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Glycerol acetylation catalyzed by an acidic styrene-*co*-dimethacrylate resin: experiments and kinetic modeling

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Abstract

This work reports an experimental study and a kinetic model for glycerol acetylation. A sulfonated resin of styrene cross-linked with ethylene glycol dimethacrylate (EGDMA) was synthesized and applied as a catalyst in the referred reaction. Furthermore, the commercial sulfonated styrene-divinylbenzene resin Amberlyst 36® was also tested in the glycerol acetylation and the results were compared to those obtained with the synthesized resin. The reactions were carried out at two different temperatures: 80 and 90 °C. The experimental data were collected and compared to predictions of a homogeneous kinetic model of a second-order reaction using the Scilab software. The blank experiments had lower conversions than the catalyzed reaction. The difference found between the ion exchange capacities for PSEGDMA $(3.45 \text{ mmol g}^{-1})$ and Amberlyst 36 $(5.45 \text{ mmol g}^{-1})$ did not produce significant differences in the catalysis results. The average R^2 obtained for the model fitting was 0.89733 and the rate constants of the catalyzed portion were found to be in the ranges: $0.01 \times 10^{-5} - 1.30 \times 10^{-5} \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$ for Amberlyst 36 and 0.01×10^{-5} - 2.74×10^{-5} L² mol⁻² min⁻¹ for PSEGDMA. According to the rate constants obtained herein, it is concluded that PSEGDMA resins has a higher efficiency for application in the referred reaction. This conclusion can be verified by calculating the efficiency per catalytic sites, which were 51.78 and 104.24 for Amberlyst 36 and PSEGDMA, respectively. This calculation can be used because it is the same catalyst but supported in different structures, proven by calculating the swelling index of the resins, which are shown in the "Results" section.

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Keywords Glycerol acetylation · Acidic resins · Styrene · EGDMA · Catalysis · Kinetic model

Introduction

Fossil fuel depletion has motivated researchers to implement new technologies in order to prevent a high impact on the environment. Biodiesel is considered a to be a high value fuel for the world, since it is obtained by renewable means, in addition to having no sulfur or aromatics in its composition [1]. However, a major problem occurring during the transesterification reaction to obtain biodiesel, is the formation of a lot of glycerol. Due to its abundance, this by-product cannot be fully accommodated by industry [2]. Over the last decades, studies were conducted to refine the crude glycerol into esters of great commercial interest: mono, di and triacetin. These products can be applied as plasticizers to fuel additives, especially in liquid fuels with octane [2–4]. One route for the formation of these three products is the acetylation reaction, which applies an acetylation agent (acetic acid or anhydride) as one of the reactants [5, 6]. The drawback of acetic anhydride is that it is a controlled acquisition compound, since it can be used for narcotic production [5, 7].

Even promoting autocatalytic esterification, acetic acid is ionized in small proportions and, therefore, the use of cationic ion exchange resins is therefore highly recommended for this type of reaction [8]. In addition, catalyzed reactions promote faster reactions at lower temperatures compared to non-catalyzed reactions. Heterogeneous catalysts are more advantageous than homogeneous ones due to their method of mechanical separation, reuse, non-toxicity, non-contamination and non-corrosivity [3, 9–11].

In recent years, other studies have shown the influence of temperature, type of catalyst and molar ratio and proposed kinetic models to describe the acetylation process. The resin Amberlyst 15 has provided considerably high glycerol conversions (about 97%) with a molar ratio of 3:1 (acetic acid/glycerol) [12] and exhibited higher conversion rates of glycerol with high selectivity over di and triacetin products, compared to other catalysts [11]. However, the use of other commercial resins like Amberlyst 35 [13], Pr-SBA-15 [14], Lewatit catalyst [3] and Ionic liquids [15], as well as other methods like a chromatographic reactor, have favored the reaction [16].

