Synthesis of Glycerol Carbonate from Glycerol, a By-Product of Biodiesel Production

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Synthesis of Glycerol Carbonate from Glycerol, a By-Product of Biodiesel Production∗

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Abstract

Methyl esters of fatty acids (also known as biodiesel) made from transesterification of vegetable oils and animal fats with methanol, have shown a lot of promise as alternative diesel fuels. Glycerol is the inevitable byproduct of transesterification process. While there are existing markets for glycerol, a significant increase in availability of glycerol, resulting from the expanded use of vegetable oils and animal fats, would destabilize the glycerol market. In this study, the synthesis of glycerol carbonate from glycerol and dimethyl carbonate was investigated. Glycerol carbonate is a key multifunctional compound employed as a solvent, additive, monomer and chemical intermediate. The resulting glycerol carbonate was obtained in almost quantitative yield. According to measured data a well-elaborated mathematical model of the reactor was used for experiments can be adequate to assign parameters of kinetic equations of the assumed reaction mechanism. Component mass balances were built into the reactor model and order of reactions was fixed.

KEYWORDS: glycerol, biodiesel, glycerol carbonate

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**Introduction**

Utilization of glycerol has a significant role on biodiesel production since large amount of glycerol is obtained as a by-product of vegetable oil methanolysis. Glycerol holds the potential of being an extremely versatile building block within the biorefinery. Although many uses have been developed for glycerol, most product markets are currently small and fragmented. However, development of a biodiesel market could have a huge impact on the availability and use of glycerol. Since glycerol is a key coproduct of biodiesel manufacture, increasing use of biodiesel will lead to much greater glycerol availability and lower cost. At lower projected costs, there is a tremendous potential to develop a variety of new processes and product lines from glycerol, taking advantage of its unique structure and properties. As a renewable and cheap raw chemical, conversion processes of glycerol to useful materials have received increasing attentions, and recently several examples have been reported: acid-induced dehydration of glycerol to acrolein in supercritical water (Ott *et al*., 2006), glycerol oxidation to dihydroxyacetone and glycric acid using carbon-supported gold catalysts (Demirel *et al*., 2007), and 1,3-propanediol production by metabolic engineering approach.

Glycerol carbonate is a stable and colorless liquid that offers useful applications as a novel component of gas separation membranes, a surfactant component, a new solvent for several types of materials or a nonvolatile solvent in the paint industry, a component in coatings, and a component of detergents. Also glycerol carbonate can be utilized as a source of new polymeric materials (Kim *et al*., 2007). Glycerol carbonate can be obtained according to various methods, using epoxy compounds as well as glycerol as raw materials. It was reported that glycerol carbonate can be formed in the reaction of epichlorohydrin with KHCO$_3$ carried out at 80 °C in the presence of 18-crown ether. Promising methods of glycerol carbonate preparation comprise the reaction of glycerol with CO$_2$ or carbon monoxide and oxygen in the presence of Cu(I) catalysts (Rokicki *et al*., 2005).

In our approach, the glycerol carbonate synthesis was carried out under mild conditions without any solvent, using glycerol and dimethyl carbonate as environmentally benign and renewable reagents. Due to the almost quantitative reaction yield there is no need for product purification by distillation at high temperature and recovery of unreacted glycerol.
Materials and methods

Dimethyl carbonate, glycerol, glycerol carbonate and K2CO3 were purchased from Sigma-Aldrich and used without further purification.

As first step reactions were carried out in a 500 ml glass flask equipped with a mechanic stirrer, thermometer and Liebig cooler. Glycerol (92 g, 1 mol) and dimethyl carbonate (270 g, 3 mol) were mixed in the flask.

When reactor temperature reached 60°C, K2CO3 (4.14 g, 0.03 mol) was added to the mixture as catalyst. In case of lower catalyst concentrations (weight proportion catalyst/glycerol: 0.02-0.03), reaction time was approximately two times longer. Catalyst dissolved in reaction media within 5 minutes. Dimethyl carbonate (DMC) was used in a molar excess (3:1) (Rokicki et al., 2005) and methanol was removed continuously to shift the reaction equilibrium towards the product. Methanol forms a minimum boiling azeotrop with DMC (Table 1), so when methanol is removed, DMC leaves the flask, as well.

