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

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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

As known, the glycerol is resulting as a byproduct from the triglycerides transesterification with alcohols in the aim of biodiesel production, a process largely practiced in the last period. The production of biodiesel in 2020 is estimated to be 42 million cubic meters, which translates to 4.2 million cubic meters of glycerol produced in the market [1].

The rise of biodiesel production registered in the last decades conducted to the increase of glycerol availability and decline of its selling price. This increased supply of glycerol on the market triggered efforts to find new valorization technologies, particularly by its conversion into medium tonnage chemicals, replacing petroleum derivatives.

By its chemical structure and physical properties, the glycerol is one of the most versatile and valuable organic compounds. Chemically, glycerol is a highly functionalized molecule used in the synthesis of more than a thousand chemical products [1-6]. A great number of processes for glycerol conversion into commodity chemicals are based on the heterogeneous catalysis (hydrogenolysis, dehydration, etherification, esterification, oxidation, reforming etc.). An important category of glycerol derivatives are its esters with acetic acid (acetates or acetins). As the glycerol is a tri-alcohol, it has three esterification derivatives (glycerol monoacetate, glycerol diacetate and glycerol triacetate), usually called monoacetin (MA), diacetin (DA), and triacetin (TA), respectively. The acetins have multiple destinations: liquid fuels additive, antimicrobial and emulsifying agent in pharmaceuticals and cigarette filters (triacetin), solvent, plasticizer and softening agent (diacetin); explosives manufacturing, solvent for dye and treatment of animal skin for leather manufacturing (monoacetin).

The acetates of glycerol can be prepared by direct esterification with acetic acid or with acetic anhydride and by transesterification of different organic acetates with glycerol respectively. Among these, the most common way is the glycerol esterification with acetic acid. The main inconvenient of this method is a relatively low triacetin selectivity. However, this can be avoided by eliminating continuously the water from the reaction medium (using an entrainer such as toluene) or by applying the reactive distillation technology. The highest yields in triacetin can be achieved by the glycerol esterification with acetic anhydride, but the method has the drawback of a much higher price of acetic anhydride, as compared with acetic acid. The acetates transesterification with glycerol presents also the inconvenient of low selectivity in di- and tri- acetates[7].

The glycerol esterification with acetic acid is conducted in presence of acid catalysts. From the kinetic point of view, the most convenient catalysts are the mineral acids (sulfuric, hydrochloric, nitric, p-toluenesulfonic acid etc.) soluble in the reaction mixture (homogeneous catalysis) [8, 9]. However, these catalysts present the in-conveniencies of corrosivity, non-reusability and environmental challenges in terms of disposal. These drawbacks of homogeneous catalysts can be eliminated by using solid materials with acidic properties (heterogeneous catalysis). Among the materials featuring the properties of solid acid catalysts the most investigated in the glycerol esterification are: the acidic ion-exchange resins such as those in the class of Amberlyst [10-12], tungstophosphoric acid on different porous supports [8, 13, 14], sulfated zirconia [15], silica functionalized with propio-sulfonic acid [16], active carbon and alumina treated with sulfuric acid [17, 18], different zeolites [19, 20] and mesoporous materials [15, 21]. Reviews of the catalysts performances tested in the glycerol acetylation process were published by Kim et al. [22] and Okoye and Hameed [23] respectively.

Among the tested solid acidic catalysts, the ionexchange resins feature a relatively good activity and selectivity toward di- and tri-acetates, in the direct esterification of glycerol with acetic acid [24]. The performances of the main catalysts used in the glycerol acetylation with acetic acid are presented in table 1.

The aim of this study was to investigate the kinetics of glycerol esterification with acetic acid, catalyzed by Amberlyst-35 resin. The experiments were performed in

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 Table 1

 CATALYSTS PERFORMANCES IN THE GLYCEROL ACETYLATION WITH ACETIC ACID

Catalyst	T (°C)	Ac:G (mol)	t _r (h)	Cat (wt %)	X _G (%)	MGA Sel (%)	DGA Sel (%)	TGA Sel (%)	Ref.
Amberlyst-70	105	6	10	5	100	0	9.4	85.4	[12]
Amberlyst-15	80	6	8	5	100	21.1	63.8	15.1	[22]
Amberlyst-15	120	9	5	10	97	8.5	50	41.5	[24]
Ag modified HPW	120	10	0.25	1	96.8	48.4	46.4	5.2	[25]
3wt% Y/ SBA – 3	110	4	3	4	100	10	35	55	[26]
C3H7-SO3H/ SBA- 15	105	3	3	5	100	5	62	33	[27]
$SO_4{}^{2-\!\!/}\gamma-Al_2O_3$	110	9	0.5	5	97	27	50	23	[28]
SO4 ²⁻ /CeO ₂ - ZrO ₂	120	3	1	5	~100	25.8	57.7	16.5	[29]
Act. Carbon trt. with H ₂ SO ₄	120	8	3	4	91	38	28	34	[17]

