

## ENHANCED USE OF RENEWABLE RESOURCES: TRANSESTERIFICATION OF GLYCEROL, THE BYPRODUCT OF BIODIESEL PRODUCTION

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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 for which new uses need to be found. 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 glycerol market. In this study synthesis of glycerol carbonate from glycerol and dimethyl carbonate was investigated. Glycerol carbonate is a key multifunctional compound employed as solvent, additive, monomer and chemical intermediate. 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:** biodiesel, glycerol, glycerol carbonate

### Introduction

Crude glycerol is a considerable by-product of biodiesel production. Approximately 10% of the converted feedstock is released as crude glycerol. This product fraction comprises several impurities, e.g. residues of vegetable oil and esters, salts, different alkaline catalysts and water.

However, the process is far from being environmentally friendly as the final mixture needs to be separated, neutralised and thoroughly washed, generating a great amount of waste in terms of salt residues. The catalyst cannot also be recycled. These several additional steps inevitably put the total overall biodiesel production costs up, reducing at the same time the quality of the glycerol obtained as by-product [1]. The lowest price that crude glycerol could fall to is equivalent to its energy content, i.e. incineration is the lowest value utilisation pathway. Pure glycerol (pharma or kosher quality) is a high price commodity, because of the energy-intensive step that is required during the processing. Hence it is viable only at a certain economic scale. Typically, SMEs operate small scale biodiesel production plants and don't purify small quantities of crude glycerol for economical reasons. 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 [2], glycerol oxidation to dihydroxyacetone and glyceric acid using carbon-supported gold catalysts [3], and 1,3-propanediol production by metabolic engineering approach [4].

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 and. Also glycerol carbonate can be utilized as a source of new polymeric materials [5].

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  $\text{KHCO}_3$  carried out at 80 °C in the presence of 18-crown ether [6].

Nevertheless, more attractive methods are those utilizing glycerol as a renewable and cheap raw material. Taking into consideration that biofuels for diesel engines are being introduced on the market in increasing amounts,

a large amount of glycerol will be available as a side-product of the vegetable oils methanolysis. A typical method of obtaining carbonate derivatives of glycerol is its transesterification with ethylene carbonate or dialkyl carbonate. In the reaction with ethylene carbonate carried out at 125 °C in the presence of sodium bicarbonate the product was formed in a yield of 81% [7].

Recently, in the patent literature, a glycerol carbonate synthesis was reported in which urea was used as reaction partner of glycerol to give the product with a good selectivity (92%) [8].

Promising methods of glycerol carbonate preparation comprise the reaction of glycerol with CO<sub>2</sub> or carbon monoxide and oxygen in the presence of Cu(I) catalysts [9].

The reaction of glycerol with carbon dioxide was carried out in a scCO<sub>2</sub> medium in the presence of zeolite and ethylene carbonate as a co-source of carbonate groups [10].

Nevertheless, according to all the above mentioned methods glycerol carbonate should be purified by distillation under reduced pressure at a relatively high temperature (125–150 °C). 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 K<sub>2</sub>CO<sub>3</sub> were purchased from Sigma-Aldrich and used without further purification.

### *Apparatus and procedure*

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, K<sub>2</sub>CO<sub>3</sub> (4.14 g, 0.03 mol) was added to the mixture as catalyst. Dimethyl carbonate (DMC) was used in a molar excess (3:1) and methanol was removed continuously to shift the reaction equilibrium towards the product. Methanol forms a minimum boiling azeotrope with DMC (*Table 1*), so when methanol is removed, DMC leaves the flask, as well.

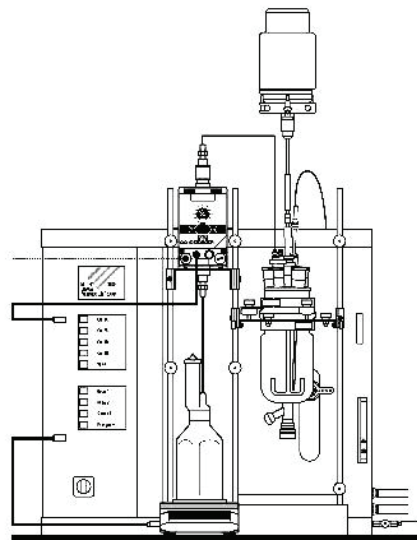
*Table 1:* Composition of methanol-DMC azeotrope

	Boiling point (C°)	Molecular weight
Binary azeotrope (70% methanol + 30% DMC)	63.2	-
Methanol	64.6	32.04
DMC	89.8	90.01

Reaction was carried out at 71–76 °C in presence of K<sub>2</sub>CO<sub>3</sub> 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 (*Fig. 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.



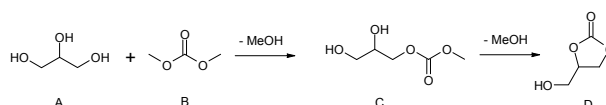
*Figure 1:* Mettler Toledo LabMax Automatic Lab Reactor

### *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.

## Result and discussion

We have developed a convenient method for synthesis of glycerol carbonate from glycerol and dimethyl carbonate (*Fig. 2*) using K<sub>2</sub>CO<sub>3</sub> 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. This mechanism is supported by analytical spectrums. On the analytical spectrums it can be seen that there is an unknown peak at retention time 12.58-12.59, which is probably intermediate C.