Two kinetic models can be highlighted for the acetylation of glycerol: a homogenous second-order model [2, 17] and a first-order model [4]. In spite of exploring the use of both first and second orders, the literature does not approach the contributions of catalyzed and uncatalyzed reactions separately, as reported by Akbay and Altiokka [18] for *n*-amyl alcohol acetylation. This approach is more precise when comparing the efficiency of different catalysts, which is why it was applied in the present study.

Sulfonated styrene resins cross-linked with triethylene glycol dimethacrylate (TEGDMA) and ethylene glycol dimethacrylate (EGDMA) have already been studied as catalysts in the esterification of isoamyl alcohol with acetic acid, and their performance was promising compared to styrene–divinylbenzene resins [19, 20].

Despite these preliminary results, it is understood that the use of dimethacrylate cross-linkers in the resin formulation is not fully explored. Assuming the extensive use of the resin Amberlyst 36 as a catalyst, allied to the study of new cross-linkers, this work reports the comparison between two sulfonated resins: Amberlyst 36 and PSEGDMA as catalysts in glycerol acetylation. A mathematical model was proposed and fitted to the experimental data, enabling the estimation of the rate coefficients involved in the process.

Experimental method

Materials

The solutions were prepared with distilled water and phenolphthalein was used as indicator in the titrations. The reagents used and their respective purity and supplier were: acetic acid (99.8%—Ultra); nitric acid (1 mol L⁻¹—Dinâmica); hydrochloric acid (0.1 mol L⁻¹—Ultra); sulfuric acid (95–98%—Química Moderna); glycerol (99.5%—Ultra); NaOH (97%—Ultra); Toluene (99.5%—Isofar); Heptane (99%—Synth); benzoyl peroxide (BPO) (72–80%—Vetec); styrene (99%—Sigma Aldrich); ethylene glycol dimethacrylate (EGDMA) (98%—Sigma Aldrich); polyvinyl alcohol (95%—Dinâmica); methanol (100%—Synth). All the reagents were used as received, without purification.

Copolymerization in suspension

The copolymerization reactions were carried out in a 1-L glass reactor at 80 and 90 °C under 350 rpm agitation. This reactor was fed with a liquid phase containing 1% of polyvinyl alcohol (707 mL of water and 0.70 g of PVA used as dispersant), which was purged with nitrogen for 1 h, followed by an organic phase containing the monomers: heptane, toluene and an initiator (benzoyl peroxide) were added. A monomer fraction of 0.4 (vol) was used in the organic phase (21.53 g); 0.4 of crosslinker agent (13.8 g of EGDMA) molar fraction in the monomer mixture; and 0.5 (vol) of toluene in the toluene + heptane mixture (23.93 and 18.77 g of toluene and heptane, respectively) and 1% (mol) of initiator (0.6 g of benzoyl peroxide) in the monomer mixture. The reactions were conducted for 6 h [21].

Sulfonation reaction

The dried copolymer (about 10 g) was kept in contact with sulfuric acid (140 mL, 98%) at 57.5 °C for 1 h under mechanical stirring at 175 rpm. When the sulfonation was finished, the content was diluted in distilled water and the particles were filtered and dried. The resin particles were then washed with distilled water in order to remove all the residual sulfuric acid. The resin was put to rest for 24 h in a volumetric flask with distilled water at a ratio of 1 g of resin to 50 mL of distilled water. One mL of that solution was then withdrawn in duplicate, which was submitted to

titration with a NaOH solution 0.1 mol L^{-1} , using phenolphthalein as indicator. This washing procedure was repeated (replacing the water after each titration) during 10 days and finished when there was no pH variation in the solution containing the particles [22, 23].

lon exchanging capacity

Nitric acid (8 mL, 1 mol L^{-1}) was added to 0.5 g of dried resin and this content was kept at rest during 4 h. The particles were then filtered and left to rest in a 0.1 mol L^{-1} NaOH solution for 24 h. Afterwards, the solution was titrated with a 0.1 mol L^{-1} HCl solution. Equation 1 was used to calculate the ion exchange capacity [24]:

$$IEC = C_{HCl} \cdot \frac{V_{NaOH} - V_t}{w_d}$$
(1)

where IEC is the ion exchanging capacity (mmol g^{-1}), C_{HCl} is the HCl concentration (mmol mL⁻¹), V_{NaOH} is the volume of NaOH solution used in the titration (mL), V_t is the titrated volume of HCl (mL) and w_d is the resin's dried mass (g).

