# Bioadditives synthesis from selective glycerol esterification over acidic ion exchange resin as catalyst

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ABSTRACT

In this work, fuel bioadditives production from glycerol esterification with acetic acid was performed over acidic ion exchange resin as acid catalyst in a batch reactor. The influence of several parameters such as temperature, molar ratio of acetic acid to glycerol and catalyst loading on glycerol conversion and product distribution were evaluated following an experimental design. Additionally, the process variables were optimized applying response surface methodology (RSM) based on central composite design (CCD). High glycerol conversion (99.6%) and elevated selectivity towards the interest products triacetylglycerol (TAG = 34%) and diacetylglycerol + triacetylglycerol mixture (DAG + TAG = 88%) were reached at 240 min of reaction time using 4 wt.% catalyst concentration, 393 K reaction temperature and 9:1 molar ratio of acetic acid to glycerol. Also, the catalyst was reusable in five catalytic cycles without regeneration and no leaching of the active species was detected.

## 1. Introduction

Glycerol is low-cost polyol obtained as a byproduct of triglycerides transesterification with methanol or ethanol. In recent years, the fast increase of biodiesel production results in a large amount of generated glycerol. However, considering conventional uses of glycerol, the actual market seems unable to consume all the generated glycerol, which furthermore requires an additional purification step to achieve the industrial grade purity [1]. In this context, it is important to convert glycerin into high value-added products. Glycerol esters production could provide one of the promising approaches because its synthesis contributes to the optimum solution from the technical, economic and strategical point of view. An interesting alternative to glycerol re-evaluation is the production of monoacetylglycerol (MAG), diacetylglycerol (DAG) and triacetylglycerol (TAG) which are widely applied in food, cosmetic, pharmaceutical and plastic industries [2]. However, special interest has been placed on TAG and mixed DAG + TAG which are used as high-quality fuel bioadditives to improve fuel property [2]. Further, the presence of MAG in the final reaction product is not desired because of its relatively high solubility in water [3].

Acetylglycerides production could be performed by the glycerol reaction with acetic acid (esterification) or acetic acid anhydride (acetylation). Particularly, acetylation process with acetic anhydride has considerably higher reaction rate and acetylating ability than esterification reaction using acetic acid. However, acetic anhydride is both much more expensive than acetic acid and hazardous to health [4,5]. Conventionally, glycerol esterification is carried out using conventional Brønsted acid as homogeneous catalysts which are highly corrosive and generate several technical and environmental drawbacks [6]. As an alternative, a variety of materials such as sulfonic or organosulfonic acid functionalized porous materials [7,8], silica supported heteropolyacids [9–13], zeolites and other acid solids [14–16] have been used as solid acid catalysts in order to overcome liquid acid critical limitations. Some heterogeneous catalysts showed good activity in esterification reaction; nevertheless, their costs, complex synthesis and functionalization methods, pore size limitation and reuse are still unresolved issues for industrial applications.

Esterification processes are frequently carried out using two main types of strong acid resins; namely, Amberlyst and Dowex types, composed by polystyrene–divinylbenzene matrix bearing sulfonic acid as functional groups [17]. The high acid site concentration allows the reaction to operate under mild reaction conditions and provides a better selectivity to desired products [18–21]. However, previous studies [22–25] indicated that the catalytic activity of several polymeric resins decreases because of water adsorption on the internal or external surface and sulfur leaching.

In most studies of the acetylglycerides synthesis, Amberlyst-15 resin was applied as a heterogeneous catalyst. This acidic resin showed high conversion and selectivity [26–28]. Goncalves et al. studied the catalytic activity of different solid acids. The results evidence that

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Amberlyst-15 was the most active acid solid, with glycerol conversion of 97% and TAG selectivity of 13% at 383 K and 30 min of reaction time. Additionally, at the used reaction conditions, by-product α-hydroxy acetone (acetol) was obtained via glycerol dehydration. On the other hand, Zhou et al. found a glycerol conversion of 97.1% with the highest TAG selectivity (43.2%) over acidic Amberlyst-15, after 300 min of reaction time at 383 K and using an 9:1 acetic acid to glycerol molar ratio.

Moreover, Kale et al. [29] proposed glycerol esterification with acetic acid via azeotropic distillation in toluene presence as entrainer in order to shift the equilibrium towards the product side. Amberlyst-70 resin shows a better catalytic performance than Amberlyst-15. The reusability tests for both catalysts indicated that glycerol conversion was retained and TAG selectivity decreased. This fact could be attributed to sulfur leaching and/or deposition of carbonaceous products on the catalyst surface. Also, Rezayat et al. [30] achieved approximately 60% selectivity of TAG in the continuous esterification of glycerol with acetic acid in supercritical carbon dioxide (scCO$_2$) at 383 K and high molar ratio (24:1 acetic acid: glycerol) and pressure (200 bar) using the same polymeric resin. The catalyst durability test showed that the solid acid retained its activity even for 25 h, but TAG selectivity decreased significantly.

In this work, an economical and alternative strong acidic ionic exchange resin (Dowex Monosphere 650C) is proposed as catalyst in the acetylglycerides synthesis. At first, the activity, selectivity and stability of commercial polymeric resin were evaluated in glycerol esterification using acetic acid. Also, the parameters influence (acetic acid to glycerol molar ratio, temperature and catalyst loading) on glycerol conversion and selectivity to desirable products TAG and DAG + TAG was studied following an experimental design. Additionally, the process variables were optimized applying response surface methodology based on central composite design and the catalyst reusability was analyzed in five reaction cycles.

## 2. Experimental

The esterification reaction of glycerol with acetic acid was carried out using acetic acid (Anedra, Glacial 99.8%), glycerol (Cicarrelli, 99.9%) and commercial strong acidic ion exchange resin Dowex Monosphere 650C (Dow Chemical Co) as heterogenous catalyst.

The acid sites concentration on polymeric acidic resin was determined by neutralization titration. The solid (0.05 g) was treated with 20 mL of aqueous NaCl solution (1 M) for 1 h at room temperature using sonication. Subsequently, the supernatant was removed by centrifugation and titrated with NaOH aqueous solution (0.01 M) using phenolphthalein as indicator [7]. Additionally, catalyst carbon and hydrogen contents were analyzed quantitatively before and after reaction by elemental analysis performed on Exeter Analytical CEE 440. Moreover, sulfur content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using high-resolution Shimadzu 9000 multitype instrument. Previous analysis, the used solid catalyst was recovered by filtration and washed with ethyl alcohol, in order to remove residues retained on the catalyst surface.

