Autocatalyzed and heterogeneously catalyzed esterification kinetics of glycolic acid with ethanol

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The chemical equilibrium and reaction kinetics in homogeneously and heterogeneously catalyzed systems were investigated for the reversible esterification reaction of glycolic acid with ethanol. In a first approach, the thermodynamic equilibrium of the reaction was established for temperatures between 50°C and 75°C. To differentiate catalytic from homogeneous contribution, the esterification was first studied without catalyst and data obtained were then used to model the autocatalyzed-homogeneous reaction kinetics. The impact of different commercial solid catalysts such as zeolites, oxides and ion-exchange resins over the esterification reaction was also investigated. For the latter, the amount of total acid sites was quantified in order to correlate this parameter to the reaction rate and glycolic acid conversion. Finally, the effects of catalyst loading, temperature, presence of water and recyclability were examined for the most efficient catalyst, Amberlyst 70. Moreover, a kinetic adjustment of the experimental results was carried out by fitting the data to a pseudo-homogeneous model and comparing to adsorption-based models.

Introduction

The esterification of carboxylic acids has been widely studied as it is a highly appealing reaction for the chemical industry. Beyond glycolic acid production, derived esters also find direct applications. The industrial application of glycolates is wide, ranging from solvents, intermediates for the production of fine chemicals, biodegradable polymers, additives for fuels, beauty products and pharmaceuticals. [1–3] The ester production processes such as hydrogenation or partial oxidation generally require catalysts based on precious metals, high temperature and/or pressure.[4] Generally, the production of esters derived from glycolic, catalyzed or not, are petroleum-based.[5] Nowadays, with the transition of the industry to long-term and more sustainable processes, the use of renewable materials as feedstock has been encouraged.[6]Therefore, the development of more efficient, greener and practical ester production processes remains a significant challenge in the modern chemical industry. Under this framework it has even been suggested that esters of carboxylic acids and hydroxy acids with short carbon chain can be recovered industrially from biomass wastes such as black liquor.[7]

At large scale, esterification reactions are usually catalyzed by strong mineral acids (H_2SO_4, HCl, and H3PO4). Still, these homogeneous catalysts have been related to problems such as waste toxicity, corrosion and malfunctions in the industrial set ups.[8] Therefore, there is a need for heterogeneous acid catalysts capable to compete in activity with the traditional homogenous ones. Moreover, with the shift of the chemical industry to greener processes the use of heterogeneous catalyst is privileged.[9,10] The employment of heterogeneous catalysts represents some benefits as providing an ease in the separation of products and catalyst, avoiding laborious separations and recovery processes.[10] Among the most reviewed solid catalysts for the esterification of carboxylic acids are polymer resins,[11–16] zeolites[17–20] and oxides.[21–23]

The esterification of glycolic acid, as well as other carboxylic acids, can be catalyzed by the acid itself. Autocatalysis can be due to undissociated acid molecules of the acid as well as the proton resulting from its dissociation.[24] In order to better describe the kinetics of these reactions, a term that accounts for the autocatalysis phenomenon was added to the homogeneous model traditionally employed.[24] For glycolic acid, the use of this so-called homogeneous-autocatalyzed model was not found in the literature. However, it has already been described for short chain carboxylic acid esterification reactions, primarily in studies of acetic and lactic acids.[13,24–27]

Studies on the heterogeneously catalyzed esterification of glycolic acid mainly report the use of ion exchange resins,[4,28,29] heteropolyacids,[30] and super acids (TiO_2/SO_4^{2-} , SO_4^{2-}/ZrO_2, $SO_4^{2-}/ZrO_2/La^{3+}$).[31–33]The use of enzymatic catalyst has been also investigated for this reaction.[3] Concerning the alcohol involved in the reaction, research has mainly been focused short chain alcohols (C1-C4) as the case for most of others carboxylic acids esterification.[4,28,30–32,34,35] Glycolic acid esterification with fatty alcohols ranging from C8-C16 has also been studied.[3]It is important to highlight that even though the employment of an acid catalyst can increase the rate of esterification, it does not determine its end point due to the fact that this type of reaction is governed by thermodynamic equilibrium.[36]

Usually, the conception of separation and recovery process requires, among other things, information on the reaction kinetics to correctly model the reaction-separation unit.[37] Several studies have been addressed on the reaction kinetic models in presence of solid catalysts. The reported studies focus on not only pseudo homogeneous models but also adsorption models such as Langmuir-Hinshelwood and Eley-Rideal.[14,38–42]

This study focuses on the esterification reaction of glycolic acid with ethanol as a reaction model (Scheme 1). Preliminary tests were performed in order to determine the nature of the autocatalytic activity and to obtain the optimum operational parameters, which were later employed in the catalytic screening. A variety of zeolites, resins and oxides were selected as heterogeneous acid catalysts for the catalytic test. Following the screening study, for the best performing catalyst, the

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influences of water, temperature and catalyst loading were investigated. Finally, kinetic parameters were obtained by fitting the experimental data to the most commonly employed kinetic models.

Scheme 1 Esterification reaction of glycolic acid with ethanol

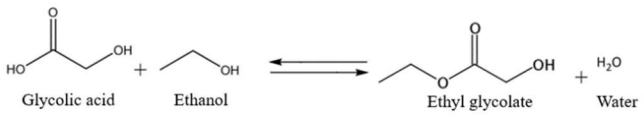
Experimental

Materials

Synthetic pure glycolic acid (Alfa Aesar 98 %), anhydrous ethanol (VWR Chemicals) and ethyl glycolate (Aldrich 98 %) were used without further purification. All catalysts tested were commercial. Five different zeolites (powder) were screened: Pentasil (MFI) 40:1 Si/Al, ZSM-5 11.5:1 Si/Al and Faujasite (FAU) 40:1 Si/Al were supplied by Zeolyst and FAU 2.5:1 Si/Al and Mordenite (MOR) 10:1 Si/Al from Alfa Aesar. Six resins were also selected for this study: Amberlyst 15, 36 and 70 were supplied by Dow Chemicals whereas Dowex 50XW8100 and Nafion NR50 were purchased from Sigma Aldrich. Titanium oxide IV (powder) was also acquired from the latter supplier.

Experimental Procedure

The study on the autocatalytic esterification of glycolic acid with ethanol, as well as the heterogeneous catalytic tests, were carried out in a stainless steel autoclave (120 mL) operating in



batch mode. The temperature inside the reactor was controlled within ±0.5 °C. Solid catalysts were suspended in the reaction mixture by mechanical stirring. A rubber seal allowed sampling by means of a syringe and needle, thus granting to work in a closed system.

All reactants were weighed and then loaded into the reactor, when working with heterogeneous catalysts, the latter was charged directly with the reactant solution as the system worked in batch mode. The zero time for a given run was established as the time at which the reaction medium reached the set temperature.

Analytical Methods

Each sample was filtered with hydrophobic syringe filters (0.45 µm), diluted (1g sample/10 g ACN) in a pre-cooled vial containing acetonitrile (ACN) and kept in the freezer until analysis. The analysis of the compounds (glycolic acid, ethanol, and ethyl glycolate) was carried out by HPLC Shimadzu with a Phenomenex Kinetex XB-C18 column (250x4.6 mm), equipped with a refractive index and a UV detector. The mobile phase employed was acidified water (0.0025 N H_2SO_4 and acetonitrile in a 90/10 (v/v %) proportion. Glycolic acid and glycolate ester are detectable in UV at a wavelength of 210 nm whereas ethanol was analyzed by refractive index. Solutions of known concentrations were used as external standards. The correlation of the concentration to the peaks area allowed to determine the concentration of each compound (ESI).The concentrations obtained by HPLC analysis were used to calculate the evolution of the molar concentration with reaction time. From the data obtained, selectivity and yield were calculated using the equation shown below.

$$Acid\ conversion\ (\%) = \frac{n_{iacid} - n_{acid}}{n_{iacid}} * 100 \quad (1)$$

$$Yield\ [\%] = \frac{n_{ester}}{n_{iacid}} * 100 \quad (2)$$

Where n_{iacid} and n_{acid} represent the number moles of acid at t=0 and at the corresponding sampling time respectively, and n_{ester} corresponds to the number of moles of ethyl glycolate produced. Due to the lack of an instrument capable of determining the amount of water such as Karl Fischer, the mass balance could not be determined. However, to corroborate the reliability of the analysis method, a carbon balance was formulated as illustrated by equation 3. Additionally, it has been shown that the experiments are repeatable with a margin of error of ±5% as illustrated in the ESI.

$$Carbon\ balance\ (\%) = \frac{(n_{iacid}*2)+(n_{iEtOH}*2)-(n_{acid}*2)-(n_{EtOH}*2)-(n_{ester}*4)}{(n_{iacid}*2)+(n_{iEtOH}*2)} * 100 \quad (3)$$

Titration of Acid Catalytic Sites

The potentiometric titration of the solid catalyst was carried out with a compact titrator Mettler Toledo G20S. The protocol followed for this measurement was the same for all the catalysts, 250 mg of fresh catalyst, previously dried at 100° C for one hour, was suspended by stirring in 50 mL of a 0.1 M NaCl solution and 0.1 M NaOH solution was used as titrant. The Gran plot method was applied to determine equivalence points corresponding to strong, medium, weak and total acidities, as described by K. Yu et al,.[43]

Results and discussion

Autocatalyzed reaction

The first steps aimed to optimize the parameters for the catalytic study on the esterification of glycolic acid with ethanol as well as to get an insight into the autocatalyzed nature of this reaction. The influences of temperature, acid/alcohol ratio and the presence of water in the initial reaction mixture were investigated in the absence of an external catalyst. Table 1 summarizes the experiments carried out for the parametric study.

