

Catalytical conversion of carbohydrates in subcritical water: A new chemical process for lactic acid production

M. Bicker, S. Endres, L. Ott, H. Vogel^{*}

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

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Abstract

In the last years the production of lactic acid has increased due to growing polymer markets (biodegradable synthetics), elevated demand in the chemical sector (oxygenated chemicals, ecologically friendly solvents) and many applications in the food industry. At present, the annual lactic acid production is about 100,000 t, most of that from the fermentation of carbohydrates. The disadvantages of this process are small space-time-yields and the production of stoichiometric amounts of salt. In pure sub- and supercritical water (SCW) only small amounts of lactic acid are obtained from the degradation of carbohydrates. But by adding small quantities of metal ions such as Co(II), Ni(II), Cu(II) and Zn(II) to that reaction media, the lactic acid yield is increased up to 42% (g g^{-1}) starting from sucrose and 86% (g g^{-1}) starting from dihydroxyacetone at 300 °C and 25 MPa. Zn(II) gave the best results with regard to the lactic acid yield. The function of the catalyst in the complex reaction network of carbohydrate degradation is discussed. An alternative lactic acid production process is proposed.

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1. Introduction

Lactic acid (2-hydroxypropionic acid) is a commodity chemical with a growing market. In 2003 the world's production capacity was about 100,000 t a⁻¹ [1]. The main part is used in the food industry for mild acid flavor, pH-regulation or as a preservative. An emerging product is poly(lactic acid), PLA, used in the manufacture of biodegradable plastics.

The state-of-the-art production process for lactic acid is the fermentation of glucose from starch hydrolysates, a process which replaced the older chemical synthesis, e.g. the addition of hydrogen cyanide onto acetaldehyde and the subsequent hydrolysis of the resulting lactonitrile. The biotechnological process, however, has some disadvantages such as small space-time-yields and the production of stoichiometric amounts of salt due to pH-regulation during fermentation.

Sub- and supercritical fluids (SCF) have proved to be alternative solvents for chemical synthesis [2,3]. Although high equipment costs caused by extreme reaction conditions for supercritical water (SCW, $T_c = 374^\circ\text{C}$ and $p_c = 21 \text{ MPa}$) must be taken into account, a series of reactions have successfully been performed in this medium [4].

Cellulose, cellobiose, glucose and fructose as model substances for biomass have been treated in sub- and supercritical water by several groups [5–8]. Here, numerous decomposition products were found, as displayed in Table 1.

Sulfuric acid as the homogeneous catalyst increases the yield of HMF, the influence of salts on the product yields was not examined. A recent review [9] on hydrogen production from biomass gasification in supercritical water ($T = 400\text{--}500^\circ\text{C}$) describes the effect of salts on the water gas shift reaction that takes place during the decomposition of glucose as model substance. The authors report that KHCO_3 immensely influences the product distribution. The influence of ZnCl_2 on 1,2-propylene glycol conversion in nearcritical water ($T = 360^\circ\text{C}$) is reported by Dai [10].

* Corresponding author. Tel.: +49 6151 162165; fax: +49 6151 163465.
E-mail address: vogel@ct.chemie.tu-darmstadt.de (H. Vogel).

Nomenclature

A	constant from the Debye–Hückel-Theory
$c(i)$	concentration of reactant i after reaction at STP (mol L $^{-1}$)
$c_0(i)$	starting concentration of reactant i at STP (mol L $^{-1}$)
c_i	concentration of ion i (mol L $^{-1}$)
$c^{\#}$	standard concentration (1 mol L $^{-1}$)
I	ionic strength
k	velocity constant (s $^{-1}$) (first order)
k_0	velocity constant without salt (s $^{-1}$) (first order)
K_{la}	lactic acid distribution coefficient
L	ligand
N^C	number of carbon atoms per reactant
S_j^C	(integral) carbon-selectivity of product j (%)
STP	standard temperature and pressure, 25 °C and 0.1 MPa
V_R	reactor volume (cm 3)
\dot{V}	volume flow (cm 3 s $^{-1}$).
X_i	degree of conversion of reactant i (mol.%)
Y_j^C	carbon-yield of product j (mol.%)
z_A, z_B, z_i	charge of the ions A and B (or i)
ρ_{Reactor}	fluid density at process pressure and temperature (g cm $^{-3}$)
ρ_{STP}	fluid density at STP (g cm $^{-3}$)

With the deficiencies of the fermentation process in mind, we opted to investigate the influence of metal ions on the reaction of biomass-relevant sugars such as sucrose, glucose and fructose in subcritical water ($T = 200\text{--}360\text{ }^{\circ}\text{C}$). The reaction pathway for carbohydrate degradation under these reaction conditions is very complex. Based on the kinetic analysis of the experimental data the catalyst's mode of operation in this reaction network is discussed.