The esterification reaction was carried out in a glass batch reactor with a reflux condenser and a temperature control system. The glycerol was heated in a silicone bath to the required temperature and then acetic acid and catalyst were added into the reactor. In the first stage, the influence of catalyst pretreatment and mass transfer effect was evaluated.

The samples were taken periodically and analyzed by capillary column gas chromatography, using a Hewlett-Packard 4890D instruments equipped with a flame ionization detector (FID) and Perkin Elmer Elite Wax column (15 m length, 0.25 mm diameter and 0.25 μm film thickness). The quantification of all reactants was done via internal standard technique and using specific response factors determined from GC analysis of standard compounds of known composition. Glycerol

**Table 1**
Experimental factors and levels used for the central composite design.

| Variables | Code | Level | | |
|---|---|---|---|---|
| | | −1 | 0 | +1 |
| Temperature (K) | T | 353 | 373 | 393 |
| Acetic acid to glycerol molar ratio (mol/mol) | MR | 3:1 | 6:1 | 9:1 |
| Catalyst loading (wt.%)[a] | CL | 4 | 6 | 8 |

[a] Respect to glycerol weight.

conversion ($X_{Gly}$) and selectivity ($S_{AG}$) to different acetylglycerides (MAG, DAG and TAG) were calculated according to the following expressions:

$$X_{Gly} = \frac{mol_{Gly\ converted}}{mol_{Gly\ fed}} \quad (1)$$

$$S_{AG} = \frac{mol_{AG formed}}{mol_{Gly converted}} \quad (2)$$

The variables effect on the process and the interaction between them were studied using an experimental design. Moreover, the optimization of the variable process was done applying response surface methodology. The proposed experimental design in this study was a full factorial central composite design $2^3$ with face centered. In order to obtain the required data, three experimental factors were chosen: temperature (T), acetic acid to glycerol molar ratio (MR) and catalyst loading (CL) with two levels on each parameter (Table 1). The factor level was selected based on previous reports [3,28] and economic and practical considerations. The selected response factors were glycerol conversion ($X_{Gly}$) and selectivity to TAG ($S_{TAG}$) and DAG + TAG ($S_{DAG + TAG}$).

The experiments were carried out in randomized order to minimize the errors because of possible systematic trends in the variables. The central point experiment was repeated three times in order to determine the variability of the results and to assess the experimental errors. The experimental design and statistical analysis were performed using the commercial software STATGRAPHICS Centurion, version XV. The quality of the developed model was determined by the correlation value ($R^2$) and the statistical significance of the model was evaluated using the analysis of variance (ANOVA).

The catalytic stability was evaluated in five consecutive catalytic cycles using the recover polymeric resin without previous treatment and maintaining the same operating conditions at 240 min reaction time.

## 3. Results and discussion

### 3.1. Influence of catalyst pretreatment

The strong acid cation resin Dowex Monoesphere 650C used in this study consists primarily of a polystyrene matrix with sulphonic groups (-SO$_3$H) coated with di-vinylbenzene (12%) forming gel beads. Water content is around 46–51% and ion exchange acidity obtained by titration over dry polymer is 4.8 mmol g$^{-1}$. This resin is prepared for specific use in heterogeneous reactive destillation columns [31]

In order to verify the influence of resin moisture content on the catalytic performance, glycerol esterification reaction was carried out at 353 K for 240 min reaction time using wet (stock sample) and dry catalyst under the same reaction conditions. Previous to catalytic run, the acidic resin Dowex Monosphere 650C was dried at 353 K under vacuum conditions for 24 h. As shown in Fig. 1, the results indicated that the pre-treatments do not have influence over the catalytic activity. However, resin mostiure has a moderated effect on the selectivity to TAG and DAG + TAG. Thus, it could suggest a similar adsorption affinity of resin for acetic acid and water preventing glycerol access to the
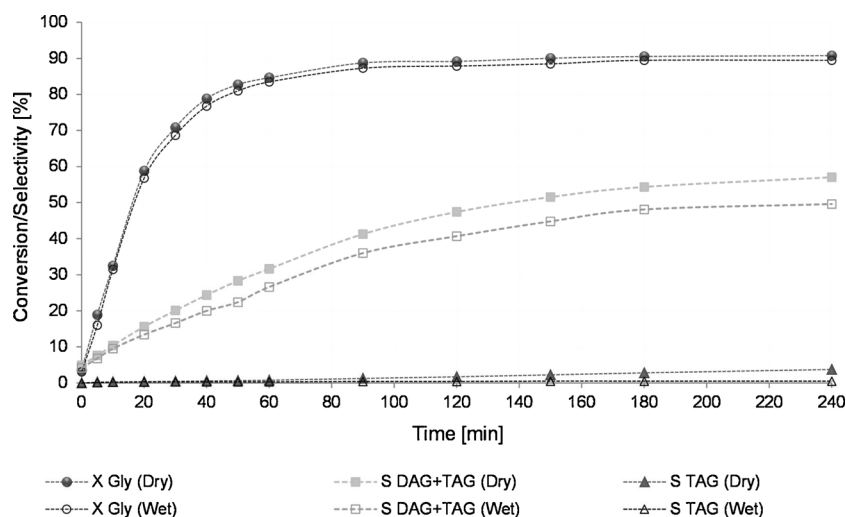
**Fig. 1.** Influence of catalyst pretreatment on glycerol conversion and selectivity to TAG and DAG + TAG (Temperature = 353 K, acetic acid to glycerol molar ratio = 3:1, catalyst loading respect to glycerol = 4 wt.%).

pores.

In general, water in many polymeric resins is adsorbed more strongly than other species and probably concentration gradients can appear. The adsorbed water molecules occupy the acid sites and prevent other species from entering the resin pores [18,32]. Consequently, the kinetics or thermodynamic parameters could be affected compared to a homogeneous catalyst [25], resulting in a lower performance. Moreover, water also promotes the reverse reaction and consequently, eventual hydrolysis of esters is produced [33–35]. Hence, a drying step is desirable in order to minimize esters hydrolysis.