Table 1. Summary of the parametric study experiments

Parametric study		
Temperature [°C]	Acid/Alcohol [mole ratio]	Water/Alcohol [mole ratio]
50	1/4	-
60	1/4	-
70	1/4	-
75	1/4	-
60	1/3	-
60	1/6	-
60	1/4	1:3

In studies on the esterification reactions of glycolic acid, the formation of by-products has been reported, with glycolide being the most common one.[2] Moreover, products of the

polymerization of glycolic acid have been described as relevant by-products in the distillation of glycolic acid with glycol. The sutdy reports on by-products formed from 2-4 glycolic acid molecules: (2- Hydroxyacetoxy) - acetic acid, 2- (2 - Hydroxyacetoxy) - acetoxyacetic acid and 2- (2 - (2 "- Hydroxyacetoxy) - acetoxy) - acetoxyacetic acid.[44] However, the presence of by-products was not found in the experiments carried out in this work. Additionally, the ethyl glycolate yield matched glycolic acid conversion in all experiments. Furthermore, the carbon balance determined using equation 3, meant the formation of by-products could be ruled out.

Influence of the temperature

The temperature was varied between 50-75°C. Tests at higher reaction temperatures were excluded due to possible degradation of the glycolic acid, and to avoid ethanol stripping. In addition, reactions below 50°C slowed down to the point where hardly any conversion was observed. Figure 1 compares the glycolic acid conversion at four different temperatures.

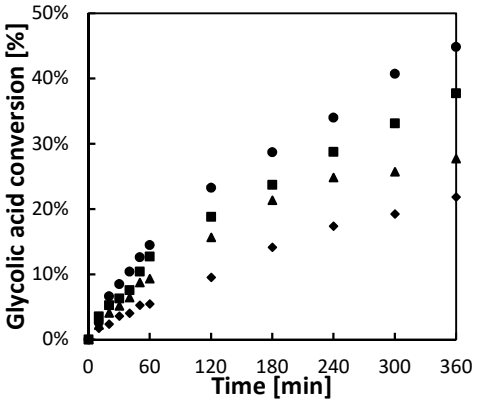


Figure 1. Temperature influence in the esterification reaction. Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm. (●) 75°C ; (■) 70°C; (▲) 60°C; (◆) 50°C.

Sun et al. [45] demonstrated that an esterification reaction with ethanol working close to its boiling point of the ethanol (78°C at atmospheric pressure) can lead to a higher conversion. However, past this point the conversion declines because the vaporized ethanol filling the head space of the reactor is no longer available for the reaction.[45] Since the initial reaction rate is directly correlated to the temperature, it is logical to observe that when the temperature decreases, the reaction slows down. It was also noted that even at 75 °C, equilibrium was not obtained after 6 hours of reaction.

Influence of the Acid/Alcohol ratio

The stoichiometry of the glycolic acid esterification requires an equimolar ratio between the alcohol and the acid. However, due to the low solubility of glycolic acid in ethanol at molar equivalences of 1 to 3, the selected molar ratios for the study of the impact of the acid to ethanol ratio were 1/3, 1/4 and 1/6. Figure 2 compares these three molar ratios for the glycolic acid conversion.

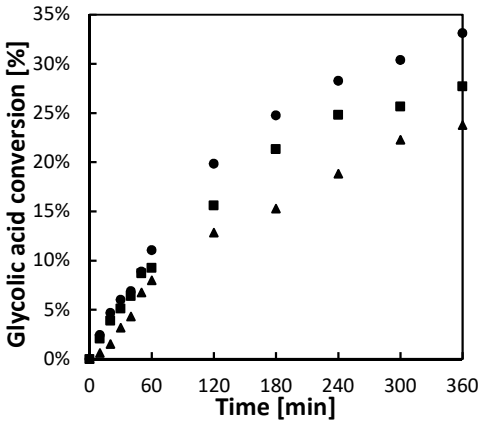


Figure 2. Acid/Alcohols molar ratio influence in the esterification reaction. Conditions: 60°C, 1400 rpm. (●) 1/3; (■) 1/4; (▲) 1/6.

At first glance, the ratio between the two reactants has little influence on the reaction speed within the first hour of reaction for the ratios 1/3 and 1/4. However, regarding the more diluted system a clear trend is marked. At stronger acid concentrations the reaction is favored while in dilute systems the reaction rate decreases.

The initial reaction rate was determined for all experiments by plotting the glycolic acid concentration against time and performing a linear regression of the data on the early part of the curve. Figure 3 illustrates the influence of the acid/alcohol molar ratio on the initial reaction rate, where a direct relationship between the initial reaction rate and the acid concentration was found.

This trend can be explained by the nature of the reaction. It is known that esterification reactions can be catalyzed by acids, hence a higher concentration of acid should favor the reaction due to a higher concentration of protons in the medium. This behavior has already been described in literature, as for example in the kinetics study of the esterification of acetic acid with isobutanol by M.R Altıokka and A. Çıtak.[39] The authors concluded that in these reactions, the relationship between the initial reaction rate and the alcohol concentration is linear at low alcohol concentrations, and the two variables become of each other at high alcohol concentration.[39]

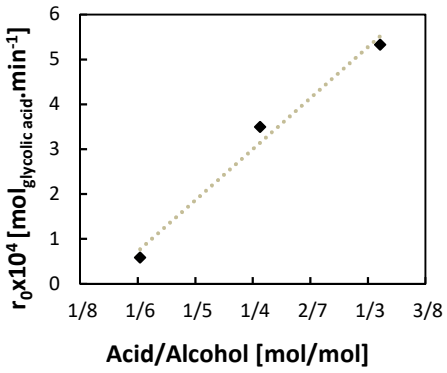


Figure 3. Acid/Alcohols molar ratio influence over initial reaction rate. Conditions: 60°C, 1400 rpm

Influence of the water content

The ffect of adding water to the initial reaction medium was studied. Water was added to the initial mixture with a water/ethanol molar ratio of 1 to 3, which corresponded approximately to 10 % wt. Figure 4 illustrates the impact of this on the reaction rate and conversion. The addition of water to the initial reaction medium strongly affects the reaction by decreasing the conversion and slowing down the reaction rate. As the reaction has not reached the equilibrium, the inhibitory effect of the water presence in the departure solution may be attributed to dilution of the system. As previously mentioned, a high concentration of acid in the solution favors the conversion, therefore it is as expected that a drop in the glycolic acid conversion is observed due to the dilution of the catalyst, glycolic acid itself, in the reaction medium.

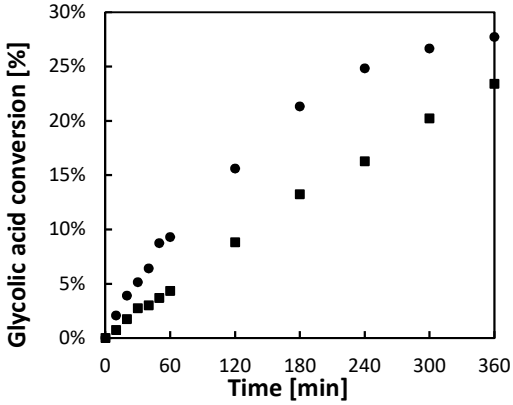


Figure 4. Influence of the water presence in the initial mixture Conditions: Acid/Alcohol 1/4 [mol/mol], 60°C, 1400 rpm. (●) No water added; (■) Water/Ethanol 1/3 [mol/mol]

After the preliminary study of the operational parameters, it was concluded that the optimal temperature for the reaction is 70°C. Even though at 75°C slightly better conversion was achieved, working so close to the boiling point of the ethanol might cause ethanol volatilization from the liquid phase reaction. Additionally, it was found that there is a direct linear correlation between the acid concentration in the medium and the reaction rate. Finally, it was also determined that presence of water in the initial reaction mixture has a great influence on the reaction whereby the rate is slowed down significantly.

