

## Dehydration of 2,3-butanediol to methyl ethyl ketone in sub- and supercritical water

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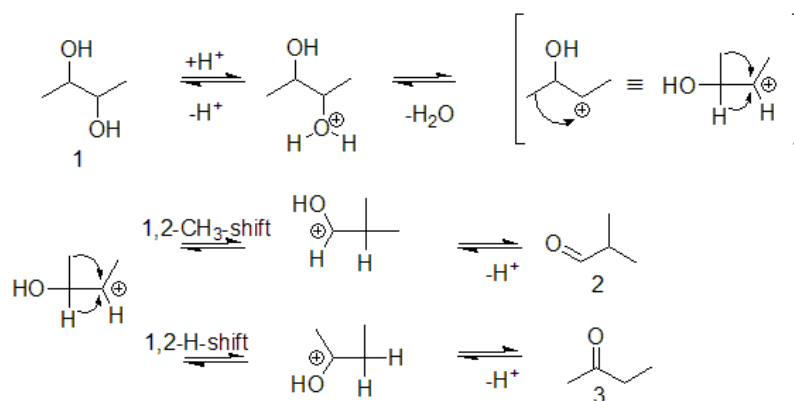
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Polyols can be synthesized from carbohydrates in bio- or chemo-catalytic way. The conversion of polyols with two hydroxyl groups in 1,4-positions, for example 1,4-butanediol, results in furan derivatives. In contrast, during the dehydration of diols with two vicinal hydroxyl groups, for example, 1,2-propane- and 1,2-butanediol, aldehydes or ketones are formed<sup>[1]</sup>. This will be presented exemplarily with the dehydration of 2,3-butanediol into methyl ethyl ketone. 2,3-butanediol is fermentative available from carbohydrates such as hexoses and pentoses or from lignocellulosic wastes<sup>[2]</sup>. The reaction in water allows to directly convert the fermentative available 2,3-butanediol solution into methyl ethyl ketone without water separation.

### Introduction

In the face of growing awareness of sustainability issues, increasing CO<sub>2</sub>-content in the atmosphere and climate protection renewable resources have continuously been assuming greater importance over the past years. An alternative to fossil resources is the production of important intermediates derived from biomass. 2,3-butanediol is fermentative available from carbohydrates (hexoses and pentoses) and lignocellulosic wastes, an alternative route for the production of biomass substrates to liquid fuels and chemical feedstock<sup>[3]</sup>. It can be used as fuel additive and be converted to diacetyl, which is used as a flavouring agent<sup>[3]</sup>. The dehydration of 2,3-butanediol in sub- and supercritical water leads to methyl ethyl ketone and isobutyraldehyde as by-product. Methyl ethyl ketone is used as a fuel additive, as solvent for plastics, resins, lacquers and for the de-paraffination of lubricants<sup>[2]</sup>. Isobutyraldehyde can be used as intermediate for the production of fertilizers, neopentyl glycol, the amino acids D,L-valine and D,L-leucine and methacrylic acid<sup>[2]</sup>.

The acid-catalyzed dehydration of 2,3-butanediol **1** (Scheme 1) occurs in two steps: first, one of the hydroxyl groups is protonated and water is eliminated. In the second step isobutyraldehyde **2** or methyl ethyl ketone **3** can be formed via pinacol-pinacolone rearrangement<sup>[5]</sup>.



**Scheme 1.** Reaction scheme for the dehydration of 2,3-butanediol to methyl ethyl ketone and isobutyraldehyde.

Bourns synthesized methyl ethyl ketone at 225 °C with aluminosilicates and achieved a yield of 85 %. At higher temperatures the yield decreases, at 450 °C only gaseous products of the decomposition remain<sup>[7]</sup>. Bucsi obtained with an almost complete conversion a selectivity of 83 %, the formation of isobutyraldehyde could nearly be suppressed ( $S = 3\%$ )<sup>[8]</sup>. The kinetic analysis of the formation of methyl ethyl ketone was examined by Neish via the addition of sulfuric acid (3-20 % ( $\text{g g}^{-1}$ ))<sup>[10]</sup>.