Glycerol acetylation

Glycerol acetylation is a series of reactions between acetic acid and glycerol where acetates are substituted by OH Groups to form mono, di and triacetin according to Fig. 1 (Adapted from [25]).



Fig. 1 Glycerol acetylation scheme. 1-monoacetin and 1,3-diacetin are illustrated but 2-monoacetin and 1,2-diacetin are also likely to be formed

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The reaction in this work was conducted at 80 °C and 90 °C in the presence of 10 g L⁻¹ of resin, with a 4:1 molar ratio (305 and 97 mL of acetic acid and glycerol, respectively) and under mechanical stirring at 350 rpm. Samples were withdrawn at prescribed times and titrated with a solution of NaOH 2 mol L⁻¹.

A Shimadzu Nexis GC 20–30 gas chromatograph, operating with a SH-Rtx-5 column and FID detector, was used to evaluate the medium composition along the acetylation process. Two different setups were used to analyze the samples: one for the acetic acid; and a second for glycerol and its esters. In the quantification methodology for acetic acid, the injection and column temperatures were 160 and 30 °C respectively, while the detector operated at 260 °C. The analysis ramp for the acetic acid started at 30 °C ending at 50 °C at a ratio of 5 °C min⁻¹ [26]. For glycerol and its esters, the injector, column and detector temperatures were 210, 125 and 250 °C respectively. The ramp started and stayed at 125 °C for 5 min and then increased to 160 °C at a ratio of 5 °C min⁻¹ [27]. Before each GC run, the samples were diluted in methanol at the ratio of 0.02 to 0.008 L (sample/methanol) and the analyses were carried out in duplicate.

The samples were submitted to an acid–base titration to quantify the acetic acid concentration and compare it to the GC data. The water concentration was determined through stoichiometric calculation.

Swelling index

After the catalysis process, the moist mass of the resin was measured and then dried until constant weight. The swelling index (S_w) was calculated by dividing the moist mass (w_m) by the dry mass (w_d) of the resin (Eq. 2) [24].

$$S_{w} = \frac{w_{m}}{w_{d}}$$
(2)

Efficiency per catalytic site

The efficiency per catalytic site was calculated by dividing the consumed number of mols of glycerol (mmol) by the number of catalytic sites (mmol). Equation 3 can be used, since both resins (Amberlyst 36 and PSEGDMA) have the same catalytic sites.

$$E_{f} = \frac{N_{C}}{C_{cat}}$$
(3)

where E_f is the efficiency per catalytic site, N_c is the number of mols of consumed glycerol (mmol) and C_{cat} is the catalyst active sites (mmol).

Kinetic model

The esterification of glycerol (G) with acetic acid (AA) is a series reaction which produces monoacetin (M), diacetin (D), triacetin (T) and water (W), as represented by Eqs. 4–6 [2].

$$AA + G \rightleftharpoons M + W \tag{4}$$

$$AA + M \rightleftharpoons D + W \tag{5}$$

$$AA + D \rightleftharpoons T + W$$
 (6)

The rate law (in mol L^{-1} min⁻¹) for these three reactions was written considering a pseudo-homogenous approach, as described in Eqs. 7–9—i.e., absorption/desorption effects were neglected [2, 4, 17].

$$r_1 = -k_1^* C_{aa} C_g + k_2^* C_m C_w$$
(7)

$$r_2 = -k_3^* C_{aa} C_m + k_4^* C_d C_w$$
(8)

$$r_3 = -k_5^* C_{aa} C_d + k_6^* C_t C_w$$
(9)