Kinetic model

Thermodynamic equilibrium

Little information is found in literature on the thermodynamic equilibrium in the esterification of glycolic acid with ethanol. In the absence of a literature reference value, the concentration equilibrium constant was calculated using the equilibrium compositions determined in experiments on a homogeneous system, catalyzed by H_2SO_4, at different temperatures (ESI).

To account for the non-ideal mixing behavior of the bulk liquid phase, the activity of the components(K_γ) was used instead of the concentration of the components (K_x). Considering that molecules with different sizes and molecular interactions are found in the solution, the mixture cannot be considered as an ideal system and so a model capable of representing these non-idealities is required. In strongly non-ideal systems at low pressure (P < 10 bar) it is standard procedure to use an activity coefficient model to describe behavior far from ideality, such as UNIFAC, UNIQUAC or NRTL.[46]

Correlative models such as NRTL or UNIQUAC are preferred if the experimental parameters are known. Otherwise, in the absence of experimental data, as is the case here, UNIFAC can be employed as a predictive model.[47] For a non-ideal liquid phase reaction, the chemical equilibrium can be described by the expression:

$$K_{Eq}(T) = \prod_i \gamma_i x_i^{v_i} \qquad (4)$$

In which v represents the stoichiometric coefficient, γ the activity coefficient and x the molar fraction at the equilibrium for each component i in the mixture. This can be translated as the product of the ratio of the molar fractions of the products over the reactants, by the ratio of the activity coefficients of products over reagents, for a reaction in general. The equation below represents this expression fitted to the studied reaction.

$$K_{Eq} = K_x\, K_\gamma = \left(\frac{x_{EG}\, x_{H2O}}{x_{GA}\, x_{EtOH}}\right)_{eq}\left(\frac{\gamma_{EG}\, \gamma_{H2O}}{\gamma_{GA}\, \gamma_{EtOH}}\right)_{eq} \quad (5)$$

In which x_{EG}, x_{H2O} and γ_{EG}, γ_{H2O} represent the products (ethyl glycolate and water) concentrations and activity coefficients calculated at equilibrium, and x_{GA} , x_{EtOH} and γ_{GA}, γ_{EtOH} represent the reactants (glycolic acid and ethanol) concentrations and activity coefficients at equilibrium. The activity coefficients of glycolic acid, ethanol, ethyl glycolate and water were estimated by using the UNIFAC model, using the equilibrium compositions for a temperature range of 50°C-75°C. The obtained values were used to plot a Van't Hoff diagram, shown in Figure 5, from which it was possible to extract the information on the equilibrium constant as a function of temperature. Equation 6 represents the correlation obtained from the regression of the experimental data on activity coefficients.

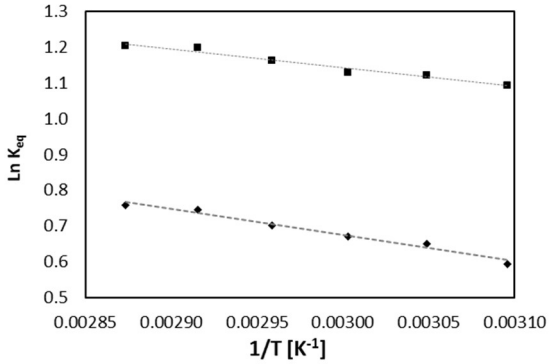


Figure 5. Van't Hoff diagram for glycolic acid esterification ethanol regressed from experimental data (■) Molar concentration and activity; (◆) Molar concentration.

$$Ln(K_{eq}) = 2.7 - \frac{523}{T} \qquad (6)$$

The Van't Hoff diagram shows that the slopes of the curves present a similar trend. Still, the K_{eq} and K_x values differ by a factor around 1.5-1.6, confirming that the behavior of the system is far from ideal within this range of temperatures. Moreover, using the regression extracted from the Van't Hoff plot, it is also possible to estimate the values of the entropy and enthalpy of the chemical reaction as it is shown by the correlation:

$$Ln\ K_{eq} = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R} \qquad (7)$$

Where, $\Delta_r H^\circ$ and $\Delta_r S^\circ$ represent the standard enthalpy and entropy of the reaction and R the universal gas constant.

The calculated values for the enthalpy and entropy of reaction were 4.3 kJ.mol^{-1} and -22.5 J.mol^{-1}.K^{-1} respectively. The reaction enthalpy value as well as the behavior of the correlation curve of the equilibrium constant with temperature suggest that the reaction can be considered slightly endothermic.

Usually, esterification is considered as an athermic or even slightly endothermic reaction.[48] Regarding the esterification of glycolic acid with methanol, values for the reaction enthalpy of approximately 15 kJ.mol^{-1} have been reported in studies which also used UNIFAC to correct the non-ideality of the system.[4,28] Additionally, in the kinetic study of the esterification of glycolic acid with propanol, butanol and octanol, J. Aparicio[35] reported values of 30.73 kJ.mol^{-1}, 23.76 kJ.mol^{-1} and 16.36 kJ.mol^{-1} respectively. However, in this case a different thermodynamic model was employed (NRTL). Thus, predictive and correlative thermodynamic models presents similar trends agree with the slightly endothermic values for the enthalpy of reaction in the esterification of glycolic acid.

Despite the enthalpy value obtained in this study being low, similar observation have been reported for the esterification of other carboxylic acids with ethanol when comparing to references or theoretical values.[15,40,49] C. Pereira et al.,[15] found a reaction enthalpy of around 4.28 kJ.mol^{-1} in the esterification of lactic acid with ethanol. Moreover, A. Orjuela[40,49] found that the slope for the equilibrium constant of succinic acid esterification with ethanol to be close to zero, showing little dependence on the temperature and so assuming heat of reaction as zero.

Parameter fitting

The experimental results of the parametrical study were used to form composition versus time profiles that were fitted to the kinetic equation. Usually, esterification reactions studied without the presence of a heterogeneous catalyst are modeled as homogeneous reactions whether or not they are catalyzed by another compound other than the main acid. This is represented by the equation below:

$$r = k^+ \left(a_{GA}a_{EtOH} - \frac{a_{EG}a_{H2O}}{K_{eq}}\right) (8)$$

In which k^+ stands for: $k_0^+ exp\left(-\frac{E_A}{RT}\right)$, where k_0^+ and E_A represent the pre-exponential factor and the activation energy and R the universal gas constant, a_{GA}, a_{EtOH}, a_{EG}, a_{H2O} represents the activity of the reagents (ethanol and glycolic acid) and products (ethyl glycolate and water) respectively and K_{eq} accounts for the equilibrium constant.

However, it is known that the esterification of carboxylic acids can be catalyzed by undissociated molecules of the acid and/or by the proton resulting from its dissociation.[24]Pöpken et al.[25] developed a kinetic model for this type of reaction, in which the autocatalytic factor is taken into account.

$$k^+ a_{RCOOH}^a \left(a_{RCOOH}a_{R'OH} - \frac{a_{ROR'}a_{H2O}}{K_{eq}}\right) (9)$$

Where a_{RCOOH}, $a_{R'OH}$, a_{ROR} and a_{H2O} are the activities for the carboxylic acid, alcohol, ester and water respectively. The application of this model to short chain carboxylic acid esterification reactions has been already studied mainly focused in acetic and lactic acids.[13,24–27] The difference between this model and the traditional homogeneous model is based on the addition of the term a_{RCOOH}^a, which accounts for the activity of the protons dissociated from the main acid (glycolic acid). [25] As mentioned above, this serves as a catalyst both for the straightforward reaction of the esterification as well as for the hydrolysis of the ester formed.

The alpha (a) parameter can take two values depending on whether the reaction occurs via a dissociated acid or not. If it is assumed that catalysis occurs via an undissociated acid, giving rise to a trimolecular reaction where two acid molecules are present, with one acting as a reactant and the other as a catalyst, the value for this constant becomes 1. [25] Alternatively, if the reaction occurs via the dissociation of the acid, this parameter takes the value of 0.5[25]

The employment of the ordinary differential equations solver ode45 in MATLAB® enabled the numerical integration of the mass balance equations in a batch reactor that describes the kinetic model using the ordinary differential equations by the fourth-order Runge-Kutta method. Parameter estimation for the different models was carried out by the minimization of the sum of residual squares (SRS) between the calculated and experimental values as presented in equation 10.