An average value of 1,53 for the reaction rate of sulfuric acid (2,5 – 10 vol %) during the conversion of 2,3-Butandiol was established by Emerson<sup>[9]</sup>. The distillation of the *racemic*- and *meso*-2,3-butanediol (mixture of (*R,R*)-, (*S,S*)-, and *meso*-2,3-butanediol) in 85 % phosphoric acid leads to a combined yield of methyl ethyl ketone and isobutyraldehyde of 59 %<sup>[11]</sup>. The dehydration of the polyols requires a high acid concentration, which leads to an increased corrosion and needs additional neutralization. These disadvantages can be avoided if 2,3-butanediol is converted in subcritical water with the addition of catalytic quantities of zinc sulfate.

The dehydration of the polyols accessible from biomass in sub- and supercritical water has been the subject of research for several years. Due to the high self-dissociation of water under near critical conditions, the dehydration often proceeds adequately fast without additives or with only small quantities of mineral acid. The use of electrolytes can have the same effect as acids, which also results in an increase of the selectivity. There are different explanations for the catalytic effect of electrolytes on the dehydration of polyols in sub- and supercritical water<sup>[14]</sup>.

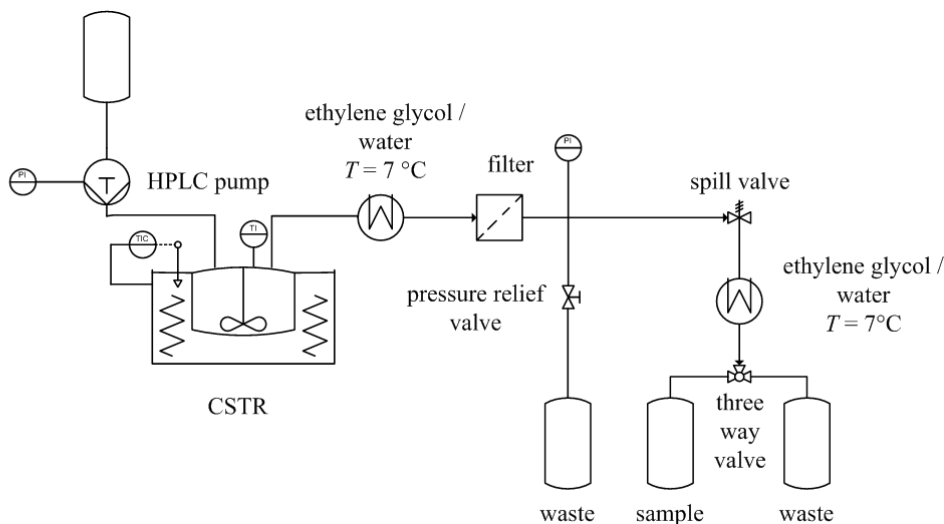
The benefit of these reaction conditions is the direct conversion of aqueous 2,3-butanediol derived from biomass into methyl ethyl ketone and isobutyraldehyde, without the separation of water. To obtain the data for the design of the technical process, the influence of the temperature, different reactants and the catalytic effect of electrolytes, such as zinc sulfate, were investigated.

## Materials and Method

### Continuous high pressure reactor

The experiments were conducted in an electrically heated continuously-stirred-tank-reactor (CSTR) (stainless steel, specification: 1.4571), which is attached to a block of aluminum. This aluminum cylinder is heated via five 400 W electrical heating cartridges, which are controlled with two thermocouples by a temperature controller. One of the Ni-Cr/Ni-thermocouples is attached to the aluminum cylinder and the other is placed directly into the fluid. The reactor volume is 5  $\text{cm}^3$ .