Here C_I is the concentration of the species 'I' (in mol L⁻¹), while k_j^* is the rate constant (in L mol⁻¹ min⁻¹). Contributions of both uncatalyzed (k_{0j} , in L mol⁻¹ min⁻¹) and catalyzed (k_j , in L² mol⁻² min⁻¹) reactions were considered as shown in Eq. 10 [18].

$$k_{j}^{*} = (k_{0j} + k_{j}C_{S})$$
(10)

Here C_S is the concentration of catalytic sites in the resin (in mol L⁻¹), described in Eq. 11.

$$C_{\rm S} = C_{\rm part} \cdot \rm{IEC} \tag{11}$$

Here IEC is the resin ion exchange capacity (in mol g^{-1}) and C_{part} is the concentration of catalyst particles (in g L^{-1}) loaded to the reaction medium. The rate equation of each species can be written as follows (Eqs. 12–17).

$$\frac{dC_{aa}}{dt} = -k_1^* C_{aa} C_g + k_2^* C_m C_w - k_3^* C_{aa} C_m + k_4^* C_d C_w - k_5^* C_{aa} C_d + k_6^* C_t C_w$$
(12)

$$\frac{\mathrm{d}C_{g}}{\mathrm{d}t} = -k_{1}^{*}C_{aa}C_{g} + k_{2}^{*}C_{m}C_{w}$$
(13)

$$\frac{dC_m}{dt} = k_1^* C_{aa} C_g - k_2^* C_m C_w - k_3^* C_{aa} C_m + k_4^* C_d C_w$$
(14)

$$\frac{dC_d}{dt} = k_3^* C_{aa} C_m - k_4^* C_d C_w - k_5^* C_{aa} C_d + k_6^* C_t C_w$$
(15)

$$\frac{dC_{t}}{dt} = k_{5}^{*}C_{aa}C_{d} - k_{6}^{*}C_{t}C_{w}$$
(16)

$$\frac{dC_w}{dt} = k_1^* C_{aa} C_g - k_2^* C_m C_w + k_3^* C_{aa} C_m - k_4^* C_d C_w + k_5^* C_{aa} C_d - k_6^* C_t C_w \quad (17)$$

The uncatalyzed rate constants were estimated by fitting the model to the results of two experiments conducted without a catalyst (one at 80 °C and one at 90 °C). Equations 12–17 were numerically integrated in Scilab by using the algorithm ODE. The selectivity of a given glycerol acetate 'a' (S_a) was calculated as follows [4, 11–15]:

$$S_{a}(\%) = \frac{C_{a}}{C_{a} + C_{b} + C_{c}} \cdot 100$$
 (18)

Here a, b and c are the three esters formed in the esterification. The confidence interval (CI) with an unknown variance was calculated through the standard deviation, with a t-student equal to 2.447 for a 95% confidence [28, 29].

Results and discussion

Table 1 shows the characterization results obtained for each resin studied and the efficiency per catalytic sites (obtained from Eq. 3).

The presence of ether and ester groups in the PSEGDMA structure may favor resin swelling in the glycerol acetylation medium due to its high polarity [30]. Since DVB is a nonpolar cross-linker, the PSEGDMA had a swelling index value that was 44% higher than that of Amberlyst 36. This network expansion may favor the catalytic activity by improving the contact between the catalytic sites and the reagents, as reported by Soto et al. [31], who found the specific volume of the swollen polymer to be one of the main catalyst properties.

Although Amberlyst 36 has a higher number of sulfonic groups (higher CTI), the comparison between efficiency per catalytic sites (almost 2 times higher for PSEG-DMA) shows that a considerable part of these groups may not participate in the catalysis. This result can be explained by the difference in the length of the cross-linkers. Since EGDMA is longer than DVB, the accessibility of molecules to the inner PSEGDMA regions seems to be higher than in Amberlyst 36.

