A Kinetic Study of Glycerol Esterification with Acetic Acid Over a Commercial Amberlyst-35 Ion Exchange Resin

IONUT BANU1, GRIGORE BOZGA2*, GHEORGHE BUMBAC1, ALIN VINTILA1, SANDA VELEA2, ANA-MARIA GALAN2, MIHAELA BOMBOS2, OLIUMPI BLAJ2, AUGUSTIN CONSTANTIN CRUCEAN2

1Department of Chemical and Biochemical Engineering, University Politehnica, 1-7 Polizu Str., 011061 Bucharest, Romania
3CPO Medias, 8 Carpatic Str., 551022, Medias, Romania

The increased quantities of glycerol available on the market initiated research efforts oriented to new valorization technologies, particularly by its conversion into medium tonnage chemicals, replacing petroleum derivatives. In this work it was investigated the valorization of glycerol by its transformation in glycerol acetates, by direct esterification with acetic acid, over a commercial Amberlyst-35 resin. Experiments were carried out batch-wise, in an autoclave reactor under controlled working conditions, at temperatures between 95 and 112 °C and initial acetic acid to glycerol molar ratios between 4 and 9. The experimental data evidenced that the glycerol conversion to monoacetate is faster than the next esterification steps. A relatively simple kinetic model was proposed and its parameters were evaluated from the experimental measurements. It proved reasonable predicting capacity for products distribution dependencies on the reactants molar ratio and reaction temperature.

Keywords: glycerol, acetylation, acetic acid, Amberlyst, kinetic model
an autoclave reactor under stirring, in controlled working conditions. A kinetic model was proposed and its parameters were evaluated from the experimental data.

**Experimental part**

As catalyst, we used commercial Amberlyst-35 (Rohm and Haas), having the characteristics given in table 2. The size of the dry grain size was practically smaller than 1 mm (the fraction of dry resin grains with the size larger than 1 mm was negligible). Before use, the resin was washed several times with distilled water and finally with ethanol, in order to remove the water from the pores of the pellets. Finally, the catalyst pellets were dried in an oven at 90°C under vacuum, for at least 12 h. Glycerol and acetic acid of analytical purity were used in all the experiments. The liquid phase esterification experiments were carried out batch-wise in a stainless steel autoclave (BERGHOF) having the capacity of 300 mL, provided with a heat transfer jacket, a magnetically driven mixing impeller and standard transmitters for internal pressure, temperature and impeller rotation frequency.

The reaction temperature was controlled by circulating a low volatility thermal oil, fed from a thermo-regulated bath. The stirring speed was maintained at 1000 rpm, in order to minimize the limiting influence of liquid-particle mass transfer on the process kinetics. The experiments were conducted under a nitrogen atmosphere at 10 bar, at temperatures in the interval 80 - 100°C, initial acetic acid to glycerol molar ratios ranging from 4:1 to 9:1. In all the experiments it was used a catalyst loading of 0.052 g catalyst/g glycerol. The composition analyses were performed by gas chromatography (Varian CP-3800, VF-5ms capillary column, 30 m x 0.25 mm x 0.25 μm). The chromatograph analyses program was calibrated with etalons for glycerol, diacetin and triacetin. The concentration of the monoacetin was calculated by mass balancing among the reacted glycerol and reaction products.

The appropriate amounts of acetic acid and ion exchange resin were charged into the autoclave and heated to approximately 80°C, when it was fed the glycerol in the desired molar ratio and the autoclave was sealed, starting the timing of the experimental run. Further, the autoclave heating was continued until a pre-specified temperature level was reached, which was kept till the final reaction time. The temperature evolution during the reaction was monitored by a thermocouple placed in the autoclave.