The homogeneous feed solution is fed into the reactor system by a two-piston HPLC pump (10 mL pump head) and is cooled down afterwards by a heat exchanger (ethylene glycol/water, 7 °C) before the pressure is completely released by a spill valve. The sample vessel is also cooled (ethylene glycol/water, 7 °C), which should prevent the evaporation of volatile substances. Behind the heat exchanger there is a filter (90 µm) for the separation of solid substances from the fluid. Fig. 1 illustrates the high pressure reactor schematically.



**Figure 1.** Schematic flow sheet of the high pressure miniplant.

Depending on the flow rate of the pump, the resulting residence time varies from 25 to 180 seconds. The flow rate is calculated by using the density of pure water, as a first assumption.

### Analysis of the reactor samples

Before injecting a 20 µL reactor sample into the column, the solution is spiked with acidic exchangers (Amberlite IR-120H<sup>+</sup>). This prevents the contamination of the column with heavy metal ions.

The quantitative analysis of the reactor sample was carried out by HPLC via a cation exchanger column (ION-300H, Interaction Chromatography). 2 mM sulfuric acid is used as the eluent. The column temperature is held constant at 25 °C, while the temperature of the RI-detector is at 40 °C. The flow is 0.5 mL min<sup>-1</sup>.

### Results and Discussion

The dehydration of 2,3-butanediol accessible from biomass was investigated and the following parameters were varied.

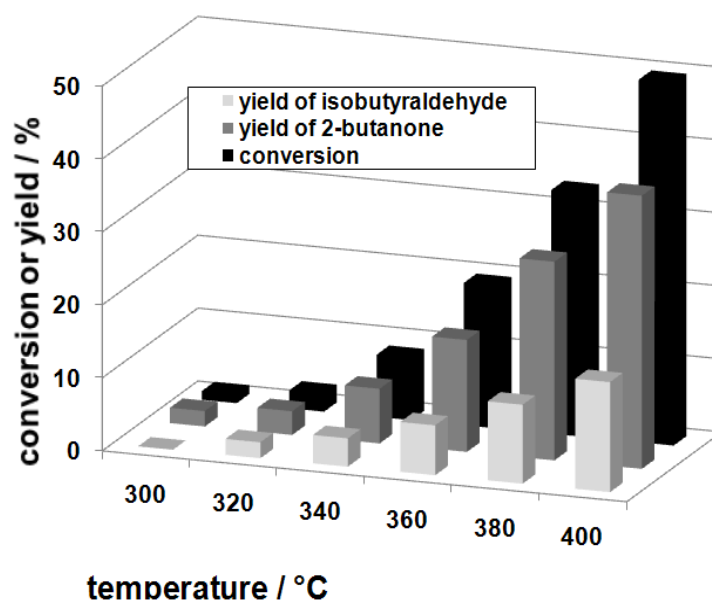
- Temperature (300-400 °C)
- Type of reactant: *meso*-2,3-butanediol, (*R,R*)-2,3-butanediol, *rac-meso*-2,3-butanediol
- Type of electrolyte (transition metal sulfates 800 ppm (g g<sup>-1</sup>))
- Residence time (15 – 180 s)

In all experiments, methyl ethyl ketone was identified as the main product and isobutyraldehyde as the by-product. Both were quantified via HPLC. For the kinetic analysis a corrected concentration is introduced and can be obtained by using Eq (1):

$$c_{corr}(i) = c_{STP}(i) \frac{\rho_{water,reactor}}{\rho_{water,STP}} \quad (1)$$

