

**Kinetics of the esterification reaction of glycol ethers with acetic acid to produce glycol ether acetates**

**Cinética de la esterificación de éteres de glicol con ácido acético para la obtención de acetatos de éteres de glicol**

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**Abstract**

Glycol ether acetates are solvents of great industrial interest due to their low water solubility and slow evaporation rate. In the present work, the kinetics of esterification of glycol ethers with acetic acid to obtain glycol ether acetates was studied. Different synthesis conditions were evaluated, such as reaction temperature, catalyst type, catalyst loading and molar ratio between reactants. Uncatalyzed, catalyzed under homogeneous conditions with pTSA and under heterogeneous conditions with Amberlyst 15 were carried out. Second order kinetic model for the homogeneous system and Langmuir-Hinshelwood kinetic model for the heterogeneous system were proposed and the fit to the experimental data was performed to estimate the reaction rate constants. It was found that the maximum in reaction conversion depends mostly on the ratio between reactants, while temperature, catalyst type and catalyst loading have a significant effect on the reaction rate. Models' predictions are in good agreement with the experimental data and the values of the reaction rate constants are consistent with values reported in other studies.

*Keywords:* glycol ether acetate, esterification, kinetics, Amberlyst 15, pTSA.

**Resumen**

Los acetatos de éteres de glicol son disolventes de gran interés industrial por sus características de baja solubilidad en agua y velocidad de evaporación lenta. En el presente trabajo se estudió la cinética de esterificación de éteres de glicol con ácido acético para obtener acetatos de éteres de glicol. Se evaluaron diferentes condiciones de síntesis, tales como temperatura de reacción, tipo de catalizador, carga de catalizador y relación molar entre reactivos. Se realizaron pruebas no catalizadas, catalizadas en condiciones homogéneas con pTSA y en condiciones heterogéneas con Amberlyst 15. Se plantearon modelos cinéticos de segundo orden para el sistema homogéneo y de Langmuir-Hinshelwood para el sistema heterogéneo y se realizó el ajuste a los datos experimentales para estimar las constantes de velocidad de reacción. Se encontró que el máximo en conversión de reacción depende en mayor grado de la relación entre reactivos, mientras que la temperatura, el tipo de catalizador y la carga de catalizador tiene un efecto significativo sobre la velocidad de reacción. Los modelos permitieron un ajuste aceptable a los datos experimentales y los valores de las constantes de velocidad de reacción son consistentes a valores reportados en otros estudios.

*Palabras clave:* acetato de éteres de glicol, esterificación, cinética, Amberlyst 15, pTSA.

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## 1 Introduction

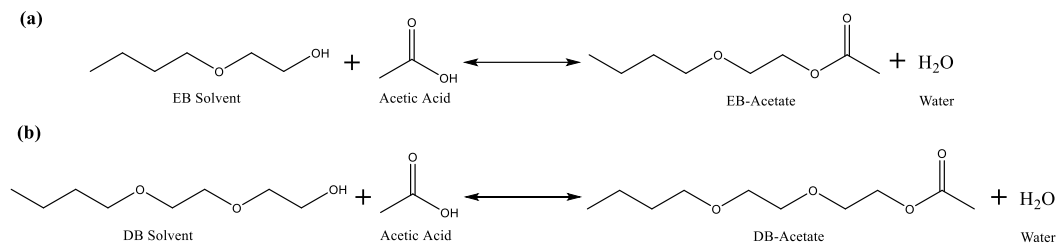
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Glycol ethers acetates (GEA) are a family of solvents with an important number of industrial applications that include coating, textile, leather, and printing industries. Also, they are used as cleaning solvents, as a carrier in insecticides and herbicides formulation, and for specialty printing inks. This versatility of applications is due to its particular characteristics such as high boiling temperature, slow evaporation, compatibility with organic solvents, and low water solubility. Within this family of solvents, those identified as EB-Acetate and DB-Acetate, which correspond, respectively, to 2-butoxyethanol acetate (also known as Ethylene glycol monobutyl ether acetate) and 2-(2-butoxyethoxy)ethyl acetate (also known as Diethylene glycol monobutyl ether acetate), stand out for their commercial consumption.

A known route to produce glycol ether acetates involves the esterification reaction of glycol ether (GE) with acetic acid (AA), as is shown in Scheme 1. The esterification reaction of alcohols with AA has long been reported in many studies to obtain acetates using both homogeneous and heterogeneous catalytic systems. Most of these works emphasized the importance of the kinetic parameter's estimation to improve the reaction conversion using different models for a better understanding of the effect of experimental conditions on the reaction, such as temperature, reactants concentrations, and molar ratios (Rönnback *et al.* 1997, Lilja *et al.* 2002, Gangadwala *et al.* 2003, Liu *et al.* 2006, Liu, Lotero *et al.* 2006, Vahteristo *et al.* 2008, Suman *et al.* 2009). Among the homogeneous catalytic systems, mineral acids are the most common, with sulfuric acid as the main one. Sulfuric acid in homogeneous catalysis has recently been used for the synthesis of novel acetates such as nopyl acetate from the esterification of nopol with acetic acid (Eliana and Luz 2018), or in reaction systems involving the use of mordenite membranes for the removal of water from the reaction medium (Zhu *et al.* 2016). Nevertheless, better conversion in esterification reaction has been reported using p-toluene sulfonic acid (pTSA) as homogeneous catalyst (Ren *et al.* 2013, Inayat *et al.* 2018). On the other hand, heterogeneous catalytic systems applied for esterification reaction include principally ion-exchange resins, such as Amberlyst 15 (Gangadwala *et al.* 2004, Sert 2010, Sharma *et al.* 2014, Lux *et al.* 2015) or Amberlyst 70 (Orjuela *et*

*al.* 2012), but other substrates can be used, such as WO<sub>3</sub> (Mitran *et al.* 2015), silica nanocomposites (Liu, Lotero *et al.* 2006), or an innovative heterogeneous system based on supported ionic liquids (Yang *et al.* 2015). Other interesting esterification processes whose kinetic behavior has been studied include the enzymatic esterification of fatty acids (Correa-Leyva 2019) or the production of biodiesel through a heterogeneous catalytic process (González-Brambila 2020). These last two papers present interesting examples of how to solve more complex kinetic models using computational tools such as Matlab or Fortran. One of the most relevant factors for the esterification reaction process is how to shift the chemical equilibrium to favor acetate conversion, given the reversible nature of the reaction. Several methods have been proposed to shift the equilibrium, most of them related to the use of catalysts or the recovery of the products from the reaction medium. Among these methods, the most important is to carry out the reaction under reactive distillation conditions, since through this process is possible to break the azeotropic mixture formed by acetates with water and acetic acid, as has been reported in several works (Hanika *et al.* 1999, Gangadwala *et al.* 2004, Suman *et al.* 2009). Nevertheless, in the case of glycol acetates, reactive distillation conditions can be more complicated due to the high boiling temperatures of these compounds. Wang and coworkers implemented an innovative entrainer-enhanced reactive distillation process to produce high-purity butyl cellosolve acetate. The function of the entrainers is to favor the separation between water and acetic acid (Wang and Huang 2011). Another option contemplates the use of a chromatographic reactor, as proposed by Deshmukh *et al.* for the same esterification reaction of butyl cellosolve with acetic acid to produce butyl cellosolve acetate (Deshmukh *et al.* 2009). Aside from these two research papers, there is scarce information related to the kinetic behavior of the esterification reaction of glycol ethers, so it is relevant to study the effect of various reaction parameters on the esterification reaction kinetics at both homogeneous and heterogeneous catalysis conditions for this type of compounds.