### 3.2. Mass transfer resistance

#### 3.2.1. Effect of external mass transfer

In order to check the influence of external diffusional resistance, glycerol esterification with acetic acid was conducted at different stirring rate and same reaction conditions. The catalyst tests were carried out at 353 K, 30 min reaction time, using acetic acid to glycerol molar ratio of 3:1 and catalyst loading of 4%. Mass transfer is characterized by reactant species and product transport from the bulk-fluid phase to the external surface of the catalyst particle (interphase transport). The results obtained in this study (Fig. 2) indicate that glycerol conversion and selectivity to TAG and DAG + TAG mixture are unaffected by the

stirring speed. Thus, it can be assumed that external mass transfer resistances are negligible. Hence, all further experiments were conducted at a stirring rate of 500 rpm to ensure the absence of external mass transfer resistances.

#### 3.2.2. Effect of internal mass transfer

The existence of mass transfer resistance, inside the catalyst particles was screened using particle with different sizes. The experimental tests were conducted at 353 K, using acetic acid to glycerol molar ratio of 3:1 and catalyst loading of 4%. Initial glycerol conversion and selectivity to DAG + TAG mixture were taken into account for this study. Fig. 3 displays that catalyst particle size have a significant influence on the overall reaction rate under experimental conditions.

The accessibility of active centers in gel type resin depends strongly on the swelling capacity. Additionally, the swollen state porosity and the pore size only depend on the divinylbenzene proportion because cross-linking limits the polymer structure swelling; therefore, it also controls the internal diffusion resistances [36,37]. Previous reports [25,38] indicate that the internal diffusional resistence cannot be neglected in the case of the ion exchange resin with high crosslinking degree (>8%).

It is worth noticing that the smallest particles (<100 μm) glycerol conversion and TAG + DAG selectivity remain constant, pointing out
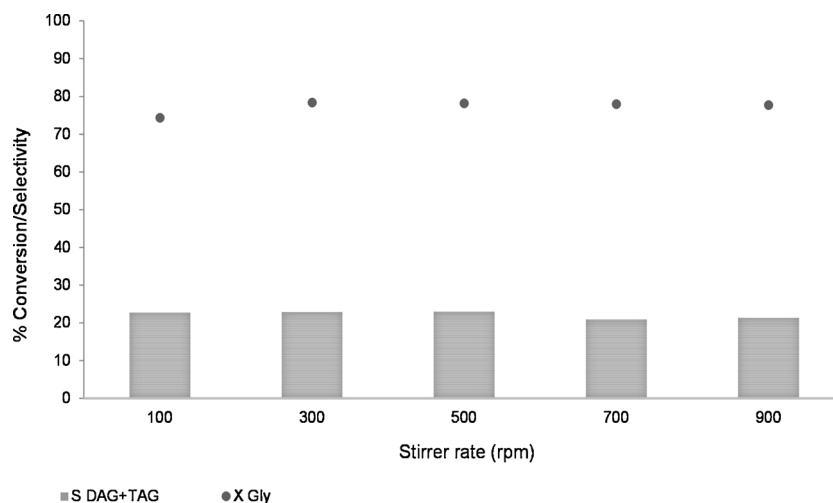


**Fig. 2.** Effect of stirring rate on glycerol conversion and DAG + TAG selectivity (Temperature = 353 K, acetic acid to glycerol molar ratio = 3:1, catalyst loading respect to glycerol = 4 wt.%).

**Fig. 3.** Effect of catalyst particle sizes on glycerol conversion and DAG + TAG selectivity (Temperature = 353 K, acetic acid to glycerol molar ratio = 3:1, catalyst loading respect to glycerol = 4 wt.%).
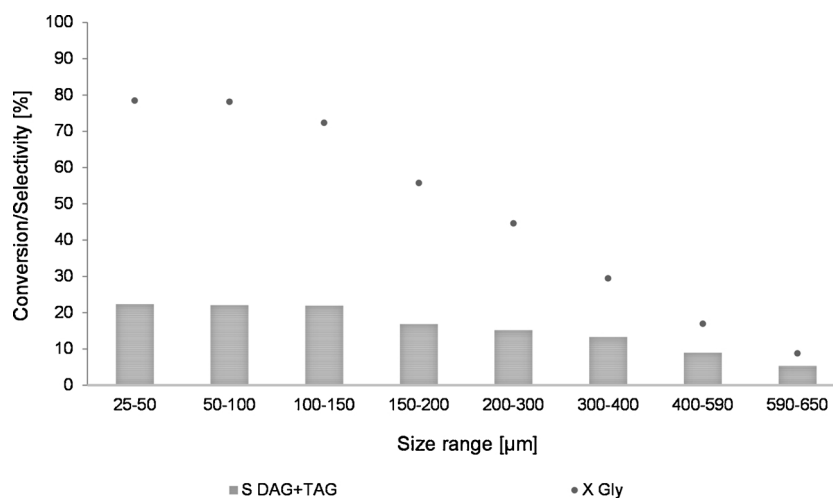
that the intraparticle diffusional limitation can be eliminated making the acid centers easily accessible, therefore this particle sized was used for all further experiments.

### 3.3. Standard esterification of glycerol with acetic acid

At first, the evolution of the reactants and products over time for acetylglycerides synthesis was evaluated in order to set the reaction time at which the experimental design will be performed. To ensure that the reaction equilibrium is not achieved by any experimental tests, the reaction tests were carried out at the highest values of the studied variables (T = 393 K, MR = 9:1, CL = 8 wt.%) defined for the experimental design.

Fig. 4 shows glycerol esterification with acetic acid over time. The evolution of products and reactants evidence a typical curve for consecutive reactions. At initial reaction stage, the glycerol conversion evidences rapid reactant consumption within the initial reaction time. The reaction conversion reaches the maximum value close to 100%. Also, a notably high MG selectivity is observed at low reaction time and drastically decreases to subsequently produce DAG and finally TAG. The intermediary product DAG achieves a maximum after 20 min while TAG attains the equilibrium concentration at 150 min of reaction. At equilibrium (150 min), the products distribution was MAG (12.9%),

DAG (52.8%) and TAG (34.5%). In view of the experimental results, the reaction time for the experimental design was set at 60 min.

For comparative purposes, the non-catalytic glycerol esterification was performed under the same operating conditions. The reaction in absence of catalyst (Fig. 5) proceeds at a visible reaction rate which is associated with the auto-catalytic activity of acetic acid presents in the reaction medium because of its weak acid nature [39]. As it can be seen in the blank test, the chemical equilibrium composition was not achieved at 360 min. Final glycerol conversion was above 95% and MAG and DAG were the major products with selectivities close to 37 and 54%, respectively.