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. Fig. 3 contains composition of samples.

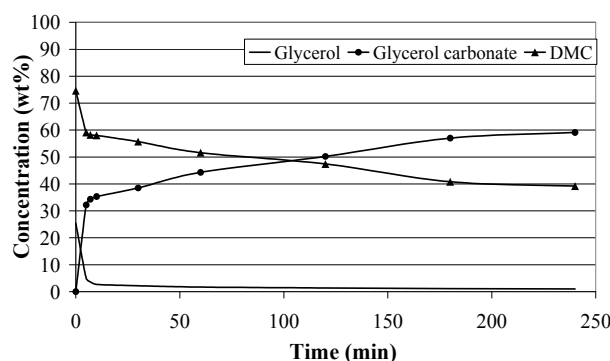


Figure 3: Influence of time on reaction of glycerol and dimethyl carbonate

#### 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. Determination of unknown

parameters can be achieved by using well-carried out experiments to collect accurate analytical data, but nowadays different kind of modeling 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 Fig. 4.



where:

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

$$k_i = k_{i,0} \cdot \exp\left(-E_{A,i}/R \cdot T^R\right), \quad (3)$$

$$i = \{1; 2; 3; 4\}$$

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 as it can be seen in Fig. 4 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. As it can be seen in Fig. 4 the reactions takes place only in the liquid phase since the catalyst doesn't evaporate.

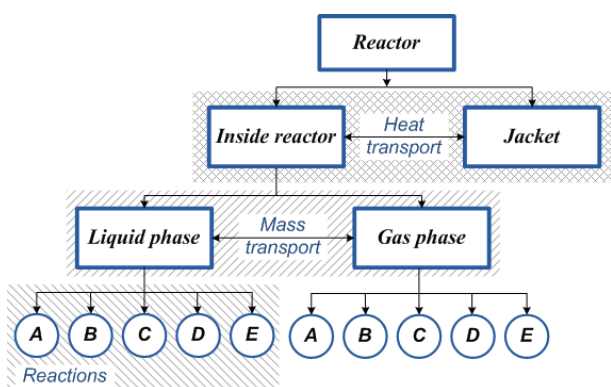


Figure 4: The structure of the reactor model

To check the assumed reaction mechanism the component balances in the liquid phase were completed with component sources based on equations 1-2. 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 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 [11]. 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 [12, 13]. Another application of CMA-ES in an engineering problem can be found in [14].

The result of the identification of missing model parameters is summarized in Table 2 while measured and calculated trajectories can be compared in Fig. 5. 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.

Table 2: Identified reactor model parameters

$k_{01}$ [ $\text{m}^{-3}\cdot\text{mol}\cdot\text{s}^{-1}$ ]	$k_{02}$ [ $\text{s}^{-1}$ ]	$E_{A1}$ [ $\text{J}\cdot\text{mol}^{-1}$ ]	$E_{A2}$ [ $\text{J}\cdot\text{mol}^{-1}$ ]
16.08	664.8	4.40e4	2.12e4
$AK_1$ [ ]	$BK_1$ [ ]	$AK_2$ [ ]	$BK_2$ [ ]
5.122	1.00e4	3.328	5.75e4
$\Delta H_{\text{reac},1}$ [ $\text{J}\cdot\text{mol}^{-1}$ ]	$\Delta H_{\text{reac},2}$ [ $\text{J}\cdot\text{mol}^{-1}$ ]	$\alpha^{\text{RJ}}$ [ $\text{W}\cdot\text{m}^{-2}$ ]	$c_v$ [ $\text{kg}\cdot\text{s}^{-1}\cdot\text{bar}^{-1}$ ]
-4.97e4	-6.43e4	6.057e3	0.2546

As it can be seen in Fig. 5 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.

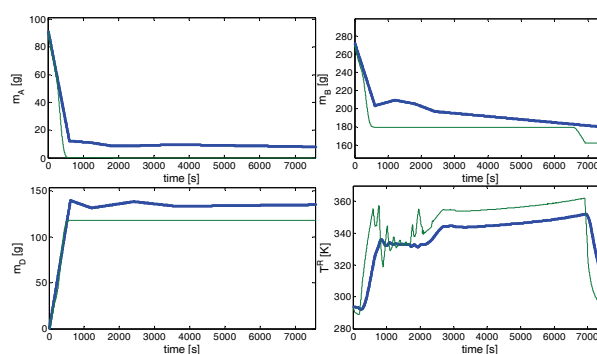


Figure 5: Calculated (thin) and the measured (thick) trajectories of state-variables

#### Summary

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  $\text{K}_2\text{CO}_3$  as catalyst. Resulting glycerol carbonate was obtained in almost quantitative yield. Created reaction mechanism was supported by analytical spectrums. 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.

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