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## Reaction network analysis and continuous production of isosorbide *tert*-butyl ethers

Rebecca Pfützenreuter<sup>a</sup>, Marta Helmin<sup>a</sup>, Stefan Palkovits<sup>b</sup>,  
Regina Palkovits<sup>a,\*</sup>, Marcus Rose<sup>a,\*</sup>

<sup>a</sup> Chair of Heterogeneous Catalysis and Chemical Technology, RWTH Aachen University, Worringerweg 1, D-52074 Aachen, Germany

<sup>b</sup> Center for Molecular Transformations, RWTH Aachen University, Worringerweg 1, D-52074 Aachen, Germany

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### ABSTRACT

Isosorbide is considered a versatile biogenic platform compound for the production of chemicals. The functionalization of its two hydroxyl groups is challenging since they exhibit a different configuration and thus, different reactivity as well as sterical accessibility. We investigated the formation of the respective *tert*-butyl ethers by an addition reaction of isosorbide to isobutene heterogeneously catalyzed by acidic ion exchange resins. An efficient liquid phase process under ambient conditions in a batch reactor has been developed. The reaction network was unravelled by detailed investigation of the reaction kinetics. Additionally, the feasibility of continuous processing was successfully demonstrated on the lab-scale applying a continuously stirred-tank reactor.

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### 1. Introduction

The development of future biorefinery schemes in competition to established refineries based on fossil resources poses quite a challenge. Especially the different chemical properties such as the high degree of functionalization of the renewable feedstock compared to fossil resources require the development of new chemical processes and technologies. In this context various platform chemicals have been identified in recent years [1–3]. Especially isosorbide is considered a versatile intermediate due to its chemical properties [4,5]. Particularly the two hydroxyl groups are interesting for further transformations. Yet, it cannot be neglected that they possess different configurations and thus, a different reactivity. The hydroxyl group in position 2 is *exo*- whereas the one in position 5 is *endo*-configured.

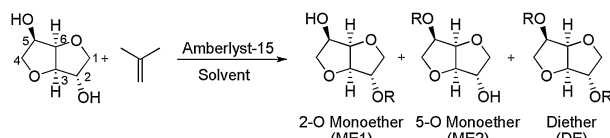
Isosorbide is produced from the C<sub>6</sub> sugar alcohol sorbitol by an acid catalyzed two-fold dehydration reaction yielding 1,4:3,6-dianhydro-glucidol. Sorbitol is a bulk chemical with a world-wide annual production of 1.7 Mt (2011) derived from sugar- or starch-containing plants [6]. One of the largest isosorbide manufacturers today is the French company Roquette with a production capacity

of several thousand tonnes per year [7]. A potential market for isosorbide is estimated to be 45 kt annually by 2020 [8]. However, a significantly greater market share seems feasible considering the production of sorbitol and isosorbide directly from lignocellulose as abundant renewable resource since the competition with the production of edibles can be avoided. Recent research proved the feasibility of this pathway [9–16], hence, promising novel fields of application of isosorbide and its derivatives can be identified.

Main applications of isosorbide derivatives can be found within the pharmaceutical industry. E.g., isosorbide dimethyl ether is considered a versatile, non-toxic solvent. By varying the substituents various properties of high-boiling compounds can be tailored including the boiling point as well as the polarity of the molecules by etherification of either one of the two hydroxyl groups or even both. In the last decades the etherification of isosorbide was investigated mainly using the Williamson method [17–24]. Thereby, organic halides are used as reactants. Microwave heating in combination with phase transfer catalysis enabled the production of long chain ethers of isosorbide in high yields within a few minutes [25,26]. However, ethers are formed in quantitative yields under elimination of stoichiometric amounts of halides as by-products exhibiting rather low atom efficiency. An alternative route for the production of specifically isosorbide dimethyl ethers was reported by Tundo et al. [27]. Dimethyl carbonate was used as a solvent as well as a reactant and the reaction was catalyzed homogeneously with bases such as sodium methanolate. Another method for the

\* Corresponding authors. Tel.: +49 241 8026466/8026497.  
E-mail addresses: [palkovits@itmc.rwth-aachen.de](mailto:palkovits@itmc.rwth-aachen.de) (R. Palkovits),  
[rose@itmc.rwth-aachen.de](mailto:rose@itmc.rwth-aachen.de) (M. Rose).

