Homogeneously catalyzed batch reactor glycerol etherification by CsHCO₃

Manfred Richter a,*, Yuni K. Kirsna ndi b, Reinhard Eckelt a, Andreas Martin a

a Leibniz-Institut für Katalyse an der Universität Rostock, Außenstelle Berlin, Richard-Willstätter-Strasse 12, D-12489 Berlin, Germany
b Department of Chemistry, Faculty of Mathematics and Science, University of Indonesia, Depok 16424, Indonesia

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ABSTRACT

The CsHCO₃ catalyzed liquid-phase etherification of glycerol to oligomers was studied in a discontinuous batch reactor at 260 °C under normal pressure. Concentration vs. time profiles at 0.1, 0.2 and 0.4 wt% CsHCO₃ addition confirmed the consecutive reaction of diglycerol to higher oligomers. Maximum concentration of the target product, linear diglycerol, was observed after intermediate reaction times of 8 h. Independent of the catalyst concentration, a unique conversion–selectivity profile was observed with 100% linear diglycerol at low glycerol conversion but only 10% at complete glycerol conversion. The α,α′ configurational diglycerol isomer prevailed and was preferentially oligomerized. Interconversion of the configurational isomers was not observed. The conversion of glycerol obeyed a 1st order kinetics.

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1. Introduction

Glycerol is a 10% by-product of biodiesel production (via the transesterification of vegetable oils). This has led to a glut of crude glycerol in the market. Thus, valorization routes of glycerol to attractive consumer products are being sought [1]. Polylglycerols with low condensation degree (di- and/or triglycerol) are a product class of interest, being used as starting material for production of emulsifiers in the food and cosmetics industry, or of additives in polyvinyl chloride manufacturing [1,2]. Therefore, there is a market for diglycerols, and the challenge consists in finding a selective conversion of glycerol, avoiding formation of acrolein as well as formation of cyclic compounds, and higher glycerol oligomers.

Commercially, synthesis of diglycerol is accomplished by base hydrolysis of epichlorohydrine using NaOH or Na₂CO₃ solution [2]. The batch conversion requires fractional distillation to separate glycerol, diglycerols and higher oligomers. Moreover, epichlorohydrine has carcinogenic effects.

Etherification of glycerol over solid bases has been studied by the group of Barrault [3–7]. In a discontinuous batch reaction mode at atmospheric pressure, 17% glycerol conversion was observed on Cs ion-exchanged ZSM-5 (Si/Al ratio 28) at 260 °C after 24 h reaction time [5]. The percentage of diglycerol in the liquid products amounted to 92%. On cesium-ion-exchanged zeolite 13X (2 wt%), 79% glycerol conversion was obtained [5]. Liquid products comprised 62% of diglycerol, 33% of triglycerol, 4% of tetragercerol and 1% of higher oligomers. Clacens et al. [6] applied mesoporous aluminum-containing MCM-41-type catalysts impregnated with different amounts of Cs (6.4 × 10⁻⁴ mol/g up to 40.7 × 10⁻⁴ mol/g) for glycerol conversion at 260 °C and found about 85% glycerol conversion after 8 h at the highest Cs loading, but only 40% conversion at the lowest Cs loading after 24 h. The understanding of the reaction and the influence of the solid catalyst is not clear, the more so, because Cs leaching during reaction was observed for some of the materials [6]. Indeed, CsOH catalyzes the reaction as well and showed higher activity compared to the Cs loaded solid [5], but poor selectivity of diglycerol formation. This lead to the conclusion that the good activity of Cs ion-exchanged zeolites and impregnated mesoporous solids is associated with the overlapping homogeneously catalyzed reaction by leached cesium.

Therefore, the question is of relevance about the catalytic role of Cs and the homogeneous reaction pathway. This has been studied by using CsHCO₃ at varied concentration as catalyst, including Cs₂CO₃ as well as CsOH for comparison. The reaction was evaluated for temporal glycerol conversion and product distribution with focus on linear diglycerol. Conversion of glycerol to diglycerol gives three configurational isomers of linear dimers, viz. α,α′, α,β and β,β′-diglycerol (Scheme 1). The ratio of α,α′:α,β:β,β′-diglycerol should be 4:2:1 if the reaction is governed by the probability that two terminal OH groups of glycerol (α position) can react with two terminal OH groups of a second molecule (α′) while the middle OH group (β position) has two positions at a second glycerol to form α,β and only one to form β,β′-diglycerol. To study consecutive reaction of diglycerol, the
feed has been varied taking linear diglycerol. Kinetic analysis of the batch reaction was performed and conclusions on the reaction mechanism were drawn.

