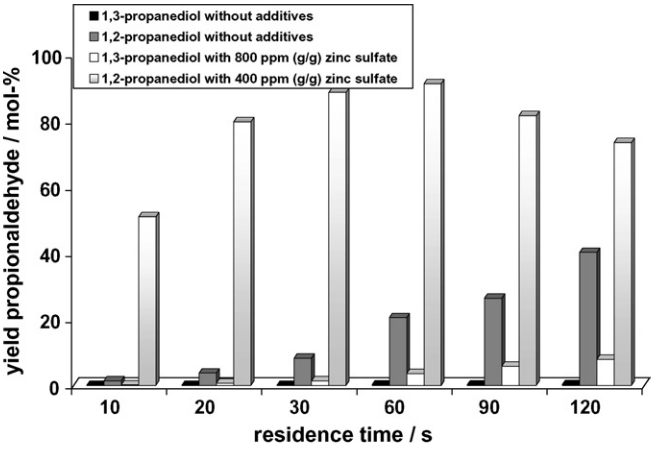


Fig. 5. Comparison of the influence of 400 (800) ppm (g g^{-1}) $ZnSO_4$ on the propionaldehyde yield for the dehydration of aqueous 5% (g g^{-1}) 1,2- and 1,3-propanediol solutions.

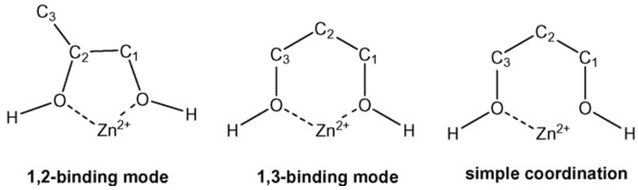


Fig. 6. Different complex geometries for 1,2- and 1,3-propanediol.

The rate of consumption of 1,2-propanediol is, under the experimental limiting conditions: 5% 1,2-propanediol solution, 280–360 °C, 34 MPa, 400 ppm (g g^{-1}) and $ZnSO_4$ [15]:

$$r_{\mathrm{V}} = k(T) \times c_{\mathrm{ZnSO_4}}^{0.23} \times c_{1,2\text{-propanediol}}^{1}$$

$$k(T)(\mathrm{l}^{0.23})(\mathrm{s\,mol}^{0.23})^{-1} = 4\times10^{13}\times\exp\left(-\frac{177(6)\,(\mathrm{kJ\,mol}^{-1})}{RT}\right).$$

Without the addition of a catalyst the activation energy is calculated to 195(9) kJ mol^{-1} with a pre-exponential factor of 6×10^{13} s^{-1}.

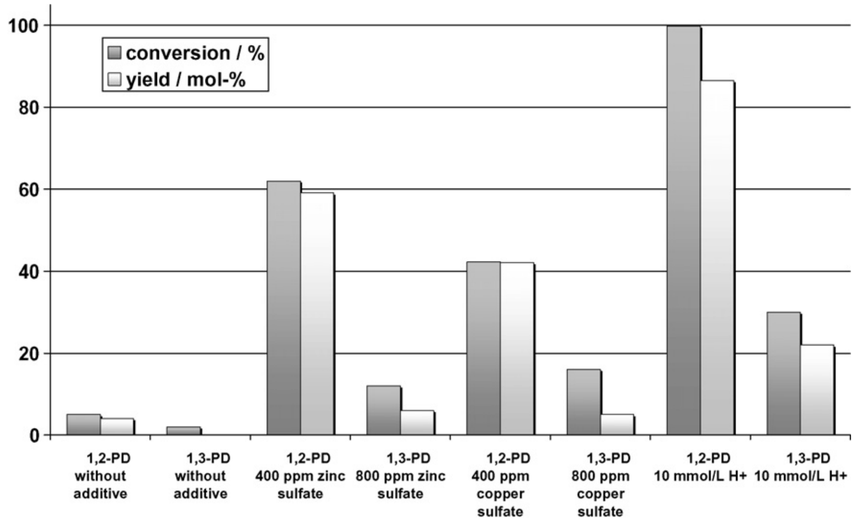


Fig. 7. Comparison of the conversions of 1,2- and 1,3-propanediol and yield of propionaldehyde with various additives. Conditions: aqueous 5% (g g^{-1}) 1,2- and 1,3-propanediol solutions at 34 MPa, 90 s residence time; it should be noted that the temperature for 1,2-propanediol was 320 °C but for 1,3-propanediol 360 °C.