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**Scheme 1.** Etherification of isosorbide via addition of the different hydroxyl groups to isobutene (R = *tert*-butyl).

production of O-C<sub>8</sub> ethers of isosorbide was reported by Lai et al. using a telomerization reaction of isosorbide with butadiene homogeneously catalyzed by a Pd catalyst [28]. This reaction is not suited for the production of short chain ethers (C<sub><8</sub>) and several isomers are obtained.

Recently, we reported for the first time the etherification of isosorbide with *tert*-butanol as well as with isobutene heterogeneously catalyzed by acidic ion exchange resins [29]. We observed an almost full conversion of isosorbide with isobutene to its mono- and di-*tert*-butyl-ether derivatives under mild conditions, i.e., at ambient temperature and pressure. Accordingly, the production of biogenic glycerol *tert*-butyl ethers (GTBE) in the liquid phase exhibits a quite complex reaction network due to the different availability of the hydroxyl groups. Few kinetic studies have been carried out and the continuous production has been proven for this system [30,31]. In contrast, the production of isosorbide *tert*-butyl ethers (ITBE) appears to be even more challenging since the substrate isosorbide is a solid and has to be converted in solution (Scheme 1).

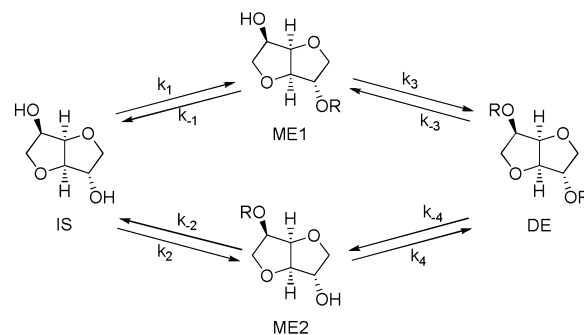
Our recent research focuses on the determination of the reaction kinetics as well as on understanding of the reaction network posing a challenge due to the differently configured hydroxyl groups. Since isosorbide exhibits only two of these groups it can be considered a valuable model compound for investigation of etherification reactions of other sugar alcohols with varying conformation. Additionally, we developed a continuous reaction setup for the quite demanding reaction system involving a liquid substrate solution, a solid acidic catalyst as well as a gaseous reactant to prove the feasibility of a continuous large-scale production of ITBE.

## 2. Experimental

### 2.1. Reaction network analysis

Isosorbide (98%) and dimethyl carbonate (99%) were purchased from Alfa Aesar and used as received. Isobutene (2.0) was purchased from Westfalen and the catalyst Amberlyst-15 (hydrogen form, dry) from Sigma–Aldrich. Methyl undecanoate (≥98%) from Roth was used as internal standard for the gas chromatography. Details of the analytic method have been described previously [29].

For a typical experiment 4.5 g (30.8 mmol) isosorbide were dissolved in 75 mL (80 g, 0.89 mol) dimethyl carbonate. 1.5 g (7.5 mmol) methyl undecanoate as well as 0.45 g Amberlyst-15 (acid sites: 2.12 mmol) in particle sizes of 100–250 μm were added. Isobutene was sparged through the solution with a flow of 129 mL min<sup>-1</sup>. The reaction mixture was stirred with 375 rpm. Experiments were executed at 22, 40 and 60 °C. At defined time intervals samples were taken and analyzed via GC. For the reaction network analysis always two experiments were combined. In both trials eight samples were taken with certain checkpoint times ensuring both experiments can be combined. In the additional experiments at room temperature and 40 °C ten samples were taken in one run.



