

## Systematic kinetic modeling of the propyl *tert*-butyl ether synthesis reaction

Jordi Hug Badia, Carles Fité\*, Roger Bringué, Montserrat Iborra, Fidel Cunill

*Chemical Engineering and Analytical Chemistry Department, Faculty of Chemistry, University of Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain*

\*Corresponding author. Tel.: +34 93 402 1304; Fax: +34 93 402 1291; E-mail address: fite@ub.edu

### Abstract

The kinetics of the liquid-phase addition of 1-propanol to isobutene to produce propyl *tert*-butyl ether (PTBE) has been studied using the ion-exchange resin Amberlyst™ 35 as the catalyst. Reaction rates free from mass transfer limitations have been experimentally determined in the temperature range 303–352 K, for different initial proportions of alcohol and isobutene, and using two different reactor types (i.e., a batch stirred tank reactor, to obtain most of the experimental data, and a tubular reactor, to validate those results). To find out the best kinetic model, a systematic approach has been adopted. The overall etherification reaction has been decomposed as the result of elementary steps based on Langmuir–Hinshelwood–Hougen–Watson or Eley–Rideal mechanisms. Candidate kinetic equations have been originated from all possible combinations of adsorbed and non-adsorbed compounds, and rate-determining step. The possible effect of the interaction between the reaction medium and the resin on reaction rates has been also examined. Since all experimental data have been used at once in the fit of the kinetic equations, all combinations of significant or non-significant temperature dependence of model parameters has been also considered. As a result, 1,404 candidate kinetic equations have been fitted separately to experimental data. Discrimination among models is based on mathematical and physico-chemical criteria. The final choice of the best kinetic model involves multimodel inference. It corresponds to an Eley–Rideal mechanism where one 1-propanol molecule adsorbed on the catalyst reacts with one isobutene molecule from the liquid phase to form one adsorbed PTBE molecule, the surface reaction being the rate-determining step.

Keywords: Kinetic modeling; Propyl *tert*-butyl ether; Amberlyst™ 35; Multimodel inference

## 1. Introduction

Alkyl *tert*-butyl ethers can be obtained through the addition of an alcohol molecule to 2-methylpropene (isobutene). Common examples of this reaction are the production of methyl *tert*-butyl ether (MTBE) from methanol, and ethyl *tert*-butyl ether (ETBE) from ethanol. Both are used as oxygenate additives for the gasoline pool and they are produced at industrial scale catalyzed by sulfonic macroreticular ion-exchange resins [1-3]. Kinetics of MTBE and ETBE production has been studied extensively for decades now. In the earliest works, kinetic equations were expressed in terms of concentrations [4,5], and later activity-based expressions were found to be more appropriate, given the high non-ideality of olefin-alcohol-ether mixtures [6,7]. Usually, the proposed rate equations for these reactions are derived from Langmuir–Hinshelwood–Hougen–Watson (LHHW) or Eley–Rideal (ER) mechanisms, where the surface reaction is considered as the rate-determining step. Depending on the assumptions adopted by each author, the reported kinetic models differ mainly on the compounds that adsorb on the catalyst, and on the number of active sites that participate in the rate-determining step of the reaction [6-10].

The next analogous reaction in the alcohol series is the synthesis of propyl *tert*-butyl ether (PTBE), which is obtained by addition of 1-propanol (1-PrOH) to isobutene (IB) (Fig. 1).

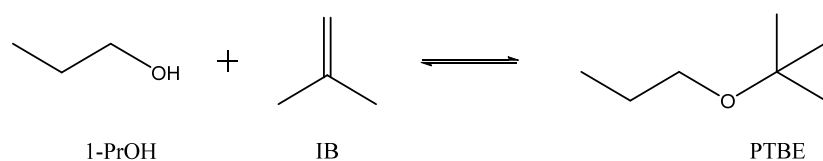


Figure 1. PTBE synthesis reaction

PTBE presents suitable properties to be used also as oxygenate additive for the gasoline pool.

Moreover, it is good candidate to accomplishing the biofuel target, since 1-propanol can be obtained through fermentative processes of non-edible biomass [11,12]. To date, a kinetic model for the PTBE synthesis in the liquid phase over ion-exchange resins as catalysts cannot be found in the literature.