### Table 1

**CATALYSTS PERFORMANCES IN THE GLYCEROL ACETYLATION WITH ACETIC ACID**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>Ac:G (mol)</th>
<th>t (h)</th>
<th>Cat (wt %)</th>
<th>Xa (%)</th>
<th>MGA Sel (%)</th>
<th>DGA Sel (%)</th>
<th>TGA Sel (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlyst-70</td>
<td>105</td>
<td>6</td>
<td>10</td>
<td>5</td>
<td>100</td>
<td>0</td>
<td>9.4</td>
<td>85.4</td>
<td>[12]</td>
</tr>
<tr>
<td>Amberlyst-15</td>
<td>80</td>
<td>6</td>
<td>8</td>
<td>5</td>
<td>100</td>
<td>21.1</td>
<td>63.8</td>
<td>15.1</td>
<td>[22]</td>
</tr>
<tr>
<td>Amberlyst-15</td>
<td>120</td>
<td>9</td>
<td>5</td>
<td>10</td>
<td>97</td>
<td>8.5</td>
<td>50</td>
<td>41.5</td>
<td>[24]</td>
</tr>
<tr>
<td>Ag modified HPW</td>
<td>120</td>
<td>10</td>
<td>0.25</td>
<td>1</td>
<td>95.8</td>
<td>48.4</td>
<td>46.4</td>
<td>5.2</td>
<td>[25]</td>
</tr>
<tr>
<td>2wt% Y/SBA - 3</td>
<td>110</td>
<td>4</td>
<td>3</td>
<td>4</td>
<td>100</td>
<td>10</td>
<td>35</td>
<td>55</td>
<td>[26]</td>
</tr>
<tr>
<td>C2H2SO3H/SBA-15</td>
<td>105</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>100</td>
<td>5</td>
<td>62</td>
<td>33</td>
<td>[27]</td>
</tr>
<tr>
<td>SO4²⁻/γ - Al₂O₃</td>
<td>110</td>
<td>9</td>
<td>0.5</td>
<td>5</td>
<td>97</td>
<td>27</td>
<td>50</td>
<td>23</td>
<td>[28]</td>
</tr>
<tr>
<td>SO4²⁻/CeO₂ - ZrO₂</td>
<td>120</td>
<td>3</td>
<td>1</td>
<td>5</td>
<td>~100</td>
<td>25.8</td>
<td>57.7</td>
<td>16.5</td>
<td>[29]</td>
</tr>
<tr>
<td>Act. Carbon ut. with H₂SO₄</td>
<td>120</td>
<td>8</td>
<td>3</td>
<td>4</td>
<td>91</td>
<td>38</td>
<td>28</td>
<td>34</td>
<td>[17]</td>
</tr>
</tbody>
</table>

### Table 2

**CHARACTERISTICS OF THE CATALYST (AMBERLYST 35)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange capacity</td>
<td>4.7 Eq H⁺/g</td>
</tr>
<tr>
<td>Bulk (dry) density</td>
<td>610 kg/m³</td>
</tr>
<tr>
<td>Wet (and swelled) pore fraction</td>
<td>0.4 m³/m³</td>
</tr>
<tr>
<td>Harmonic mean size of grains</td>
<td>0.7 - 0.95 mm</td>
</tr>
<tr>
<td>Surface area</td>
<td>50 m²/g</td>
</tr>
<tr>
<td>Average pore diameter</td>
<td>300 Å</td>
</tr>
</tbody>
</table>

2326  
http://www.revistadechimie.ro  
REV.CHIM.(Bucharest) • 70 • No. 7 • 2019
reaction was registered rigorously and used in the kinetic calculations.

Results and discussions

Using the described procedure, there were performed experiments at different working conditions. The temperature evolutions during the experiments are presented in figure 1 (in the figure are also presented the polynomial interpolations used in the calculations). Note that, besides the evolutions given in figure 1, there was used also another lower temperature regime, not presented in figure, which was registered only after the temperature stabilization (95°C). In what follows, the reaction temperature regimes will be named using the final temperature level, as specified in figure 1. The concentration measurements, performed at different reaction times, were used to calculate the glycerol conversion (fraction of consumed glycerol) and the yields of the three esters, using the relation:

\[
\text{yield of } j = \frac{\text{mole } j \text{ in the mixture}}{\text{initial moles of glycerol}}
\]

The experimental results are presented graphically in the figures 2 to 5, as well as in the next ones, where are compared calculated and experimental values. The most important products of the glycerol esterification process are diacetin and triacetin. The influences of temperature and reactant molar ratio on diacetin and triacetin yields are presented in figures 2 to 5. The maximum TAG yield was around 22 %, being achieved at rather severe conditions (Ac:G=9 and temperature 108 °C, see Figure 5). The time evolutions of MAG and DAG yields present maximum points, being intermediate products (see figures 2, 4, 7 and 9). The most evident are the maxima of MAG evolutions, those of DAG being less pronounced.

As expected, the glycerol conversion increases with the temperature and the reactants molar ratio respectively. From these results it appears that the glycerol conversion to MAG occurs relatively faster than the MAG conversion to DAG, the transformation of DAG to TAG representing the slowest step of the overall esterification process. Practically, the glycerol conversion is achieving the maximum value (around 98 %) in the first three hours, after this reaction time occurring the accumulation of DAG and TAG by the last two steps of esterification process.

Development of a kinetic model for the glycerol esterification process

The glycerol esterification consists of three consecutive-parallel steps, whose stoichiometry is described by the equations:

\[
G + Ac \leftrightarrow MAG + H_2O \quad (r_1)
\]

\[
MAG + Ac \leftrightarrow DAG + H_2O \quad (r_2)
\]

\[
DAG + Ac \leftrightarrow TAG + H_2O \quad (r_3)
\]

Fig. 1. The time evolutions of reaction temperature (points- experimental values; solid lines calculated by polynomial interpolation).

Fig. 2. Temperature influence on glycerol diacetate (DAG) yield. In the figure’s legend are given the reagents molar ratio (Ac:G) and temperature profiles

Fig. 3. Temperature influence on the glycerol triacetate (TAG) yield

Fig. 4. The influence of reagents (Ac:G) molar ratio on DAG yield

Fig. 5. The influence of reagents (Ac:G) molar ratio on TAG yield
As underlined by different studies [1, 30] the product distribution of this process is strongly influenced by the reactions reversibility. Therefore, the accuracy of the chemical equilibrium constants determination is one of the main prerequisites of the esterification process modeling.