Kinetic studies continue to be relevant today to predict reaction or transformation rate parameters for processes as different as the growth of microorganisms (González-Figueroa 2021), polymerization reactions (López-Badillo 2019) or chemical adsorption (Chel-Galicia 2020).



Scheme 1 Synthetic route to produce glycol ether acetates: (a) EB-Acetate synthetic route, and (b) DB-Acetate synthetic route.

Table 1. Reagents.

Reagent	Acroniym	Supplier	Purity, %
Acetic acid	AA	Alveg	>98.87%
2-butoxiethanol or butylglycol	EB	Polioles	>99%
2-(2-butoxyethoxy)ethyl or butyldiglycol	DB	Polioles	>98.5%
p-Toluenesulfonic acid	pTSA	Sigma-Aldrich	>98.5%
Ambelyst 15	-	Sigma-Aldrich	-

Several models have been proposed to obtain kinetics parameters for both homogeneous and heterogeneous catalytic systems in esterification reactions. In the case of the homogeneous system, second-order kinetics with quasi-equilibrium approximation has been used for several esterification reactions between AA and different alcohols, using both concentrations and activities for model fitting (Lilja *et al.* 2002, Liu *et al.* 2006, Eliana 2018). Regarding heterogeneous catalyzed esterification, proposed kinetics models include pseudo-homogeneous (PH), Eley-Rideal (RE), Langmuir-Hinshelwood-Hougen-Watson (LHHW), and modified LHHW (LH). In general, PH and LHHW models have performed well in predicting the kinetic behavior of the esterification reaction of AA with alcohols catalyzed by Amberlyst 15 (Gangadwala *et al.* 2003, Deshmukh *et al.* 2009, Sert 2010, Lux *et al.* 2015).

In this study, the kinetic behavior of the esterification reaction of GE with AA to synthesize glycol ether acetate was evaluated with both a homogeneous (pTSA) and heterogeneous (Amberlyst 15) catalyst. Additionally, it was studied the effect of reaction parameters such as temperature, catalyst concentration, and molar ratio between AA and GE on the esterification kinetics. A second-order kinetics model was applied to obtain reaction rate constants

for the homogeneous catalytic system, whereas a LH model was employed for the heterogeneous system.

## 2 Materials and methods

### 2.1 Experimental

#### 2.1.1 Materials

The reagents were used without any further purification according to the Table 1.

#### 2.1.2 Reaction setup

Isothermal batch kinetic experiments were carried out in a 500 mL three neck round-bottom flask equipped with reflux condenser, placed in a heating mantle and magnetic stirring plate, as is shown in Fig. 1. The temperature was maintained within accuracy of  $\pm 0.1^\circ\text{C}$  using a thermocouple type J and controller. Reaction mixture was continuously stirred, the minimum stirring speed was maintained at 240 rpm. A reflux condenser was connected vertically to the reactor flask to prevent the loss of volatile compounds. A syringe was used to sampling at definite time intervals.

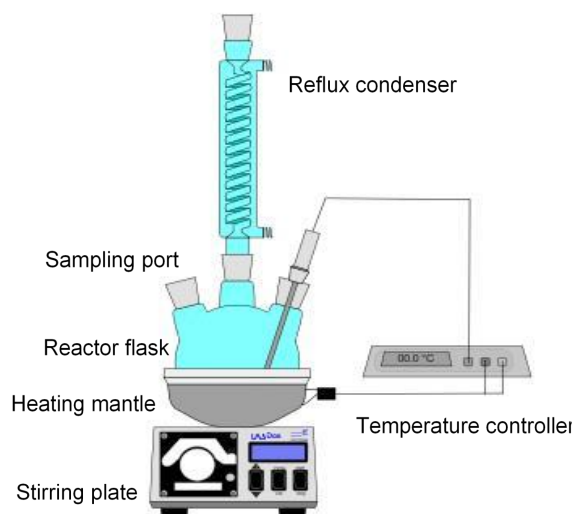


Fig. 1 Experiment setup diagram of batch reaction.

### 2.1.3 Reaction procedure

The amount of AA and glycol ether (GE), EB or DB, were placed into the reactor flask at room temperature in predetermined molar ratios according with the catalyst type. Those reactants were mixed and heated, after the temperature had been stabilized the first sample for analysis was withdrawn, this moment was taken as time zero. The reaction initiated by adding the catalyst, pTSA or Amberlyst 15. Liquid samples of 1 mL were taken out with a syringe at regular intervals, 15 minutes intervals during the first hour, followed by 120 minutes intervals until the reaction reached equilibrium conversion. The samples were analyzed for the acetic acid concentrations and water content. The reaction in the analytical samples was quenched by diluting and cooling the sample with acetonitrile, according to the method described by Rönnback (1997).

For homogeneous experiments molar ratio between AA:GE were 1:1, 1:2 and 2:1 and for heterogeneous experiments were 1:1 and 2:1. The reaction temperatures were 90 and 100°C. The catalyst pTSA with 2 different loads (2.5 and 5 meq) and the catalyst dosage of 5 meq of Amberlyst 15 were studied. All experiments were carried out at reflux and for sufficient time to reach equilibrium conversion.

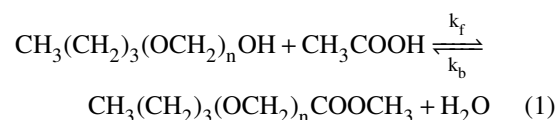
### 2.1.4 Analysis

The acetic acid concentration was analyzed by titration of reaction mixture sample with standard solution of KOH (0.1N) using phenolphthalein as the indicator. The moisture content of the reaction sample was

determined by titration using Karl Fisher method. The concentrations of glycol ether were calculated from stoichiometric relations.

## 2.2 Kinetic models

The esterification reaction is given as:



Where  $n = 2$  for EB and  $n = 3$  for DB.

### 2.2.1 Homogeneous catalysis

Homogeneous acid catalyzed esterification has been reported as a second-order kinetics (Lilja *et al.* 2002, Liu *et al.* 2006, Mekala 2015, Eliana 2018). The reaction rate expression is:

$$-r_A = -\frac{dC_A}{dt} = k_f C_A C_B - k_b C_C C_D \quad (2)$$

Where  $k_f$  and  $k_b$  represent the forward and backward reactions rate constants.  $C_A$ ,  $C_B$ ,  $C_C$  and  $C_D$  are the AA, glycol ether (EB or DB), GEA and water (W) concentrations.