Finally, a lactic acid production process based on sucrose or glucose as feedstock is proposed.

Table 1
Products from carbohydrate degradation in sub- and supercritical water

Starting material	Temperature (°C)	Pressure (MPa)	Catalyst	Products	Reference
Cellulose	215	34.5	H ₂ SO ₄	Glucose ^a , HMF	[5]
Celllobiose	350–400	25–40	–	Glucose, erythrose, glycolaldehyde, glyceraldehyde, dihydroxyacetone, pyruvaldehyde, HMF, furfural	[6]
Glucose, fructose	300–400	25–40	–	Glyceraldehyde, dihydroxyacetone, erythrose, glycolaldehyde, pyruvaldehyde, 1,6-anhydroglucose, HMF, acetic acid, formic acid	[7]
Fructose	250	34.5	H ₂ SO ₄	HMF ^a , glucose, mannose, glyceraldehyde, dihydroxyacetone, erythrose, glycolaldehyde, pyruvaldehyde, hydroxyacetone, 1,6-anhydroglucose, furfural, acetic acid, formic acid, levulinic acid, lactic acid	[8]

^a Main product.

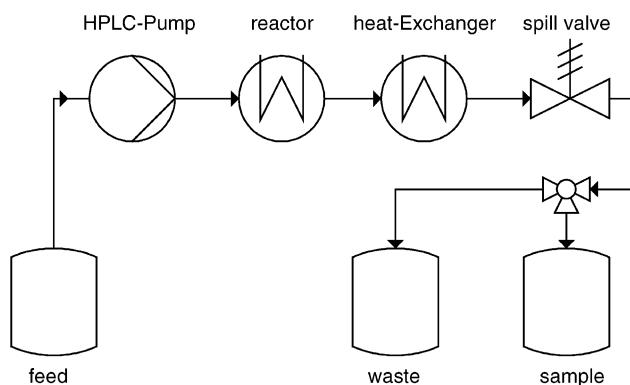


Fig. 1. High pressure tube reactor.

2. Experimental

2.1. Continuous high pressure reactor

The reactors consist of stainless steel tubes (tube 1: i.d. 1.0 mm, length 700 mm, volume 0.55 cm 3 ; tube 2: i.d. 3.0 mm, length 700 mm, volume 4.95 cm 3). These reactors are placed in a block of aluminium that can be heated electrically up to 500 °C. The hydrodynamic residence time τ was calculated via Eq. (1):

$$\frac{\tau}{s} = \frac{V_R \rho_{\text{Reactor}}}{\dot{V} \rho_{\text{STP}}} \quad (1)$$

The residence time can be varied by adjusting the volume flow of the pump to the calculated value. To secure that the reactor is in steady-state condition the reactor volume plus the heat exchanger volume was flushed five times before sampling.

Fig. 1 displays the high pressure tube reactor schematically. For further details see [11].

A HPLC pump delivers the feed into the reactor. A heat exchanger (pipe-in-pipe system) cools down the fluid after reaction to 15 °C. Pressure is relieved in a spill valve. After that, a three-way valve permits switching between waste or sample reservoirs.

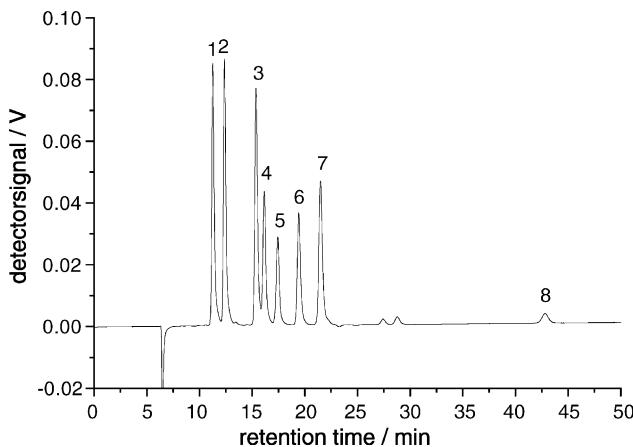


Fig. 2. Chromatogramm of sugars and some degradation products. (1) glucose, (2) fructose, (3) pyruvic aldehyde, (4) DL-lactic acid, (5) dihydroxyacetone, (6) acetic acid, (7) levulinic acid and (8) HMF.

2.2. Preparation of feed solution

For all experiments a 1% (g g^{-1}) carbohydrate and 400 ppm (g g^{-1}) catalyst (as sulfate salt) solution in deionized water was prepared.