The most relevant references related to this reaction system are the kinetic study of the PTBE gas-

phase synthesis by Słomkiewicz [13] and the work on propanol reactivity and equilibrium of the PTBE liquid-phase synthesis by Linnekoski et al. [14], both using Amberlyst<sup>TM</sup> 15 as the catalyst.

Commonly, the adopted procedure in kinetic modeling is to propose a reduced number of candidate equations and to discriminate among them by selecting the one that better predicts experimental rate data. If temperature dependence is analyzed, kinetic equations are usually fitted using separately data subsets, each obtained from different reaction temperature experiments. The main weak points are: i) one cannot assure that the true model is included in the set of candidate equations; ii) when fitting separately data subsets, the best fitting equation could differ for some subset, although the actual mechanism does not change; iii) the true model could be discarded if overfitting occurs, because at least one fitted parameter is statistically non significant.

In the present work, some actions have been undertaken to overcome the commented weak points in the search of the true kinetic model of the synthesis of PTBE:

- i) Trying to ensure that the true model is contained in the set of candidate models, the overall etherification reaction has been decomposed in the elementary steps, according to LHHW and ER mechanisms: reactants adsorption on the catalyst, surface reaction and product desorption. A kinetic equation has been derived from every combination of these steps, i.e., the choice of adsorbed compounds and rate-determining step. In addition, it has been considered that the reaction medium can affect the catalyst activity, hence reaction rates. A kinetic equation has been derived from every combination of elementary steps and the possible effect of the reaction medium, what results in the base set of candidate kinetic equations.
- ii) All terms of every kinetic equation have been expressed as a function of the experimental variables (composition and temperature), so all experimental data are used at once to fit each kinetic equation.
- iii) For every kinetic equation in the base set, all plausible combinations of significant and non-significant parameters have been considered, each combination originating a different kinetic equation to be fitted.

A more detailed explanation on obtaining the base set of kinetic equations and the derived equations to be fitted is described in section 3.2.

Some studies adopting this kinetic analysis approach for a similar reaction system can be found in the literature: the kinetics of the ETBE synthesis, from ethanol and an industrial FCC C<sub>4</sub> cut as the isobutene source [15] and, more recently, the kinetics of a more complex reaction system, the simultaneous synthesis of ETBE and TAAE (*tert*-amyl ethyl ether) by etherification of isobutene and isoamylenes with ethanol [16]. In those investigations, several combinations of adsorbed and non-adsorbed species on the catalyst, and the possible temperature-dependence of parameters were considered. Also, the inclusion in the kinetic model of a term that accounts for the possible effect of the interaction between the reaction medium and the catalyst on reaction rates was taken into account.

## **2. Experimental section**

### **2.1. Materials**

Reactants were 1-propanol (>99.7% GC, Sigma-Aldrich) and isobutene, supplied as pure isobutene (>99.9% GC; Air Liquide) or as a component of a synthetic C<sub>4</sub> mixture (25%wt isobutene, 40%wt isobutane, 35%wt *trans*-2-butene; Abelló-Linde). Chemical standards were used for chromatographic analysis: 2-methyl-2-propanol (TBA, >99.7% GC, Panreac), 2,4,4-trimethyl-1-pentene (TMP-1, >98% GC, Sigma-Aldrich), 2,4,4-trimethyl-2-pentene (TMP-2, >98% GC, Sigma-Aldrich). 2-Methyl-2-propoxypropane (PTBE, >99% GC) was synthesized and purified in our laboratory.

As the catalyst, the ion-exchange resin Amberlyst™ 35 (A35, The Dow Chemical Company) was used. A35 is a sulfonic macroreticular polymer of styrene-divinylbenzene. Physical properties are listed in Table 1.

Table 1. Physical properties of A35.

Catalyst		Amberlyst 35
Structure		Macroreticular
Divinylbenzene	[%]	20
Skeletal density, $\rho_{sk}$	[g cm <sup>-3</sup> ]	1.542
Acid Capacity <sup>a</sup>	[meq H <sup>+</sup> g <sup>-1</sup> ]	5.32
Mean particle diameter, $d_{p,m}$ <sup>b</sup>	[ $\mu$ m]	623
BET surface area, $S_{BET}$	[m <sup>2</sup> g <sup>-1</sup> ]	29.0
Swollen-state pore volume, $V_g$ <sup>c</sup>	[cm <sup>3</sup> g <sup>-1</sup> ]	0.720
Volume of the swollen polymer phase, $V_{sp}$ <sup>c</sup>	[cm <sup>3</sup> g <sup>-1</sup> ]	0.613
Porosity in polar medium, $\phi_p$ <sup>d</sup>		0.513
Max. temperature operation, $T_{max}$	[K]	423