At time zero, in the beginning of the reaction, the products water and glycol ether acetate are no present, in terms of acetic acid conversion:  $C_A = (1 - X_A)C_{A0}$ ,  $C_B = (1 - X_A)C_{A0}$  and  $C_C = C_D = C_{A0}X_A$ , and  $K_{eq}$  is the equilibrium constant of the reaction:

$$K_{eq} = \frac{k_f}{k_b} = \left[ \frac{C_C C_D}{C_A C_B} \right]_{eq} = \left[ \frac{X_A^2}{(1 - X_A)^2} \right]_{eq} \quad (3)$$

The rate expression is rearranged as:

$$-r_A = k_f C_{A0}^2 \left[ (1 - X_A)^2 - \frac{X_A^2}{K_{eq}} \right] \quad (4)$$

Integrating and rearranged the equation (4):

$$-r_A = H k_f t = \ln \left( \frac{1 + F X_A}{1 - G X_A} \right) \quad (5)$$

Where  $H = 2 \sqrt{\frac{1}{K_{eq}}} C_{A0}$ ,  $F = \sqrt{\frac{1}{K_{eq}}} - 1$  and  $G = \sqrt{\frac{1}{K_{eq}}} + 1$ .

With the equations (3) and (5), the parameters  $K_{eq}$ ,  $k_f$  and  $k_b$  were estimated from the experimental data fitting with the proposed model.

### 2.2.2 Heterogeneous catalysis

The model Langmuir-Hinshelwood was used to fit the experimental data obtained in the batch reaction with Amberlyst 15 (Deshmukh *et al.* 2009, Sert 2010, Sharma *et al.* 2014, Lux *et al.* 2015). The reaction rate expression is:

$$-r_A = -\frac{dC_A}{dt} = \frac{k_f C_A C_B - k_b C_C C_D}{(1 + K_a C_A + K_w C_D)^2} \quad (6)$$

Where  $K_a = 0.08587$  L/mol and  $K_w = 0.01639$  L/mol are the adsorption constants for acetic acid and water respectively (Deshmukh *et al.* 2009). According to the stoichiometry of the reaction in terms of acetic acid conversion:  $C_A = (1 - X_A)C_{A0}$ ,  $C_B = (m - X_A)C_{A0}$  and  $C_C = C_D = C_{A0}X_A$ , where  $m$  is the initial molar ratio of GE:AA. For the equilibrium constant the equation is:

$$K_{eq} = \frac{k_f}{k_b} = \left[ \frac{X_A^2}{(1 - X_A)(m - X_A)} \right]_{eq} \quad (7)$$

The rate expression is rearranged as:

$$-r_A = C_{A0} k_f \frac{\left[ (1 - X_A)(m - X_A) - \frac{1}{K_{eq}} X_A^2 \right]}{(1 + K_a C_{A0}(1 - X_A) + K_w C_{A0} X_A)^2} \quad (8)$$

The Euler's method was used to solve the differential equation (8), the parameters  $K_{eq}$ ,  $k_f$  and  $k_b$  were estimated from the experimental data fitting with the proposed model.

### 2.2.3 Pre-exponential factor and activation energy

The temperature dependency of the reaction rate constants is expressed by the Arrhenius law.

$$k = k_0 e^{-E_a/RT} \quad (9)$$

Where  $k_0$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the gas constant and  $T$  is the temperature.

Using the linear form of the equation (9), the parameters  $k_0$  and  $E_a$  can be calculated from the estimated  $k$  of the kinetic model.

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (10)$$

## 3 Results and discussion

### 3.1 Effect of reaction conditions on the conversion to glycol acetate for homogeneous catalytic system

Different reaction conditions were studied to analyze the effect of the molar ratio between reactants (acetic acid to glycol ether ratio), the reaction temperature and the amount of homogeneous catalyst (pTSA) on the synthesis of glycol ether acetates. The experiments were carried out at isothermal conditions in a batch reactor. Fig. 2 shows the conversion to produce EB-Acetate versus time at different AA:EB ratios. Curves obtained at 90 or 100 °C with pTSA catalyst loadings of 0.25 or 0.5 meq and the concentration curves of the non-catalytic homogeneous esterification reactions can be observed. The addition of the homogeneous catalyst pTSA reduces the reaction time by almost two orders of magnitude to reach the same conversion of the produced EB-Acetate. That is, to reach, for example, a conversion of 0.4, with the addition of pTSA are required only 5 to 20 minutes while for the non-catalytic reactions are needed more than 1000 minutes. The reaction temperature also shows a significant effect on the conversion to EB-Acetate. Higher reaction temperature favors acetate formation, being more evident at AA:EB molar ratio of 1:1.

The amount of pTSA catalyst also shows a very clear effect on the reaction conversion, since the experiments performed with a 0.5 meq load of pTSA show higher conversion values compared to the curves obtained with 0.25 meq. Finally, better results were obtained for the conversion to EB-Acetate produced with AA:EB reagent molar ratios of 1:1 and 1:2. Experiments performed with the AA:EB ratio of 2:1 showed lower conversion values. The effect of the molar ratio between acetic acid and alcohol in esterification reactions has been reported in other studies. What they have reported in these works is that the conversion of the reaction increases when the molar ratio has a higher content of the higher boiling temperature reagent (Suman *et al.* 2009, Zhu *et al.* 2016, Eliana 2018). In the case of the reaction between AA and EB, it was observed that reactions with higher EB concentration improved the reaction conversion.

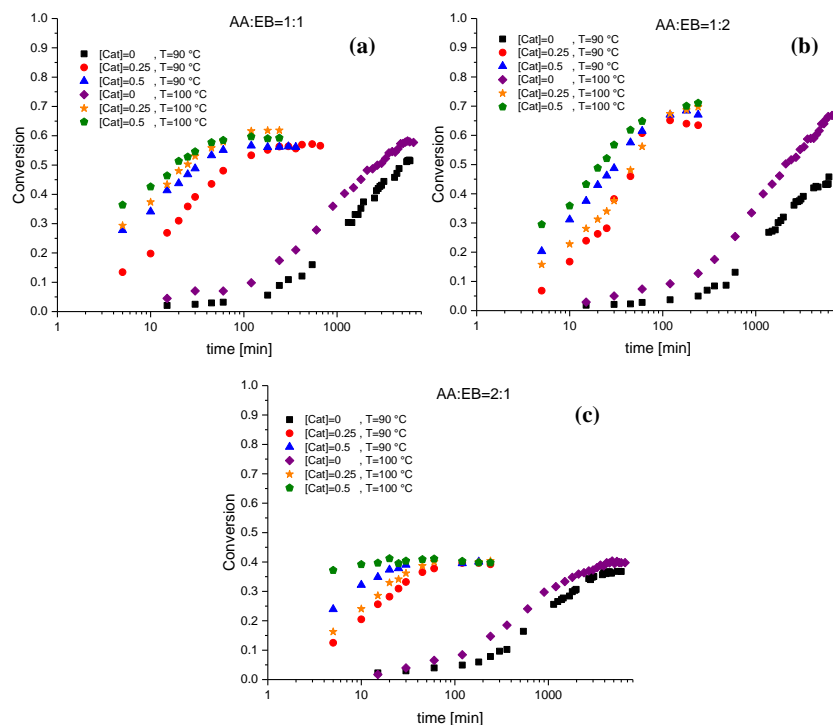


Fig. 2 Reaction conversion for EB-Acetate production at different catalyst loads and temperatures: (a) AA:EB ratio 1:1, (b) AA:EB ratio 1:2, and (c) AA:EB ratio 2:1.