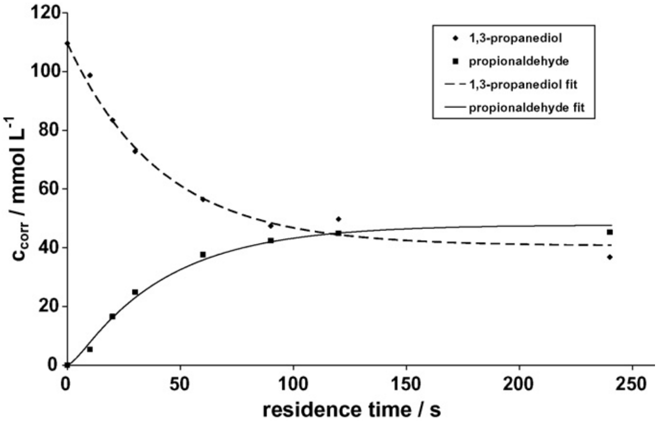


Fig. 8. Kinetics of the dehydration of 1,3-propanediol at 400 °C, 34 MPa with 800 ppm (g g^{-1}) $ZnSO_4$.

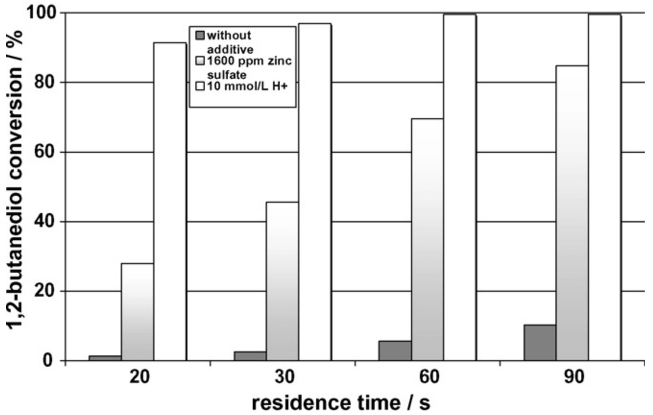


Fig. 10. Influence of different additives on 1,2-butanediol conversion at 320 °C and 34 MPa.

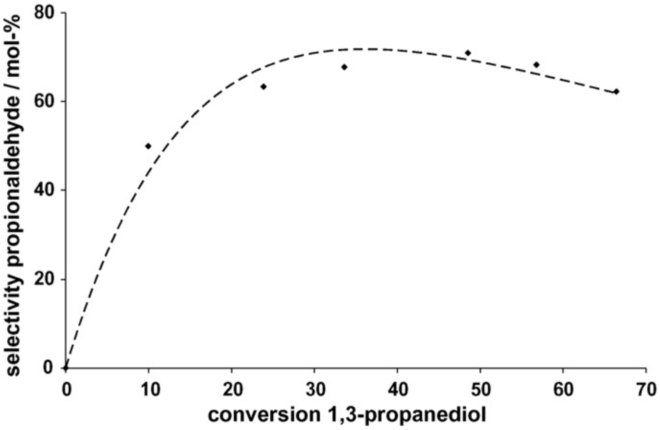


Fig. 9. *S*/*X*-diagram of the dehydration of 1,3-propanediol at 400 °C, 34 MPa with 800 ppm (g g^{-1}) $ZnSO_4$.

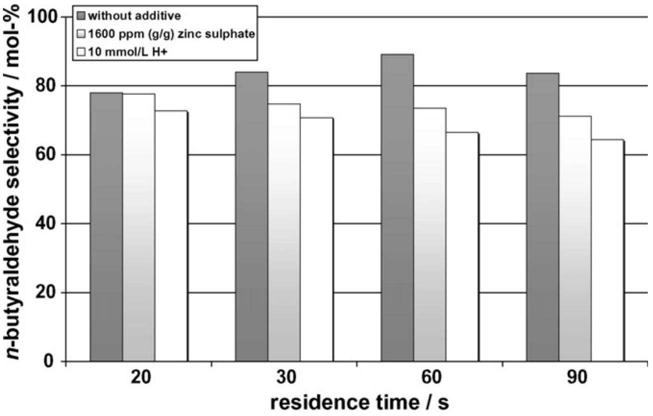


Fig. 11. Influence of different additives on *n*-butyraldehyde selectivity at 320 °C and 34 MPa.