### Influence of the temperature

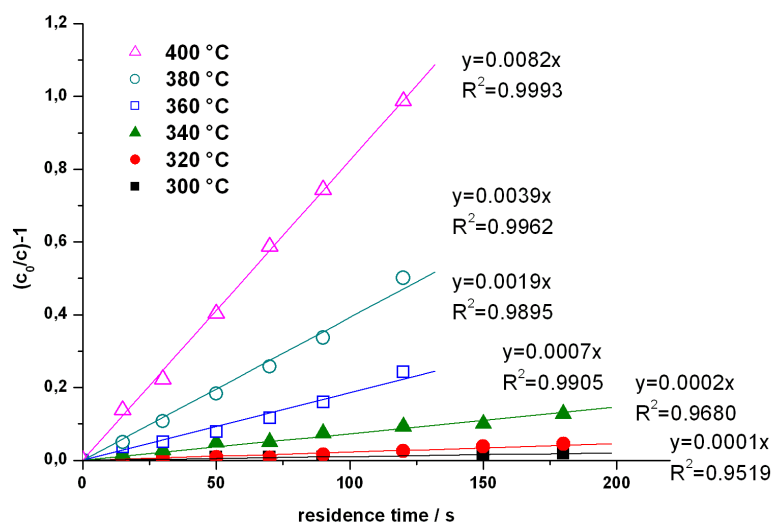
The temperature was varied from 300 to 400 °C at 34 MPa and the educt was an aqueous 0.5 % (g g<sup>-1</sup>) *rac-meso*-2,3-butanediol. As can be seen in Fig. 2, the conversion and yield of methyl ethyl ketone raise with increasing temperature and residence time. The maximum conversion of about 50 % and a maximum yield of methyl ethyl ketone about, 40 % are reached after 120 s at 400 °C and 34 MPa.



**Figure 2.** Influence of temperature on the maximum achieved conversion of *rac-meso*-2,3-butanediol and the yield of methyl ethyl ketone and isobutyraldehyde . Conditions 0.5 % (g g<sup>-1</sup>) 2,3-butanediol solution, 120 s residence time, 34 MPa.

Above a temperature of 300 °C isobutyraldehyde is achieved and its maximum yield is about 15 % at 400°C, 34 MPa and after 120 s.

The kinetic analysis was done on the assumption of an ideal continuously stirred tank reactor (CSTR) and a reaction order of one concerning 2,3-butanediol. The assumption of a CSTR was clarified via mean residence time distribution experiments <sup>[15]</sup>. The graphical analysis is presented in Fig 3..



**Fig.3** Plot for determining the reaction constants in an ideal continuously stirred tank reactor for the dehydration of *rac-meso*-2,3-butanediol at 34 MPa.

The resulting activation energy amounts to  $147 \text{ kJ mol}^{-1}$  and the frequency factor is  $2 \cdot 10^9 \text{ s}^{-1}$ . The corresponding straight line correlation coefficient  $R^2$  is 0.997. Table 1 gives an overview on other activation energies and frequency factors for dehydration of diols in sub- and supercritical water. The activation energy regarding the dehydration of 2,3-butanediol in sub- and supercritical water has a similar value as those for the glycerol dehydration (Tab. 1).

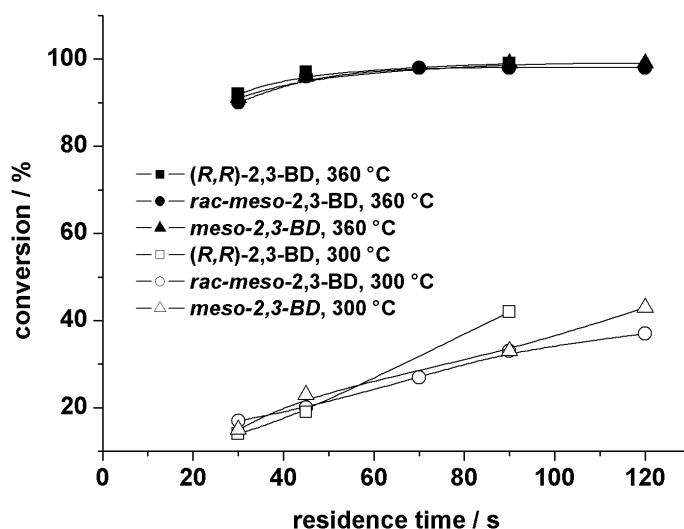
**Table 1:** Overview of activation energies and frequency factors for dehydration of diols and triols in sub- and supercritical water.