<sup>a</sup> Titration against standard base. <sup>b</sup> Laser diffraction technique in air. <sup>c</sup> Inverse Steric Exclusion Chromatography technique [17,18]. <sup>d</sup>  $\phi_p = (V_g + V_{sp} - 1/\rho_{sk}) / (V_g + V_{sp})$

## 2.2 Apparatus, procedure, and analysis

Experiments have been performed at temperatures ranging from 303 to 352 K in two different reactor setups: most of experiments were run in a batch stirred tank reactor, the rest in a continuously operated fixed-bed catalytic reactor, with the main purpose of validating the results obtained in the batch reactor. The initial reaction mixture in batch experiments, and the reactor feed in continuous experiments did not contain ether. Catalyst beads were crushed and sieved to obtain a specific particle diameter,  $d_p$ , of 0.25-0.40 mm that avoids internal mass transfer effects on the measured reaction rate, according to a previous work [19].

### 2.2.1 Batch stirred tank reactor setup

This setup consisted of a 200 cm<sup>3</sup> stainless-steel jacketed batch reactor. Isothermal experiments were carried out in the range of 320 to 352 K at 2.0 MPa. The initial alcohol to isobutene molar ratio ( $R_{A/IB}^0$ ) varied between 1.0 and 2.0. Pure isobutene was used as reactant for all the experiments carried out in the batch reactor. The stirring speed was set to 750 rpm, because in previous works on similar reaction systems it had been proved to avoid internal mass transfer effects [20,21].

Before each experimental run, the catalyst was dried at room temperature for 48 h, introduced in an atmospheric oven at 383 K for 2.5 hours and, afterwards, placed in a vacuum oven at 0.001 MPa and

373 K for 12 h. This procedure ensures a 3-5%wt maximum final water content in the resin beads (analyzed by Karl-Fischer titration in the laboratory). A known amount of 1-propanol was introduced into the reactor vessel and heating and stirring were switched on. The isobutene was first kept in a pressurized burette and then introduced into the reactor by pressure difference, impelled by nitrogen. After the reactant mixture reached the desired temperature, controlled within  $\pm 0.1$  K by a 1,2-propanediol-water thermostatic mixture, a known amount of catalyst (0.1-10% of the total reactant weight) was added from an injection device pressurized at 2.0 MPa with nitrogen ( $> 99.9995$ , Air Liquide). This instant was considered as the starting point for the reaction. Each experimental run lasted about 5-8 h.

To determine the evolution of the reaction medium composition during each experimental run, samples were taken inline from the reaction medium every 20 min through a sampling valve that injected 0.2  $\mu$ L of pressurized liquid into a gas chromatograph (GC, Agilent 6890, Agilent Technologies) coupled to a mass selective detector (HP5973N, Hewlett Packard), which allowed to identify and quantify reactants, products, and byproducts, if formed. The GC was equipped with a capillary column (HP-PONA 19091S-001, J&W Scientific; 100% dimethylpolysiloxane, 50 m  $\times$  0.20 mm  $\times$  0.50  $\mu$ m). The oven temperature was set at 333 K and the carrier gas flow rate at 0.6 mL/min (helium,  $>99.998\%$ , Abelló-Linde). The electron source of the mass detector was set to 503 K and the quadrupole to 423 K.

The formation rate of compound  $j$ ,  $r_j$ , at each sampled time was obtained from the derivative with respect to time of an appropriate empirical function fitted to the experimental mole evolution of that compound, as follows:

$$r_j = \frac{1}{W_{\text{cat}}} \left( \frac{dn_j}{dt} \right) \quad (1)$$

where  $W_{\text{cat}}$  is the mass of dry catalyst,  $n_j$  is the number of moles of compound  $j$  and  $t$  is time.