2. Experimental

Glycerol was of synthetic grade (Acros Chemicals). Diglycerol was provided by courtesy of Solvay Deutschland GmbH (CAS-Nr. 59113-36-9), composed of ca. 84% α,α′-diglycerol, ca. 14% α,β and <1% β,β′-diglycerol, ca. 0.2% of cyclic diglycerol, and remaining 10% of triglycerol. Glycerol etherification was carried out in a stirred batch glass reactor, in the presence of 0.1, 0.2 and 0.4 wt% of catalyst. Water formed during the reaction was evaporated and separated from the reaction batch by a sideward condenser. The reaction was performed at 260 °C under isothermal conditions, using 50 g of glycerol (0.54 mol), and a slow flow of argon (15 cm³ min⁻¹) to support water removal, and for inertization of the reactor free volume. The vapor pressure of glycerol at 260 °C amounts to ca. 45 kPa [8]. Nevertheless, evaporated glycerol was condensed back to the reactor due to the low temperature at the top of the reactor equipment (ca. 100 °C), and glycerol in the sideward condenser was found negligible. The water withdrawn and condensed outside the reactor did not contain any organic compounds to a significant extent as has been proven by GC analysis. Before heating the glycerol, the corresponding amount of CsHCO₃, Cs₂CO₃ and CsOH powder (Sigma–Aldrich) was added, dissolved in 500 μl of distilled water. Reaction time zero was taken as the glycerol concentration in the side product was ca. 100 °C. Samples of the liquid (0.2 g at maximum) were withdrawn at 2, 4, 8, 12 and 24 h for analysis. Blank experiments yielded only minor conversion of glycerol, viz. 2% after 12 h and 4% after 24 h reaction time.

Reagents and products were analyzed after silylation according to the method of Sweeney et al. [9]. Weighed amounts (5–10 mg) of the liquid sample were mixed with 1.5 cm³ of carefully dried pyridine in a screw cap septum vial (4 cm³), and n-dodecanol added as internal standard. After dissolution, 0.2 cm³ hexamethyldisilazane (HMDS) and 0.1 cm³ trimethylchlorosilane (TMCS) were added and the mixture heated to 70 °C for 1 h. 0.05 cm³ of the solution were diluted by 2 cm³ of dried toluene.

This solution (1 μl) was injected into the GCD 1800 system (Agilent Technologies) GC analysis on a capillary column HP-5 (30 m × 0.25 mm × 0.25 μm, Agilent Technologies) was accomplished in a temperature-programmed mode (ramp 10 K min⁻¹) from 60 to 250 °C. Results were recorded by a mass spectrometric detector in the total ion chromatogram (TIC) mode. Retention times of the silylated components amounted to tR = 6.22 min (glycerol), tR = 11.75 min (linear β,β′-diglycerol), tR = 12.11 min (linear α,β-diglycerol), and tR = 12.32 min (linear α,α′-diglycerol). For calibration of the dimer products, the reference diglycerol was used.

Kinetic analysis was performed using the nonlinear least squares fitter of the ORIGIN software package, version 6 (Microcal Software Inc.).

3. Results and discussion

3.1. Glycerol conversion and diglycerol selectivity

An overview on the reaction characteristics is given in Fig. 1a–c. It can be seen that the amount of catalyst influences the conversion of glycerol as well as the product formation. Within the first 2 h after start of the reaction, ca. 10% glycerol conversion is achieved.

![Scheme 1. Glycerol dimerization and configurational isomers of linear diglycerol.](image-url)
at the lowest catalyst amount applied (0.1 wt%), while with higher amounts of catalyst a higher conversion is observed, viz. ca. 15% at 0.2 wt% and ca. 20% at 0.4 wt% of catalyst. Products comprises linear diglycerol (sum of configurational isomers), triglycerols, tetruglycerols and higher oligoglycerols. Oligoglycerols higher than tetruglycerols could not be resolved by the GCD system. Therefore, the concentration of oligoglycerols resulted from the balance deficit of product analysis.

The concentration vs. time profile of the etherification products is indicative of a consecutive reaction pathway. Specifically, at 0.2 and 0.4 wt% CsHCO₃, the percentage of linear diglycerols passes a maximum of about 40% after 6–12 h reaction time while further consecutive consumption of diglycerol to oligoglycerols takes place at longer reaction times.