2.3. HPLC analysis

A quantitative analysis of the reactor discharge was done by HPLC (Model ProStar 210, Varian). A cation exchanger column (ION-300H, Interaction Chromatography, Inc.) was held at 50 °C, the RI-Detector's temperature was set at 40 °C. Sulfuric acid (2 mM in water) was the eluent. Fig. 2 displays a chromatogram of carbohydrates and some degradation products.

2.4. NMR analysis

Product identification was performed by $^1\text{H-NMR}$. Proton signals of a solution of pure DL-lactic acid in water (^1H (d^6 -DMSO, 500 MHz, water suppression) ppm: 4.36 (q , 1H), 1.43 (d , 3H)) were compared with signals recorded from a reactor sample. The addition of DL-lactic acid to that sample and re-recording increased these signals.

2.5. Extraction procedure

The extraction procedure used for downstream processing of the reactor discharge was taken from literature [12].

3. Results and discussion

Calculation of conversion, yield and selectivity were as follows:

$$X_i \text{ (mol.\%)} = \frac{c_0(i) - c(i)}{c_0(i)} \times 100 \quad (2)$$

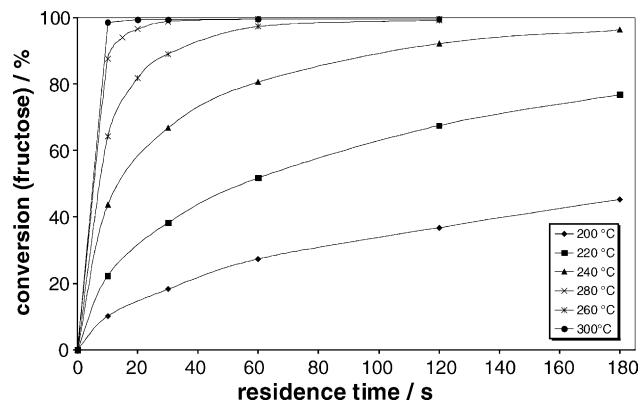


Fig. 3. Zinc-catalyzed fructose conversion at 200–300 °C, $\tau = 10–180$ s, $p = 25$ MPa, c_0 (fructose) = 55.5 mmol L $^{-1}$ and c (ZnSO_4) = 400 ppm (g g^{-1}).

$$Y_j^C \text{ (mol.\%)} = \frac{N_j^C}{N_i^C} \frac{c(j) - c_0(j)}{c_0(i)} \times 100 \quad (3)$$

$$S_j^C \text{ (\%)} = \frac{Y_j^C}{X_i} \times 100 \quad (4)$$

3.1. Zinc-catalyzed fructose conversion at different temperatures

Experiments in the temperature range from 200 to 360 °C and residence times from 3 to 180 s were conducted to study temperature dependence and kinetic behavior of the zinc-catalyzed fructose degradation. The reaction pressure was kept at 25 MPa and the ZnSO_4 concentration at 400 ppm (g g^{-1}) (Fig. 3).

Complete conversion of fructose can be achieved at 260 °C within 2 min or at higher temperatures within shorter reaction times. Lactic acid selectivity was determined as described above. The values obtained (with corresponding residence times) are presented in Fig. 4.

Up to 300 °C lactic acid selectivity rises continuously until it reaches 48%. No further increase of that value can be achieved above that temperature, but space-time-yields

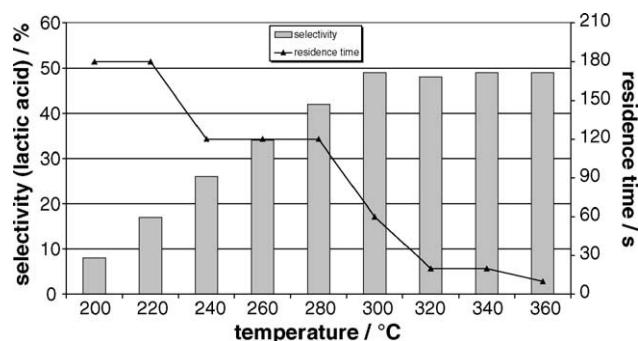


Fig. 4. Lactic acid selectivities (columns) with corresponding residence times (triangles) obtained by the zinc-catalyzed fructose conversion at 200–360 °C, $p = 25$ MPa, c_0 (fructose) = 55.5 mmol L $^{-1}$ and c (ZnSO_4) = 400 ppm (g g^{-1}).