Table 2. Summary of autocatalytic kinetic models

Model		Kinetic law
Homogeneous		$k^{+}\left(a_{GA}a_{EtOH}-\frac{a_{EG}a_{H2O}}{K_{eq}}\right)$
Homogeneous-Autocatalyzed	Autocatalysis mechanism is assumed to take place via the solvated protons of the dissociated acid	$k^{+}(a_{GA})^{0.5}\left(a_{GA}a_{EtOH}-\frac{a_{EG}a_{H2O}}{K_{eq}}\right)$
	Autocatalysis mechanism is assumed to take place via the molecular acid (undissociated acid)	$k^{+}(a_{GA})^{1}\left(a_{GA}a_{EtOH}-\frac{a_{EG}a_{H2O}}{K_{eq}}\right)$

$$SRS=\frac{1}{n}\sum_{j}^{Ns}\sum_{i}^{Nc}\left(x_{exp}-x_{cal}\right)^{2} \quad (10)$$

With Nc as number of compounds, Ns as number of samples per experiments, n as the number of experiments and x_{exp} , x_{cal} as the experimental and predicted molar concentrations. For the estimation of the two parameters (activation energy and pre-exponential factor), the concentration profiles of the 7 experiments in Table 1, which accounts for 12 individual concentrations of glycolic acid, ethanol and ester were employed, thus guaranteeing sufficient independent data to perform the error minimization and parameter regression.

In order to differentiate between the three models, the experimental data was fitted to each one of the models in Table 2. Additionally, for the optimized parameters the absolute error and mean average relative residual were using equations 11 and 12. The results of the parameter estimation are displayed in Table 3.

$$Err_{Abs}=\frac{1}{n}\sum_{j}^{Ns}\sum_{i}^{Nc}\left|x_{exp}-x_{cal}\right| \quad (11)$$

$$MARR\ (\%)=100*\frac{1}{n}*\frac{1}{n_{parameters}}\sum_{j}^{Ns}\sum_{i}^{Nc}\frac{\left|x_{exp}-x_{cal}\right|}{x_{exp}} \quad (12)$$

Moreover, a statistical analysis was performed to estimate the correlation coefficients between pairs of determined parameters and their corresponding p-values (95 % confidence intervals). The optimization was performed several times starting from different initial values to avoid local minima. The correlation coefficients were estimated from the covariance calculated with the Jacobian Matrix.

Considering the estimation of the activation energy, the choice of model has little impact on the value regressed, as all the models are in agreement with values between 46-48 kJ.mol^{-1}. This is not the case for the value of the pre-exponential factor, as it is logical, due to the structure of the kinetic model. Little attention has been paid to the autocatalytic element of esterification with carboxylic acids; most of the reported literature is focused on studies of the kinetics of the reaction catalyzed by external sources different to the acid itself. Moreover, for the esterification of glycolic acid with ethanol no reference was found. Still, the estimated value is in agreement with the energy of activation reported in the literature for short chain carboxylic acids such as acetic acid and also for alpha hydroxy carboxylic acids, such as lactic, acid ranging between 42-63 kJ.mol^{-1}. [13,24–27]

As can be seen in Table 3 the experimental kinetics correspond better to the models that take into account the catalytic properties of the glycolic acid itself. Moreover, they are better reproduced when alpha takes the value 1 rather than 0.5, suggesting that the reaction is more likely catalyzed by molecular glycolic acid. However, due to the small difference between both autocatalytic models, it is difficult to differentiate between them, leading to the alternative where the acid is partially dissociated. It could also be considered as a valid and consistent hypothesis supported by the corresponding low pKa value for this acid (3.83). Similarly for the case of lactic acid (pKa 3.8), the obtained error values for the two homogeneous-autocatalytic models lead to a narrow deviation between them, making difficult to distinguish. P. Delgado et al.[13] reported that for the esterification of lactic acid with ethanol, the autocatalysis occurs via dissociated molecules, whereas M. T. Sanz et al.[26] reported that the autocatalysis is more likely due to the interaction of the molecular acid in the reaction of lactic acid with methanol.

A parity plot describing this adjustment for the molecular catalyzed reaction is shown in Figure 6A. Calculated and predicted concentrations are illustrated in Figure 6B, where it is also possible to appreciate that the concentration profiles correspond with good precision to those obtained through experiments.

(A)

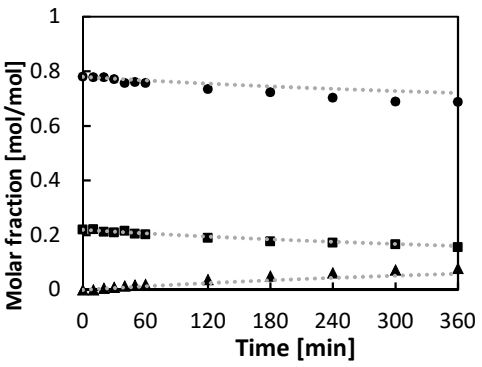
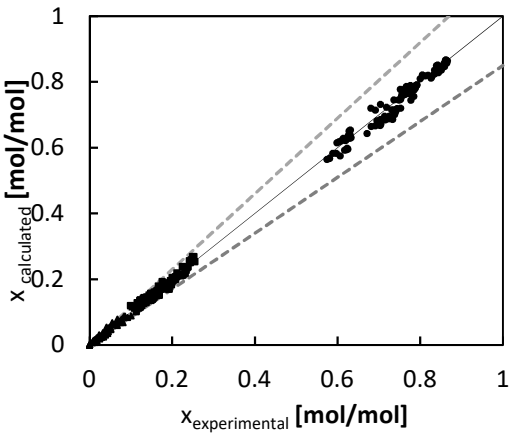


Table 3. Optimized parameters with 95% confidence intervals for the different kinetic models

Model	k_0^+ mol.min^{-1}	E_A J.mol^{-1}	SRS	Err_{Abs}	MARR (%)
Homogeneous	2.29E+04±1.04E+00	46491±90	0.00060	0.03512	20.11
Homogeneous-Autocatalyzed undissociated acid	1.64E+05±1.01E+00	47344±44	0.00044	0.02957	13.94
Homogeneous-Autocatalyzed dissociated acid	1.92E+04±1.01E+00	47615±35	0.00049	0.03167	16.21



(B)

Figure 6. (A) Parity plot of the autocatalyzed glycolic acid esterification with ethanol fitted to the molecular autocatalyzed model (B) Experimental and predicted molar concentrations of autocatalyzed glycolic acid esterification with ethanol fitted to the molecular autocatalyzed model. Conditions: Acid/Alcohol ratio 1/4 [mol/mol], 60°C, 1400 rpm; Mole fractions: Experimental (●) Ethanol; (■) Glycolic acid; (▲) Ethyl glycolate; (---) ±15%; dotted lines: predicted profile concentrations.

Heterogeneous catalyzed reaction

Catalysts screening

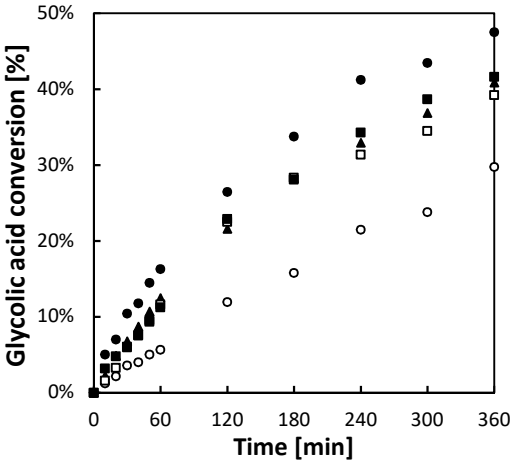
For this study a series of heterogeneous acid catalysts were selected to be tested in the glycolic acid esterification with ethanol. Following the results of the initial parametric study the temperature and acid/alcohol ratio were fixed at 70°C and 1/4 respectively. External diffusion limitations were discarded for all catalysts and for the best performant one, the kinetic regime was ensured (see Table 4 and Figure 16).