Fig. 2 summarizes the selectivity data of diglycerol for the three catalyst concentrations applied, in dependence on the glycerol conversion. Diglycerol selectivity was calculated according to Eq. (1):

\[
S = \frac{n_{DG}}{n_G - n_C} \cdot \frac{v_C}{v_{DG}} \cdot 100
\]  

where \(n_{DG}\) means the moles of linear diglycerol, \(n_G\) and \(n_C\) the moles of glycerol at the beginning of the reaction and at reaction time \(t\), respectively, with \(v_C\) and \(v_{DG}\) as stoichiometric coefficients of reaction according to Eq. (2).

\[
2C_3H_8O_3 \rightarrow C_6H_{14}O_5 + H_2O
\]

It follows from Fig. 2 that (i) diglycerol selectivity of 100% is achieved only at low glycerol conversion up to maximal 20%, (ii) the selectivity declines with higher glycerol conversion. Only 10% selectivity to diglycerol is maintained at nearly full glycerol conversion, and (iii) no significant influence of the amount of CsHCO₃ is observed. Some beneficial influence might be prevailing at higher CsOH concentration, but due to the scattering of data, a reliable conclusion could not be obtained.

Further results using Cs₂CO₃ and CsOH with the same molar Cs concentration (1.85 mmol Cs/mol glycerol), equivalent to the run with 0.4 wt% CsHCO₃ showed no influence of the three anions on the reaction course as displayed in Fig. 3, where the same selectivity–conversion profile is obeyed for the linear diglycerols. This means, that the different anions, although leading to modified basicity if dissolved in water (pH 12.4, 11.2 and 9.2 for 0.01 molar CsOH, Cs₂CO₃, and CsHCO₃ solution, respectively) do not alter the reaction characteristics. Rather the Cs cation seems to be of relevance. Further investigations are in progress using Na and K salts, in order to elucidate the influence of different alkaline cations as well as of different anions on the reaction.

Comparing the results with data of Clacens et al. [5] for homogeneously CsOH catalyzed glycerol conversion, the selectivity-conversion profile is found in good agreement: 70–75% diglycerol at 50% glycerol conversion, and 40–45% diglycerol at 80% glycerol conversion were achieved in both cases.

3.2. Diglycerol isomer distribution

Distribution of the linear configurational isomers during reaction is shown in Fig. 4, together with the conversion of glycerol, for 0.4 wt% CsHCO₃ addition. It can be concluded, that formation of the \(\alpha,\alpha'\) isomer is favoured (69.5% after 2 h), followed by the \(\alpha,\alpha'\) isomer (27.5% after 2 h) and the \(\beta,\beta'\) isomer (3%, after 2 h). Also at lower CsCHO₃ concentration, the distribution of linear diglycerols is maintained at short reaction time (2 h), as can be seen from data summarized in Table 1. The use of CsOH and Cs₂CO₃ lead to the same profile of diglycerol distribution with reaction time.

The prevalence of \(\alpha,\alpha'\)-diglycerol could be related to a higher probability for coupling of OH groups in terminal \(\alpha,\alpha'\) position. Additionally, however, \(\alpha,\alpha'\) and \(\alpha,\alpha'\) isomers are energetically favoured in comparison with \(\beta,\beta'\) isomer as followed from preliminary DFT calculations [10]. Experimentally, it can be seen from the observed dimer distribution, that indeed \(\alpha,\alpha'\) is preferably formed.
at short reaction times and, confirming the DFT view, the percentage of \(\alpha,\beta\)-diglycerol is minor.

At longer reaction time, the dimer distribution is modified, specifically at higher catalyst concentration, and the percentage of \(\alpha,\beta\)-diglycerol decreases, with corresponding increase of \(\alpha,\alpha\)- and \(\beta,\beta\)-percentages. This means that \(\alpha,\beta\)-diglycerol is preferentially involved in further oligomerization. Interconversion between the linear diglycerol configurational isomers does not occur to an appreciable extent as is derived from experiments with diglycerol as reactant instead of glycerol (see Section 3.3).

### 3.3. Diglycerol conversion

The reactivity of diglycerol seems to be comparable to that of glycerol as follows from the conversion-time curves shown in Fig. 5. Analysis results at zero time reflect the composition of the commercial diglycerol product with 94.2% of linear diglycerol, and 5.8% of triglycerol. No glycerol and no cyclic diglycerols could be detected. Complete conversion of the diglycerol has been achieved within 24 h. As expected, the product composition is different. Prevailing reaction is the dimerization of diglycerol to tetraglycerol, whereas no additional triglycerols are formed. The latter fact indicates that no back-scission of diglycerol to glycerol occurs under reaction conditions. Instead, cyclization of linear diglycerols is observed, and, the percentage of oligoglycerols higher than tetraglycerol is significantly enhanced. The initial distribution of the linear diglycerols (ca. 84% \(\alpha,\alpha\), ca. 14\% \(\alpha,\beta\) and <1\% \(\beta,\beta\)-diglycerol) is only moderately modified throughout the reaction with a slight shift in favor of the \(\alpha,\beta\)- and \(\beta,\beta\)-diglycerol (Fig. 6).

#### 3.4. Kinetics and mechanism

As shown experimentally, conversion of glycerol to diglycerols can result in three configurational isomers according to the OH groups of glycerol that interact.