The results obtained in this study (Fig. 4) indicated that the presence of polymeric resin improves the reaction rate, thus confirming that it is a suitable catalyst for acetylglycerides synthesis. In general, the high activity of ion exchange resin is attributed to three main factors: high density of acid sites, polymers matrix swelling ability and preferential adsorption of one compounds [26,32]. It is well known that catalyst acid sites have a considerable influence on the catalytic activity and selectivity [3,7,8,40]. The esterification reaction involves Fischer mechanism. The proton of ion exchange resin proton attaches to the lone electron pair of the oxygen atom of the acetic acid carbonyl group. Consequently, the carbon atom of the carbonyl group becomes positively charged. Immediately after that, the negative charged hydroxyl
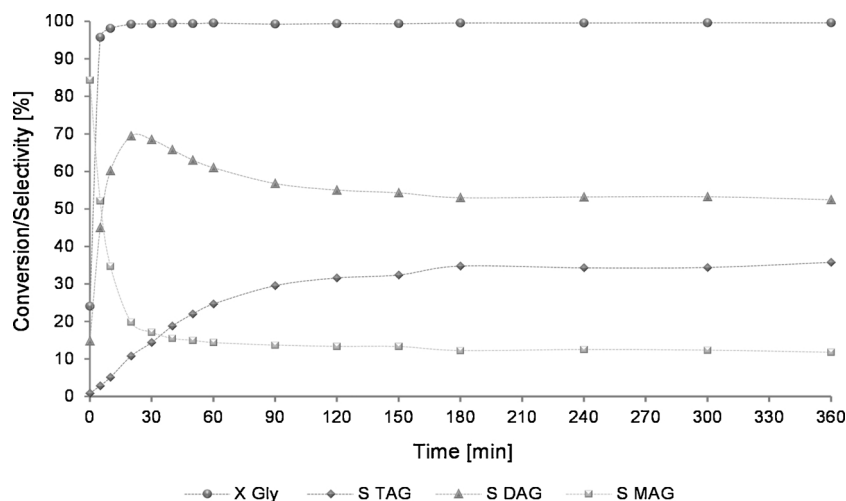


**Fig. 4.** Evolution of products and reactants for the glycerol esterification with acetic acid catalyzed by Dowex Monosphere 650C exchange resin (Temperature = 393 K, acetic acid to glycerol molar ratio = 9:1, catalyst loading respect to glycerol = 8 wt%).
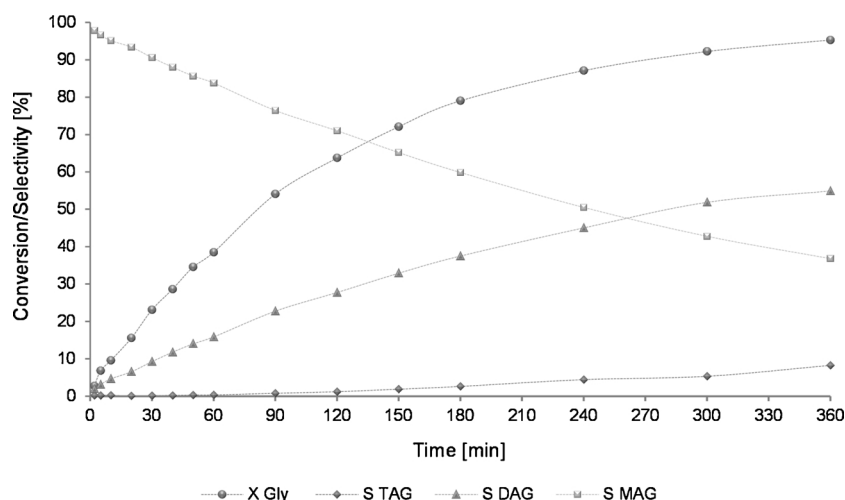
**Fig. 5.** Evolution of products and reactants for the non-catalytic glycerol esterification with acetic acid (Temperature = 393 K, acetic acid to glycerol molar ratio = 9:1).

**Table 2**
Central Composite Design matrix and experimental results of response variables (Stirrer rate = 500 rpm, reaction time = 60 min).

| Run | Type | T (K) | MR | CL (wt%) | $X_{Gly}$ (%) | $S_{TAG}$ (%) | $S_{DAG+TAG}$ (%) |
|-----|------|-------|-----|----------|---------------|----------------|---------------------|
| 1 | Fact | +1 | +1 | +1 | 99.6 | 24.7 | 85.6 |
| 2 | Fact | −1 | −1 | −1 | 84.7 | 0.8 | 31.6 |
| 3 | Fact | −1 | +1 | −1 | 91.8 | 1.5 | 36.2 |
| 4 | Fact | −1 | +1 | +1 | 97.6 | 2.9 | 55.9 |
| 5 | Fact | −1 | −1 | +1 | 89.5 | 1.5 | 45.0 |
| 6 | Fact | +1 | −1 | +1 | 90.5 | 9.2 | 60.2 |
| 7 | Fact | +1 | +1 | −1 | 99.3 | 19.3 | 84.0 |
| 8 | Fact | +1 | −1 | −1 | 90.8 | 7.1 | 59.3 |
| 9 | Center | 0 | 0 | 0 | 97.4 | 7.4 | 72.2 |
| 10 | Center | 0 | 0 | 0 | 97.4 | 5.9 | 70.3 |
| 11 | Center | 0 | 0 | 0 | 97.7 | 8.9 | 74.4 |
| 12 | Axial | 0 | 0 | +1 | 98.0 | 7.5 | 73.6 |
| 13 | Axial | +1 | 0 | 0 | 98.1 | 18.2 | 79.3 |
| 14 | Axial | −1 | 0 | 0 | 95.0 | 1.5 | 44.7 |
| 15 | Axial | 0 | −1 | 0 | 91.0 | 4.3 | 57.5 |
| 16 | Axial | 0 | +1 | 0 | 98.9 | 6.9 | 75.1 |
| 17 | Axial | −1 | 0 | −1 | 97.3 | 4.4 | 65.2 |

**Table 3**
Predictive second order polynomial models obtained from Central Composite design.

| Second order Polynomial models | $R^2$ | p-value | F-ratio |
|---|---|---|---|
| $X_{Gly}$ = -565.80 + 5.516 MR + 3.132 T-0.35 $MR^2$- 0.03312 TCL + 12.92 CL-0.003799 $T^2$ (3) | 0.9873 | 0.0000 | 130.35 |
| $S_{TAG}$ = 752.95-4.079 T-18.81 MR + 0.05333 TMR + 0.005496 $T^2$ +0.001737 TCL (4) | 0.9568 | 0.0000 | 48.78 |
| $S_{DAG+TAG}$ = -3486.85 +17.898T −17.71 MR − 0.02276 $T^2$ + 37.87 CL + 0.07208 TMR-0.09562 TCL-0.53396 $MR^2$ (5) | 0.9911 | 0.0000 | 143.83 |

group of glycerol attack to protonated carbonic acid, leading to the ester formation accompanied by water molecule leasing [41]. Regarding the swelling property, when a gel type resin is totally dry, the polymeric matrix collapses and polystyrene chains will be as close as atomic force allows. Therefore, for catalytic applications, the swelling ability is essential because the swollen gel type resins allow access to the higher amount sulfonic sites found within inner structure [18,42].