Zeolites

Zeolites can be employed in a broad number of applications such as molecular sieving, purification of effluents by adsorption, ionic exchange and catalysis.[50] However in the context of this investigation the zeolites were selected for their qualities as acid catalysts required for esterification reactions. Three different commercial zeolite structures were studied: Faujasite (FAU), Penstasil (MFI) and Mordenite (MOR). In addition to the diversity of the structures, different Si/Al ratios were tested. Figure 7 compares the progress of glycolic acid conversion between different commercial zeolites. In general, zeolite structure seems to have an impact on the conversion of glycolic acid. Comparing the FAU, MOR and MFI (40:1, 10:1 and 40:1, respectively) with acidity in a similar range, the FAU structure presented the highest glycolic acid conversion. Mordenite and MFI (10:1 and 40:1, respectively) showed a similar behavior, with MFI displaying a slightly better catalytic performance. Furthermore, for two FAU structures with different Si/Al ratio and acidity values, the resulting conversion differs. In this case, it was observed that the lower the Si/Al ratio, lower the catalytic activity and thus glycolic acid conversion.

Figure 7. Influence of the zeolite structure and Si/Al ration in the esterification reaction. Conditions: Acid/Alcohol 1/4 [mol/mol] , 1400 rpm, 70°C, Catalyst 2 wt%. Zeolites (●) FAU 40/1 ; (■) MFI 40/1; (▲) MOR 10/1; (□) MFI11.5/1;(○) FAU 2.5/1.

It is important to mention that the FAU 5.1/1 zeolite presented



a lower performance compared to the uncatalyzed reaction under the same operating conditions. A drop of approximately 7 % in conversion compared to the benchmark suggests an inhibitory rather than a reaction-promoting behavior by this zeolite, suggesting that not only the structure but also the alumina content has an impact on the catalytic activity of zeolites in the esterification reaction of glycolic acid.

The differences in the performances of the different structures can be explained by the relationship between the average pore diameter and the yield. Maheria et al.[51] stated that bulkier acid molecules can suffer from diffusional and geometrical limitations with respect to the pore size and geometry affect significantly the levulinic acid conversion.[51] Furthermore Prinsen et al.,[52] suggested that hydrophobicity/hydrophilicity and pore size éare also relevant factors in esterification reactions rather that only the acidity. [52] The influence of the structure, Si/Al ratio and the acidity on the catalytic properties of zeolites is not straightforward. The rate and efficiency of proton transfer in zeolites, as discussed previously, depends on a variety of factors linked to the ease of the molecules to diffuse or transport through narrow confined cavities and closed channels in the zeolites to the acid sites, and the concentration of active sites and their enclosed geometry.

Ion-exchange resins

The choice of the resins tested was based on their chemical composition and morphological structure properly adapted to the model reaction. These polymeric materials present different morphological characteristics such as surface area, average pore diameter and even physical shape, but also differ in catalytic properties as the concentration of acids sites. The latter one is directly related to the availability of acid sites for either per volume or mass of catalyst. Figure 8 compares the evolution of glycolic acid conversion for different commercial ion exchange resins as catalysts.

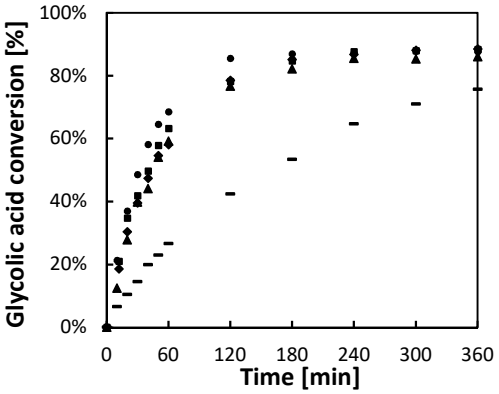


Figure 8. Influence of the ion exchange resin in the esterification reaction. Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm, 70°C, Catalyst 2 wt%. Ion exchange resin: (●) Amberlyst 70 ; (■) Amberlyst 15; (◆) Amberlyst 36; (▲) Dowex 50XW8-100;(━) Nafion NR50.

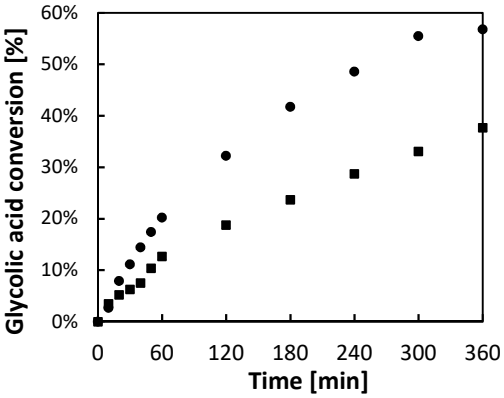
All ion exchange resins tested presented a significant catalytic activity in the esterification of glycolic acid. The Amberlyst series performed better than to Dowex and Nafion polymers. When using Amberlyst 70 the equilibrium was reached faster than with Amberlyst 15 and 36, which presented similar reaction times to reach equilibrium. These experimental results are in agreement with the work described by Orjuela et al.[40] which stated that the catalytic activity of Amberlyst 70 may over perform Amberlyst 15 in esterification reactions even though if the former one exhibits lower pore volume and surface area. It was also found that Amberlyst 70 is a more effective catalyst in the esterification reaction than Amberlyst 36, consistent with the results obtained by Hoşgün & Çitak[53] in the kinetic study of propionic acid with isobutyl alcohol.

Despite the fact that Amberlyst catalyst and Dowex have different surface areas and pore diameters, the four catalyst presented similar final conversions. However, the faster reaction rate presented by Amberlyst 70 may be related to the fact that this resin has a lower degree of polymerization in comparison to the other macro reticular polymers, which could play a role in the accessibility and transport of reactive molecules to the active sites. Moreover, the performance of the Nafion catalyst being below the average presented by the other resins tested is probably linked to its low ionic exchange capacity.

Titanium oxide

Along with zeolites and resins, mixed and metal oxides are the most commonly employed solid acids.[54] Figure 9 shows the conversion of glycolic acid with and without the presence of TiO_2 as catalysts.

Figure 9. Comparison between benchmark (non-catalyzed at same operational



conditions) and TiO_2 catalyzed reaction of glycolic acid esterification with ethanol. Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm, 70°C. (●) TiO_2 catalyst amount 2 wt%. (■) non-catalyzed reaction

When comparing TiO_2 the reaction with the benchmark (autocatalyzed reaction) at same operational conditions, it is clear that the reaction is promoted by the acidic properties of the titanium oxide. Titanium oxide displayed a significant activity in the reaction with a conversion value around 57 % at the end of 6 hours, approximately 20 % higher than that of the benchmark reaction. Moreover, the titanium oxide presented a better performance as an acid catalyst in the glycolic acid esterification with ethanol than all the zeolites tested in this study.

Comparative study and selection of catalysts

To further establish the parameters that favor the production of ethyl glycolate, the acid-base titration of all the commercial catalysts employed in this study was carried out. This allowed to differentiate and quantify the different acid sites: strong, medium and weak, that were present in each solid. The results of the titration are presented in Figure 10.The quantification of acid sites by potentiometric titration is a straightforward procedure that consists of the direct titration of an aqueous suspension of the sample of powdered solid with a dilute base to a neutral endpoint.[55] The disadvantage of this technique is related to the imprecise representation of the phenomena occurring on the solid surface during its use as an acid catalyst, which might be radically different in a water suspension. Water can also drastically alter the structural properties of the solid, causing decantation, structural collapse and swelling.[55]

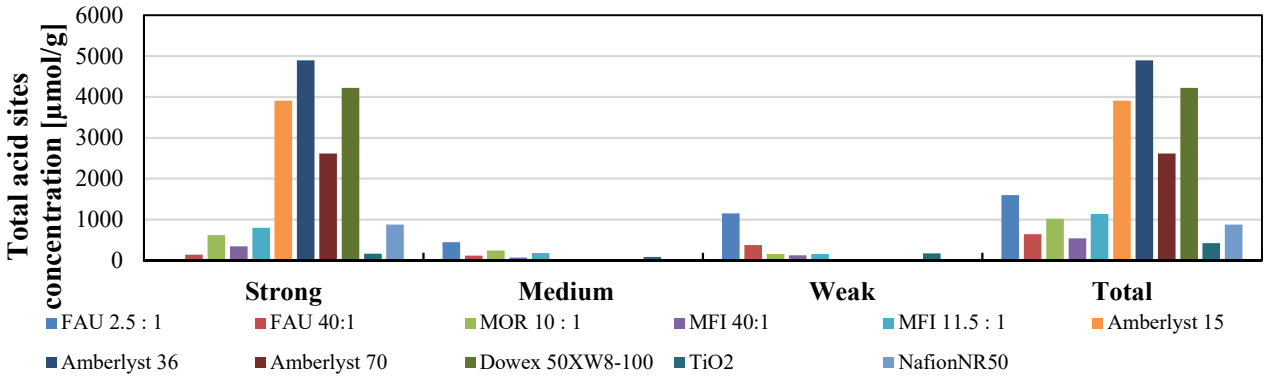


Figure 10. Characterization by titration of different acid sites present in the commercial catalyst

However, as water is one of the reaction products, these phenomena would occur albeit to a lesser extent, over the course of the reaction. Despite this, the results obtained during this study are accurate approximations of the values described in the literature for the solid catalysts studied, with a variation of 15 % inherent to this type of technique. With the exception of FAU 2.5 in which no strong sites were found, zeolites were shown to have all three types of acid sites. Titanium oxide presented similar values regarding weak and strong sites, with fewer medium acid sites. Contrary to the characterization of the other two types of solids, the ion exchange resins did not show medium or weak acid sites, thus the total number of acid sites represents only strong acid sites.