**Scheme 2.** Reaction network of the formation of mono- and diethers from isosorbide which was used for modelling the reaction kinetics (R = *tert*-butyl).

### 2.2. Continuous reaction set-up

The set-up consists of a glass reactor with an incorporated frit in its lower third on which top the catalyst spheres are placed but not fixed. Two metering pumps (digital regulated Ritmo R05/3 pumps by Fink Chem+Tec OHG) connected via PTFE-tubes to the reactor pump the substrate solution in and the product solution out, respectively. The tube used for pumping the product solution is equipped with a mesh keeping the catalyst spheres from leaving the system. A glass tube connected to the bottom of the reactor serves as the gas inlet. The gas flow is controlled using a mass flow controller by Brooks Instrument.

As initial volume 150 mL of a dimethyl carbonate solution containing isosorbide (0.03 g mL<sup>-1</sup>) was placed in the reactor together with 1 g Amberlyst-15 spheres (diameter approximately 600–850 μm) as provided by the supplier. The mixture was stirred with 375 rpm at room temperature (22 °C). The gas flow was set to 65 mL min<sup>-1</sup>. The substrate solution was pumped in with 1 mL min<sup>-1</sup> and the products were pumped out with 1.2 mL min<sup>-1</sup>. At certain time intervals samples were taken and after degassing them using a freeze–pump–thaw method they were analyzed by means of GC.

## 3. Results and discussion

### 3.1. Reaction network analysis

The formation of the isosorbide di-*tert*-butyl ether (DE) occurs as a consecutive reaction of the formation of the two different monoethers (ME1 and ME2) (Scheme 2). Additionally, the possibility of reaction equilibria has to be considered. For investigation of the reaction kinetics the whole network should be taken into account. Nevertheless, for modelling of the reaction kinetics it is assumed that the solution is saturated with the gaseous substrate isobutene and its concentration remains constant since excess amounts are sparged continuously through the reaction solution. Therefore, the reaction rates only depend on the concentrations of isosorbide (IS) and its ether derivatives (Scheme 2).

The optimal reaction conditions for the etherification of isosorbide with isobutene have been identified in our previous study [29]. The reaction gave the highest conversion of isosorbide and yields of the mono- and diethers by using dimethyl carbonate as a solvent and sparging isobutene through the solution under atmospheric pressure and at ambient temperature. Despite using dimethyl carbonate as solvent no methyl ethers of isosorbide were observed under these reaction conditions. However, isobutene di- and trimers have been detected by GC analysis. As reported in literature, isobutene undergoes an oligomerization reaction in the presence of acidic catalysts, forming preferably liquid products [30,32]. Since it would exceed the scope of this study, the mass

**Table 1**  
Results of the DFT calculations estimating  $\Delta G$  and  $\Delta H$  for all four reactions at 25 °C.

Reactions		$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )
1	IS + IB → ME1	-27.4	-79.0
2	IS + IB → ME2	-25.4	-80.5
3	ME1 + IB → DE	-21.8	-76.1
4	ME2 + IB → DE	-23.8	-74.5

balance of the exclusively isobutene-based by-products was not investigated in detail. Thus, considering only isosorbide and its ether derivatives, the mass balance was found to be closed.

Preliminary to the kinetic investigations different temperatures were screened, in order to determine the best suited temperature range. Below 20 °C the solubility of isosorbide decreases significantly, enabling only very low concentrations to be converted. With increasing temperature on the one hand the formation of the unwanted isobutene oligomer by-products increases significantly. On the other hand the conversion of isosorbide decreases and accordingly the equilibrium involving all the isosorbide ether derivatives is shifted to the side of the substrates indicating the addition reaction of the isosorbide hydroxyl groups to isobutene to be an exothermic reaction.