Table 2 shows the experimental conditions of the acetylation reactions.

Table 1 Ion exchangingcapacity (IEC), swelling index (S_w) and efficiency per catalyticsite after 6 h of reaction	Resins	IEC (mmol g ⁻¹)	S _w	Efficiency catalytic	Efficiency per catalytic site	
				80 °C	90 °C	
	Amberlyst 36	5.45	1.73	51.78	57.88	
	PSEGDMA	3.45	2.49	104.24	108.45	

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Table 2 Glycerol acetylation conditions	Experiments	Resins	$C_{part} \left(g \ L^{-1} \right)$	MR	T (°C)
	B80	Blank	-	4:1	80
	B90	Blank	-	4:1	90
	A80	Amberlyst 36	10	4:1	80
	A90	Amberlyst 36	10	4:1	90
	E80	PSEGDMA	10	4:1	80
	E90	PSEGDMA	10	4:1	90

T temperature, MR acetic acid/glycerol molar ratio, C_{part} catalyst loading

Table 3 Kinetic and equilibrium
parameters fitted with CI for
the uncatalyzed esterification of
glycerol with acetic acid at 80
and 90 °C

Parameter	$T = 80 \degree C$	T=90 °C
$k_{01} \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	15.93 ± 7.81	21.15 ± 11.51
$k_{02} \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	0.09 ± 0.06	0.16 ± 0.09
$k_{03} \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	6.90 ± 5.96	10.52 ± 6.58
$k_{04} \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	0.53 ± 0.79	0.86 ± 0.19
$k_{05} \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	1.65 ± 2.68	1.74 ± 1.84
$k_{06} \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	0.86 ± 0.44	1.27 ± 0.06

Table 3 presents the kinetic constants fitted for the uncatalyzed experiments.

No significant effect can be observed from the results presented in Table 3 when the temperature changes from 80 to 90 °C, even though a slight increase in the rate constants is noted as temperature increases [32]. The parameter with the highest variation was k_{01} (from $(15.93 \pm 7.81) \times 10^{-5}$ to $(21.15 \pm 11.51) \times 10^{-5}$ L mol⁻¹ min⁻¹), which is related to glycerol consumption and monoacetin formation. The literature provides that the range of the kinetic parameters is 6.54×10^{-3} to 7.22 L mol⁻¹ min⁻¹ at 120 °C with a molar ratio of 12:1 (acid/glycerol) for 480 min of reaction at a pressure of 1070 kPa [2]. The higher rate constant values obtained in the literature are expected since their reactions were conducted at a higher temperature and molar ratio.

The modeling results for the experiments without catalyst (blank) are illustrated in Fig. 2. The model fitting provided an average R^2 of 0.89733. Experiments at 90 °C are reported in Supplemental Material (Fig. S1).

Fig. 2 shows a minimal, but important, increase in the concentration of products when the temperature is raised from 80 to 90 °C. 1.86 and 1.96 mol L^{-1} of monoacetin and 0.29 and 0.46 mol L^{-1} of diacetin were obtained at 80 and 90 °C. Very little formation of triacetin was observed for both temperatures. According to these experimental data, there is a consumption of 12.70 (80 °C) and 37.99% (90 °C) of glycerol.

Fig. S2 illustrates the selectivity of blank experiments at both temperatures and the results show the predominance of monoacetin formation among the glycerol acetates for both temperatures. At 80 °C, the selectivities of monoacetin,



Fig. 2 Model fitting with blank experiments at 80 °C. Where M is monoacetin, D is diacetin, T is triacetin, AA is acetic acid, G is glycerol, W is water, (exp) is experimental data and (mod) is model prediction. Molar ratio: 4:1 for acetic acid/glycerol and stirring speed of 350 rpm

diacetin and triacetin are 85.83%, 13.48% and 0.69% rescpectively; at 90 °C, they are 79.48%, 18.85% and 1.66% respectively.