In general, all the catalysts tested in the catalytic screening showed catalytic activity in the esterification reaction. Resins presented the highest conversion, followed by titanium oxide and finally the group of zeolites. The common property of these catalysts is their acidic characteristics. Figure 11 displays the relation between the initial reaction rate and total acid site concentration of the catalyst.

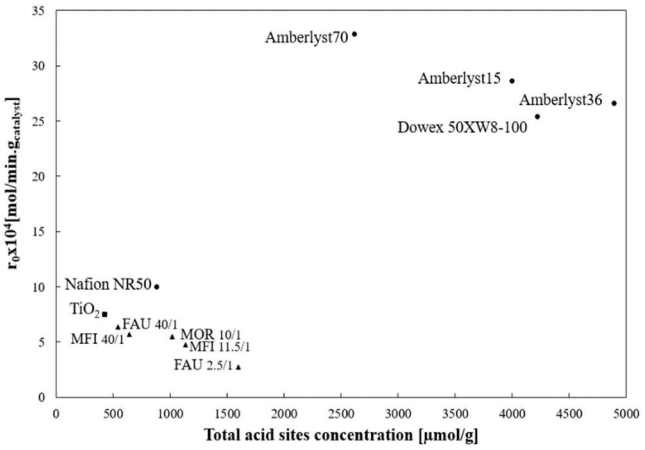


Figure 11. Influence of the total acid sites concentration over the initial reaction rate. Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm, 70°C, Catalyst 2 wt%. (●) Ion exchange resin; (■) Oxide; (▲) Zeolite.

The illustration gives a clear trend among the different families of solid catalysts used in this study. It also suggests that the primary influencing factor of the heterogeneously catalyzed glycolic acid esterification with ethanol is the total amount of acid sites. However, it is necessary to emphasize that this is valid as long as these sites are accessible to the reagents. The reactive molecules contrast in molecular sizes, where glycolic acid is a much more bulky molecule than ethanol. Catalysts such as resins and oxides have a larger pores, making the active sites more accessible. On the contrary, catalytic materials such as zeolites have smaller pore sizes in addition to the complex structures of channels and cages in which bulkier molecules can be trapped before arriving to the active site, thus decreasing their catalytic performance. Even if zeolites have a larger surface area and in some cases a notably higher concentration of active sites than oxides, their low accessibility may be the cause of their poor performance. The comparison between resins and oxides can also fit in this hypothesis. In this case, the Amberlyst series of resins present superior values in pore size and concentration of active sites, which makes them more efficient.

Furthermore, the characterization suggests that not only the total amount but also the strength of the acid sites can be an influencing parameter in the reaction, indicated by the fact the best performing catalysts were ion exchange resins and, that only strong acid sites were found in these solids. This allows us to hypothesize that these might be the sites that have the biggest influence on the esterification of glycolic acid with ethanol.

Parametric study with Amberlyst 70

To continue the study the effects of temperature, catalyst loading, presence of water and reusability have been examined in detail for the glycolic acid esterification with ethanol in presence of Amberlyst 70 as a result of being the most efficient of all catalyst tested in the reaction.

Influence of the temperature

The influence of the reaction temperature on the esterification of glycolic acid was studied in the temperature range 50-70°C keeping the other reaction parameters constant. Figure 12 illustrates the effect of the three different temperatures. It has been observed that the glycolic acid conversion at a set reaction time increases with the increase of reaction temperature. The reaction at 50 °C did not reach constant conversion even in the last hour of reaction, while the reaction at 70 °C required only

half this time to reach this point. The glycolic acid conversion in the reaction catalyzed by Amberlyst 70 increases from 83 to 88 % by changing the reaction temperature from 50 to 70°C at the end of 6 hours of reaction. In contrast an increase in the temperature had a much greater impact the autocatalyzed reaction, with 16% difference between the tests carried out at 50 and 70°C in the same period of time (Figure 1). The low variation in the final conversion achieved for the reactions in the presence of Amberlyst at different temperatures is explained by the fact that the tests either reached or got close to thermodynamic equilibrium.

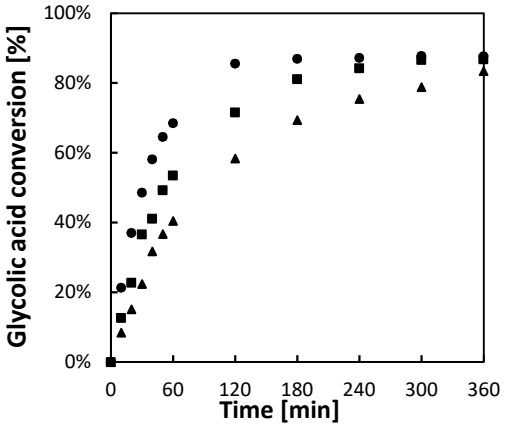


Figure 12. Influence of the temperature over the reaction catalyzed by Amberlyst 70. Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm, Catalyst 2 wt%. (●) 70°C; (■) 60°C; (▲) 50°C

Influence of the water content

The effect of initial water amount on the reaction rate and conversion of glycolic acid was investigated by adding a molar ratio of 1 mol water to 3 mol of ethanol, corresponding to around 10 wt% of water, to the departure solution. The comparison of impact of the water addition over the autocatalyzed and heterogeneously catalyzed reaction is displayed in Figure 13.

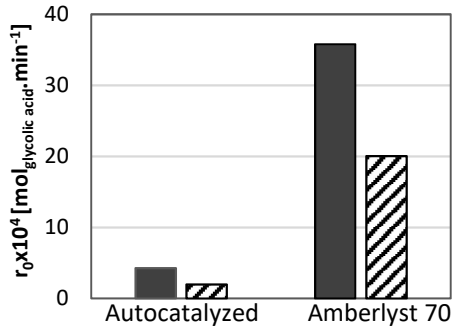


Figure 13. Influence of water in the departure solution over glycolic acid conversion. Conditions: Acid/Alcohol 1/4 [mol/mol], 70°C, Catalyst 2 wt%. (■)Without water; (▨) Water 10 wt%.

In the two scenarios, with or without catalyst, the presence of water in the initial solution has an inhibitory effect. These results agree with those found by Nguyen et al.,[56] in the study of the esterification of lactic acid in dilute media, where it was found that resins and even the uncatalyzed reactions suffer from decrease in conversion due to the presence of water. In this case, the presence of water in the starting reaction medium shows a similar trend for the reaction catalyzed by the polymeric and the autocatalyzed reaction as the initial reaction rate decreased in both cases. However, the conversion was more affected at the end for the heterogeneously catalyzed reaction, as it decreased by around 15 % compared to 8 % for the autocatalyzed reaction after 6 hours of reaction. This may be due to the fact that when working with catalyzed reactions in presence of water in the reaction medium not just one but two negative effects may arise: the catalyst may be deactivated due to a fast interaction between the water and the catalyst, and the reaction itself may be affected. Since this is a reversible and equilibrium reaction, the presence of a product from the beginning of the reaction could shift the equilibrium towards the reactants, and therefore a lower final conversion is achieved. Moreover, the intentional addition of water can also cause a dilution effect, decreasing the reactant as well as the catalyst concentration in the medium, thus resulting in lower conversion.

Influence of catalyst loading and reusability

Heterogeneous catalyst greatly influence the reactions by providing active sites for the reaction to take place in. An increase in the catalyst loading increases the number of available catalytic sites. In order to test the effect of the catalyst loading, the reaction was tested in the presence of three different mass percentages of Amberlyst 70 :1 % , 2 % and 3 % (Figure 14).