educt	activation energy / $\text{kJ mol}^{-1}$	frequency factor / $\text{s}^{-1}$
glycerol <sup>[16]</sup>	150	$10^{18}$
1,2-propanediol <sup>[17]</sup>	195	$6 \cdot 10^{13}$
1,4-butanediol <sup>[18]</sup>	116	$1,9 \cdot 10^7$

A kinetic analysis and the temperature dependency (138 to 180 °C) of the dehydration of *rac-meso*-2,3-butanediol in presence of 2.5 to 10 vol.% sulfuric acid as catalyst leads to a reaction order of 1.53 concerning the acid and  $36 \text{ kJ mol}^{-1}$  as activation energy<sup>[9]</sup>. The activation energy under sub- and supercritical water for dehydrations of diols and triols without catalysts is considerably larger.

## Dehydration of the different stereo-isomers of 2,3-butanediol

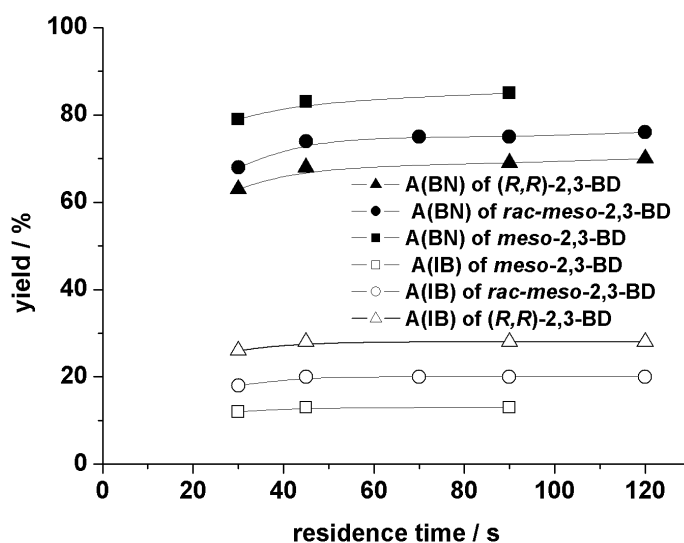
Compared to *rac-meso*-2,3-butanediol, the dehydration of *meso*-2,3-butanediol and (*R,R*)-2,3-butanediol leads to similar results under comparable conditions (Fig. 4). The feed concentration of the 2,3-butanediol is 1 % (g g<sup>-1</sup>).



**Figure 4.** Conversion of an aqueous 1% (g g<sup>-1</sup>) 2,3-butanediol as a function of the residence time at 300 and 360 °C, 34 MPa and with the addition of 800 ppm (g g<sup>-1</sup>) ZnSO<sub>4</sub>.

The selectivity of methyl ethyl ketone during the dehydration of (*R,R*)-2,3-butanediol is in the range of 10 to 30 % larger than the corresponding values of *meso*-2,3-butanediol. This is in accordance with the results of Bucsi, who also observed a higher reaction rate of the *c2*-symmetric-isomers<sup>[6]</sup>. One explanation is the different stability of the transition states based on the *meso*- and *rac*-isomers during the elimination and rearrangement.

Fig. 5 clarifies, that the yield of methyl ethyl ketone (during the conversion of (*R,R*)-2,3-butanediol) is about 10-15 % larger for the *meso*-isomers. The yield of methyl ethyl ketone during the dehydration of *rac-meso*-2,3-butanediol lies between the yield achieved with the other isomers.