The stoichiometry is given by Eq. (2) with further consecutive reaction of the diglycerols to higher oligoglycerols. The full reaction model consists of competing-consecutive reaction pathways not accessible to an analytical solution of the kinetic equations. However, a simplified approach is possible, taking into account, that triglycerol (and higher oligoglycerols) are not formed within 6 h after start of the reaction. Then, the reaction is described by Eq. (2). If, further, the molecularity of the reaction corresponds to the order of reaction with respect to glycerol, a second order rate Eq. (3) should describe the concentration change of glycerol during reaction in the discontinuous batch reactor.

\[
\frac{dc_G}{dt} = -kc_G^2
\]

with the solution (Eq. (4))

\[
c_G = \frac{c_G^0}{1 + (c_G^0/kt)}
\]

where \(c_G\) and \(c_G^0\) represent the glycerol concentration at time \(t\), and the initial glycerol concentration, respectively, and \(k\) the rate constant.

However, it follows from the example shown in Fig. 7 that the 2nd order equation does not describe the concentration vs. time course of glycerol adequately. It should be noted that the concen-

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**Table 1**

<table>
<thead>
<tr>
<th>(t) (h)</th>
<th>Catalyst (wt%)</th>
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<tr>
<td></td>
<td>0.1</td>
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<tr>
<td>(\alpha,\alpha)</td>
<td>(\alpha,\beta)</td>
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<tr>
<td>2</td>
<td>74.9</td>
</tr>
<tr>
<td>4</td>
<td>72.2</td>
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<td>67.1</td>
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<td>8</td>
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<td>12</td>
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**Table 2**

<table>
<thead>
<tr>
<th>(n)</th>
<th>Rate equation</th>
<th>(W) (wt%)</th>
<th>(k) (h(^{-1}))</th>
<th>(\rho^2)</th>
<th>(x^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(x = 1 - (kt)^{c_0})</td>
<td>0.1</td>
<td>0.0195 ± 0.0013</td>
<td>0.93363</td>
<td>0.0045</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>0.0256 ± 0.0008</td>
<td>0.77578</td>
<td>0.0231</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>0.0275 ± 0.0005</td>
<td>0.68888</td>
<td>0.0358</td>
</tr>
<tr>
<td>1</td>
<td>(x = \exp(-kt))</td>
<td>0.1</td>
<td>0.0582 ± 0.0022</td>
<td>0.99114</td>
<td>0.0006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>0.1011 ± 0.0026</td>
<td>0.99675</td>
<td>0.0003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>0.1209 ± 0.0053</td>
<td>0.99138</td>
<td>0.0010</td>
</tr>
<tr>
<td>2</td>
<td>(x = 1/(1 + c_G^0/kt))</td>
<td>0.1</td>
<td>0.1493 ± 0.0182</td>
<td>0.94235</td>
<td>0.0039</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>0.2902 ± 0.0418</td>
<td>0.94166</td>
<td>0.0060</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4</td>
<td>0.3606 ± 0.0621</td>
<td>0.92695</td>
<td>0.0084</td>
</tr>
</tbody>
</table>

\(^a\) \(n\): Reaction order, \(c_G^0\): initial glycerol concentration (0.54 mol), \(W\): catalyst weight, \(k\): reaction constant with standard deviation, \(\rho^2\): correlation coefficient, \(x^2\): sum of squares of the deviations between the theoretical curve and the experimental points.
An explanation could be derived from the mechanistic suggestions that the reaction starts with the attack of a base (OH−) on a terminal proton to convert the neutral glycerol molecule in an anionic charged form. This anionic glycerol can attack a second glycerol molecule with splitting off a water molecule. Because of the abundance of neutral glycerol, its concentration can be viewed as unchanged. Consequently, the reaction is observed as of pseudo 1st order with respect to the rate-determining reaction of anionic glycerol. It has to be noted, that the initial glycerol concentration is formally contained in the values of the rate constant.

Fig. 8 shows the dependence of activity (expressed as rate constant k) of the pseudo-first order consumption of glycerol on the amount of catalyst (expressed as mmol Cs/mol of glycerol). It is evident that the effect of catalyst concentration levels off at approximately 2 mmol Cs/mol glycerol (equivalent to 0.4 wt% CsHCO₃).

4. Conclusion

The etherification of glycerol to oligoglycerols is catalyzed by CsHCO₃ in a batch mode at 260 °C, with full conversion after 24 h reaction time. High selectivity of the target product, linear diglycerols, is achieved at low glycerol conversion. The reaction obeys a pseudo-first order kinetics with consecutive conversion of diglycerols to higher oligoglycerols. The distribution of linear diglycerol configurational isomers is in favour of the α,α-dimer. Interconversion between the linear diglycerols is negligible.

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