### 2.2.2 Fixed-bed reactor setup

Isothermal experiments in the range of 303 to 333 K at 1.5 MPa were performed in a catalytic fixed-bed reactor to validate the results obtained in the batch reactor system. This setup consisted of a tubular microreactor (length: 150 mm, i.d.: 7 mm) submerged in a thermostatic bath to maintain the reactor at the desired temperature, controlled within  $\pm 0.01$  K with a polydimethylsiloxane thermostatic oil. In order to get an isothermal reactor bed, the catalyst was diluted with silicon carbide of the same particle size range. Silicon carbide had been proven to be inert in terms of reaction by means of a blank assay where the fixed bed was composed exclusively of silicon carbide. To avoid back-mixing and channeling, inert to catalyst mass ratios were below 300 [15,22]. The alcohol to isobutene molar ratio,  $R^o_{A/IB}$ , at the reactor inlet was 1.0. Either pure isobutene or a C<sub>4</sub> mixture was used as the isobutene source. To operate under differential regime, where the average reaction rate can be considered as representative of the overall reaction rate along the bed, the amount of used catalyst was chosen to reach a sufficiently low isobutene conversion level ( $\leq 10\%$ ) [19]. The weight hourly space velocity was higher than 500 h<sup>-1</sup> to avoid external mass transfer effects, as concluded in a previous work [19].

Before each experimental run, the catalyst was dried at room temperature for 48 h and afterwards introduced in an atmospheric oven at 383 K for 14 h. Then, known amounts of catalyst and inert were mixed up and introduced into the reactor. Before starting each experiment, the reactor was submerged in the thermostatic bath and only 1-propanol was fed to preheat the catalytic bed. While the alcohol flow rate was kept constant, the appropriate flow rate of isobutene was added to the feed, either as pure isobutene or as C<sub>4</sub> mixture, for the reaction to take place. About 3-4 h were needed for each kinetic run to reach the steady state, which was verified by repeated chromatographic analyses at the reactor outlet. Samples were taken inline from the reactor inlet and outlet streams through two sampling valves that injected 0.2  $\mu$ L of pressurized liquid into a gas chromatograph (GC, Agilent 7890A, Agilent Technologies) with a flame ionization detector. The GC was equipped with a capillary column (HP-PONA 19091S-001, J&W Scientific, Santa Clara, US; 100% dimethylpolysiloxane, 50 m  $\times$  0.20 mm  $\times$  0.50  $\mu$ m). Hydrogen (>99.99, Air Liquide) and synthetic air (>99.999, Air Liquide) were

used for the FID detector. The used carrier gas was helium, with a flow rate of  $0.75 \text{ mL min}^{-1}$ . GC oven temperature was 333 K. This analytical system allowed identifying and quantifying the reactants, the inert components of the  $C_4$  mixture, the formed ethers, and the reaction byproducts, if formed.

Experimental isobutene consumption rates were calculated by means of the following expression, which applies to a plug-flow fixed-bed catalytic reactor under differential regime:

$$-r_{\text{IB}} = \frac{F_{\text{IB}}^{\circ} (X_{\text{IB,outlet}} - X_{\text{IB,inlet}})}{W_{\text{cat}}} \quad (2)$$

where  $F_{\text{IB}}^{\circ}$  is the isobutene reference molar flow rate at null isobutene conversion,  $X_{\text{IB,outlet}}$  is the isobutene conversion at the reactor outlet, and  $X_{\text{IB,inlet}}$ , the inlet isobutene conversion, was zero.

Isobutene conversion was calculated as follows:

$$X_{\text{IB}} = 1 - \frac{F_{\text{IB,outlet}}}{F_{\text{IB,inlet}}} \quad (3)$$

### 3. Results and discussion

#### 3.1. Exclusion of mass transfer effects

To determine the kinetic equation of a given chemical reaction, experimental reaction rates should be estimated free of transport effects. Internal mass transfer effects can be avoided using a sufficiently small catalyst bead size. External mass transfer resistance could become significant at low fluid velocity at the external catalyst surface, that is, at low stirring speed in the batch reactor, or at low flow rate in the fixed-bed reactor. If mass transfer limitations exist, the reaction rate is underestimated. In particular, mass transfer resistance would become more evident at higher reaction rates, that is, at higher temperature and in the absence of products, because this situation entails a higher mass flux. To check it, experiments have been performed in the two experimental setups at different temperatures, but at the same initial composition (batch reactor) or inlet composition (fixed-bed reactor), equal to  $R_{A/\text{IB}}^{\circ} = 1.0$  and using pure isobutene. Then, the logarithm of the observed initial reaction rates (batch reactor) or steady-state reaction rates (fixed-bed reactor) has been plotted against the inverse