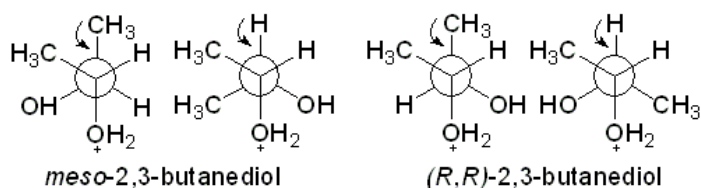


**Figure 5.** Yield of methyl ethyl ketone and isobutyraldehyde as a function of the residence time at 360 °C, at 34 MPa and with the addition 800 ppm (g g<sup>-1</sup>) ZnSO<sub>4</sub>.

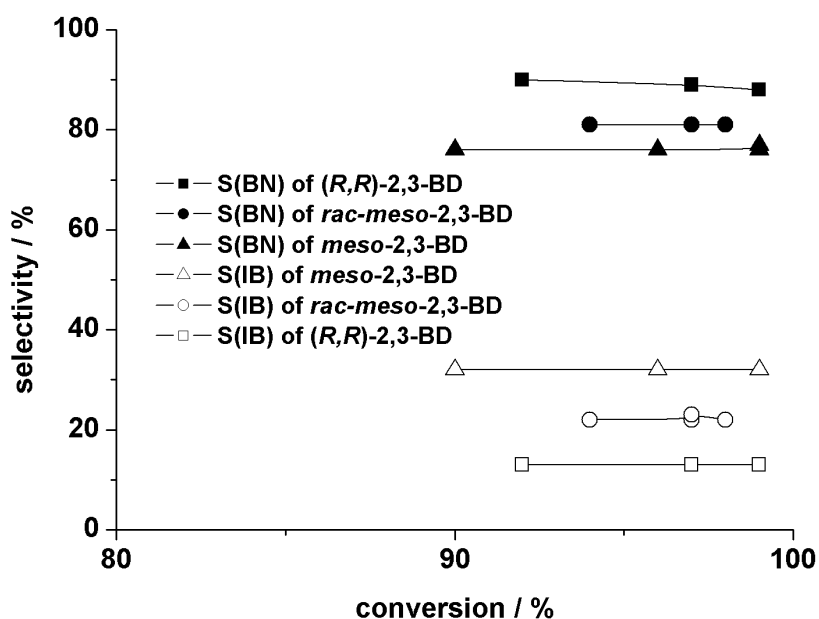
It could be shown that 2,3-butanediol can be dehydrated in subcritical water with the addition of ZnSO<sub>4</sub> with a yield of up to 77 % of methyl ethyl ketone. Without electrolytes the conversion of *rac-meso*-2,3-butanediol could also be reached with a maximum yield of 36 % of methyl ethyl ketone at 360 °C and a residence time of 120 s. Furthermore the results of Bucsi<sup>[8]</sup> and Alexander<sup>[11]</sup> could also be confirmed concerning the higher selectivity of methyl ethyl ketone at reaction of (*R,R*)-2,3-butanediol.

One possible explanation for the faster conversion of the (*R,R*)-isomer is given by Bucsi, which is based on the possible intermediate stages with steric hindrance of the methyl groups. This can lead to a slower reaction<sup>[8]</sup>.

The *rac*-isomers have an intermediate stage **5** (Scheme 3, on the right), where no steric hindrance exists. This is energetically preferred and methyl ethyl ketone is formed by a hydride shift. With this stereo chemical consideration, the distribution of the products as well as the faster reaction of the *rac*-isomers can be explained.



**Scheme 3.** Possible intermediate stage of the E2-elimination of 2,3-butanediol<sup>[8]</sup>, *meso*-2,3-butanediol **4** (on the left), (*R,R*)-2,3-butanediol **5** (on the right).



**Figure 6.** Selectivity/conversion-diagram of the dehydration of 2,3-butanediol at 360 °C, at 34 MPa and with the addition 5 mmol L<sup>-1</sup> ZnSO<sub>4</sub>.

The selectivity/conversion-diagram (Fig. 6) indicates the mechanism presented in Scheme 1 for the dehydration of 2,3-butanediol with a pinacol-pinacolone rearrangement.