Table 4 shows the comparison of the results obtained in the present study with those found in the literature.

According to Table 4, there is a predominance of monoacetin in all cases, even at high acid concentrations and temperature. For each resin (Amberlyst 36 and PSEG-DMA) at both temperatures (80 and 90 $^{\circ}$ C), the rate constants obtained in the modeling study are shown in Table 5.

Table 5 shows that there are slight differences between both resins according to these kinetic parameters. This suggests that both catalysts operate at the same capacity, even though PSEGDMA has fewer active sites. The contribution of each parameter to the reaction process is shown in Table 6. The literature shows that the range of the kinetic parameters is 0.013×10^{-5} to 262×10^{-5} L mol⁻¹ min⁻¹ at 100 °C with a molar ratio of 3:1 (acid/glycerol) and 2.5% of sulfuric acid in 90 min of reaction [17]. By calculating an average between the k₁^{*}-k₆^{*} values from Table 5, 3.34×10^{-4} L mol⁻¹ min⁻¹ for 80 °C and 4.17×10^{-4} L mol⁻¹ min⁻¹ for 90 °C is obtained. These values are below the average obtained for the aforementioned range achieved at 100 °C (4.41×10^{-4} L mol⁻¹ min⁻¹), as expected.

Table 6 shows that the first reaction (Eq. 4) has predominance over diacetin and triacetin formation. At 90 °C, the k_1 value for PSEGDMA is $(2.74 \pm 0.77) \times 10^{-5}$

$T(^{\circ}C)$	t (min)	MR	X _g (%)	S _m (%)	S _d (%)	S _t (%)	References
80	360	4:1	12.7	85.8	13.5	0.7	This work
90			38.0	79.5	18.9	1.7	
105	240	6:1	73.6	_	-	2.2	[13]
100	30	8:1	11.0	97.4	2.6	0.0	[15]
110	260	9:1	73.2	84.7	13.8	1.5	[4]
125	120		12.5	72.0	25.0	3.0	[14]
	240		37.0	59.0	36.0	5.0	

T is temperature, t is time, MR is the acetic acid/glycerol molar ratio, X_g is the glycerol conversion, S_I is the selectivity of species 'I', G is glycerol, M is monoacetin, D is diacetin and T is triacetin

 Table 4 Conversion and product distribution of glycerol

acetylation in blank experiments

Resin	Amberlyst 36		PSEGDMA	PSEGDMA		
Parameter	$T = 80 \degree C$	T=90 °C	T = 80 °C	T=90 °C		
$k_1^* \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	84.80±22.01	91.14 ± 15.27	84.80±5.10	115.69 ± 27.93		
$k_2^* \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	0.36 ± 0.15	0.44 ± 0.15	0.29 ± 0.20	0.53 ± 0.05		
$k_3^* \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	62.23 ± 40.11	69.36 ± 11.75	69.95 ± 10.71	80.05 ± 23.63		
$k_4^* \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	48.57 ± 15.54	63.02 ± 12.42	29.17 ± 17.62	53.52 ± 20.14		
$k_5^* \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	7.49 ± 0.00	8.44 ± 2.26	7.19 ± 2.01	8.48 ± 5.33		
$k_6^* \times 10^5 (L \text{ mol}^{-1} \text{ min}^{-1})$	3.89 ± 0.59	5.00 ± 1.45	3.47 ± 2.35	4.72 ± 2.26		

Table 5 Global kinetic parameters with CI for catalyzed esterification of glycerol with acetic acid at 80 and 90 $^\circ$ C

Table 6 Kinetic and equilibrium parameters with CI for the catalyzed esterification of glycerol with acetic acid at 80 and 90 $^{\circ}$ C