Table 1. Composition of methanol-DMC azeotrope

<table>
<thead>
<tr>
<th></th>
<th>Boiling point (°C)</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary azeotrope</td>
<td>63.2</td>
<td>-</td>
</tr>
<tr>
<td>(70% methanol + 30% DMC)</td>
<td>63.2</td>
<td>-</td>
</tr>
<tr>
<td>Methanol</td>
<td>64.6</td>
<td>32.04</td>
</tr>
<tr>
<td>DMC</td>
<td>89.8</td>
<td>90.01</td>
</tr>
</tbody>
</table>

Reaction was carried out at 71-76 °C in presence of K2CO3 as a catalyst for 5 h, and then unreacted dimethyl carbonate was distilled off at 40 °C under reduced pressure (4-6 kPa).

Reaction progress was monitored by collecting samples of reaction mixture. As next step reaction was carried out in a Mettler Toledo LabMax Automatic Lab Reactor (Figure 1). The transparent, double-walled glass reactor allows automatic performance of chemical syntheses in the temperature range –50 to 220 °C (TR). The pressure range varies from vacuum to ambient pressure. The working volume of the glass reactor is 0.6 liter.

Analysis

Samples of reaction products were analysed with a Merck LaChrom HPLC equipped with an Ultrahydrogel column (I.D. = 7.8 mm, L= 300 mm) and a Merck LaChrom RI detector. Water was used as eluent. Retention time of the components in minutes: glycerol – 10.97; unknown component – 12.58; glycerol carbonate – 16.31 and DMC – 19.27.
Results and discussion

We have developed a convenient method for synthesis of glycerol carbonate from glycerol and dimethyl carbonate (Figure 2) using $\text{K}_2\text{CO}_3$ as catalyst. Resulting glycerol carbonate was obtained in almost quantitative yield.
Figure 2. Synthesis of glycerol carbonate

Between two types of hydroxyl group in glycerol, two primary alcohols are presumably more reactive than a secondary hydroxyl group. Therefore, intermediate C might be formed at the first step, and subsequently formation of product D occurs through intramolecular conversion. On the chromatograms it can be seen that there is an unknown peak at retention time 12.58-12.59 min, which is probably intermediate C.

Table 2. Influence of time on reaction of glycerol and dimethyl carbonate

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>Glycerol (wt%)</th>
<th>Glycerol carbonate (wt%)</th>
<th>DMC (wt%)</th>
<th>Intermediate (area %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>3.6</td>
<td>34.3</td>
<td>58.2</td>
<td>3.8</td>
</tr>
<tr>
<td>10</td>
<td>2.7</td>
<td>35.3</td>
<td>58.0</td>
<td>3.9</td>
</tr>
<tr>
<td>30</td>
<td>2.2</td>
<td>38.5</td>
<td>55.7</td>
<td>3.5</td>
</tr>
<tr>
<td>60</td>
<td>1.7</td>
<td>44.3</td>
<td>51.6</td>
<td>2.4</td>
</tr>
<tr>
<td>120</td>
<td>1.4</td>
<td>50.2</td>
<td>47.4</td>
<td>6.6</td>
</tr>
<tr>
<td>180</td>
<td>1.1</td>
<td>57.0</td>
<td>40.8</td>
<td>0.9</td>
</tr>
<tr>
<td>240</td>
<td>1.0</td>
<td>59.1</td>
<td>39.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Samples were collected from reaction mixtures at 1, 3, 5, 7, 10, 30, 60, 120, 180, 240 and 300 minutes. Unfortunately the first three samples were not representative because during this period there are two phases in the flask (glycerol and dimethyl carbonate) and solubilization starts when mixture contains enough amount of glycerol carbonate. Table 2 contains composition of samples, amount of intermediate is given in area %, other components were factorized.