This assumption was supported by estimating the thermodynamic properties of the four occurring reactions via DFT calculation of the reaction enthalpy ( $\Delta H$ ) as well as of the Gibbs free energy ( $\Delta G$ ) using the software GAMESS [33]. Details of the calculations are given in the supporting information (S1). The reaction enthalpy of the etherification is found to be in the range of -70 to -80 kJ mol<sup>-1</sup> (Table 1). This proves the experimental observation that an increasing reaction temperature decreases the conversion of the slightly exothermic etherification reaction. The values are also in good agreement with the extensively studied thermodynamics of the formation of methyl *tert*-butyl ether from methanol and isobutene in the gas phase ( $\Delta H = -65$  kJ mol<sup>-1</sup>) [34]. In contrast, the same reaction in the liquid phase is characterized by  $\Delta H$  of around -35 kJ mol<sup>-1</sup> strongly depending on the type of solvent [35]. Estimation of the Gibbs free energy of the four isosorbide etherification reactions gives valuable insights into the reaction network (Table 1). For all reactions  $\Delta G$  is between -21 and -28 kJ mol<sup>-1</sup> implying a thermodynamically favoured reaction. The etherification of the *exo*-configured hydroxyl group (reactions (1) and (4)) exhibits lower  $\Delta G$  values of -27.4 and -23.8 kJ mol<sup>-1</sup> than the conversion of the *endo*-configured group (reactions (2) and (3)) with -25.4 and -21.8 kJ mol<sup>-1</sup>, respectively. This renders the *exo*-configured hydroxyl group the preferred one, presumably due to sterical hindrance of the *endo*-configured group for a bulky *tert*-butyl substituent. This hypothesis is experimentally supported. In all experiments always an excess of ME1 over ME2 is observed in the equilibrium (Table 2) and reaction kinetics exhibit higher reaction rate coefficients for reactions (1) and (4) than for (2) and (3).

In order to determine the intrinsic reaction kinetics despite using a solid, macroporous ion exchange resin as catalyst, the influence of the particle size (pore diffusion), stirring rate (film diffusion) as well as the gas flow (gas-liquid transfer) were investigated and chosen in a proper range to exclude mass transfer limitations (S2).

**Table 2**  
Equilibrium yields (%) of IS, ME1, ME2 and DE at different reaction temperatures.

	22 °C	40 °C	60 °C
IS	3	10	37
ME1	20	37	38
ME2	4	11	10
DE	73	42	11
$\Sigma$	100	100	96

**Table 3**  
Determined rate constants at 22, 40 and 60 °C considering the initial reaction and the chemical equilibrium.

Rate constant	22 °C	40 °C	60 °C
$k_1$ (min <sup>-1</sup> )	$1.50 \times 10^{-2}$	$2.59 \times 10^{-2}$	$3.00 \times 10^{-2}$
$k_{-1}$ (min <sup>-1</sup> )	0	$5.85 \times 10^{-3}$	$3.52 \times 10^{-2}$
$k_2$ (min <sup>-1</sup> )	$1.02 \times 10^{-2}$	$1.53 \times 10^{-2}$	$1.10 \times 10^{-2}$
$k_{-2}$ (min <sup>-1</sup> )	0	0	0
$k_3$ (min <sup>-1</sup> )	$1.27 \times 10^{-2}$	$8.59 \times 10^{-3}$	0
$k_{-3}$ (min <sup>-1</sup> )	$3.32 \times 10^{-3}$	$8.92 \times 10^{-3}$	$3.94 \times 10^{-2}$
$k_4$ (min <sup>-1</sup> )	$2.38 \times 10^{-2}$	$4.43 \times 10^{-2}$	$5.60 \times 10^{-2}$
$k_{-4}$ (min <sup>-1</sup> )	$9.47 \times 10^{-4}$	$8.63 \times 10^{-3}$	$1.20 \times 10^{-2}$
Least squares (mol <sup>2</sup> kg <sup>-2</sup> )	$3.26 \times 10^{-2}$	$1.43 \times 10^{-2}$	$8.25 \times 10^{-3}$