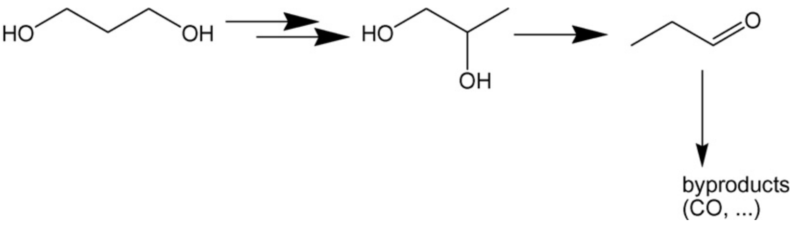
4.2. 1,3-Propanediol

The dehydration of 1,3-propanediol analogously produces propionaldehyde, however with significantly lower conversion speed and selectivity (Fig. 5).

For the catalytic effect of the electrolytes different reasons can be discussed. In the case of $NaSO_4$ a pH-value shift occurs into the alkali so that the reaction is completely prevented [14]. In the case of bivalent transition metals classical and complex salt effects can be discussed. The classical salt effects basically depend only on ionic strength. Therefore $MgSO_4$ and $ZnSO_4$ should have the same catalytic effect. As this is not confirmed for 1,2- and 1,3-propanediol, classical salt effects can be neglected. Therefore, the different complex geometries for 1,2- and 1,3-propanediol (Fig. 6) were discussed by Ott et al. [12].

If one compares the results concerning conversion and yield for both reactants 1,2- and 1,3-propanediol, it is noticeable that the same amounts of salts do not accelerate the dehydration of 1,3-propanediol to the same proportion as in the case of 1,2-propanediol (Fig. 7). This leads to the conclusion that the 1,2-binding mode and therefore the five-ring transition state is thermodynamically and kinetically favoured. This thesis is supported by other work in the area of Ni^{2+} and Zn^{2+} polyol complexes, in which the 1,2-binding mode has been found [16].

The kinetic analyses of the concentration/residence time-plot and the *S*/*X*-diagram (Figs. 8 and 9) indicate the



Scheme 1. 1,3-Propanediol dehydration.

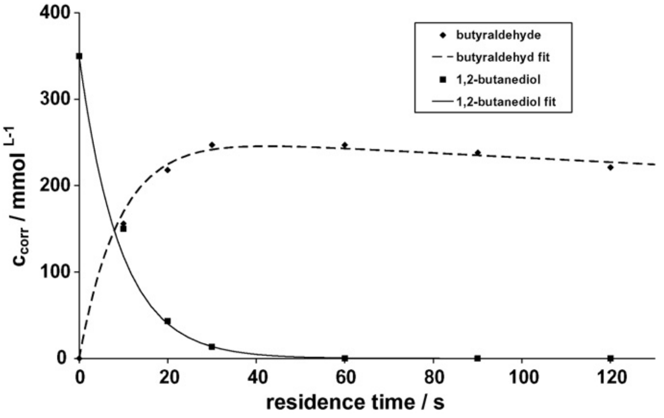


Fig. 12. Kinetics of the dehydration of 1,2-butanediol at 360 °C, 34 MPa with 400 ppm (g g^{-1}) $ZnSO_4$.