### 3.4. Influence of experimental variables and process optimization

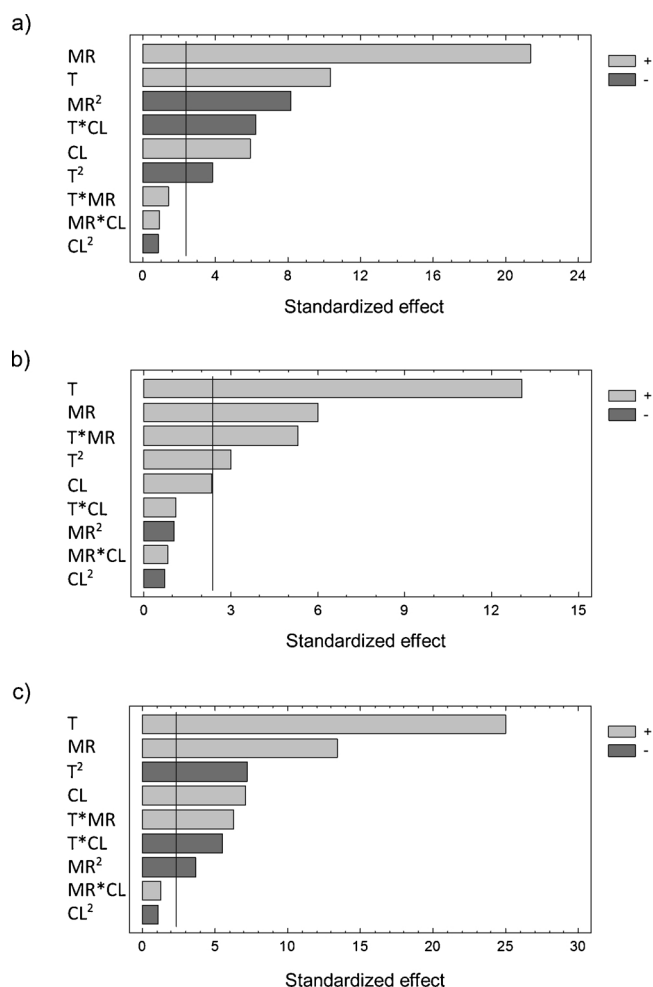The esterification of glycerol with acetic acid was investigated



**Fig. 6.** Standardized Pareto chart for (a) glycerol conversion, (b) TAG selectivity and (c) combined selectivity toward DAG and TAG.

following a three factors Central Composite Design ($2^3$ + stars). A total of 17 experimental tests were randomly carried out to determine the parameters effects. The experimental design included 8 factorial points ($2^n$), 3 center point replications and 6 axial points (or stars points, 2n). The axial points are defined by α value, corresponding to the distance from the center to the start point. The face centered design was selected
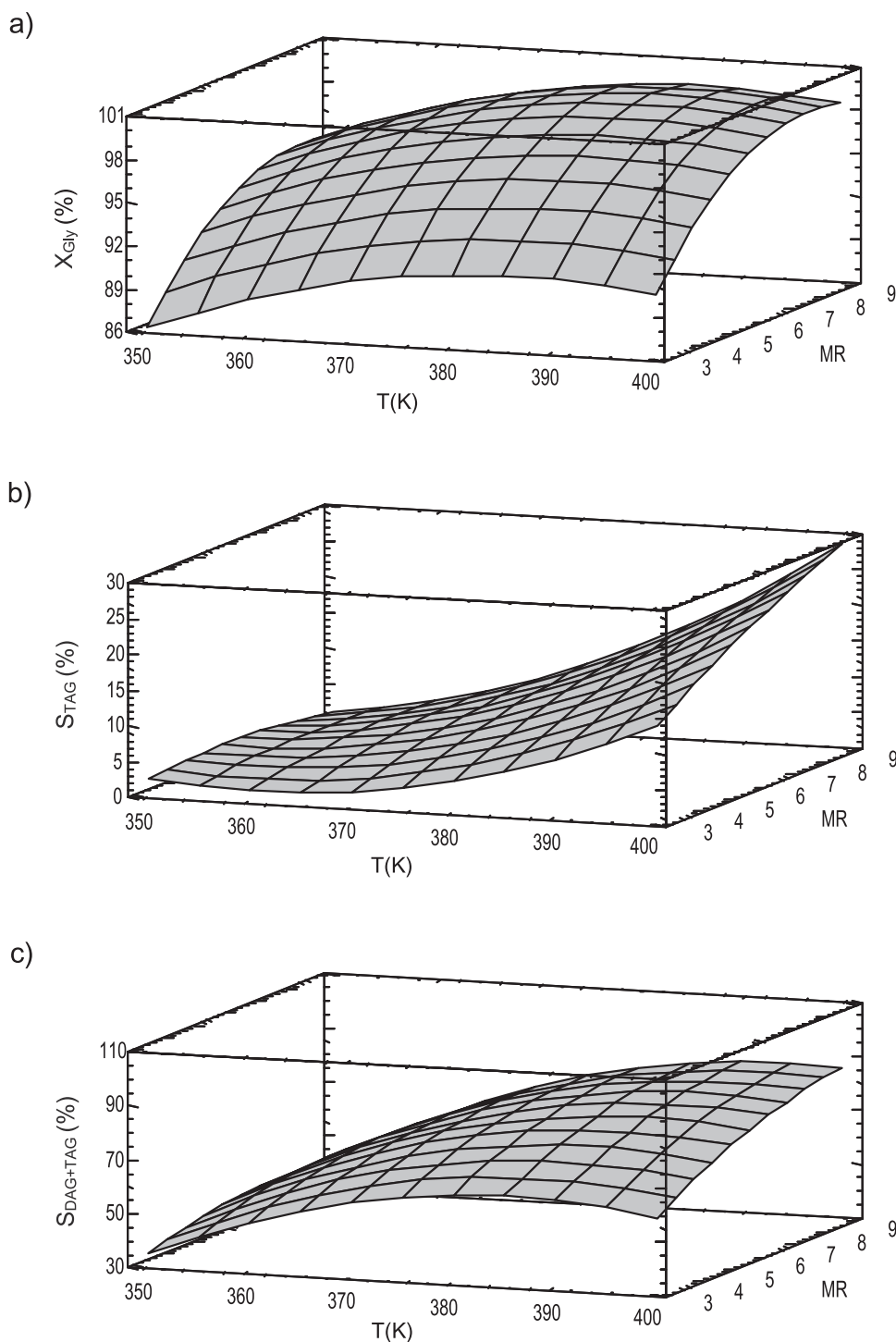
**Fig. 7.** Response surfaces for (a) glycerol conversion, (b) TAG selectivity and (c) combined selectivity toward DAG and TAG (Catalyst loading = 6 wt.%, reaction time = 60 min).