Reactor model

When a reactor is designed the first step is to investigate the possible reactions take place in reactor, all the micro and macro processes (e.g. stirring) and operating conditions which have some influence on them. Reactors are planned and used to make value added compounds, so the most important task to know how the cheap raw materials can be converted into a value added product. The conversion pathway can be demonstrated by reaction mechanism. Unfortunately, reaction mechanism does not contain all necessary information which is needed to
design a reactor because it gathers steps of conversion but does not give any information about the reaction rate.

To run a reactor under optimal operation conditions or to find the optimal operating range it is inevitable to know the rate of individual reaction steps. Many kind of correlation can be applied to describe the rate of a reaction with different number of unknown parameters.

To calculate reaction rates the Arrhenius equation (eq. 3) was used with two unknown parameters (pre-exponential factor and activation energy). The produced heat during the reactions is called reaction heat, which is over 0 if the reaction is endothermic while it is below zero if the reaction is exothermic. Every reaction has reaction heat which differs from 0.

Hence, to characterize a reaction, next to the earlier mentioned two parameters, the reaction heat must be determined too. It can be performed with some calorimetric measures.

\[
\begin{align*}
A + B & \rightleftharpoons C + E \\
\frac{k_1}{k_2} \\
C & \rightleftharpoons D + E \\
\frac{k_3}{k_4}
\end{align*}
\]

A: glycerol; B: Dimethyl-carbonate; C: Intermediate; D: Glycerol-carbonate; E: Methanol

\[
k_i = k_{i,0} \cdot \exp\left(-\frac{E_{A,i}}{R \cdot T^R}\right)
\]

\(i = \{1; 2; 3; 4\}\)

Determination of unknown parameters can be achieved by using well-carried out experiments to collect accurate analytical data, but nowadays different kind of modelling techniques can be applied to reduce the number of necessary experiments. According to measured data a well-elaborated mathematical model of the reactor was used for experiments can be adequate to assign parameters of kinetic equations of the assumed reaction mechanism. Structure of the elaborated model of reactor is shown in Figure 2 while a detailed description of all model equations can be found in the appendix.

As eq. 1-2. show both of the reactions in the assumed reaction mechanism are equilibrium reactions so next to the unknown parameters in kinetic equations it is necessary to have a correlation between the inside temperature of reactor and the equilibrium content. Arrhenius-type temperature dependent was used to calculate the reaction equilibrium. To investigate the effect of the producing methanol on the performance of synthesis the methanol is considered in back
reactions, so both of back reactions are second order. The first reaction (eq. 1) is second order since in the first step the glycerol and dimethyl-carbonate must be formed the intermediate which is decomposed into glycerol-carbonate and methanol. On this level of work based on the introduced reaction mechanism component mass balances were built into the reactor model and order of reactions was fixed.

A heat transport couples the inside and the jacket of the reactor and the heat conductivity phenomena in the reactor wall was not consider in this model. Silica oil is circulated in the jacket through a thermostat to keep the temperature of the jacket at desired value so only the heat balance of the reactor inside was built into the model. At the next level in the model hierarchy there is the level of phases. Since the reactions equilibrium is modified with the evaporation of products it is necessary to calculate the content of gas phase.

The temperature of the liquid and gas phase is equal so only the mass transport couples these phases. At the bottom of the model structure can be found the level of components. The reactions are considered at this level. The reactions takes place only in the liquid phase since the catalyst doesn’t evaporate.

To check the assumed reaction mechanism the component balances in the liquid phase were completed with component sources based on the 1-2 equations. The identification of missing model parameters was performed by comparing the analytically determined masses of components and the measured temperature trajectory of reactor inside with the calculated ones using the model.

**Identification and validation of model parameters**

Some of the missing model parameters can be determined from the literature (e.g. all the necessary properties of components) but there is no information about parameters of kinetic and equilibrium expressions so parameter identification was performed based on the comparison of measured and calculated trajectories of state-variables. The square sum of the difference was calculated in every sample time. To find the global minima of this multi variable optimization problem an Evolutionary Algorithm (EA), the Covariant Matrix Adaptation Evolutionary Strategy (CMA-ES) was applied.