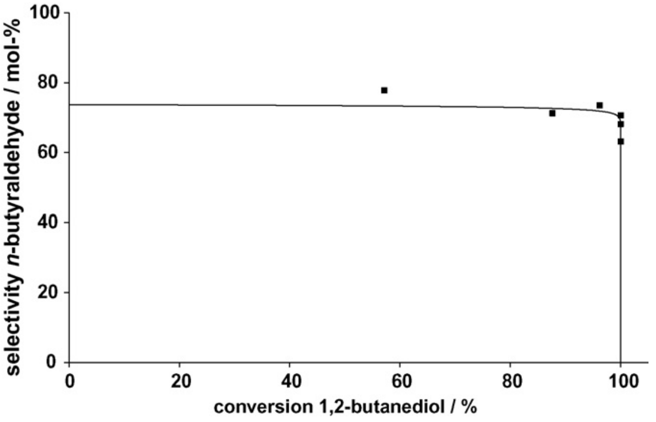


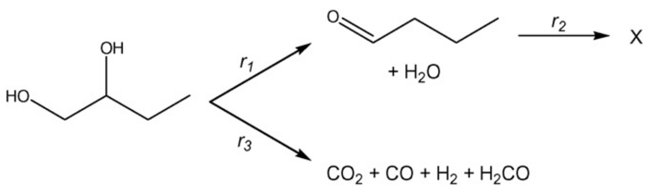
Fig. 13. *S*/*X*-diagram of the dehydration of 1,2-butanediol at 360 °C, 34 MPa with 400 ppm (g g^{-1}) $ZnSO_4$.

mechanism presented in Scheme 1 for the dehydration of 1,3-propanediol with a pinacol rearrangement.

4.3. 1,2-Butanediol

1,2-Butanediol is converted at 360 °C, 34 MPa and 400 ppm (g g^{-1}) $ZnSO_4$-additive to an extent of 98 and 77% selectivity to the main product *n*-butyraldehyde. As with the propanediols the conversion is accelerated by the addition of catalytic amounts of H_2SO_4 and/or $ZnSO_4$ (Figs. 10 and 11) and completely prevented by the addition of Na_2SO_4.

The kinetic analyses of the concentration/residence time-diagram (Fig. 12) and the *S*/*X*-plot (Fig. 13) suggest the reaction network presented in Scheme 2.



Scheme 2. 1,2-Butanediol dehydration.

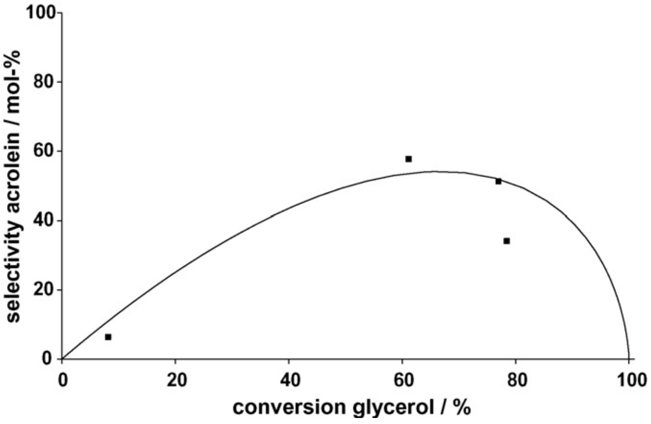


Fig. 14. Comparison of the modelled and measured *S*/*X*-behaviour of the dehydration of glycerol to acrolein at 360 °C, 34 MPa and with 791 ppm (g g^{-1}) $ZnSO_4$.

The rate of consumption can be described with the following rate equation:

$$r_V = k(T) \times c_{ZnSO_4}^{0.35} \times c^1_{1,2\text{-butanediol}}$$

$$k(T)(l^{0.35})(s\,mol^{0.35})^{-1} = 2 \times 10^{13} \times \exp\left(-\frac{173(7)\ (kJ\,mol^{-1})}{RT}\right)$$

Experimental conditions: 300–360 °C, 34 MPa, 400 ppm (g g^{-1}) $ZnSO_4$, 5% (g g^{-1}) aqueous solutions.

4.4. Glycerol

Glycerol is converted into acrolein in subcritical water with catalytic amounts of $ZnSO_4$. The kinetic analyses of the *S*/*X*-diagram (Fig. 14) as well as the concentration/residence time-profile (Fig. 15) suggest the mechanism presented in Scheme 3 [17].