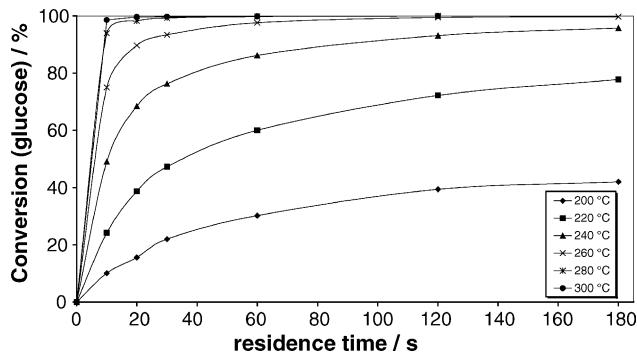


Fig. 5. Zinc-catalyzed glucose conversion at 200–300 °C, $\tau = 10\text{--}180\text{ s}$, $p = 25\text{ MPa}$, c_0 (glucose) = 55.5 mmol L⁻¹ and c (ZnSO₄) = 400 ppm (g g⁻¹).

increase due to shorter residence times. Higher concentrations of carbohydrate that would also increase the space-time-yield result in lower lactic acid selectivities due to increased formation of so-called “brown products”. These reactions are common in carbohydrate chemistry [13,14].

3.2. Zinc-catalyzed glucose conversion at different temperatures

To study temperature dependence and kinetic behavior of the zinc-catalyzed glucose degradation further experiments in the temperature range from 200 to 300 °C and residence times from 10 to 180 s were performed. Again, the reaction pressure was kept at 25 MPa and ZnSO₄ concentration at 400 ppm (g g⁻¹). Fig. 5 displays the results of these test series.

The kinetic behavior of glucose degradation is very similar to that of fructose degradation under the same reaction conditions whereas the selectivity for lactic acid is lower, as indicated in Fig. 6.

3.3. Influence of different catalysts on the lactic acid selectivity

The influence of salts on fructose conversion in subcritical water first was reported by Hirth [15]. This work was

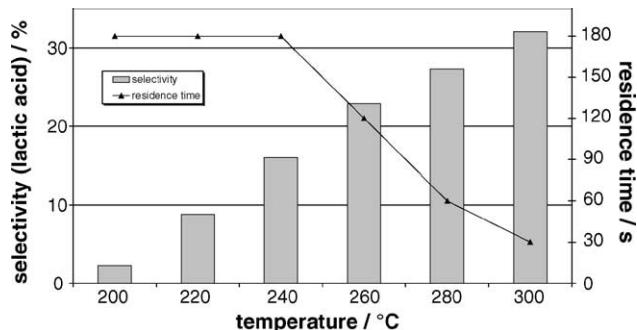


Fig. 6. Lactic acid selectivities (columns) with corresponding residence times (triangles) obtained by the zinc-catalyzed glucose conversion at 200–300 °C, $p = 25\text{ MPa}$, c_0 (glucose) = 55.5 mmol L⁻¹ and c (ZnSO₄) = 400 ppm (g g⁻¹).

Table 2

Lactic acid selectivity (%) from fructose conversion at 280 °C, $p = 25\text{ MPa}$, $\tau = 30\text{ s}$ and c (catalyst) = 400 ppm (g g⁻¹)

catalyst	Hirth [15]	This work
ZnSO ₄	42	39
CuSO ₄	—	2
NiSO ₄	—	36
CoSO ₄	—	31
MgSO ₄	20	—
(Na) ₂ SO ₄	5	—
Without	5	5

checked and the list of catalysts was extended by some transition metals. As shown in Table 2 high lactic acid selectivities can be obtained by Co(II), Ni(II) and Zn(II) whereas zinc sulfate as the catalyst gave the best results. This is very favorable as it is very cheap and absolutely non-toxic.

The influence of copper sulfate is very noteworthy, as only very small amounts of lactic acid are produced. HMF is the main product with a selectivity of 43%. Because of their Lewis-acidity transition metal cations polarize nucleophilic substrates. As Cu(II) is even more Lewis-acidic than Zn(II), the possibility that higher Lewis-acidity of the metal cation leads to higher lactic acid selectivity is eliminated. Another possible mechanism is the “salt effect” on reaction kinetics [16]. Within the scope of this theory, the influence of salts on the reaction rate is discussed. The ionic strength of the dissolved salt influences the k -values (Eqs. (5) and (6)) [17].

$$\ln k = \ln k_0 + A z_A z_B \sqrt{I} \quad (5)$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{c_i}{c^\#} \quad (6)$$

Only the charge and the concentration of the ions effect the k -value. As ZnSO₄ and CuSO₄ are the same concerning these properties the salt effect can be excluded as a possible reason for the catalytical activity of the metal ions. One more mechanism for catalytical activity is the formation of complexes. This topic is discussed later.