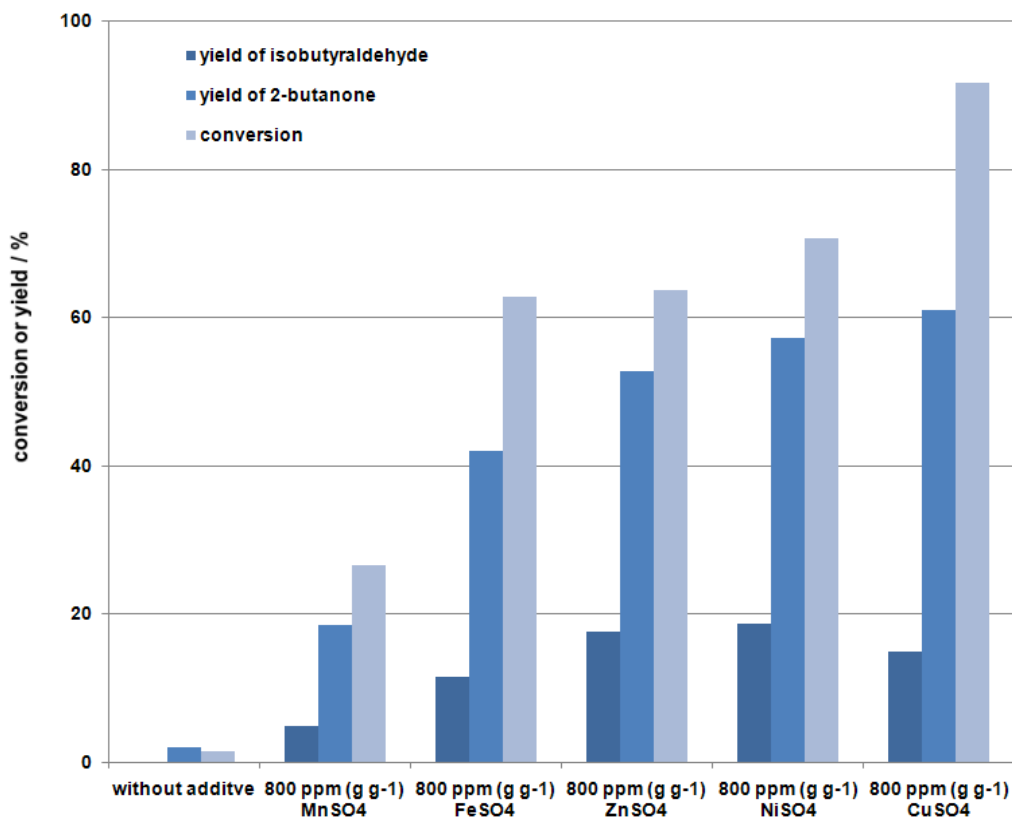
For the catalytic effect of the zinc sulfate salt two reasons can be taken into account. On the one hand this might depend on the catalytic effect of zinc, which can be traced back to the temporary complexation of 2,3-butanediol and in consequence to an easier dehydration. This thesis is supported by works on dehydration of other polyols<sup>[14]</sup>. On the other hand, a shift of the pH-value might be an explanation.

The addition of 5 mmol L<sup>-1</sup> ZnSO<sub>4</sub> resulted in good yields of methyl ethyl ketone at a temperature of 360 °C.

### Comparison of Different Electrolytes

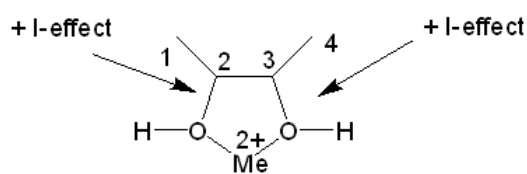
Fig. 7 compares the influence of different electrolytes on the *rac-meso*-2,3-butanediol conversion and the yield of methyl ethyl ketone and isobutyraldehyde. The addition of copper sulfate leads to the best results, 92 % conversion and about 61 % yield of methyl ethyl ketone. During the noncatalyzed reaction a conversion of only 2 % is obtained. Comparing the sulfate electrolytes the conversion and yields for the zinc and iron conduct to similar results. The lowest effect has the manganese sulfate (conversion ca. 27 % and yield of methyl ethyl ketone ca. 19 %).