The experimental data was collected at different temperatures (22 °C, 40 °C and 60 °C) in order to investigate the influence on the reaction rate and course. To trace the progress of the reaction, samples were taken at certain time intervals and analyzed via gas chromatography (cf. Section 2). The kinetic modelling was carried out using a fifth order Runge-Kutta method [36,37] on the basis of the following set of differential equations which express the reaction network displayed in Scheme 2:

$$\frac{dc_{IS}}{dt} = -k_1 c_{IS} + k_{-1} c_{ME1} - k_2 c_{IS} + k_{-2} c_{ME2} \quad (1)$$

$$\frac{dc_{ME1}}{dt} = k_1 c_{IS} - k_{-1} c_{ME1} - k_3 c_{ME1} + k_{-3} c_{DE} \quad (2)$$

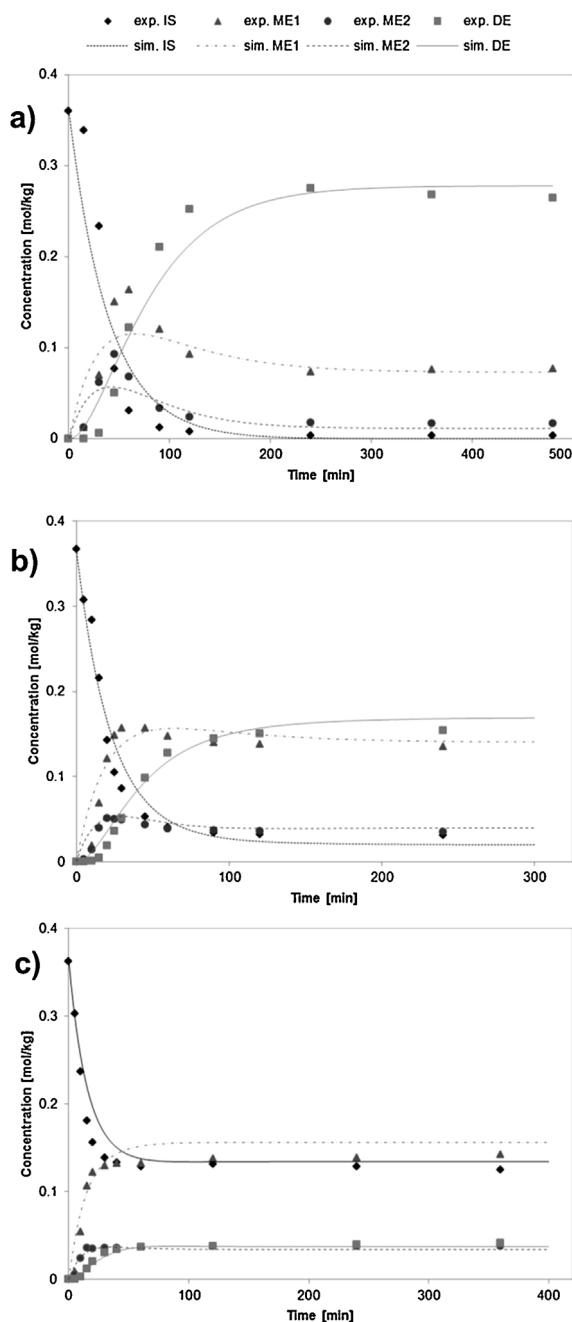
$$\frac{dc_{ME2}}{dt} = k_2 c_{IS} - k_{-2} c_{ME2} - k_4 c_{ME2} + k_{-4} c_{DE} \quad (3)$$

$$\frac{dc_{DE}}{dt} = k_3 c_{ME1} - k_{-3} c_{DE} - k_4 c_{ME2} + k_{-4} c_{DE} \quad (4)$$