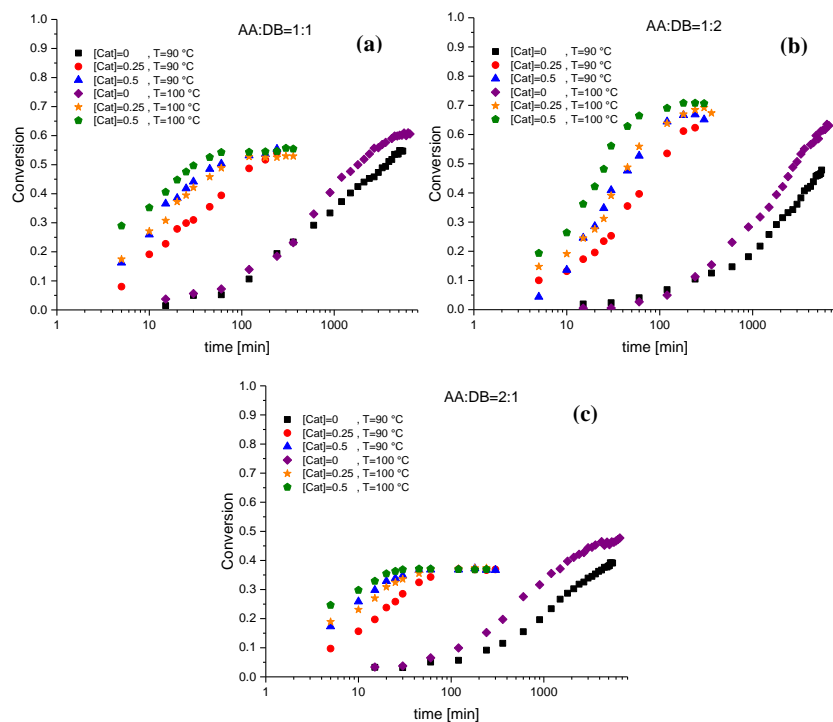


Fig. 3 Reaction conversion for DB-acetate production at different catalyst loads and temperatures: (a) AA:DB ratio 1:1, (b) AA:DB ratio 1:2, and (c) AA:DB ratio 2:1.

Fig. 3 shows the conversion curves corresponding to esterification reaction between AA and DB. As was observed with the AA:EB system, similar effects were observed for the reaction temperature, catalyst loading and reagents molar ratio for the DB-Acetate production. In general, it is observed that the conversion values obtained in the synthesis of DB-Acetate are slightly lower compared to those obtained in the reaction to produce EB-Acetate. The conversion values obtained for the esterification reactions between AA and the glycol ethers EB and DB are consistent with those reported in other works that have studied the esterification reaction of glycols with acetic acid (Deshmukh *et al.* 2009, Suman *et al.* 2009, Yang *et al.* 2015).

### 3.2 Kinetic model for homogeneous catalytic system

A second-order kinetic model for homogeneous esterification reaction was used to fit the experimental data and to estimate the reaction rate constants ( $k_f$  and  $k_b$ ). Fig. 4 and Fig. 5 show the experimental conversion curves and the fitted model at several reaction conditions for EB-Acetate and DB-Acetate synthesis. It is observed that the fit of the model to the experimental data is reasonably good regardless of the experimental conditions used in this study. It can also be observed that the effect of the molar ratio between AA and GE is more significant as the conversion of the reaction approaches chemical equilibrium. It is clear that the value of the maximum conversion of the reaction depends on the AA:GE ratio and has little dependence on temperature and catalyst loading. In the experiments catalyzed with pTSA, the AA:GE ratio of 1:2 yields the highest conversion values, while the 2:1 ratio yields the lowest conversion values. This result is consistent with previous works for other homogeneous catalytic systems that reports that an increase in alcohol concentration causes increments in maximum conversion (Eliana 2018).

On the other hand, there is few information in the literature on the behavior of the pTSA catalyst in homogeneous esterification reactions of alcohols with acetic acid, since it is commonly used in supported systems and for the esterification of fatty acids (Liu *et al.* 2020), so it is relevant to obtain information on the kinetic parameters with this type of catalyst. In the Table 2 are reported the equilibrium constant  $K_{eq}$ , calculated by equation (3), the reaction rate constants  $k_f$  and  $k_b$ , estimated by fitting experimental data to equation (5) using the non-linear fit app of Origin Pro

software, and the square of the correlation coefficient  $R^2$  for EB-Acetate and DB-Acetate experiments at different conditions of catalyst loading, temperature, and AA:GE ratio. The equilibrium constant values show the effect of the AA:GE ratio on the esterification reaction discussed above, while the  $R^2$  values confirm the observation that the proposed kinetic model adequately represents the experimental data. Both the equilibrium constant and correlation coefficient values are consistent with values reported for esterification reactions of alcohol with organic acids (Lilja *et al.* 2002, Eliana 2018).

The reaction rate constants show a correlation with pTSA catalyst loading. With an increasing in catalyst loading, the values of the constants increase. The same effect occurs with temperature, although the change is not as high as with increasing catalyst. This behavior was observed with both glycol acetates. Regarding the differences in the values of the reaction constants and equilibrium constant between the AA:EB and AA:DB systems, the non-catalyzed experiments show no clear behavior or significant differences between the two systems, but the pTSA-catalyzed experiments show that the EB-Acetate synthesis presents higher values of the equilibrium and reaction rate constants compared to the DB-Acetate synthesis. This may be attributed to the glycol chain length as was observed for alcohols in other esterification studies (Lilja *et al.* 2002). Moreover, the order of magnitude of the values of the reaction rate constants is consistent with values reported for esterification reactions using homogeneous catalysts (Liu *et al.* 2006, Eliana 2018).

Table 3 presents the results of the calculation of the activation energies  $E_a$  and the pre-exponential factor  $k_0$ . No evident correlation is observed between  $E_a$  and reaction parameters such as catalyst loading, AA:GE molar ratio or type of glycol ether.  $E_a$  values range from 30,000 to 130,000 J/mol. Other studies have reported  $E_a$  values in the same magnitude range, so it can be estimated that the values obtained are consistent in magnitude order (Rönneck *et al.* 1997, Liu *et al.* 2006, Liu, Lotero *et al.* 2006).

### 3.3 Heterogeneous catalytic system

The esterification reaction between AA and glycol ethers was evaluated with a heterogeneous catalytic system based on an ion exchange resin (Amberlyst 15). Experiments were performed using 5 meq of Amberlyst 15 per mole of AA at two temperatures (90 and 100 °C) and at two molar ratios between reagents (AA:GE of 1:1 and 2:1).