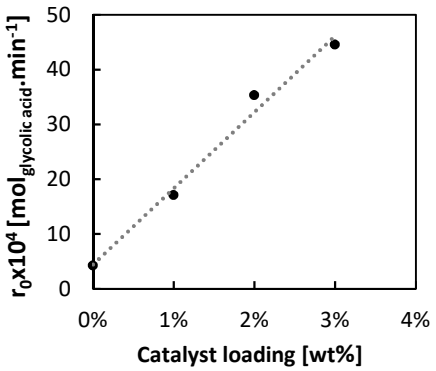


Figure 14. Influence of the catalyst amount in the reaction. Conditions: Acid/Alcohol 1/4 [mol/mol], 1400 rpm, 70°C.

As the catalyst amount increases the glycolic acid conversion rate increases. Moreover, in the plot of the initial reaction rate against catalyst amount a linear correlation between the two variables was observed.

The recyclability of the heterogeneous catalysts is an important factor in their economical applicability.[57] Heterogeneous catalysts may suffer from phenomena such as leaching decreasing their activity. The resins can be deactivated by SO_3H groups leaching from the matrix.[56] For the recycling tests, the catalyst was recovered by filtration from the reaction medium and washed with ethanol, then dried in an oven overnight at 60°C. Higher temperatures of drying were avoided as resins suffer from gradual desulfurization when subjected to temperatures higher than 120°C.[26]

Amberlyst 70 was used over 3 consecutive runs, for a total reaction time of 18 hours of reaction. No significant variations were observed in the performance of the resin (ESI). The initial reaction rates presented in the reaction with the fresh and recycled catalysts are presented in Figure 15. Amberlyst 70 showed promise to be recyclable compared to fresh catalysts with little variation in initial rate possibly due to product or reagent residues resulting from the previous reaction blocking the active sites, or partial loss of acidity and/or strength of the active sites when exposed to the reaction medium.

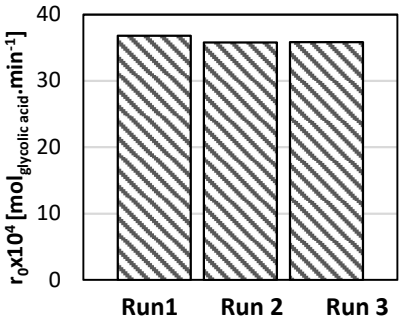


Figure 15. Influence of the reuse of Amberlyst 70. Conditions Acid/Alcohol 1/4 [mol/mol], 70°C, Catalyst 2 wt%.

Mass transfer limitations

Before performing rigorous kinetic modeling, an analysis of diffusion limitations should be conducted, in which the two sensitive variables are the transport of the reactants from within the fluid to the surface and their transport from the catalyst surface to the active sites. All this is to guarantee that the reaction is being developed in a kinetic regime.

The intraparticle mass transfer limitations were estimated for each experience by the Weisz-Prater criterion.[58] Table 4 displays the parameters employed for the evaluation of mass transfer resistances for the Weisz-Prater criterion.

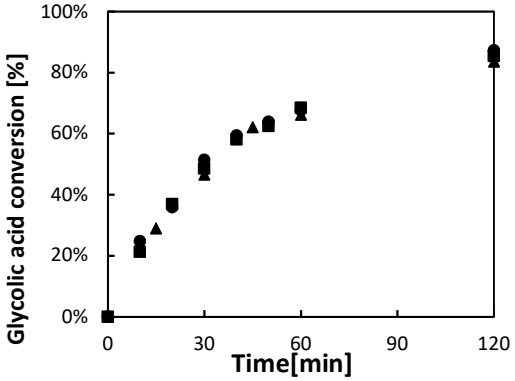
Table 4. Parameters employed for the evaluation of mass transfer resistances. Conditions: Acid/Alcohol 1/4 [mol/mol], 70°C, Catalyst 2 wt%.

Parameter	value
Catalyst loading by mass of reacting media (w_{cat}) [kg_{cat}. kg_{sln}^{-1}]	0.020
Density of the reacting media (ρ_{sln}) [kg. m^{-3}]	789
Density of the catalyst (ρ_{Cat}) [kg. m^{-3}]	1000[40,59]
Association factor Wilke -Chang model (ethanol)	1.50[60]
Glycolic acid molar volume at normal boiling point [$cm^3.mol^{-1}$]	75.80*
Observed reaction rate for the heterogeneously catalyzed reaction (r_{0cat}) [kmol. $kg_{cat}^{-1}s^{-1}$]	5.27E-05
Diffusion coefficient for glycolic acid (D_{GA}) [m^2. s^{-1}]	2.73E-09
Effective diffusivity of glycolic (D_{Eff}) [m^2. s^{-1}]	9.00E-10
Weisz-Prater criterion	0.08

*Calculated by Group/Atom contribution for Le bas method[61]

Values significantly inferior to the unit (0.05-0.08) were obtained for the Weisz-Prater criterion, thus t can be stated that the internal mass transfer resistance has minimal impact in the glycolic acid esterification on presence of Amberlyst 70. Moreover, tests varying the stirring rate at similar operational conditions demonstrated that external diffusional limitations do not impact the heterogeneously catalyzed reaction (Figure 16). This in agreement with several authors that have stated that for reactions catalyzed by Amberlyst type resins these kind of resistances are usually negligible.[40,56,62–65]

Figure 16. Influence of the stirring rate over the reaction catalyzed by Amberlyst 70.



Conditions: Acid/Alcohol 1/4 [mol/mol], 70°C, Catalyst 2 wt%. (●) 1600 rpm; (■) 1000 rpm; (▲) 800 rpm.

Kinetic parameter fitting

It is important to highlight that even if earlier in this study the catalytic component from glycolic acid was taken into account in the parametric adjustment, this contribution becomes negligible when compared to the catalytic effect of the ion exchange resin due to the important amount of acid sites provided by the solid catalyst. Catalytic tests at different initial acid concentrations allowed to corroborate this hypothesis (ESI). Therefore, only conventional heterogeneous kinetic models were considered for fitting the experimental data. Several studies have been undertaken on the kinetic models for the esterification reactions in the presence of a solid catalyst. The reported studies focus on Langmuir-Hinshelwood, Eley-Rideal and pseudo homogeneous type models.[14,38–42]

Pseudo-homogeneous (PH) model assumes that the reactants reach the active surface on the catalyst easily thus reacting as in a homogeneous system. The Eley-Rideal (ER) model assumes that only one of the two reactants adsorbs onto the active site, forms the adsorbed species and then reacts with the other reactant forming the products, only one of the resultants is generated as an adsorbed state on the surface of the solid. On the contrary, Langmuir-Hinshelwood model (LH) states that the all the species generated as adsorbed species on active sites. These species are product of the interaction, in the same way, of two absorbed species. The kinetic models adapted for the esterification reaction of glycolic acid with ethanol in a heterogeneous system are listed in Table 5, where K_{ET},K_{GA}, K_{EG} and K_{H2O} stand for the adsorption constants of the reactants (ethanol and glycolic acid) and products (ethyl glycolate and water) in the corresponding order.

Table 5. Kinetic laws developed for the different kinetic models

Model		Kinetic law
Pseudo-Homogeneous	The reaction takes place as if it were a homogeneous system	$k^{+}\left(a_{GA}a_{EtOH}-\frac{a_{EG}a_{H2O}}{K_{eq}}\right)$
Eley-Rideal	Only one reactant and one product are found as adsorbed species	$k^{+}\frac{\left(a_{GA}a_{EtOH}-\frac{a_{EG}a_{H2O}}{K_{eq}}\right)}{(1+K_{GA}a_{GA}+K_{EG}a_{EG})^{1}}$
Langmuir-Hinshelwood	All reactants and products a present as adsorbed species	$k^{+}\frac{\left(a_{GA}a_{EtOH}-\frac{a_{EG}a_{H2O}}{K_{eq}}\right)}{(1+K_{GA}a_{GA}+K_{EtOH}a_{EtOH}+K_{EG}a_{EG}+K_{H2O}a_{H2O})^{2}}$

The experimental data obtained for Amberlyst 70 was fitted to the three kinetic models, as has been already described in the autocatalytic section concerning the software, solver of equations and minimization algorithm.

Here, there is a maximum of o total parameters to be estimated, however, the number of independent data was kept sufficient as the algorithm was fed with the concentration profiles of the 8 experiments each one accounting for 12 individual concentrations of the three quantified species. The estimated parameters are shown in table 6. The optimization was initialized from different values to avoid optimization in local minimum points of the function surface.