due to its easy implementaction. Therefore, α value was set at 1. The experimental matrix and results of the response factors are shown in Table 2.

According to the high values of the determination coefficient ($R^2$, Table 3), the models for response variables are statistically adequate and can be used to predict the response values. In addition, P-values lower than 0.05 indicate there no lack of fit and the models proposed are considered statistically significant with 95% confidence level. The large values of F-ratio for the three models show high statistical significance for the regression models.

Considering the estimated effects for glycerol conversion (Fig. 6a), the acetic acid to glycerol molar ratio (MR) turns out to be the most significant factor, followed by temperature (T) and catalyst loading (CL); all of them have a positive effect on the responses factor. Additionally, quadratic factors ($T^2$ and $MR^2$) and interaction between T and MR are less significant and even display a detrimental effect evidenced by negative coefficients of the estimated effect. Fig. 7a shows the surface plot of glycerol conversion versus temperature and acetic acid to glycerol molar ratio at 6 wt.% catalyst loading. As it can be seen, MR variable produces an effective rise on glycerol conversion, whereas

**Table 4**
Catalyst loading influence on reaction rate (Stirrer rate = 500 rpm, Temperature = 373 K, acetic acid to glycerol molar ratio = 6).

| CL (wt.%) | $X_{Gly}$[a] | Selectivity (%)[a] | | | TOF (mmol/molH$^+$s)[b] |
|---|---|---|---|---|---|
| | | MAG | DAG | TAG | |
| 2 | 95.1 | 50.5 | 47.2 | 2.3 | 72.4 |
| 3 | 96.5 | 39.4 | 56.9 | 3.7 | 85.2 |
| 4 | 97.3 | 34.8 | 60.9 | 4.3 | 90.4 |
| 6 | 97.4 | 29.7 | 64.4 | 5.9 | 64.5 |
| 8 | 98.2 | 26.4 | 66.1 | 7.5 | 52.2 |

[a] Results corresponded to 60 min of reaction time.
[b] Calculated at initial time.

T variable has a smooth influence on the responses factor analyzed, although it is slightly noticeable at high MR.

The analysis of variance for TAG selectivity (Fig. 6b) recognises T and MR as the principal experimental factors, having a remarked positive influence in the studied range. On the other hand, the quadratic term ($T^2$) and the interaction between MRT and TCL have a slightly positive effect. The response surface plot (Fig. 7b) clearly demonstrates that T and MR variables in values range from medium to high increase TAG selectivity, while values from low to medium have a negligible influence. The 3D plot suggests that TAG selectivity is maximized using high values of MR and T.

As it can be seen in Fig. 6c, the selectivity toward combined DAG and TAG compounds is strongly influenced by the reaction temperature. The second factor in importance is MR followed by the MRT interaction and CL, all of them with positive impact. In addition, $T^2$, $MR^2$ and TCL present little negative effect. Fig. 7c shows the relationship between the experimental factor T and MR and the combined DAG and TAG selectivity. As it can be observed, the T variable has a marked positive impact on low to medium values range, and slight effect from medium to high ranges. On the other hand, it was found that MR shows a higher positive influence at medium and high T. According to the surface plot, the maximum DAG + TAG selectivity corresponds to the highest MR and T values.

Table 3 shows the second order polynomial models Eqs. (3–5) obtained by multiple regression analysis. The statistical models demonstrate the empirical relationships between the independent variables and the response factors. The magnitude of the influence of the experimental variables is related to the value of estimated effects for each response factor (Fig. 6). This analysis removes insignificant terms to improve the optimization results. The statistical significance and fitness

of quadratics models were assessed using the analysis of variance (ANOVA).

In general, the results obtained clearly show that T and MR are the most influential experimental factors in glycerol esterification reaction. Higher temperature increases the reaction rate favoring the production of the di and tri substituted derivatives until reaching the equilibrium. This fact is due to the endothermic nature of the subsequent reactions. From thermodynamic data, it was found that reaction Gibbs free energy relative to MAG and DAG formation is 19.2 kJ mol$^{-1}$ and 37 kJ mol$^{-1}$, respectively, while the value for TAG is 92.5 kJ mol$^{-1}$ [41]. These values explain the cause of low TAG selectivity. Likewise, the acetic acid initial concentration increase in the reaction medium promotes the esterification reaction. Glycerol esterification with acetic acid is controlled by the chemical equilibrium that determines the product distribution that can be obtained at any given temperature [28,41]. Therefore, the excess of one of the reactants shifts the equilibrium towards the side of higher substituted species (DAG and TAG). However, it is important to highlight that the elevated MR (˃9:1) is not attractive for industrial applications [29].

Regarding catalyst loading, the experimental design showed that the catalyst amount has a negligible influence on the glycerol conversion and a moderated impact on the selectivities to TAG and DAG + TAG. For a better understanding of the catalyst influence, additional tests were run out using polymeric resin loading of 2 and 3 wt.%. The initial rate and TOF values (Table 4) indicated that catalyst loading in a range of 1 to 4 wt.% has a strong influence on glycerol conversion, suggesting that the active site concentration plays an effective catalytic role in terms of activity. Besides, TOF values with the catalyst amount increases from 4 to 8 wt.% showed diminutions, indicating that the reaction reached saturation.