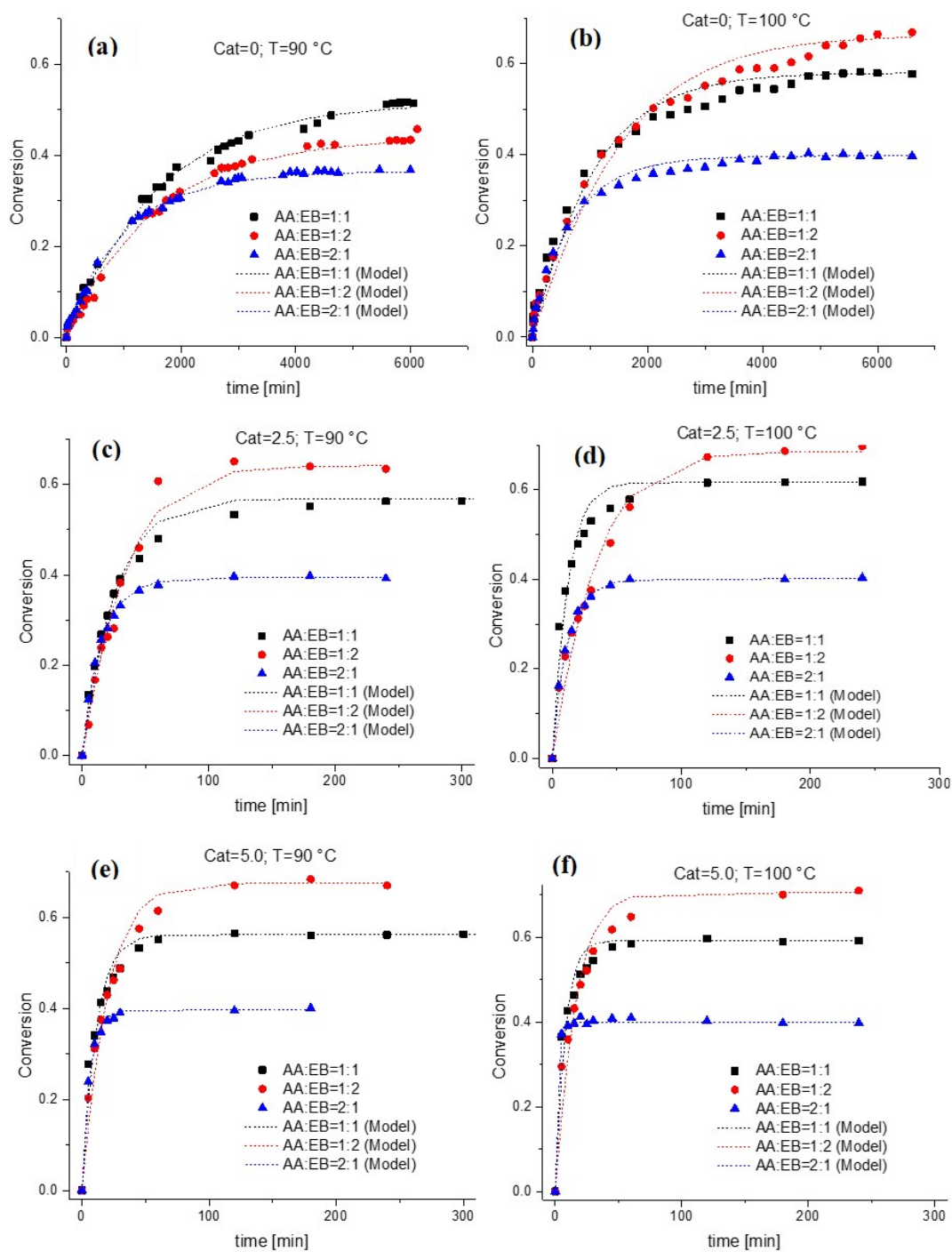


Fig. 4 Fitting of the curves obtained from the kinetic model to the experimental conversion data of the AA: EB system at different reaction conditions: (a) Cat=0, T=90°C, (b) Cat=0, T=100°C, (c) Cat=2.5 meq, T=90°C, (d) Cat=2.5 meq, T=100°C, (e) Cat=5.0 meq, T=90°C, and (f) Cat=5.0 meq, T=100°C.



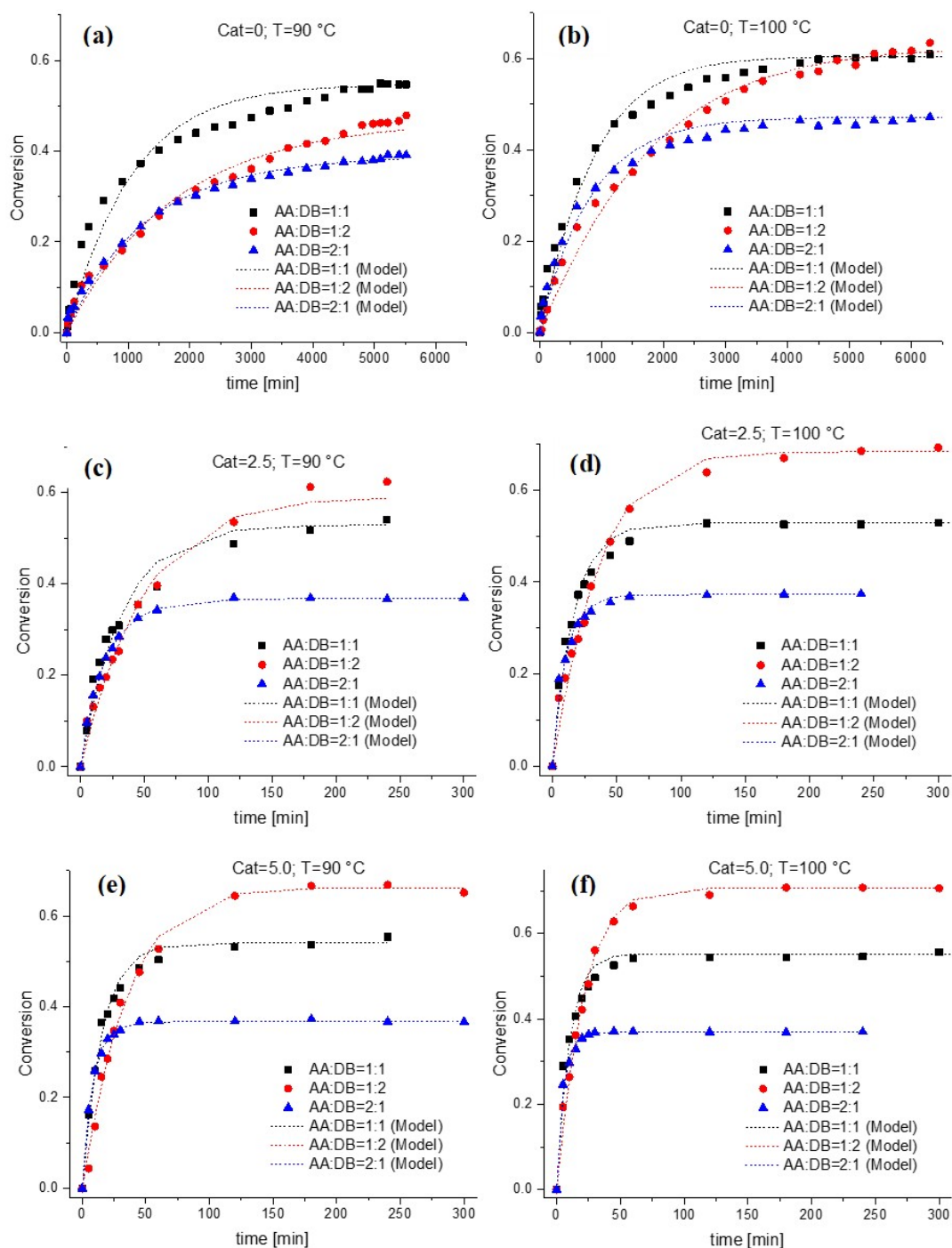


Fig. 5 Fitting of the curves obtained from the kinetic model to the experimental conversion data of the AA: DB system at different reaction conditions: (a) Cat=0, T=90°C, (b) Cat=0, T=100°C, (c) Cat=2.5 meq, T=90°C, (d) Cat=2.5 meq, T=100°C, (e) Cat=5.0 meq, T=90°C, and (f) Cat=5.0 meq, T=100°C.