The EA is an optimization method which based on the natural selection and survival of the fittest as it works in the real world. EAs consistently perform well approximating solutions to all types of problems because they do not make any assumption about the underlying fitness landscape, hence it makes EAs applicable from different fields of engineering to social sciences (Eiben et al., 2007). Learning the covariance matrix in the CMA-ES can improve the performance on ill-conditioned and/or non-separable problems by orders of magnitude. The CMA-ES overcomes typical problems that are often associated
with EAs, e.g. the poor performance on badly scaled and/or highly non-separable objective functions (Hansen et al., 2000; Hansen et al., 2005). Another application of CMA-ES in an engineering problem can be found in (Varga et al., 2007).

Table 3. Identified reactor model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{01}$</td>
<td>76.94</td>
</tr>
<tr>
<td>$k_{02}$</td>
<td>260.2</td>
</tr>
<tr>
<td>$E_{A1}$</td>
<td>4.78e4</td>
</tr>
<tr>
<td>$E_{A2}$</td>
<td>1.84e4</td>
</tr>
<tr>
<td>$A_{K1}$</td>
<td>7.79</td>
</tr>
<tr>
<td>$B_{K1}$</td>
<td>8.135e4</td>
</tr>
<tr>
<td>$A_{K2}$</td>
<td>5.75</td>
</tr>
<tr>
<td>$B_{K2}$</td>
<td>9.39e4</td>
</tr>
<tr>
<td>$\Delta H_{\text{reac},1}$</td>
<td>-4.97e4</td>
</tr>
<tr>
<td>$\Delta H_{\text{reac},2}$</td>
<td>-6.43e4</td>
</tr>
<tr>
<td>$\alpha_RJ$</td>
<td>5.018e3</td>
</tr>
<tr>
<td>$c_v$</td>
<td>0.5574</td>
</tr>
</tbody>
</table>

The result of the identification of missing model parameters is summarized in Table 3 while measured and calculated trajectories can be compared in Figure 3. As it can be seen in Table 2 only seven samples were taken and analyzed. In the identification process the measured value of state variables were linearly interpolated between nearby samples to help searching algorithm with increasing the number of learning samples.
Figure 3. Calculated (thin) and the measured (thick) trajectories of state-variables (the molar ratio of B (dimethyl carbonate) and A (glycerol) components is three)

As it can be seen in Figure 3 there are some differences between the measured and calculated trajectories after much of reagents transformed. To improve the accuracy of the worked out model more experiments with varying jacket temperature trajectory need to be performed in the reactor but results are promising.

The initial molar ratio of reagents is modified to validate the developed model. The comparison of the calculated and the measured trajectories is shown in Figure 4. and Figure 5. These figures show that the obtained model can be applied to further analyze the investigated reaction system.
Figure 4. The molar ratio of B (dimethyl carbonate) and A (glycerol) components is two. The calculated (thin) and the measured (circles) trajectories of state-variables.
Conclusion

Synthesis of glycerol and dimethyl carbonate was investigated. A convenient method has been developed for synthesis of glycerol carbonate from glycerol and dimethyl carbonate using $K_2CO_3$ as catalyst. Resulting glycerol carbonate was obtained in almost quantitative yield. A well detailed dynamic model of the reactor where the experiments were performed has been worked out.

The developed mathematical model of reactor can be applied to unfold reaction steps of other synthesis, but before a final conclusion can be drawn more experiments need to be done. Due to the reactor model other synthesis can be performed and analyzed in the reactor system in future. The result of model validation shows that obtained model can be applied to further analyze the investigated reaction system.