In a first step of the theoretical investigation of this process, we calculated time evolutions of reaction mixture composition, using different kinetic models proposed for the process catalyzed by acidic ion exchange resins. In this aim we used the mass balance equations specific for the perfectly stirred batch reactor:

\[
\frac{dn_J}{dt} = - r_{J^-,} \quad J = G, MAG, DAG
\]

Where \( n_J \) = moles number of species J in the bulk liquid; \( r_{J^-} \) = consumption rate of species J (mole/g/s); \( m_{cat} \) = mass of the catalyst in the mixture.

The triacetin (TAG), acetic acid (Ac) and water (W) number of moles in the mixture were calculated from the stoichiometric relations:

\[
n_{\infty} = n_G + n_{MAG} + n_{DAG} + n_{TAG}
\]

(6)

\[
n_{Ac} = n_{Ac,0} - (n_{MAG} + 2n_{DAG} + 3n_{TAG})
\]

(7)

\[
n_{W} = n_{W,0} - n_{Ac}
\]

(8)

As none of the published models provided adequate simulation results, we developed a relatively simple, homogeneous type kinetic model, considering the rate expressions of the three reactions:

\[
\begin{align*}
\eta_1 &= k_1 \left( C_G C_{Ac} - C_{MAG} C_{Ac} \right) \\
\eta_2 &= k_2 \left( C_{MAG} C_{Ac} - C_{DAG} C_{Ac} \right) \\
\eta_3 &= k_3 \left( C_{DAG} C_{Ac} - C_{TAG} C_{Ac} \right)
\end{align*}
\]

(9)

The rate constants, \( k_i \), and the chemical equilibrium constants, \( K_{eq,i} \), are considered temperature dependent:

\[
k_i = A_i \exp \left( - \frac{E_i}{RT} \right), \quad K_{eq,i} = \exp \left( - \frac{\Delta G_{eq,i}}{RT} \right), \quad i = 1, 2, 3
\]

(10)

The liquid phase Gibbs free energies of the three reactions were calculated from the data published by Gelosa et al. [28]: \( \Delta G_{eq,1} = -4834.2 \text{ J/mole} \); \( \Delta G_{eq,2} = 548.9 \text{ J/mole} \); \( \Delta G_{eq,3} = 6957.6 \text{ J/mole} \).

The esterification process model so defined was used to estimate the kinetic parameters \( A_i \) and \( E_i \) involved in the reaction rate expressions (9). The calculus was performed by the least squares method implemented in the Matlab function lsqlin and lsqlinest. The estimated values of the kinetic parameters are given in Table 3. Note that the activation energies values for the three reaction steps are apparent ones, due to global representation of the chemical-physical process and the disregarding of reaction mixture non-ideality.

In the figures 6 to 9 are presented simulated evolutions of the glycerol conversion and transformations yields into DAG and TAG respectively. As observed, the concordance between the calculated and experimental measurements is satisfactory.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>( A_i (L^\text{\textsuperscript{3}} \text{mol}^\text{-1} \text{gcat}^{-1} \text{s}^{-1}) )</th>
<th>( E_i (\text{kJ/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction 1 ((r1) (i=1))</td>
<td>7.312 \times 10^6</td>
<td>8.633 \times 10^6</td>
</tr>
<tr>
<td>Reaction 2 ((r2) (i=2))</td>
<td>2.333 \times 10^6</td>
<td>1.671 \times 10^6</td>
</tr>
<tr>
<td>Reaction 3 ((r3) (i=3))</td>
<td>6.334 \times 10^6</td>
<td>8.7302 \times 10^6</td>
</tr>
</tbody>
</table>

In the figure 10 are presented the observed and simulated evolutions of TAG yields at two initial reagents ratio, which are evidencing an important influence of the Ac:G ratio to TAG yield. The results presented in the figures 6 to 9 are evidencing a trend of stabilization of composition, to the chemical equilibrium state. The proposed kinetic model proved a good predictive capacity of the temperature and composition dependencies of it, is usable in conceptual design studies for glycerol acetylation plants.
Conclusions

The Amberlyst-35 ion exchange resin presents a good catalytic activity in the glycerol esterification with acetic acid. Even at relatively low resin concentration, a practically total glycerol conversion is achieved in a reasonably time, operating batch-wise. The experimental observations are evidencing a relatively fast glycerol conversion, as compared with the following steps of MAG and DAG transformations. In order to obtain high DAG and TAG yields in batch systems, there are necessary high initial reagents molar ratios. Higher product yields are possible in semi-continuously reaction systems, by eliminating the water from reaction mixture, or alternatively, using continuous reactive distillation. A relatively simple kinetic model was proposed, which can be used in the process design studies.

Acknowledgments: This work has been funded by Romanian Government, UEFISCDI Bridge Grant Research Project PN-III-P2-2.1-BG-2016-0324 through the Financial Agreement 80BG/2016.

References