Table 2 Equilibrium and rate constants  $k_f$  and  $k_b$  for various ratio molar AA:GE, catalyst load and temperatures, determined by homogeneous kinetic model fitting of the experimental data.

AA:GE molar ratio	Temperature, °C	meq pTSA/mol AA	Keq(a)	$k_f$ , [L mol <sup>-1</sup> min <sup>-1</sup> ](b)	EB-acetate $k_b$ , [L mol <sup>-1</sup> min <sup>-1</sup> ](c)	R <sup>2</sup> (d)	Keq	$k_f$ , [L mol <sup>-1</sup> min <sup>-1</sup> ](b)	DB-acetate $k_b$ , [L mol <sup>-1</sup> min <sup>-1</sup> ](c)	R <sup>2</sup> (d)
1:01	90	0	1.1356	0.000066	0.000059	0.9958	1.4604	0.000142	0.000097	0.9634
		2.5	1.7414	0.00546	0.003135	0.987	1.2592	0.00423	0.003359	0.9632
		5	1.6483	0.01196	0.007256	0.967	1.3839	0.00894	0.00646	0.9878
	100	0	1.8993	0.000134	0.000071	0.9755	2.3487	0.000227	0.000097	0.9831
		2.5	2.6062	0.0125	0.004796	0.9512	1.252	0.00759	0.006062	0.9834
		5	2.1286	0.01839	0.00864	0.9511	1.5253	0.01374	0.009008	0.9669
1:02	90	0	0.6234	0.000078	0.000125	0.9954	0.7804	0.000092	0.000118	0.9845
		2.5	3.2154	0.0099	0.003079	0.9855	2.0725	0.00646	0.003117	0.9858
		5	4.3244	0.01978	0.004574	0.9721	3.8393	0.01378	0.003589	0.9936
	100	0	3.8566	0.000245	0.000064	0.9812	2.8407	0.000219	0.000077	0.9921
		2.5	4.7657	0.01297	0.002722	0.9752	4.6645	0.01397	0.002995	0.9885
		5	5.7453	0.02671	0.004649	0.9415	5.8329	0.02839	0.004867	0.9932
2:01	90	0	0.3327	0.000032	0.000095	0.9966	0.4144	0.00003	0.000073	0.9913
		2.5	0.4245	0.00245	0.005772	0.9976	0.3387	0.00175	0.005167	0.9991
		5	0.4375	0.00626	0.014309	0.9963	0.3363	0.00409	0.012161	0.9991
	100	0	0.4357	0.000056	0.000128	0.9904	0.7994	0.000077	0.000097	0.9852
		2.5	0.4498	0.00322	0.007158	0.9968	0.3544	0.00351	0.009903	0.9836
		5	0.4426	0.01996	0.045098	0.9969	0.3428	0.00661	0.019281	0.9947

(a)  $K_{eq} = [X_A^2 / (1 - X_A)^2]_{eq}$ (b)  $k_f$  was estimated by fitting experimental data to equation (5) using the non-linear fit app of Origin Pro software(c)  $k_b = k_f / K_{eq}$ (d) R<sup>2</sup> is the squared correlation coefficientTable 3. Pre-exponential factor  $k_0$  and activation energy  $E$  for various ratio molar GE:AA, catalyst load and temperatures.

AA:GE molar ratio	meq pTSA/mol AA	EB-acetate		DB-acetate	
		$k_0$	Ea, J/mol	$k_0$	Ea, J/mol
1:01	0	5.09E+07	82642	5.44E+03	52717
	2.5	1.45E+11	93336	2.48E+07	67974
	5	1.07E+05	48317	9.19E+04	48764
1:02	0	6.79E+13	124608	1.45E+10	98738
	2.5	2.28E+02	30333	2.48E+10	87513
	5	1.46E+03	33841	1.99E+10	84623
2:01	0	4.27E+04	63467	5.79E+10	106272
	2.5	8.10E+01	31437	3.06E+08	78162
	5	1.82E+16	128388	2.32E+05	53909

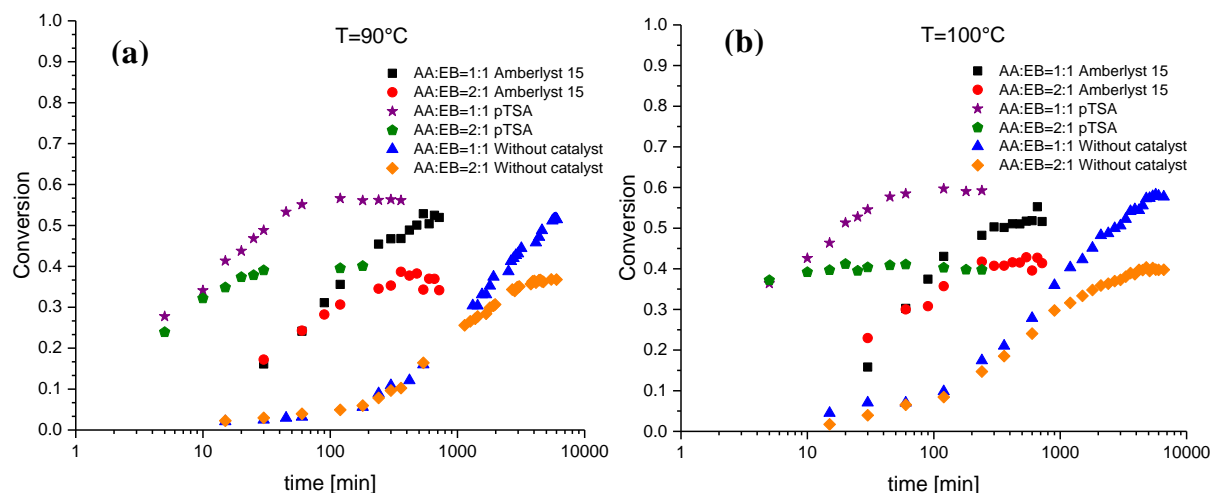


Fig. 6 Reaction conversion for EB-Acetate production with 5 meq of homogeneous or heterogeneous catalyst and without catalyst at different temperatures: (a) 90 °C (b) 100 °C.