3.4. Lactic acid yield obtained from various carbohydrates

With optimized reaction parameters a number of carbohydrates were converted to lactic acid. Fig. 7 displays the obtained lactic acid selectivities.

Best results are obtained starting from trioses such as dihydroxyacetone or glyceraldehyde. Hexoses give less lactic acid. In both cases, the lactic acid yield is higher starting from ketoses than from aldoses. Sucrose (a very cheap sugar) is converted to lactic acid in an agreeable 42% yield. Sorbitol (hydrogenated glucose, not shown in Fig. 7) is not converted at all under these reaction conditions.

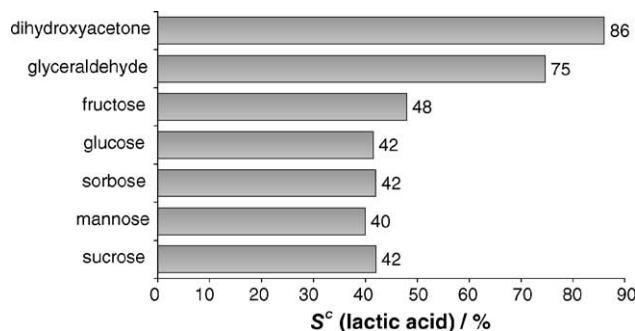


Fig. 7. Lactic acid yields obtained by the zinc-catalyzed conversion of various sugars at 300 °C, $p=25$ MPa, c_0 (sugar)=1% (g g^{-1}) and c (ZnSO_4)=400 ppm (g g^{-1}).

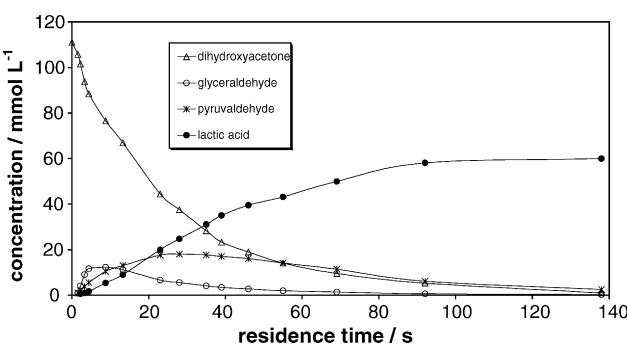


Fig. 8. Kinetics of dihydroxyacetone degradation at 260 °C, $p=25$ MPa, c_0 (dihydroxyacetone)=1% (g g^{-1}) and c (ZnSO_4)=400 ppm (g g^{-1}).

3.5. Kinetic analysis

As mentioned before, the degradation kinetic of carbohydrates in water at high temperatures is very complex. For a better understanding of the reaction network and catalyst mechanism c/τ -diagrams of dihydroxyacetone (Fig. 8), fructose (Fig. 9) and glucose (Fig. 10) degradation were determined.

The curves represent typical courses of consecutive, parallel and equilibrium reactions. Fructose conversion at 260 °C without a catalyst was investigated, too. The c/τ -data of the main products are presented in Table 3.

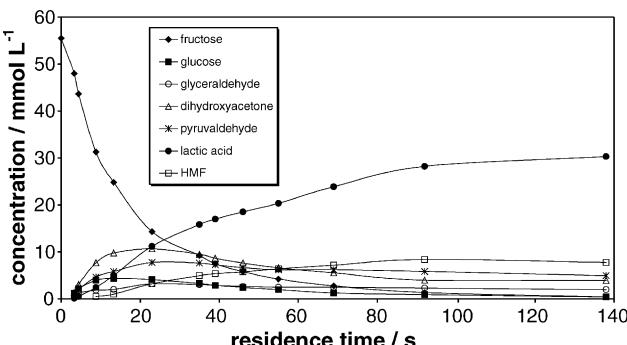


Fig. 9. Kinetics of fructose degradation at 260 °C, $p=25$ MPa, c_0 (fructose)=1% (g g^{-1}) and c (ZnSO_4)=400 ppm (g g^{-1}).

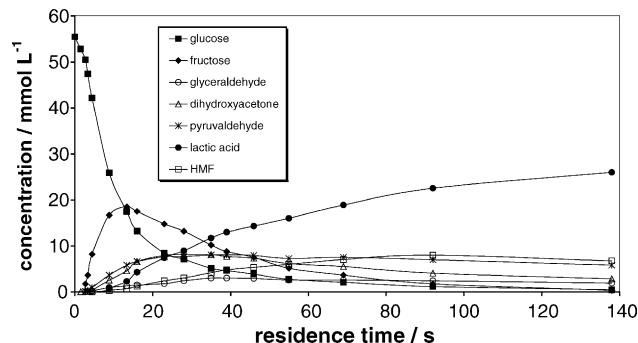


Fig. 10. Kinetics of glucose degradation at 260 °C, $p=25$ MPa, c_0 (glucose)=1% (g g^{-1}) and c (ZnSO_4)=400 ppm (g g^{-1}).