temperature. As a result, a linear trend is obtained (Figure 2). The agreement between results obtained from both setups is noteworthy. As a consequence, it can be assumed that the observed PTBE formation rates are not significantly affected by neither external nor internal mass transport effects, within the margin of experimental error, in the whole assayed range of temperatures. In addition, the apparent activation energy of the PTBE formation can be estimated from the slope of the straight line:  $(75 \pm 4) \text{ kJ mol}^{-1}$ . This value is similar to those quoted in literature for analogous reactions over the same catalyst, namely  $84 \text{ kJ mol}^{-1}$  for the MTBE synthesis, and between  $72$  and  $83 \text{ kJ mol}^{-1}$  for the ETBE synthesis [15,22].

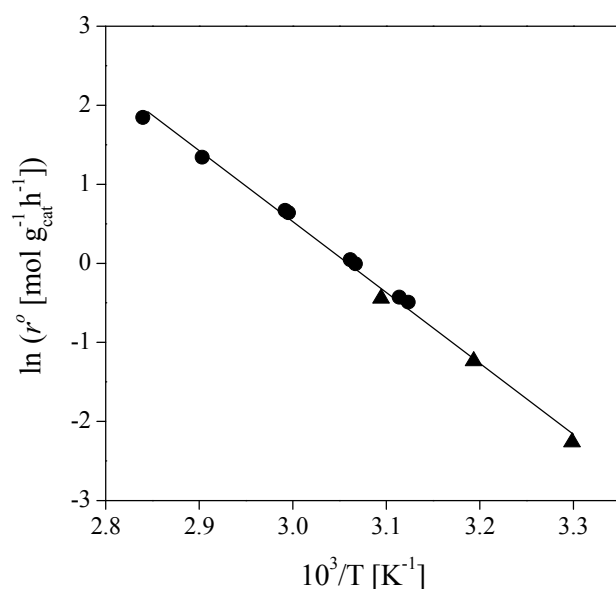


Figure 2. Arrhenius plot of experimental PTBE formation rate in the absence of ether.  $R_{A/IB}^\circ = 1.0$ , pure isobutene. Symbols: batch reactor setup (●), fixed-bed reactor setup (▲)

### 3.2. Systematic kinetic modeling

Experimental intrinsic rate data, free from mass transfer limitations, were used to fit kinetic equations based on LHHW and ER mechanisms. UNIFAC-Dortmund activities were used instead of concentrations due to high non-ideality of the reacting mixtures [23]. A large number of candidate kinetic equations has been considered. They have been systematically obtained from all possible combinations concerning four aspects: i) the rate-determining step, ii) the set of adsorbed and non-adsorbed species on the catalyst, iii) the number of active sites that participate in the rate-determining

step, and iv) the significance of the temperature dependence for every parameter included in the kinetic equation. All proposed equations present the following general form:

$$r_i = \{\text{kinetic factor}\} \frac{\{\text{driving force}\}}{\{\text{adsorption term}\}^n} \{\text{resin-medium interaction}\} \quad (4)$$

This general kinetic expression is composed of five different terms: i) the kinetic factor, ii) the driving force, iii) the adsorption term, iv) the exponent of the adsorption term, and v) a factor that accounts the possible effect of the interaction between the reaction medium and the catalyst on its catalytic activity, since it has been found to enhance the reaction rate prediction in analogous reaction systems [9].

The kinetic factor contains the rate constant of the rate-determining step, the total concentration of active sites, and eventually the etherification and adsorption equilibrium constants. Because of their expected temperature dependence according to the Arrhenius and the van't Hoff equations, the kinetic factor can be expressed as follows:

$$\{\text{kinetic factor}\} = k' = \exp \left[ k'_1 + k'_T \left( \frac{1}{T} - \frac{1}{\bar{T}} \right) \right] \quad (5)$$

where  $k'_1$  and  $k'_T$  are the parameters to be fitted. The mean experimental temperature,  $\bar{T}$ , is included to reduce the correlation between both parameters.

The driving force accounts for the distance to the reaction equilibrium position in terms of composition. It drops progressively to zero as the reaction approaches equilibrium. Its form depends on the considered rate-determining step, with a result of three different forms (Table 2).