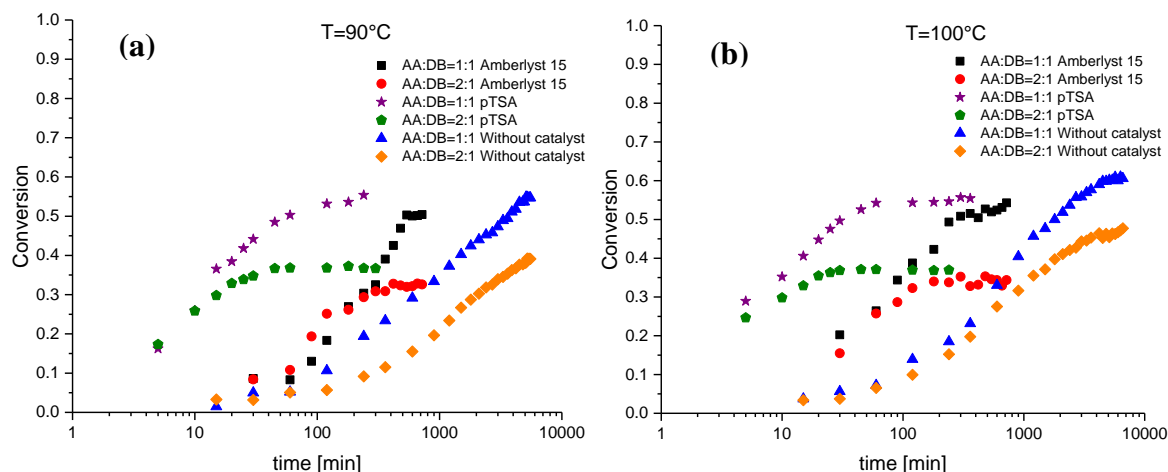


Fig. 7 Reaction conversion for DB-Acetate production with 5 meq of homogeneous or heterogeneous catalyst and without catalyst at different temperatures: (a) 90 °C (b) 100 °C.

Fig. 6 shows the conversion data corresponding to experiments carried out with AA and EB, whereas Fig. 7 shows conversion curves obtained from reactions between AA and DB. In both figures the conversion curves obtained from the tests without catalyst and with homogeneous catalyst (pTSA) at the same loading level (5 meq) were included to compare the catalytic systems. For both the reaction between AA and EB and the reaction between AA and DB, it can be seen that with the homogeneous catalytic system high conversion values are achieved in short reaction times, while with the heterogeneous system longer times are required to achieve the same conversion. When equilibrium is reached, similar conversion values are obtained with both catalytic systems, or even without the use of catalyst, being the reaction time the most important difference between the selection of one system or the other. This behavior is associated with homogeneous catalysts having higher esterification reaction rates compared to heterogeneous catalytic systems due to factors such as adsorption and diffusion of reactants on the catalyst surface, as has been reported in other studies (Lilja *et al.* 2002, Liu *et al.* 2006, Khire *et al.* 2012).

The molar ratio of reactants, AA:EB and AA:DB, has a significant effect on the conversion of the esterification reaction regardless of the catalytic system or whether the reaction is uncatalyzed. This effect is most noticeable as the reaction approaches chemical equilibrium. This dependence of the conversion on the molar ratio of the reactants has

been reported for the esterification reaction of other acid/alcohol systems (Sert 2010, Sharma *et al.* 2014). As discussed above, the highest conversion values are reached when the content of the reagent with the highest boiling point is higher than the content of the reagent with the lowest boiling point, in this case it is observed when the content of glycol ether is equal to or higher than the content of acetic acid.

### 3.4 Kinetic model for heterogeneous catalytic system

A Langmuir-Hinshelwood (LH) model was used to fit the experimental data obtained from the heterogeneous esterification reaction of AA with EB and DB using Amberlyst 15 as catalyst. The experimental conversion data and the model fitting corresponding to EB-Acetate and DB-Acetate synthesis is shown in Fig. 8. It is observed that the fit of the model to the experimental data works acceptably for the two reactions at the different experimental conditions. Unlike the kinetic model used to fit the esterification reactions with the homogeneous catalytic system, in which an analytical solution was developed to obtain an algebraic equation, the LH model was solved from the differential equation (8) using a Euler method. Despite employing two different solution routes, both models worked adequately to obtain the values of the rate constants as a result of fitting the experimental data for the respective catalytic systems.

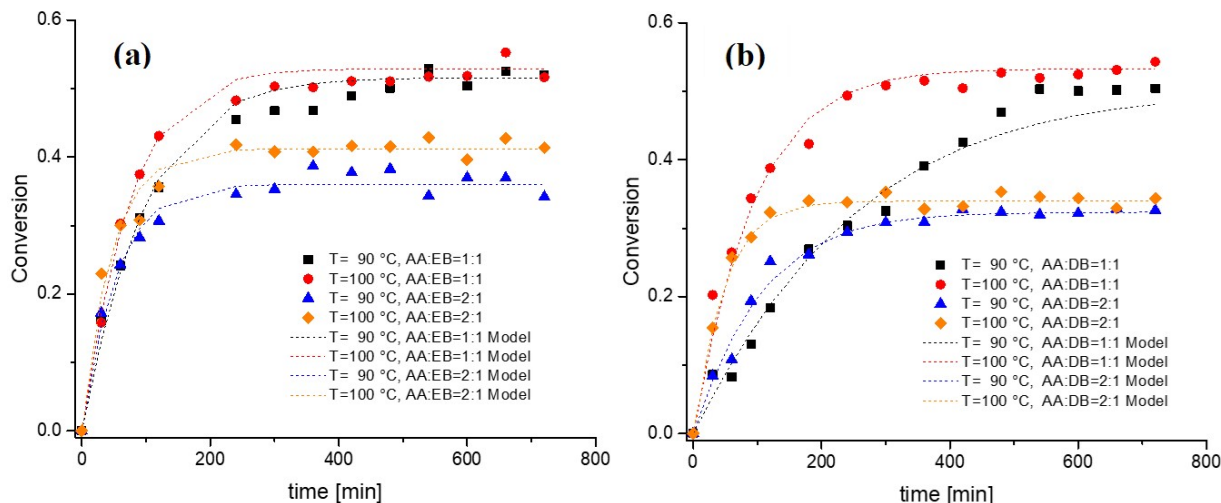


Fig. 8. Fitting of the curves obtained from the heterogeneous kinetic model to the experimental conversion data with catalyst addition of 5 meq Amberlyst15 for: (a) EB-Acetate, and (b) DB-Acetate.

Table 4. Rate constants  $k_f$  and  $k_b$  for various ratio molar AA:GE and temperatures using a catalyst load of 5 meq Amberlyst 15, determined by heterogeneous kinetic model fitting of the experimental data.