Figure 5. The molar ratio of B (dimethyl carbonate) and A (glycerol) components is four. The calculated(*thin*) and the measured(*circles*) trajectories of state-variables.
Appendix

Dynamic reactor model

Based on the model assumptions and the supposed reaction mechanism the following expressions were applied to calculate states of reactor during the experiment. At first on components level the component source must be calculated so reaction rate constants are the following assuming an Arrhenius-type correlation between reactor temperature and the reaction rate:

\[ R_1 = \frac{k_1}{K_1} [m^3 \cdot mol^{-1} \cdot s^{-1}] \]

\[ R_2 = \frac{k_2}{K_2} [m^3 \cdot mol^{-1} \cdot s^{-1}] \]

Rate of reactions and component sources were calculated applying the following expressions which all have the same dimension \([mol \cdot m^{-3} \cdot s^{-1}]\):

\[ r_1 = k_1 \cdot c_A \cdot c_B \]

\[ r_2 = k_2 \cdot c_C \]

\[ r_1^- = k_1^- \cdot c_C \cdot c_E \]

\[ r_2^- = k_2^- \cdot c_D \cdot c_E \]

\[ R_A = -r_1 + r_1^- \]

\[ R_B = -r_1 + r_1^- \]

\[ R_C = r_1 - r_1^- - r_2 + r_2^- \]

\[ R_D = r_2 - r_2^- \]
\[ R_x = r_1 - r_1^- + r_2 - r_2^- \]  

(16)

On level of phases some differential equations must be used to calculate the change of value of state-variables in time, so the volume of liquid phase is changed only by the evaporation:

\[ \frac{dV^F}{dt} = -V^{FG} \left[ m^3 \cdot s^{-1} \right] \]  

(17)

since mass and temperature measurements are applied to follow the experiment, the following correlation is applied to calculate the volume of liquid phase in the model:

\[ V^F = \frac{\sum m^F_i}{\rho^F} \left[ m^3 \right] \]  

(18)

and the density of liquid phase is evaluated with:

\[ \rho^F = \frac{\sum m^F_i \cdot \rho^F_i}{\sum m^F_i} \left[ kg \cdot m^{-3} \right] \]  

(19)

expression, where the density of pure components is the function of temperature \( \rho^F_i = f(T^R_i) \) and the constants of these correlation were collected from database of ASPEN. The reactor is operated as a batch reactor so there is no reagent feed during the process and the evaporation couples the liquid and gas phases. Based on these assumptions the following differential equations used to calculate the mass of liquid and gas phase:

\[ \frac{dm^F_i}{dt} = V^F \cdot R_i \cdot M_i - m_i^{FG} \left[ kg \cdot s^{-1} \right] \]  

(20)

\[ \frac{dm^G_i}{dt} = m_i^{FG} - m_{kond,i} \left[ kg \cdot s^{-1} \right] \]  

(21)

To calculate the temperature of reactor it is necessary to know the heat of vaporization of each component (source: database of ASPEN) and heat of reactions (source: identification):
where the heat flux between the reactor and the jacket is:

\[ j_{Q}^{RJ} = A_{RJ} \cdot \alpha_{RJ} \cdot (T_{R}^{R} - T_{J}^{J}) \quad [\text{K} \cdot \text{s}^{-1}] \]  (23)

The next module of reactor model calculates the mass flux from liquid to gas phase. The vapour pressure of pure components was calculated with Antoine-equation applying constants found in ASPEN. The gas phase is treated as an ideal gas so the component mass of gas phase:

\[ \sum_{i=[A;B;C;D;E]} n_{i}^{G} = \frac{p_{G}^{0} \cdot V_{G}^{R}}{R \cdot T_{R}^{R}} \quad [\text{mol}] \]  (24)

where the component mass of each component is calculated with Raoult-Dalton’s law:

\[ n_{i}^{G} = \frac{x_{i} \cdot p_{0}^{G}}{p_{G}^{0}} \cdot \sum_{i=[A;B;C;D;E]} n_{i}^{G} \quad [\text{mol}] \]  (25)

The evaporated liquid is removed from the gas phase through a Liebig cooler, which is treated as a valve with a valve constant (c_v):

\[ \sum_{i=[A;B;C;D;E]} m_{i}^{G} = c_{v} \cdot \sqrt{p_{G}^{G} \cdot (p_{G}^{G} - p_{A}^{A})} \quad [\text{kg} \cdot \text{s}^{-1}] \]  (26)

where \( p_{G}^{G} \) and \( p_{A}^{A} \) represent the pressure of gas phase and the ambient in bar.
References