The above mentioned kinetic model has been optimized for the reaction system. The concentration-time profiles of the etherification reaction at 22, 40 and 60 °C (Fig. 1) show good agreement of the experimental and the modelled data. However, there are still some inconsistencies mainly for the monoether compounds. Overall, small values are slightly overestimated while large values are underestimated by the model (cf. parity plots in the supporting information S3-S5). This is probably due to the wide time range which is considered, including the reaction reaching the chemical equilibrium. Thus, the model includes the values for the concentrations in the chemical equilibrium rather than describing exclusively the initial, non-equilibrium data. A model of higher accuracy is achieved by only considering the non-equilibrium data points. This is explained in more detail at the end of this chapter. However, to give a full insight into the reaction network the equilibrium has to be considered. For this purpose the accuracy of the model is sufficient.

In general, the profile supports the assumption that the isosorbide di-*tert*-butyl ether is formed in a consecutive reaction from isosorbide via ME1 and ME2, respectively. At 22 °C the concentration of both monoethers level to a constant value and thus, the chemical equilibrium is reached after 240 min. Under these conditions isosorbide is converted to 97%. This suggests that the reaction towards the diether is indeed an equilibrium reaction while the back reactions from the monoethers to isosorbide do not likely occur at low temperatures. The modelling resulted in zero for the rate constants  $k_{-1}$  and  $k_{-2}$  (Table 3) describing these two reverse reactions.

As expected the reaction at a higher temperature of 40 °C is faster and the equilibrium is reached already after 90 min (Fig. 1b). A full conversion of isosorbide at this temperature is not achieved anymore, thus, implying the back reactions of the monoethers to isosorbide to occur. However, taking the rate constants for these reaction steps into account ( $k_{-1}$  and  $k_{-2}$ , Table 3) it is obvious that only ME1 exhibits the reverse reaction since  $k_{-2}$  is zero. On the



**Fig. 1.** Concentration-time profiles of the etherification reaction of isosorbide to monoethers 1 and 2 and the diether at 22 °C (a), 40 °C (b) and 60 °C (c). Symbols mark experimental values while lines represent the modelled data, respectively.

other hand, ME2 is converted five times faster towards the diether (cf.  $k_3$  and  $k_4$ ) avoiding therefore its back reaction.

This observation is in accordance with the above mentioned different *Gibbs* free energies rendering the formation of DE from ME2 by etherification of the *exo*-configured hydroxyl group the preferred reaction. Raising the reaction temperature to 60 °C, the reaction rate increases further (Fig. 1c). The equilibrium is reached after 60 min. Back reactions seem more pronounced at this temperature since a smaller amount of isosorbide is converted (63%) and less diether (11%) is formed in the equilibrium. Considering the rate constants, the back reactions are indeed faster with one exception: the value for  $k_{-2}$  is still zero. Hence, the reaction does not occur. Interestingly, the rate constant  $k_3$  is also zero meaning the diether is exclusively formed via ME2 at elevated temperatures. The rate

**Table 4**

Determined rate constants at 22 and 40 °C exclusively considering the initial reaction phase before reaching the chemical equilibrium.

Rate constant	22 °C	40 °C
$k_1$ (min <sup>-1</sup> )	$2.83 \times 10^{-2}$	$5.61 \times 10^{-2}$
$k_{-1}$ (min <sup>-1</sup> )	0	$1.57 \times 10^{-2}$
$k_2$ (min <sup>-1</sup> )	$1.72 \times 10^{-2}$	$2.83 \times 10^{-2}$
$k_{-2}$ (min <sup>-1</sup> )	0	0
$k_3$ (min <sup>-1</sup> )	$1.18 \times 10^{-2}$	$6.13 \times 10^{-3}$
$k_{-3}$ (min <sup>-1</sup> )	0	$5.21 \times 10^{-3}$
$k_4$ (min <sup>-1</sup> )	$3.04 \times 10^{-2}$	$6.45 \times 10^{-2}$
$k_{-4}$ (min <sup>-1</sup> )	0	$7.45 \times 10^{-3}$
Least squares (mol <sup>2</sup> kg <sup>-2</sup> )	$1.22 \times 10^{-2}$	$1.19 \times 10^{-3}$