Table 3

c/τ -data, conversion, yield and selectivities for the uncatalyzed conversion of fructose in subcritical water at 260 °C, 25 MPa and c_0 (fructose)=55.5 mmol L⁻¹

τ (s)	Substance	c (mmol L ⁻¹)	X (mol.%)	Y^C (mol.%)	S^C (%)
10	Fructose	38.9	29.9	—	—
	Lactic acid	0.0	—	0.0	0.0
	HMF	1.4	—	2.6	8.7
20	Fructose	30.4	45.3	—	—
	Lactic acid	0.0	—	0.0	0.0
	HMF	4.6	—	8.3	18.4
30	Fructose	20.6	62.8	—	—
	Lactic acid	1.1	—	1.0	1.6
	HMF	9.5	—	17.1	27.2
60	Fructose	7.2	87.0	—	—
	Lactic acid	2.8	—	2.5	2.9
	HMF	14.2	—	25.5	29.3
120	Fructose	1.0	98.1	—	—
	Lactic acid	6.1	—	5.5	5.6
	HMF	9.3	—	16.8	17.1

The addition of zinc sulfate influences the fructose degradation rate only slightly but has a great influence on lactic acid and HMF selectivities. Carbon balance decreases due to the formation of “brown products” that were not qualified nor quantified in this work.

Further kinetic data of the zinc-catalyzed reactions were measured in a temperature range from 200 to 300 °C to quantify activation energies (Table 4) via Arrhenius plots (Fig. 11).

Mok and Antal [5] report activation energies for the acid-catalyzed cellulose and glucose degradation in subcritical

Table 4

Activation energies for carbohydrate degradation in subcritical water at 200–300 °C, $p=25$ MPa, c_0 (carbohydrate)=1% (g g^{-1}) and c (ZnSO_4)=400 ppm (g g^{-1})

	A (s ⁻¹)	E_A (kJ mol ⁻¹)
Glucose	8.25×10^8	102
Fructose	1.79×10^8	96
Pyruvaldehyde	5.21×10^4	58

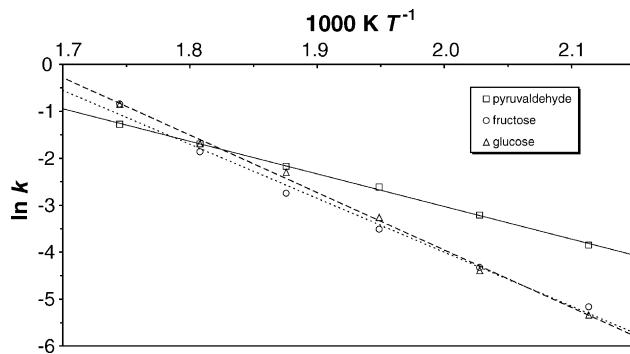


Fig. 11. Arrhenius plots for the determination of activation energies of the degradation of pyruvaldehyde (straight line), fructose (dotted line) and glucose (dashed line) in subcritical water at 25 MPa, c_0 (sugar)=1% (g g^{-1}) and $c(\text{ZnSO}_4)=400 \text{ ppm} (\text{g g}^{-1})$.

water of 144 and 100 kJ mol^{-1} , respectively. For cellobiose degradation in sub- and supercritical water without a catalyst the activation energy was found to be 111 kJ mol^{-1} [6]. Hirth [15] reports an activation energy for the uncatalyzed fructose degradation in subcritical water of 96 kJ mol^{-1} . Bonn et al. [18] reports an activation energy for pyruvaldehyde degra-

dation in subcritical water of 77 kJ mol^{-1} . Kabyemela et al. [19] discovered an activation energy of 94 kJ mol^{-1} for this reaction.

The activation energies of the glucose- and fructose degradation in the presence of zinc sulfate are more or less the same. The activation energy for the zinc-catalyzed pyruvaldehyde degradation compared to that of the hexoses' is a great deal lower.

3.6. Reaction network

Comparing our results with literature data [7,8,18,19], a simplified degradation network for the sugars is compiled (see Fig. 12).

By further kinetic simulations, the proposed reaction network was ratified. These results will be presented in another paper in the near future.