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

 Table 2

 CHARACTERISTICS OF THE CATALYST (AMBERLYST 35)

Property	Value
Exchange capacity	4.7 Eq H ⁺ /g
Bulk (dry) density	610 kg/m ³
Wet (and swelled) pore fraction	0.4 m ³ /m ³
Harmonic mean size of grains	0.7 ÷ 0.95 mm
Surface area	50 m²/g
Average pore diameter	300 A

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 μ m). 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 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 figure1. 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:

yield of J=100x $\frac{m \text{ oles } J \text{ in the } m \text{ ix ture}}{\text{ initial moles } of glycerol}$, J=MAG, DAG, TAG (1)



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

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.



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

Development of a kinetic model for the glycerol esterification process

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

$$G + Ac \leftrightarrow MAG + H_2O \qquad (r_1) \qquad (2)$$

$$\begin{array}{l} \text{MAG} + \text{Ac} \leftrightarrow \text{DAG} + \text{H}_2 \text{O} \quad (r_2) \\ \text{DAG} + \text{Ac} \leftrightarrow \text{TAG} + \text{H}_2 \text{O} \quad (r_3) \\ \end{array}$$

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:

$$\frac{dn_J}{dt} = -m_{cat} nr_J, \quad J=G, \text{ MAG}, \text{ DAG}$$

$$t=0, n_J=n_{J0}$$
(5)

 n_{1} - moles number of species J in the bulk liquid; rr_{1} 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:

$$\mathbf{n}_{\mathrm{G0}} = \mathbf{n}_{\mathrm{G}} + \mathbf{n}_{\mathrm{MAG}} + \mathbf{n}_{\mathrm{DAG}} + \mathbf{n}_{\mathrm{TAG}} \tag{6}$$

$$n_{AC} = n_{AC,0} - (n_{MAG} + 2n_{DAG} + 3n_{TAG})$$
 (7)

$$\mathbf{n}_{\mathrm{W}} = \mathbf{n}_{\mathrm{AC},0} - \mathbf{n}_{\mathrm{AC}} \tag{8}$$

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:

$$\begin{aligned} r_{1} &= k_{1} \Biggl(C_{G}C_{AC} - \frac{C_{MA}C_{W}}{K_{eq,1}} \Biggr) \\ r_{2} &= k_{2} \Biggl(C_{MA}C_{AC} - \frac{C_{DA}C_{W}}{K_{eq,2}} \Biggr) \end{aligned} \tag{9} \\ r_{3} &= k_{3} \Biggl(C_{DA}C_{AC} - \frac{C_{TA}C_{W}}{K_{eq,3}} \Biggr) \end{aligned}$$

The rate constants, k,, and the chemical equilibrium constants, K_{eq}, are considered temperature dependent:

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right); \ K_{eq,i} = \exp\left(-\frac{\Delta G_{R,i}}{RT}\right), \ i = 1, 2, 3; \ (10)$$

The liquid phase Gibbs free energies of the three reactions were calculated from the data published by Gelosa et al. [28]: $\Delta G_{R,1}$ = -4834.2 J/mole; $\Delta G_{R,2}$ =548.9 J/mole; $\Delta G_{R,3}$ =6957.6 J/mole. The esterification process model so defined was used

to estimate the kinetic parameters A, and E, involved in the reaction rate expressions (9). The calculus was performed by the least squares method implemented in the Matlab function *lsqcurvefit*. 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 nonideality.

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 3 THE ESTIMATED VALUES OF KINETIC PARAMETERS

	A _i (L ² mole ⁻¹ g _{cat} ⁻¹ s ⁻¹)	E _i (J/mole)
Reaction 2 (r1) (i=1)	7.312.10	8.6533-104
Reaction 3 (r2) (i=2)	2.333-10-4	1.6712-104
Reaction 4 (r3) (i=3)	6.334-10*	8.7302·10 ³



Fig. 6. Simulated and experimental evolutions of glycerol conversion



Fig. 7. Simulated and experimental evolutions of the three glycerol esters yields



Fig. 8. Simulated and experimental evolutions of glycerol conversion (Ac:G=6; T=100 °C).

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.



Fig. 9. Simulated and experimental evolution of the three glycerol esters yields (Ac:G=6; T=100 °C).



Fig. 10. Simulated and experimental evolutions of triacetin yield at two reagents molar ratios (T=110 °C).

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 semicontinuously 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.

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