constants describing generally the same reaction, e.g., the etherification of the *endo*-configured hydroxyl group ( $k_1$  and  $k_4$ ) show overall the same trends with changing temperatures. Yet, comparing for example  $k_3$  and  $k_2$ , the differences between both values is more distinct especially at 60 °C, when  $k_3$  becomes zero but  $k_2$  does not. The same holds true for  $k_{-1}$  and  $k_{-4}$  at 22 °C. However, this is not surprising considering the different starting materials for the individual reaction steps. The electronic and steric properties are of course different between IS and ME1.

Taking all data into consideration it can be concluded, that the etherification of the *exo*-configured hydroxyl group is faster than the etherification of the *endo*-configured one. Furthermore, with increasing temperature the equilibrium is shifted towards the starting material. However, the back reaction of ME2 does not occur under the investigated conditions. In general, with higher temperatures a reaction rate is faster and thus, the rate constant increases. This is not the case for all obtained rate constants of the investigated reaction network. Especially  $k_3$  is decreasing with increasing temperature and also partially  $k_2$ . This behaviour could be evidence of a more complex mechanism of the corresponding reaction steps which are in both cases the etherification of the *exo*-configured hydroxyl group.

In order to get more accurate rate constants from a reaction engineering point of view additional experiments were executed at 22 and 40 °C (S6–S8). Therefore, ten samples were taken in a shorter time interval to describe the initial reaction before reaching the chemical equilibrium more precisely. Moreover, an initial break-in phase for the different reaction temperatures has been considered which was 10 or 5 min, respectively. In this approach, observing only the initial phase of the reaction, there are no back reactions considered at room temperature. Additionally, also the rate constants decreased for the back reactions at 40 °C except for  $k_{-1}$  (Table 4). The other qualitative conclusions stay the same. Furthermore, the errors of the rate constants determined by the method of least squares were diminished, for the 40 °C data even in one order of magnitude.

### 3.2. Continuous production of ITBE

Additionally to the kinetic studies a continuous lab-scaled reaction set-up was designed and built in order to investigate the possibility of a continuous etherification of isosorbide. Due to the versatile parameters within the reaction system containing a dissolved substrate (IS), a gaseous reactant (IB) and an acidic ion exchange resin as solid catalyst (Amberlyst-15) a continuous-stirred tank reactor with fluidized catalyst particles was chosen (Fig. 2). The substrate IS was dissolved in the solvent (dimethyl carbonate) beforehand and pumped into the reactor via a metering pump. Ensuring a complete dissolution of isosorbide the concentration was set to 0.03 g mL<sup>-1</sup>. An initial amount of 150 mL was placed inside the reactor. The gas with a flow of 65 mL min<sup>-1</sup> entered the reactor through a ceramic frit on the bottom of the



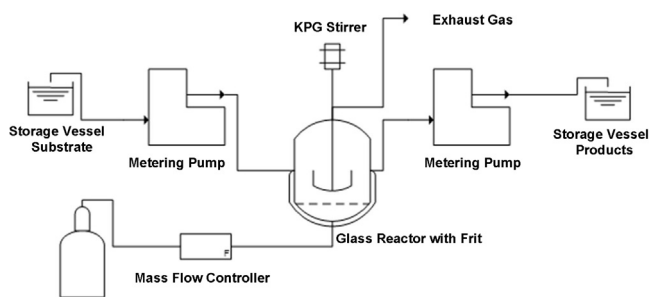


Fig. 2. Reaction set-up for the continuous production of ITBE from isosorbide and isobutene with an acidic ion exchange resin as solid catalyst.

reactor. Underneath it a small dead volume was observed. Hence, the actual volume within the reactor was 125 mL. Only the solution in the main part of the reactor had contact with the catalyst (1 g of Amberlyst-15) since it was placed on top of the frit. The outlet tube was equipped with a mesh in order to keep the catalyst inside the system. Due to the Amberlyst-15 particle size of 0.63–0.85 mm no plugging occurred during the experiments. The flow rate of the substrate solution was set to  $1 \text{ mL min}^{-1}$ . Considering all these parameters the hydrodynamic residence time in this system is 125 min and the weight hourly space velocity (WHSV) is  $1.8 \text{ g g}^{-1} \text{ h}^{-1}$ .