Resin	Amberlyst 36		PSEGDMA	PSEGDMA		
Parameter	$T = 80 \degree C$	T=90 °C	$\overline{T=80 \ ^{\circ}C}$	T=90 °C		
$k_1 \times 10^5 (L^2 \text{ mol}^{-2} \text{ min}^{-1})$	1.28 ± 0.38	1.30 ± 0.30	2.00 ± 0.22	2.74 ± 0.77		
$k_2 \times 10^5 (L^2 \text{ mol}^{-2} \text{ min}^{-1})$	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.01	0.01 ± 0.00		
$k_3 \times 10^5 (L^2 \text{ mol}^{-2} \text{ min}^{-1})$	1.02 ± 0.11	1.09 ± 0.21	1.83 ± 0.31	2.02 ± 0.63		
$k_4 \times 10^5 (L^2 \text{ mol}^{-2} \text{ min}^{-1})$	0.89 ± 0.04	1.15 ± 0.20	0.83 ± 0.46	1.53 ± 0.52		
$k_5 \times 10^5 (L^2 \text{ mol}^{-2} \text{ min}^{-1})$	0.11 ± 0.01	0.12 ± 0.05	0.16 ± 0.08	0.20 ± 0.14		
$k_6 \times 10^5 (L^2 \text{ mol}^{-2} \text{ min}^{-1})$	0.06 ± 0.00	0.07 ± 0.02	0.08 ± 0.06	0.10 ± 0.06		

 $(L^2 \text{ mol}^{-2} \text{ min}^{-1})$, which indicates that this resin promotes a higher reaction rate than Amberlyst 36 $(k_1 = (1.30 \pm 0.30) \times 10^{-5} L^2 \text{ mol}^{-2} \text{ min}^{-1})$.

Figs. 3 and 4 show the curve-fitting results for the catalyzed experiments.

Fig. S3 shows the glycerol conversion results for both resins at 80 and 90 $^{\circ}$ C, and as can be seen, there is also no considerable difference between the conversions, reaching 89.5 and 87.1% at 80 $^{\circ}$ C; and 91.9 and 93.5% at 90 $^{\circ}$ C, for Amberlyst 36 and PSEGDMA respectively.

Figs. 3 and 4 reveal there are almost no differences between the performance of the resins: at 80 °C both reach a plateau after 100 min in the concentration of monoacetin and the consumption starts at about 150 min for both catalysts at 90 °C. A poor fit can be observed for monoacetin, mainly at 80 °C. Since this process refers to a series reaction, corrections in the kinetic parameters in order to achieve a better fit for monoacetin would negatively affect the fit of the other compounds and the average fit. It cannot be asserted that the higher discrepancies (for monoacetin) between model and experimental data are associated with a specific phenomenon occurring with monoacetin. However, it can be stated that phenomena such as phase separation and catalyst/medium partition of compounds would provide additional parameters that could improve the model fitting.



Fig. 3 Model fitting for the reaction catalyzed by Amberlyst 36 where **a** and **b** 80 °C; **c** and **d** 90 °C. Where M is monoacetin, D is diacetin, T is triacetin, AA is acetic acid, G is glycerol, W is water, (exp) is experimental data and (mod) is model prediction. Molar Ratio: 4:1 for acetic acid/glycerol, 10 g L^{-1} of catalyst loading and stirring speed of 350 rpm



Fig. 4 Model fitting for the reaction catalyzed by PSEGDMA where **a** and **b** 80 °C, **c** and **d** 90 °C. Where M is monoacetin, D is diacetin, T is triacetin, AA is acetic acid, G is glycerol, W is water, (exp) is experimental data and (mod) is model prediction. Molar Ratio: 4:1 for acetic acid/glycerol, 10 g L⁻¹ of catalyst loading and stirring speed of 350 rpm

Nonetheless, this kinetic model is an acceptable approach, since it predicts the profiles depending only on kinetic parameters (Fig. S4).