**Fig.7** Comparison of the influence of different electrolytes on the *rac-meso*-2,3-butanediol conversion, yield of methyl ethyl ketone and isobutyraldehyde at 320 °C, 34 MPa and after 90 s.

It is assumed, that the positive effect of the transition metal sulfates can be traced back to the fact that both oxygen atoms of the reactants coordinate with the transition metal  $Me^{2+}$  to a five-ring transition-state, as described by Ott<sup>[14]</sup>. (Scheme2).



**Scheme2.** Postulated transitional state formed by addition of bivalent transition metal cations during the dehydration of 2,3-butanediol.

The transition metal cation and the 2,3-butanediol forms a chelate five membered ring, where the transition metal draw off the electron density from the hydroxyl groups. An electron defect is created and the bonds between C2 or rather C3 and the Hydroxylgroups are weakened. This makes the water separation easier. During the dehydration at C2 or rather C3 a secondary carbo-cation is formed which can be stabilised due to the +I-effect of the methyl groups<sup>[14]</sup>.

An explanation for the different effect of the transition metals could be given by regarding the Irving-Williams sequence ( $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ ) for complexation constants. The Irving-William sequence considers predominantly electrostatic and size effects. The stability of copper is greater than for nickel, although copper has an added anti-bonded orbital. The anomaly of the copper can be led back to the stabilised Jahn-Teller-Effekt. This

phenomenon is especially developed, if copper forms an tetragonal distortion complex with two 2,3-butanediol molecules <sup>[18]</sup>.

## Conclusions

In this article experiments for the dehydration of 2,3-butanediol under subcritical water conditions were presented. The results show that with low amounts of transition metal sulfates considerable conversions and selectivities can be achieved, for example with 800 ppm (g g<sup>-1</sup>) zinc sulphate at a temperature of 360 °C and a pressure of 34 MPa:

- for *rac-meso*-2,3-butanediol the conversion is up to 98 % with a maximum selectivity of 81 %
- for (*R,R*)-butanediol the conversion is up to 99 % with a maximum selectivity of 89 %
- for *meso*-2,3-butanediol the conversion is up to 99 % with a maximum selectivity of 77 %.

The enhancing effect of the bivalent transition metal sulfates on the dehydration of 2,3-butanediol let infer from a complexation effect. The bivalent cations form with the 2,3-butanediol a chelate five membered ring. An electron defect is determined by the bivalent cations, which makes a water separation easier <sup>[14]</sup>.

The explanation of a complexation effect can be strengthened, because the conversion and yield of methyl ethyl ketone increases after the following sequence Mn<sup>2+</sup><Fe<sup>2+</sup><Zn<sup>2+</sup><Ni<sup>2+</sup><Cu<sup>2+</sup>. This sequence is very similar to the Irving-Williams sequence, where the complexation stability increases after this sequence <sup>[18]</sup>.

The benefit of this procedure is the direct conversion of the fermentative, aqueous 2,3-butanediol solution into methyl ethyl ketone without water separation.

## Symbols used

$\rho_{\text{water, reactor}}$	[g cm <sup>-3</sup> ]	water density at process temperature and pressure
$\rho_{\text{water, STP}}$	[g cm <sup>-3</sup> ]	water density at standard temperature and pressure
$c_{\text{corr}}(i)$	[mol L <sup>-1</sup> ]	corrected concentration of compound i
$c_{\text{STP}}(i)$	[mol L <sup>-1</sup> ]	concentration of compound i at standard temperature and pressure

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