The function of Zn(II) in condensation- and hydrolysis reactions is well known. Due to its Lewis-acidity Zn(II) polarizes substrates. Vice versa the reversion of polarity of the Lewis acid Zn(II) to a Lewis base ($L_3-Zn^{2+}-OH^-$) is possible as demonstrated by the zinc-catalyzed nucleophilic attack of water on CO_2 (Fig. 13) [20,21].

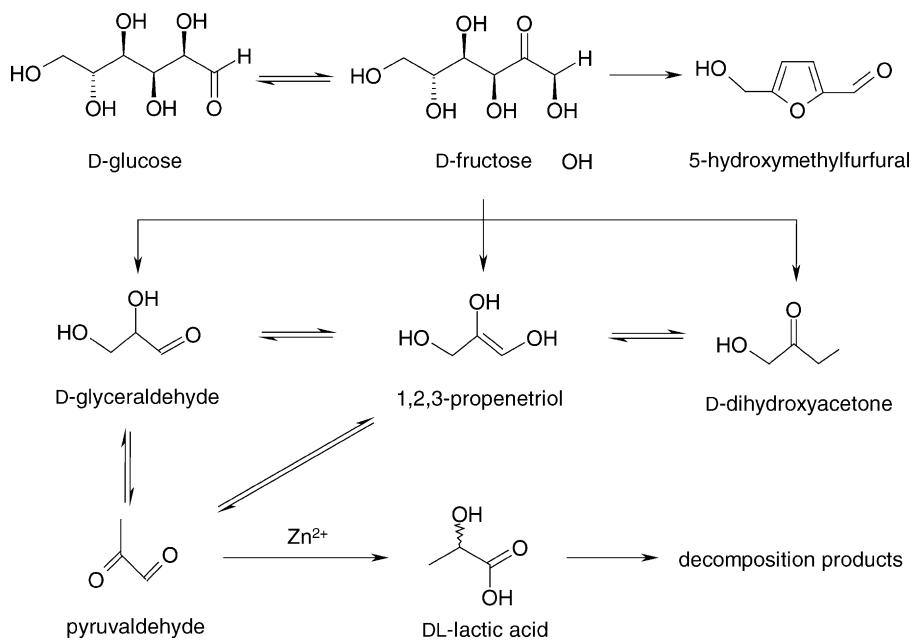


Fig. 12. Simplified reaction schema for the zinc-catalyzed degradation of carbohydrates in subcritical water.

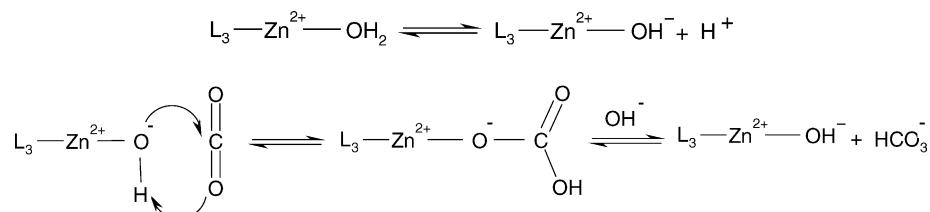


Fig. 13. Zinc-catalyzed nucleophilic attack of water on CO_2 [20,21]. $L = H_2O$.

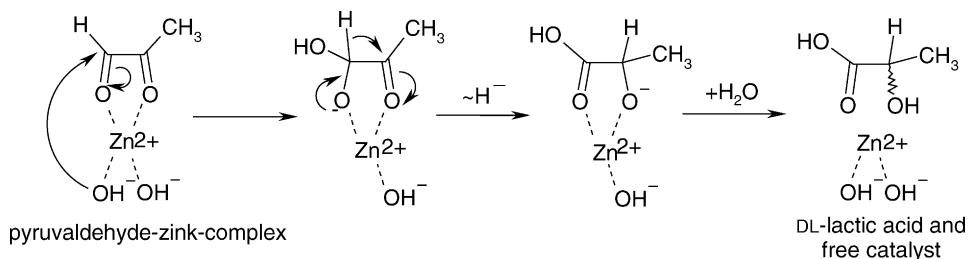


Fig. 14. Possible mode of action of Zn(II) in the formation of lactic acid from pyruvaldehyde.

This mode of action is adapted to the conversion of pyruvaldehyde to lactic acid as shown in Fig. 14.

4. Conclusion

The influence of salts on the conversion of sugars in subcritical water was investigated. Transition metal ions have a great influence on product selectivities. With ZnSO₄ as the catalyst lactic acid yields from 42 to 86% can be achieved by the conversion of a 1% (g g⁻¹) sugar solution in water at subcritical conditions of 300 °C and 25 MPa.