Moreover, under these reaction conditions a certain amount of liquid by-products was formed which were mainly isobutene di- and trimers. This led to an increase of the reaction volume by 12 mL per hour. Hence, the outlet flow was set to  $1.2 \text{ mL min}^{-1}$  to keep the volume in the reactor constant.

Already after about 6 h at  $22^\circ\text{C}$  the yields remain constant, indicating that steady state conditions are reached (Fig. 3). In the 27 h reaction time no significant decrease of the yield could be observed. Thus, Amberlyst-15 seems to be an appropriate catalyst also for longer time-on-stream reactions as already known from MTBE production. However, there is a slight decrease between 10 and 25 h of 3% in the total yield. Whether this is due to a loss in catalyst activity is not certain since it is still within the error of the GC method.

Altogether high overall yields of 95% of all three ether derivatives have been obtained. Furthermore, the fractions of DE as well as of ME1 are quite high with an average of 44 and 36%, respectively. These are the favoured products since both are liquids at room temperature and therefore feasible for the application as high-boiling solvents or fuel blends.

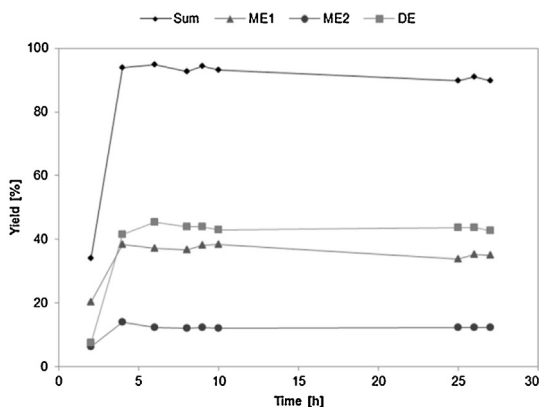


Fig. 3. Yield-time diagram of the continuous etherification of IS to ME1, ME2 and DE.

## 4. Conclusions

The reaction network analysis of the etherification of isosorbide with isobutene using the acidic ion-exchange resin Amberlyst-15 as catalyst revealed a rather complex reaction system. It consists of consecutive as well as equilibrium reactions. With rising temperature the equilibrium shifts towards the starting material. Furthermore, it displays nicely the reactivity of the two hydroxyl groups with different configurations. The *exo*-configured hydroxyl group is favoured for the investigated etherification. Hence, there are always higher amounts of the 2-O monoether (ME1) than the 5-O monoether (ME2) produced. Moreover, also the formation of the diether occurs preferably via ME2. These effects increase with increasing temperature.

Furthermore, rate constants were obtained from a reaction engineering point of view by investigating only the initial reaction and considering an initial break-in phase. Thereby, the errors of the rate constants determined by the method of least squares could be decreased significantly compared to modelling the data including the chemical equilibrium.

In addition, the applicability of a continuous process was proven in a lab-scaled continuous reaction set-up with a fluidized solid catalyst. A first long-term experiment gave good results with high conversion to the isosorbide ether derivatives of up to 95%. In terms of the possible applications of high boiling solvents and fuel blends the produced fractions of the liquid products ME1 and DE with 36% and 44%, respectively, are promising. In future, also the formation of other isosorbide ether derivatives might gain interest due to varying properties of the compounds. An adaption of the developed continuous process due to a high flexibility in process parameters seems feasible. However, also other reactor concepts such as a bubble column reactor might be reasonable especially for the often occurring issue of the transformation of biogenic chemicals in solution with gaseous substrates.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2014.03.007>.

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