4.5. m-Erythritol

The dehydration of *m*-erythritol in high-temperature water with $ZnSO_4$ delivers 1,4-anhydroerythritol (tetrahydrofuran-(3,4)-diol) via an equilibrium reaction. As already shown with

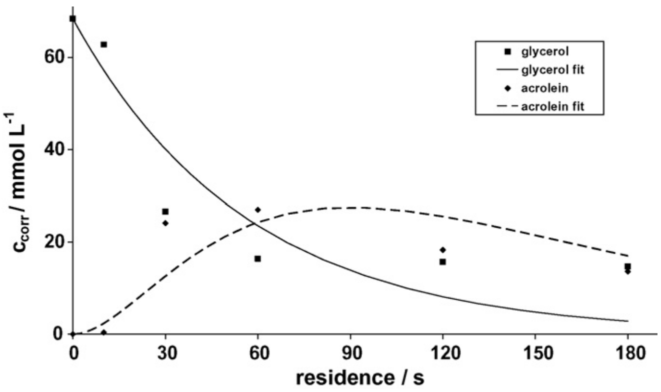


Fig. 15. Modelled and experimental concentration/residence time-plot for glycerol and acrolein at 360 °C, 34 MPa and with 791 ppm (g g^{-1}) $ZnSO_4$.

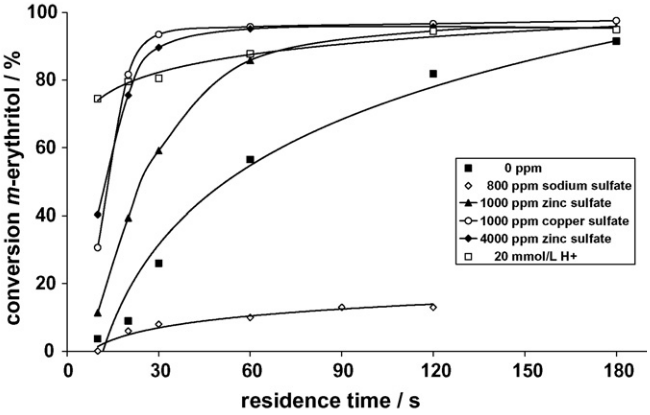


Fig. 16. Comparison of the influence of different additions on the conversion of *m*-erythritol at 360 °C and 34 MPa.

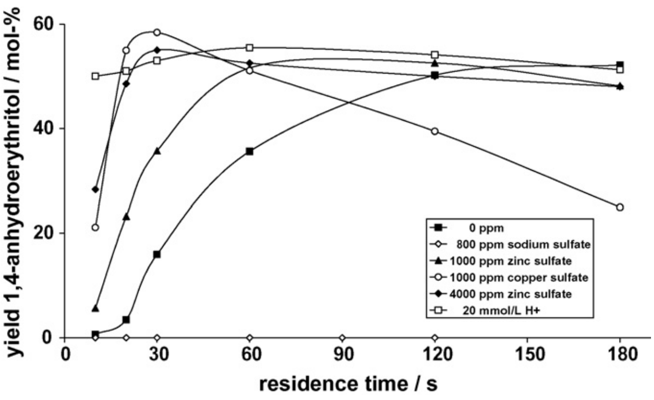


Fig. 17. Comparison of the influence of different additions on the yield of 1,4-anhydroerythritol at 360 °C and 34 MPa.

the other polyols, the dehydration reaction is promoted with $ZnSO_4$ and $CuSO_4$ and inhibited with Na_2SO_4 (Figs. 16 and 17). However, $CuSO_4$ appears to have a greater influence on the reaction than salts of other bivalent transition metals. About four times the molecular amount of $ZnSO_4$ is required to get the same conversion as with a single amount of $CuSO_4$. However, in contrast to $ZnSO_4$, $CuSO_4$ also promotes the consecutive reactions of the 1,4-anhydroerythritol, resulting in a reduction of the yield to ca. 25% after 180 s. The addition of 10 mmol L^{-1} H_2SO_4 is not as effective here as with the other diols ($X = 75\%$).

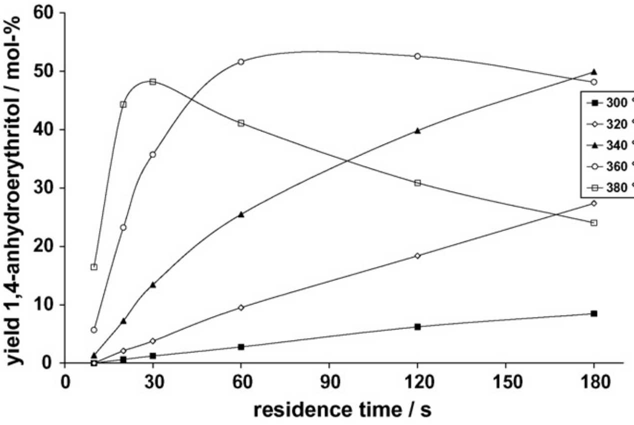


Fig. 18. Development of the 1,4-anhydroerythritol yield with temperature at 34 MPa and 988 ppm (g g^{-1}) $ZnSO_4$.