The above observations indicated that the maximum production of TAG and DAG + TAG was obtained at 393 K reaction temperature, 9:1 acetic acid to glycerol molar ratio and 4 wt.% catalyst loading. At these operating conditions, the glycerol conversion predicted by the quadratic model is 99.2%, and the selectivity towards TAG and DAG + TAG is 20.7 and 85.3% (calculated Eqs. 3–5). The optimal values obtained from response surface plots were consistent with those obtained from the optimized mathematical equation. The standard deviations were lower than 2% for all response variables. Therefore, the experimental errors are not significant.

In addition, the evolution of the products and reactants over time in the glycerol esterification with acetic acid catalyzed by Dowex Monosphere 650C on the best experimental conditions is shown in Fig. 8. In the catalytic test, glycerol reaches the equilibrium conversion
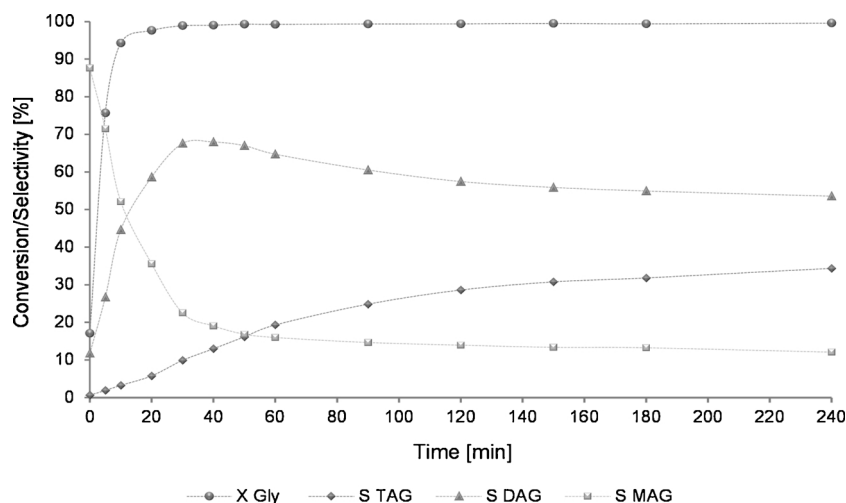


**Fig. 8.** Evolution of products and reactants for the of glycerol esterification with acetic acid catalyzed by Dowex Monosphere 650C exchange resin (Temperature = 393 K, acetic acid to glycerol molar ratio = 9:1, catalyst loading respect to glycerol = 4 wt%).
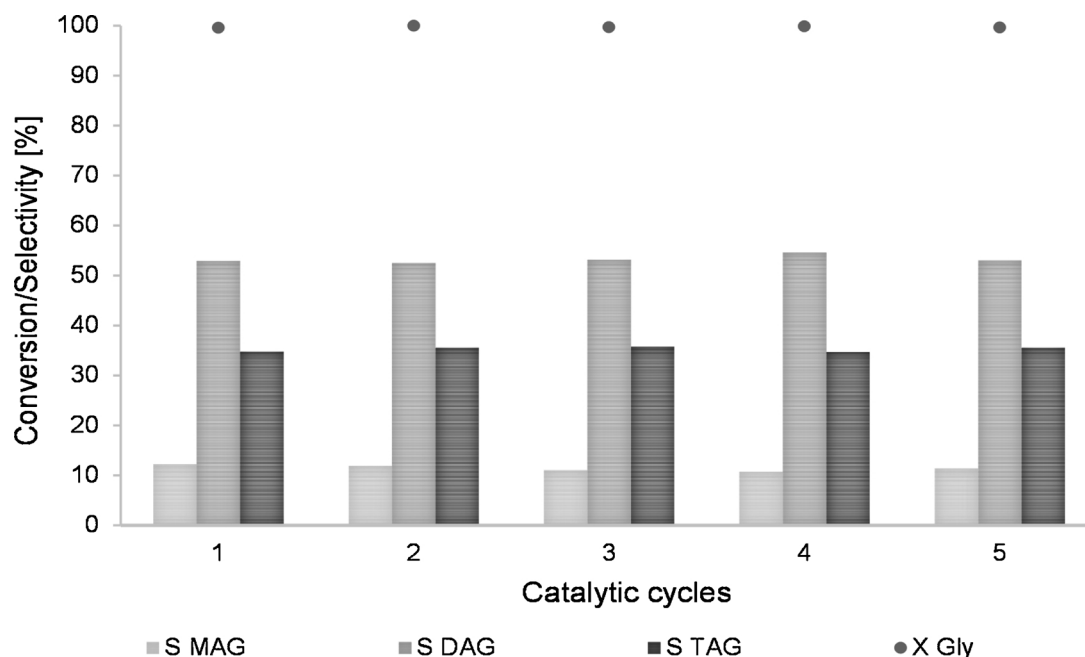
**Fig. 9.** Reuses Dowex Monosphre 650C resin in glycerol esterification with acetic acid (Temperature = 393 K, acetic acid to glycerol molar ratio = 9:1, catalyst loading respect to glycerol = 4 wt.%, reaction time = 240 min).

**Table 5**
Analysis of C, H and S of fresh and spent Dowex Monosphere 650C catalysts.

| Catalyst | C (wt.%)[a] | Element fraction | | |
|---|---|---|---|---|
| | | H (wt.%)[a] | N (wt.%)[a] | S (wt.%)[b] |
| Fresh | 48.4 | 5.2 | 0.3 | 13.8 |
| 5th run | 48.3 | 5.0 | 0.3 | 13.8 |

[a] Determinated by elementary analysis.
[b] Determinated by inductively coupled plasma atomic emission spectroscopy.

($\sim 100\%$) at 30 min of reaction time. The MAG content dropped to values close to 11 wt.% after 240 min reaction time. Also, the DAG and TAG reached a maximum concentration at 30 and 240 min, respectively. The final product distribution at 240 min reaction time was 91 wt.% for DAG + TAG and 40 wt.% for TGA.

### 3.5. Catalyst stability

Concerning catalyst recyclability, the reuse tests were performed at the optimum reaction condition (temperature = 393 K, acetic acid to glycerol molar ratio = 9, catalyst loading respect to glycerol = 4 wt.%, reaction time = 240 min) for five consecutive catalytic cycles. The obtained results are shown in Fig. 9. The catalyst performance was sustained on consecutive batch runs without activity or selectivity loss ($X_{Gly}$ = 100%, $S_{DAG}$ = 54% and $S_{TAG}$ = 34%).

In order to check the polymeric resin integrity after the reuses, carbon, hydrogen and sulfur content in spent catalysts were analyzed and compared with the fresh resin. The results (Table 5) do not show significant differences, these data reveal no sulfur leaching or strongly adsorbed species on the gel-type resin surface. Therefore, it can be concluded that Dowex Monosphere 650C resin has excellent stability and is suitable for glycerol esterification with acetic acid under studied reaction conditions.