AA:GE molar ratio	Temperature, $K_{eq}$ °C	EB-acetate			$R^2$	$K_{eq}$	DB-acetate		$R^2$
		$k_f$ , L/mol min	$k_b$ , L/mol min	$k_f$ , L/mol min			$k_b$ , L/mol min		
1:01	90	1.1359	0.001978	0.001741	0.9892	1.0162	0.000806	0.000793	0.9856
	100	1.2618	0.002696	0.002137	0.9927	1.2998	0.002306	0.001774	0.9867
2:01	90	1.4525	0.004488	0.00309	0.9771	0.8741	0.00214	0.002449	0.9866
	100	3.2914	0.006242	0.001896	0.9747	1.087	0.004901	0.004509	0.9926

Table 4 shows the values of the equilibrium constant  $K_{eq}$ , the reaction rate constants  $k_f$  and  $k_b$  and the square of the correlation coefficient  $R^2$  corresponding to the synthesis of EB-Acetate and DB-Acetate obtained from fitting the LH model to the experimental data estimated with the Amberlyst 15 heterogeneous catalytic system. It is observed that, for the synthesis of both acetates, the equilibrium constant increases with temperature, whereas on changing the AA:EB ratio from 1:1 to 2:1 the value of the constant increases but on changing the AA:DB ratio from 1:1 to 2:1 the  $K_{eq}$  constant decreases. The values of the correlation coefficients  $R^2$  confirm the proper fit of the LH model to the experimental data, as discussed above.

On the other hand, it is observed that for both glycol ether acetates the value of the rate constants increases with higher temperature, which is an expected behavior. It is also observed that the reaction rates are higher for the experiments performed with the AA:EB or AA:DB ratio of 2:1. These results indicate that the reaction rate does indeed rise with increasing acetic acid concentration but chemical equilibrium is being reached at lower conversion values. It can

also be seen that the values of the reaction rate constants obtained for EB-Acetate are higher than those obtained for DB-Acetate. This is explained by a retardation effect of the esterification reaction due to an increase in the chain length of the alcohol (Lilja *et al.* 2002).

Comparing the values of the  $k_f$  and  $k_b$  constants obtained from the reactions with the homogeneous and heterogeneous systems at the same experimental conditions, it is observed that the reaction rates with the Amberlyst 15 catalyst are lower than the rates obtained with the pTSA. On the other hand, the values obtained for the reaction rate constants are consistent in magnitude to those reported for other types of esterification reactions between an organic acid and an alcohol (Sert 2010, Sharma *et al.* 2014).

From the values of the reaction rate constants estimated from the experiments performed at 90 and 100 °C, the activation energy  $E_a$  and frequency factor  $k_0$  were calculated with Equation (10) and are reported in Table 5. The activation energy values corresponding to EB esterification are lower than those obtained for DB esterification.

Table 5. Pre-exponential factor  $k_0$  and activation energy  $E_a$  for various ratio molar AA:GE using a catalyst load of 5 meq Amberlyst 15.

AA:GE molar ratio	EB-acetate		DB-acetate	
	$k_0$	$E_a$ , J/mol	$k_0$	$E_a$ , J/mol
1:01	1.81E+02	34482	2.89E+13	115067
2:01	9.93E+02	37142	4.90E+10	92866

This indicates that the reaction rate for obtaining DB-Acetate is more sensitive to temperature changes than the reaction to obtain EB-Acetate when the heterogeneous catalyst is used. Regarding the molar ratio between AA and glycol ether, as in the case of the homogeneous catalytic system or the non-catalyzed one, there is no clear behavior of the dependence of the activation energy on this factor. The activation energy values are relevant for estimating the values of the rate constants at other temperatures. However, since no clear correlation of  $E_a$  with factors such as catalyst concentration or molar ratio between reactants is observed, it is necessary to have the data for different combinations of catalyst loading and AA:GE ratio.

The activation energy results are consistent in magnitude with values reported for the esterification reaction of alcohols with acetic acid using Amberlyst 15 catalyst. Deshmukh and coworkers reported  $E_a$  values around 60,000 J/mol for the esterification of butyl cellosolve (EB) with acetic acid in a Amberlyst 15 fixed-bed chromatographic reactor (Deshmukh *et al.* 2009). Lux and coworkers reported values of  $E_a$  around 55,000 J/mol for the esterification of methanol with acetic acid using Amberlyst 15 as catalyst (Lux *et al.*, 2015).

To evaluate the results obtained from fitting both models, AA and EB-Acetate (Fig. 9) and AA and DB-Acetate (Fig. 10) concentration curves were constructed with the estimated reaction rate constants and compared to the experimental concentration values obtained with the pTSA and Amberlyst 15 catalysts. It can be seen that the curves obtained with both models are in good agreement with the experimental concentration data for both types of glycol ether acetate.

The AA concentration curves clearly show that the esterification reaction catalyzed with pTSA generates a very fast disappearance of the acid to reach chemical equilibrium within a few minutes, whereas the reactions catalyzed with Amberlyst 15 require longer times to consume the AA to reach equilibrium. The glycol ether acetate concentration has a reciprocal behavior to that of the AA concentration, i.e., a rapid

increase in acetate concentration is observed with the homogeneous catalyst and a slower increase in concentration with the heterogeneous catalyst. Neither the molar ratio of AA:GE reagents nor temperature has a significant effect on the concentration of glycol ether acetate, since most of the experiments obtained concentrations at the equilibrium between 2 and 3 mol/L.

The results of the kinetic study of the esterification of glycol ethers with acetic acid is relevant for the design of industrial processes for the synthesis of glycol ether acetates. The information obtained in this study is the basis for studying reactive distillation processes that can employ both homogeneous and heterogeneous catalytic systems to produce these solvents with so many uses in industry.

## Conclusions

The esterification reactions of glycol ethers with acetic acid produced the glycol ether acetates EB-Acetate and DB-Acetate. The molar ratio of acetic acid to glycol ether (AA:GE) has a significant effect on the maximum conversion achievable in the esterification reaction, while temperature, catalyst type and catalyst loading have a significant effect on the reaction rate. The kinetic models proposed for the homogeneous and heterogeneous systems, a second order and LH respectively, had an acceptable fit with the experimental data and can be used to consistently predict the concentration curves for the disappearance of acetic acid and appearance of glycol ether acetate. The values of the reaction rate constants were estimated from the fit of the models, finding that they are consistent with values reported for other esterification reactions with similar catalytic systems. It was observed that the homogeneous catalytic system based on pTSA presents higher reaction rates than those obtained with the heterogeneous catalytic system based on Amberlyst 15. The results obtained are the basis for the design of reactive distillation systems that will allow a continuous reaction process for industrial applications.

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### Nomenclature

GEA	glycol ether acetate
EB-Acetate	2-butoxyethanol acetate
DB-Acetate	2-(2-butoxyethoxy)ethyl acetate
GE	glycol ether
AA	acetic acid
pTSA	p-toluene sulfonic acid
EB	2-butoxyethanol
DB	2-(2-butoxyethoxy)ethyl
meq	milliequivalents
$k_f$	forward reaction rate, $L \text{ mol}^{-1} \text{ min}^{-1}$
$k_b$	backward reaction rate, $L \text{ mol}^{-1} \text{ min}^{-1}$
$X_A$	reaction conversion
$K_{eq}$	equilibrium constant
$E_a$	activation energy, $J \text{ mol}^{-1}$
$k_0$	pre-exponential factor

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