Table 2. Possible forms of the driving force term in the kinetic equation for PTBE synthesis.  $a_j$ : activity of compound  $j$ ;  $K_{\text{Eq}}$ : equilibrium constant of the etherification reaction

Rate-determining step	{driving force}	
Surface reaction	$a_{\text{IB}} a_{1\text{-PrOH}} - a_{\text{PTBE}} / K_{\text{Eq}}$	(6)
1-Propanol adsorption	$a_{1\text{-PrOH}} - a_{\text{PTBE}} / (K_{\text{Eq}} a_{\text{IB}})$	(7)
Isobutene adsorption	$a_{\text{IB}} - a_{\text{PTBE}} / (K_{\text{Eq}} a_{1\text{-PrOH}})$	(8)
PTBE desorption	$a_{\text{IB}} a_{1\text{-PrOH}} - a_{\text{PTBE}} / K_{\text{Eq}}$	(9)

Values of the equilibrium constant used in this work have been calculated using the following expression [24]:

$$\ln K_{\text{Eq}} = 864.31 - \frac{105500}{RT} - \frac{1414.36}{R} \ln T + \frac{10.9645}{2R} T - \frac{27.836 \times 10^{-3}}{6R} T^2 + \frac{2.089 \times 10^{-5}}{12R} T^3 \quad (10)$$

The adsorption term accounts for the relative distribution of the vacant and the occupied active sites by the different adsorbed species, determined by the adsorption equilibrium constants of the compounds adsorbed on the catalyst and the reaction medium composition. The adsorption term can be expressed as follows:

$$\{\text{adsorption term}\} = \left( \alpha_1 + \sum_{j=\{\text{1-PrOH, PTBE, IB}\}} \alpha_j K_j a_j \right) \quad (11)$$

where  $K_j$  is a parameter directly related to the adsorption equilibrium constant of compound  $j$  on the resin.  $\alpha_1$  and  $\alpha_j$  are binary type parameters, defined for the ease of the fitting procedure, that indicate whereas the contribution of active sites ( $\alpha_1$  for vacant sites,  $\alpha_j$  for sites occupied by species  $j$ ) to the adsorption term is significant ( $\alpha = 1$ ) or not ( $\alpha = 0$ ). For example,  $\alpha_1 = 0$  would indicate that the number of vacant active sites is not significant, and  $\alpha_{\text{1-PrOH}} = 1$  would indicate that the contribution of the alcohol adsorption is significant. When  $\alpha_1 = 1$ , the parameter  $K_j$  refers to the actual adsorption equilibrium constant of species  $j$  on the catalyst,  $K_{a,j}$ , with the exception that  $K_{\text{PTBE}}$  corresponds to  $K_{a,\text{PTBE}} \cdot K_{\text{Eq}}$  if ether desorption is the rate-determining step. When  $\alpha_1 = 0$ , the adsorption term has to be expressed as  $\left( a_\ell + \sum_{j \neq \ell} \alpha_j K_j a_j \right)$ , the compound  $\ell$  being the first one with a significant contribution, in order to avoid overfitting due to the total correlation between every  $K_j$  and the apparent kinetic coefficient,  $k'$ . In this last case, the parameter  $K_j$  equals  $K_{a,j}/K_{a,\ell}$ , the ratio of adsorption equilibrium constants of compounds  $j$  and  $\ell$ . A possible contribution of byproducts in the adsorption term has been disregarded, because they were produced in very small amounts exclusively in some of the

experiments in the batch reactor, being always lower than 5%wt. at the end of the experimental runs. Consequently, fifteen different forms of the adsorption term have been considered (Table 3). The only combination that has been discarded to build the candidate kinetic equations is the adsorption term being equal to  $a_{PTBE}$  (i.e., only PTBE adsorbs on the catalyst and the number of unoccupied sites is negligible), because it corresponds to an unrealistic situation: in the absence of PTBE in the reaction medium (e.g., at the initial instant in batch experiments), since no other compound is adsorbed, the number of unoccupied active sites cannot be negligible, which is in contradiction with the underlying assumption.