This conversion process occurs in a very complex network of parallel, consecutive and equilibrium reactions, the last step being the Zn(II)-catalyzed Cannizzaro-type reaction of pyruvaldehyde to lactic acid.

With all results combined, a continuous production process for lactic acid based on the chemical-catalytical conversion of sucrose or glucose in subcritical water is proposed. The flow chart is presented in Fig. 15.

A high pressure pump delivers the feed (1% (g g⁻¹) glucose or sucrose and 400 ppm (g g⁻¹) ZnSO₄ in water) through a heat exchanger (pre-heater) into the reactor. The reactor discharge is simultaneously cooled down. The plug flow reactor is heated up to 300 °C, pressure is kept at 25 MPa. For downstream processing pressure is relieved to ambient pressure and lactic acid purification is accomplished by reactive extraction with *n*-butanol/tri-*n*-hexylamine [12].

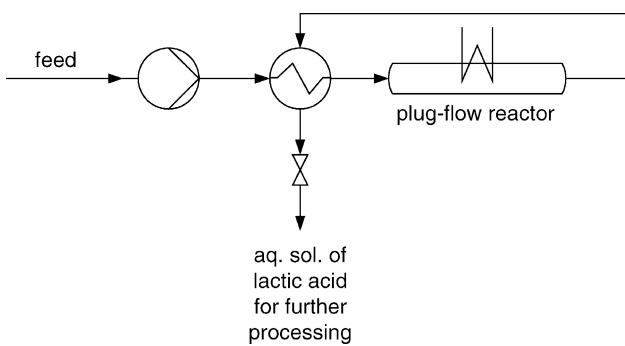


Fig. 15. Continuous lactic acid production process based on catalytical sugar conversion in subcritical water.

The extraction process was tested with the reactor discharge. The lactic acid distribution coefficient K_{la} was determined to be 10 (second coalescence time was 15 min).

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References

- [1] C.D. Skory, J. Ind. Microbiol. Biotechnol. 30 (2003) 22–27.
- [2] P.G. Jessop, W. Leitner, Chemical Synthesis Using Supercritical Fluids, Wiley-VCH, Weinheim, New York, 1999.
- [3] Y. Arai, T. Sako, Y. Takebayashi, Supercritical Fluids Molecular Interactions, Physical Properties and New Applications, Springer, Stuttgart, 2002.
- [4] E. Dinjus, A. Kruse, J. Phys.: Condens. Matter 16 (2004) 1161–1169.
- [5] W.S.M. Mok, M.J. Antal Jr., Ind. Eng. Chem. Res. 31 (1992) 94–100.
- [6] K. Arai, et al., Ind. Eng. Chem. Res. 41 (2002) 6642–6649.
- [7] B.M. Kabyemela, et al., Ind. Eng. Chem. Res. 38 (1999) 2888–2895.
- [8] M.J. Antal Jr., et al., Carbohydr. Res. 199 (1990) 91–109.
- [9] A. Kruse, E. Dinjus, Z. Phys. C 219 (2005) 341–366.
- [10] Z. Dai, B. Hatano, H. Tagaya, Appl. Catal. A 258 (2) (2004) 189–193.
- [11] M. Bicker, J. Hirth, H. Vogel, Green Chem. 5 (2003) 280–284.
- [12] M. Jung, B. Schierbaum, H. Vogel, Chem. Eng. Technol. 23 (1) (2000) 70–74.
- [13] B. Cämmerer, et al., Eur. Food. Res. Technol. 209 (1999) 261–265.
- [14] A. Hollnagel, W.L. Kroh, J. Agric. Food Chem. 48 (2000) 6219–6226.
- [15] J. Hirth, Ph.D. thesis, Ernst-Berl-Institute for Technical and Macromolecular Chemistry, Darmstadt University of Technology, 2003.
- [16] K. Schwetlick, Kinetische Methoden zur Untersuchung von Reaktionsmechanismen, VEB Deutscher Verlag der Wissenschaft, Berlin, 1971.
- [17] G. Wedler, Lehrbuch der Physikalischen Chemie, 4. Auflage, Wiley-VCH, Weinheim, New York, 1997.
- [18] G. Bonn, et al., J. Carbohydr. Chem. 4 (1) (1985) 67–77.
- [19] B.M. Kabyemela, et al., Ind. Eng. Chem. Res. 36 (1997) 2025–2030.
- [20] M.F. Dunn, Structure and Bonding, Springer Verlag, Berlin, 1975, pp. 101–102.
- [21] J.E. Coleman, Curr. Opin. Chem. Biol. 2 (2) (1998) 222–234.