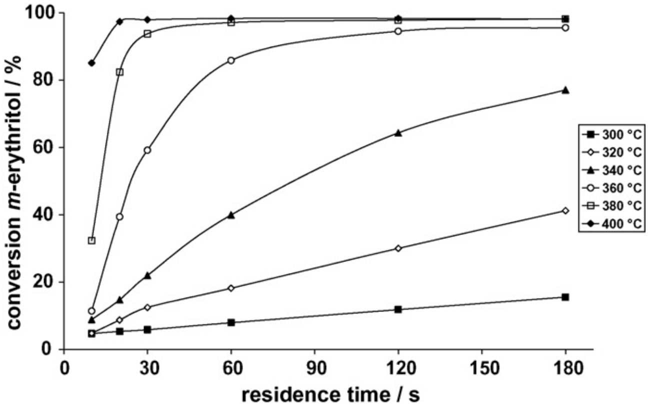
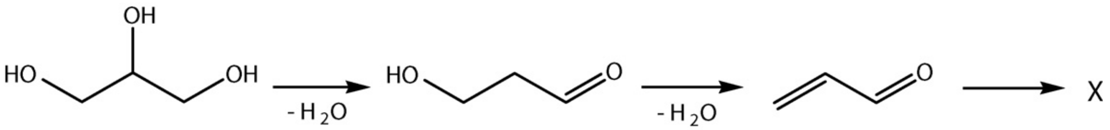


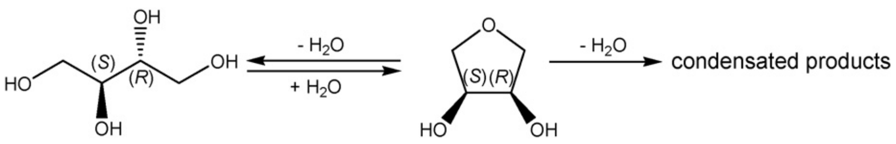
Fig. 19. Development of the *m*-erythritol conversion with temperature at 34 MPa and 988 ppm (g g^{-1}) $ZnSO_4$.

In the case of *m*-erythritol the positive effect of the salts is attributed to classical salt effects, in contrast to the results for 1,2- and 1,3-propanediol in which complex formation is assumed [12].

The yield and/or the conversion/residence time-plot of 1,4-anhydroerythritol in dependence of temperature at 34 MPa with 988 ppm (g g^{-1}) $ZnSO_4$ is shown in Figs. 18 and 19. The



Scheme 3. Glycerol dehydration.



Scheme 4. *m*-Erythritol dehydration.

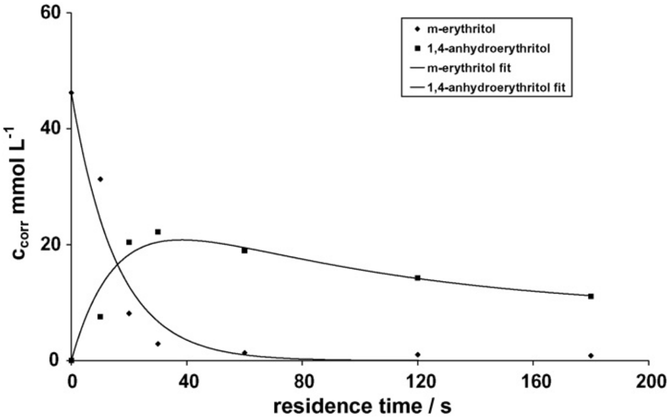


Fig. 20. Kinetics of the dehydration of *m*-erythritol at 380 °C, 34 MPa with 400 ppm (g g^{-1}) $ZnSO_4$.