Adsorption based models shown big difference concerning the pre-exponential factor. The LH model presented the highest value, whereas ER presented rather a value in the same range of PH. Considering the activation energies, the optimized values were quite similar for adsorption based models and PH (42-43 kJ.mol^{-1}). No reference value was found in the literature, however the obtained activation energy is in agreement with the reported one for glycolic acid esterification with a solid catalyst and linear chain alcohols C1-C8 (34-59 kJ.mol^{-1}).[4,34,35] On one hand J. Aparicio[35] reported values of 52 kJ.mol^{-1}, 56 kJ.mol^{-1} and 34 kJ.mol^{-1} for the activation energy of propanol, butanol and octanol respectively obtained employing ER and LH models. On the other hand C. Mutschler[34] and S. Yang et al.[4] demonstrated that the PH model is able to correctly describe the profiles for the esterification of glycolic acid with butanol (48 kJ.mol^{-1}) and methanol (59 kJ.mol^{-1}) respectively.

The narrow difference in the error criteria may suggest that both adsorption and PH model are able to describe the reaction kinetics, with ER being the less suitable to correctly represent the experimental data (higher SRS and ErrAbs values). For the ER model, two scenarios were considered: either the ester and the acid or the ester and the alcohol are present in adsorbed form on the solid. On the grounds that these were the quantified species, the best fit for the optimized parameters was the glycolic acid and ester couple where the ester is slightly more strongly adsorbed onto the catalyst. Higher adsorption constants were obtained for the LH model, however, in agreement with the trend found for ER, glycolic acid and ethyl glycolate were the most strongly absorbed species. Taking into account the fact that the values of the adsorption constants obtained are not negligible, it can be established that the model that describes the experiments more strictly is the LH model. Moreover, for the error criteria it might be inferred that the best fitting for the experimental data is the LH model. Despite the MARR value and being the simplest of the considered kinetic models, the results obtained with the PH model may also be considered as accurate for the he glycolic acid esterification with ethanol.

Table 6. Optimized parameters with 95% confidence intervals for the different heterogeneous kinetic models

	Kinetic Model					
Parameter	LH		ER		PH	
$\boldsymbol{k_0^+}$ [mol.min^{-1}.gcata-1]	1.11E+07	±1.02E+00	8.51E+04	±8.06E-04	8,86E+04	±1.00E+00
EA [J.mol^{-1}]	42825	±22	42489	±7	43348	±1
$\boldsymbol{K_{ET}}$	3.95	±1.50E-03	-		-	
$\boldsymbol{K_{GA}}$	36.10	±1.54E-02	1.53	±1.88E-04	-	
$\boldsymbol{K_{EG}}$	23.80	±2.14E+00	1.66	±3.04E-01	-	
$\boldsymbol{K_{H2O}}$	15.06	±2.86E-02	-	-	-	
SRS	0.00021		0.00029		0.00027	
Err_{Abs}	0.0227		0.0255		0.0245	
MARR (%)	2.68		4.23		12.05	

As we perform an optimization on values close to zero, low molar concentrations, and normalizing the value, the error naturally increases and so as the PH model has only 2 adjustable parameters, in contrast to 6 and 8 for the ER and LH models, the MARR calculated is higher. As previously discussed, it had been demonstrated that PH model can represent with precision the kinetics of esterification in the presence of ion exchange resins.[29,36,37,43]

A graphical representation of the adjustment of the LH model to the prediction of the concentration profiles for one of the experiments carried out is shown in Figure 17 where is illustrated that all predicted values agree with experimental data within an error of 15 %.

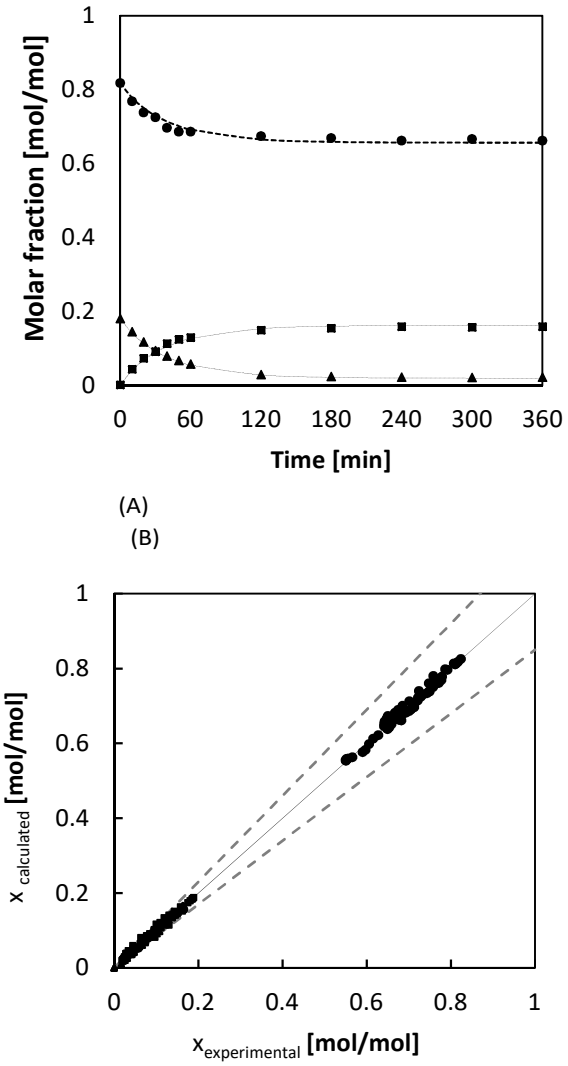


Figure 17. (A) Parity plot of the heterogeneously catalyzed glycolic acid esterification with ethanol by Amberlyst 70 fitted to LH (B) Experimental and predicted concentration profiles of heterogeneously catalyzed glycolic acid esterification with ethanol by Amberlyst70 fitted to LH. Conditions: Acid/Alcohol 1/4 [mol/mol], 70°C, 1400 rpm, Catalyst 2 wt%. Mole fractions: Experimental (●) Ethanol; (■) Glycolic acid; (▲) Ethyl glycolate; (---) ±15%; dotted lines: predicted profile concentrations.

Conclusions

In this study, the kinetics of the esterification of glycolic acid with ethanol homogeneously autocatalyzed and heterogeneously were investigated. In the parametrical study, the reaction was found to be favored by an increase in temperature and acid molar fraction, whereas the dilution of the initial mixture with water had an inhibitory effect. Under optimized conditions (Acid/Alcohol 1/4 [mol/mol], 70°C) up to 38% conversion of glycolic acid was achieved in a medium with no catalyst other than the acid itself. Additionally, it was established that the reaction is more likely to be catalyzed by glycolic acid molecules than via the solvated protons. In order to determine the relationship between the equilibrium constant and the temperature, the correction of non-idealities was performed using the UNIFAC group contribution method. This led to the conclusion that this reaction is slightly endothermic with an activation energy of 47-48 $kJ.mol^{-1}$. Among the reviewed solid catalysts, resins stand out as being the best performant in the esterification of glycolic acid with ethanol followed by the oxide and finally the zeolites the less performing (2-12% increase in conversion). Concerning heterogeneous catalysis, in the presence of Amberlyst 70 (2 w% Acid/Alcohol 1/4 [mol/mol], 70°C), equilibrium conversion (about 90%) was reached within 2 to 3 hours of the reaction. It was established that among the most sensitive parameters of the heterogeneously catalyzed reaction are the accessibility, quantity and strength of acid sites. Further studies carried out in the presence of Amberlyst 70 revealed a direct correlation between the catalyst loading and initial reaction rate. Moreover, a similar behavior was observed when temperature was increased compared to the autocatalyzed system. Contrary, when water is added to the initial solution the glycolic acid conversion is more affected when working in the presence of the ion exchange resin. Consecutive tests, evaluation of the Weizs Prater criterion and test at different stirring rates suggests that Amberlyst 70 could be recycled for several runs and that the kinetics of the glycolic acid esterification with ethanol is affected to minimum extent by internal or external mass transfer. Three kinetic models were considered to fit the experimental data obtained of the heterogeneously catalyzed reaction with Amberlyst70. The results obtained from the optimized parameters suggest that LH model is able to more accurately describe the kinetics of the esterification reaction of glycolic acid with ethanol. Still the results of the PH model were also found to be accurate when a simpler mathematical form is sought.

Author contributions

Laura Reyes: Methodology, Investigation, Visualization, Writing - Original Draft

Clémence Nikitine: Conceptualization, Resources, Supervision, Project administration, Writing - Review and editing

Léa Vilcocq: Conceptualization, Resources, Supervision, Writing - Review and editing

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Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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