With respect to the model fitting for the catalyzed reaction at 80 °C, the selectivities of monoacetin, diacetin and triacetin were 43.70, 49.79 and 6.50% for Amberlyst 36 and 43.03, 50.16 and 6.81% for PSEGDMA. At 90 °C the selectivities were 38.37, 53.35 and 8.28% for Amberlyst 36 and 37.60, 53.14 and 9.26% for PSEGDMA (Fig. S5). All information was calculated for 360 min of reaction.

At 30 min of the reaction catalyzed by Amberlyst 36, it presented similar glycerol conversions compared to the blank experiment at 360 min of reaction: 18.66% (80° C) and 25.92% (90 °C). This was similar to the PSEGDMA-catalyzed reaction at 30 min: 11.56 (80 °C) and 29.97% (90 °C). The same can be stated on the selectivities for Amberlyst 36: 70.57, 23.77 and 5.66% at 80 °C and 71.59, 23.01 and 5.40% at 90 °C (mono, di and triacetin); and for PSEGDMA: 78.18, 17.79 and 4.04% at 80 °C and 76.81, 19.40 and 3.79% at 90 °C (mono, di and triacetin). This reveals that the extent of all reactions are not significantly different when comparing autocatalyzed (acetic acid) to catalyzed (acetic acid + SO₃H sites) glycerol acetylation processes.

Table 7 shows a comparison of the glycerol acetylation results from this study with those from other works. There is coherence in the experimental results from the different studies, and the predominance of diacetin formation could be highlighted, even at low temperatures, acetic acid excess and reaction time. This is an expected result since the reaction achieves higher conversions in the presence of a catalyst when compared to the blank reactions.

An interesting aspect is revealed by Table 7. Despite the different reaction times, Amberlyst 15 (wet) at 80 °C and MR = 9:1 had the same glycerol conversion as PSEGDMA, which was conducted with a lower molar ratio.

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Resin	T (°C)	t (min)	MR	X _g (%)	S _m (%)	S _d (%)	S _t (%)	References
Amberlyst 15	_	30	3:1	97.0	31.0	54.0	13.0	[12]
Amberlyst 36	80	360	4:1	89.5	43.7	49.8	6.5	This work
	90			91.9	38.4	53.3	8.3	
PSEGDMA	80			87.1	43.0	50.2	6.8	
	90			93.5	37.6	53.1	9.3	
Amberlyst 15	80	480	6:1	100	21.1	63.8	15.1	[11]
Amberlyst 15 (dried)	110	300	9:1	97.1	7.8	47.7	44.5	[4]
Amberlyst 15 (wet)				93.5	18.5	43.2	38.3	

 Table 7 Glycerol conversion and product distribution of glycerol acetylation by resin

T is temperature, t is time, MR is the acetic acid/glycerol molar ratio, X_g is the glycerol conversion, S_I is the selectivity of species 'I', G is glycerol, M is monoacetin, D is diacetin and T is triacetin

Conclusion

The glycerol conversions obtained in the blank experiments were almost 40%lower than in the catalyzed reactions. Furthermore, Amberlyst 36 and PSEGDMA did not present significant differences in glycerol conversion. At almost the same conversion of glycerol (between 12 and 40%), both blank and catalyzed experiments favor the formation of monoacetin (selectivities ranging from 70.57 to 85.83%), but the latter reached this reaction extent after 30 min of reaction. A kinetic model based on a second-order reversible homogenous reaction was fitted to the experimental data obtained for both resins and took into consideration both uncatalyzed and catalyzed reaction rates, indicating higher catalytic activity for PSEGDMA. The blank experiments not only showed that the reaction can occur without a catalyst, but also that there is a good contribution from the uncatalyzed reaction, almost 14% of glycerol conversion for 80 °C and 41% for 90 °C. Regarding the resins' efficiency as catalysts, PSEGDMA had a lower ion exchange capacity than Amberlyst 36. Conversely, it presented a higher swelling index (favored by the presence of ether and ester groups), which may contribute to a better accessibility of the catalytic sites and, consequently, a higher efficiency per catalytic site, which leads to an equal or even better performance regarding glycerol acetylation.

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