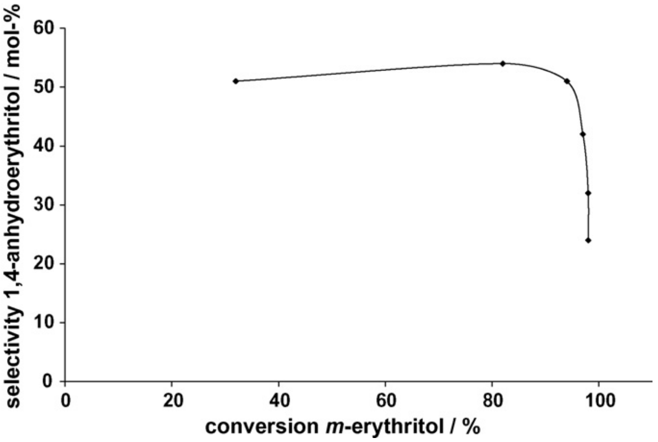


Fig. 21. *S*/*X*-diagram of the dehydration of *m*-erythritol to 1,4-anhydroerythritol at 380 °C, 34 MPa with 400 ppm (g g^{-1}) $ZnSO_4$.

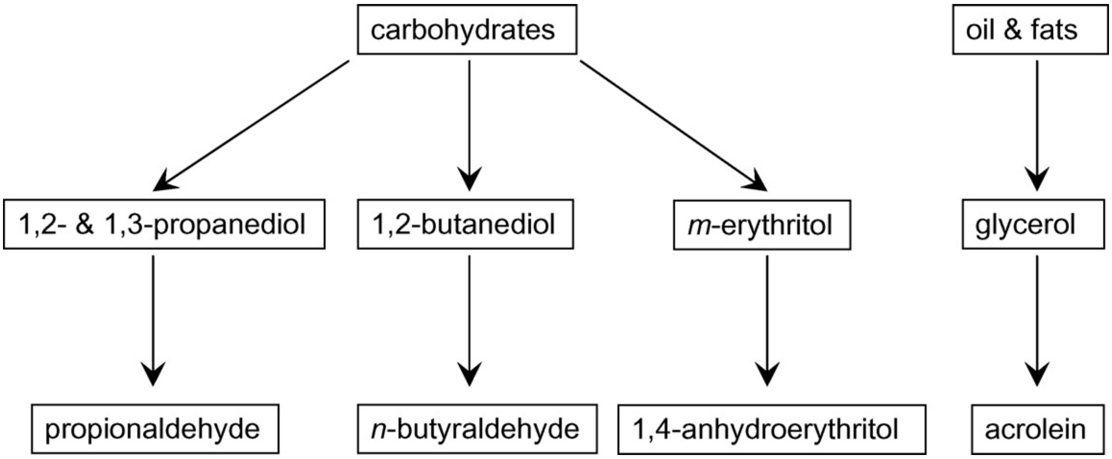


Fig. 22. Chemical conversion of renewable raw materials for the production of biomass based chemicals.

maximum yield amounts to 55 mol% at 360 °C and 60 s. Total conversion is achieved from 360 °C with a retention time of 120 s.

The kinetic analyses of the concentration/residence time-diagrams (Fig. 20) and the *S*/*X*-plot (Fig. 21) suggest the simplified reaction network presented in Scheme 4.

The rate of consumption can be described with the following rate equation [12] (conditions: 1% *m*-erythritol solution, 300–400 °C, 34 MPa, 988 ppm (g g^{-1}) $ZnSO_4$):

$$r_V = k(T) \times c_{ZnSO_4}^{0.48} \times c_{m\text{-erythritol}}^{1}$$

$$k(T)\,(l^{0.48})(\mathrm{s\,mol}^{0.48})^{-1} = 7 \times 10^{13} \times \exp\left(-\frac{175(4)\,(\mathrm{kJ\,mol}^{-1})}{RT}\right)$$

5. Conclusions

Due to the limited availability and the strongly fluctuating purchase price of the currently still dominating fossil raw material, oil, the development of biomass as a renewable raw material for the production of chemicals, plastics and fuels represents an important task of the future for modern industrialised nations. The possibilities of catalysis for the direct chemical conversion of renewable raw materials for the production of bio based chemicals (so called platform chemicals or buildings blocks and intermediates) are rarely used in consideration of their natural chemical structure, although there are already some promising results as described in this work (Fig. 22).

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