### 3.6. Comparison with reported catalyst

The glycerol esterification results obtained in this work using Dowex Monosphere 650C resin as catalyst were compared with several acid catalysts reported under identical reaction conditions (Table 6). In general, the polymeric resin shows high glycerol conversion and selectivity to desired products which are comparable with the homogeneous sulphuric acid catalyst [3]. On the other hand, most of the heterogeneous catalysts included in Table 6 present lower selectivity than acidic polymeric resin used in this work. However, the silica materials functionalized with sulfonic acids [3,8] and supported heteropoly acids [11] have a similar catalytic performance with Dowex Monosphere 650C. Melero et al. [3] obtained glycerol conversion between 78 and 89% with 36–39% TAG selectivity using sulfonic acid functionalized mesostructured materials (Pr-SBA-15, Ar-SBA-15 and F-SBA-15) as catalyst. Nevertheless, Dalla Costa et al. [8] evidenced that propylsulfonic functionalized mesoporous silica (Pr-SBA-15) was deactivated due to sulfonic groups loss and coke deposition during the glycerol esterification reaction. Furthermore, the supported heteropoly acids HPW-ZrO$_2$, HPMo-ZrO$_2$ and HSiW-ZrO$_2$ presented a complete glycerol conversion and TAG selectivity between 30 and 32%. However, this solid catalyst showed glycerol conversion drops during the consecutive uses as consequence of acid components leaching [11].

### 4. Conclusion

The acidic resin Dowex Monosphere 650C was studied in the glycerol esterification reaction with acetic acid. This study showed that the polymeric resin is a suitable catalyst for fuel bioadditive production with a notable activity and high selectivity to the desirable product TAG and DAG + TAG.

Drying step to remove the resin moisture did not have influence over the catalytic performance, but showed a moderated effect on the selectivity toward the desirable product. On the other hand, mass transfer resistance study indicated that glycerol conversion and selectivity to TAG and DAG + TAG are unaffected by the stirring speed and it can be assumed that the external mass transfer resistances are negligible. Moreover, intraparticle diffusional limitation can be eliminated making the acid centers easily accessible using particles smaller than 100 μm.

The analysis of reaction parameters indicated that the temperature and acetic acid to glycerol molar ratio are the most influential

**Table 6**

Glycerol esterification with acetic acid over different acid catalysts.

| Catalyst | Acidity (mmol/g) | Reaction parameters | | | | $X_{Gly}$ (%) | $S_{AG}$ (%) | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | MR | T (K) | CL (Wt.%) | Time (min) | | DAG + TAG | TAG | |
| Blank | – | 9:1 | 393 | – | 240 | 87.1 | 49.5 | 4.5 | This work |
| Dowex 650C | 4.8 | | | 4 | | 99.6 | 88.0 | 34.0 | |
| $H_2SO_4$ | 20.4 | 9:1 | 398 | 4 | 240 | 92.0 | 80.0 | – | [3] |
| Pr-SBA – 15[a] | 1.2 | | | | | 78.0 | 83.0 | 39.0 | |
| Ar-SBA – 15[b] | 1.0 | | | | | 93.0 | 81.0 | 37.0 | |
| F-SBA – 15[c] | 0.3 | | | | | 89.0 | 84.0 | 36.0 | |
| Pr-SBA – 15[a] | 1.8 | 6:1 | 393 | 4 | 150 | 96.0 | 87.0 | 32.0 | [8] |
| HPW-MCM – 41[d] | 0.9 | 6:1 | 373 | – | 360 | 87.0 | 75.0 | 15.0 | [9] |
| HPW-ZrO$_2$[d] | 0.8 | | | | | 80.0 | 40.0 | 5.0 | |
| HPW-ZrO$_2$[d] | 0.2 | 10:1 | 393 | 6 | 240 | 99.2 | 92.7 | 29.9 | [11] |
| HPMo-ZrO$_2$[e] | 0.1 | | | | | 98.2 | 88.0 | 26.0 | |
| HSiW-ZrO$_2$[f] | 0.2 | | | | | 100.0 | 93.6 | 32.3 | |
| Pr-SBA-15 | 1.2 | 6:1 | 353 | 5 | 480 | 100.0 | 84.2 | 19.6 | [7] |
| SO$_3$−H-SBA-15 | 0.8 | | | | | 100.0 | 88.9 | 27.0 | |
| Amberlyst-15 | 4.8 | | | | | 100.0 | 78.6 | 15.1 | |
| Amberlyst-15 | 4.8 | 9:1 | 398 | 4 | 240 | ~86.0 | 84.0 | – | [3] |
| SAC-13 | 0.1 | | | | | ~83.0 | 84.0 | – | |
| Amberlyst-35 | 5.3 | 6:1 | 375 | 5 | 240 | 99.0 | – | 25.9 | [4] |
| Amberlyst-15 | | | | | | 98.6 | – | 25.0 | |
| Amberlyst-70 | 2.8 | 6:1 | 378 | 10 | 240 | 97.0 | 60.3 | 9.3 | [29] |
| SO$_4$$^{-2}$/γ-Al$_2$O$_3$ | – | 12:1 | 383 | – | 300 | 99.2 | 76.8 | 27.3 | [16] |

[a] Pr = 3-Trimethoxysilyl-1-propanethiol.

[b] Ar = Chlorosulfonyl-phenylethyltrimethoxy-silane.

[c] F = 1,2,2-trifluoro-2hydroxy-1trifluoromethylethane-sulfonic acid.

[d] HPW = Phosphotungstic acid.

[e] HPMo = Phosphomolybdic acid.

[f] HSiW = Silicotungstic acid.

experimental variables on the esterification reaction. Besides, the catalyst loading exhibited a saturation for catalyst loading from 4 wt.%. The response surface models evidence that optimal experimental conditions obtained from response surface plots correspond to the reaction temperature of 393 K, acetic acid to glycerol molar ratio of 9:1 and 4 wt. % catalyst loading. After 240 min reaction time and reaction condition, the polymeric resin presented a good performance with high glycerol conversion (99.6%) and elevated selectivity to interest products TAG (34%) and DAG + TAG (88%).

Concerning catalyst recyclability, the experimental results showed that Dowex Monosphere 650C is reusable for five catalytic cycles without activity loss. The used solid characterization confirms the absence of active spices leaching.

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