Table 3. Possible forms of the adsorption term in the kinetic equation for PTBE synthesis

No.	Adsorption term	No.	Adsorption term
1	1	8	$1 + K_{1-PrOH} a_{1-PrOH}$
2	$a_{1-PrOH}$	9	$1 + K_{PTBE} a_{PTBE}$
3	$a_{IB}$	10	$1 + K_{IB} a_{IB}$
4	$a_{1-PrOH} + K_{PTBE} a_{PTBE}$	11	$1 + K_{1-PrOH} a_{1-PrOH} + K_{PTBE} a_{PTBE}$
5	$a_{1-PrOH} + K_{IB} a_{IB}$	12	$1 + K_{1-PrOH} a_{1-PrOH} + K_{IB} a_{IB}$
6	$a_{PTBE} + K_{IB} a_{IB}$	13	$1 + K_{PTBE} a_{PTBE} + K_{IB} a_{IB}$
7	$a_{1-PrOH} + K_{PTBE} a_{PTBE} + K_{IB} a_{IB}$	14	$1 + K_{1-PrOH} a_{1-PrOH} + K_{PTBE} a_{PTBE} + K_{IB} a_{IB}$

Based on the van't Hoff equation, the temperature dependence for every parameter  $K_j$  can be expressed as:

$$K_j = \exp \left[ K_{j_1} + K_{j_T} \left( \frac{1}{T} - \frac{1}{T} \right) \right] \quad (12)$$

$K_{j_1}$  and  $K_{j_T}$  are the parameters to be fitted. In case that the parameter  $K_j$  does not depend significantly on temperature,  $K_{j_T} = 0$ .

The exponent  $n$  of the adsorption term refers to the number of active sites, or clusters of active sites, involved in the rate-determining step, the most likely values being 1, 2 or 3.

Finally, the possible resin–medium interaction term in Eq. 4 has been expressed as a factor based on the difference between the Hildebrand solubility parameter of the reaction medium,  $\delta_M$ , and that of the polymeric catalyst,  $\delta_p$ , as suggested in analogous etherification systems [9,25]. If such effect takes

place significantly, it should be included in the kinetic equation. This interaction term has been expressed as follows:

$$\{\text{resin-medium interaction}\} = \exp \left[ \alpha_p \frac{\bar{V}_M \phi_p^2}{RT} (\delta_M - \delta_p)^2 \right] \quad (13)$$

$\alpha_p$  is a binary type parameter that is equal to 1 when the effect of the resin-medium interaction is significant, or zero when there is not a significant interaction, hence the whole factor becomes equal to unity.  $\bar{V}_M$  is the molar volume of the liquid mixture,  $\phi_p$  is the catalyst porosity in the swollen-state ( $\phi_p = 0.513$  from Table 1),  $R$  the gas constant,  $T$  the temperature, and  $\delta_M$  and  $\delta_p$  the Hildebrand solubility parameter of the liquid mixture and the catalyst, respectively.  $\bar{V}_M$  and  $\delta_M$  can be estimated from the reaction medium composition and temperature [26–28].  $\delta_p$  follows a linear dependence on temperature, according to literature [9,25]:

$$\delta_p = k_{p_1} + k_{p_T} (T - \bar{T}) \quad (14)$$

For kinetic equations where the resin-medium interaction is considered to affect kinetics ( $\alpha_p = 1$ ),  $k_{p_1}$  and  $k_{p_T}$  are parameters to be fitted ( $k_{p_T}$  equals zero in case of a non significant temperature dependence of  $\delta_p$ ). Given the form of the interaction term (Eq. 14),  $\delta_p$  being a linear function of the temperature entails a nonlinear dependence of the resin-medium interaction term, i.e., the catalytic activity. The mean temperature,  $\bar{T}$ , has been included to reduce the correlation between both parameters.

As a result, a total of 1,404 different candidate kinetic equations are obtained from all possible combinations of the different forms of the five equation terms (Equation 4), and possible non-significant dependence of parameters on temperature. Each kinetic equation has been fitted to all experimental reaction rates free of mass transfer effects at once by minimization of the residual sum of squares (*RSS*), i.e. the objective function, using the Levenberg-Marquardt algorithm:

$$RSS = \sum_{i=1}^N (r_{\text{exp}} - r_{\text{calc}})_i^2 \quad (15)$$

where  $r_{\text{exp}}$  is the experimental reaction rate,  $r_{\text{calc}}$  is the calculated one with each model, and  $N$  is the number of experimental data. Fits were also carried out using an alternative objective function that consisted of a weighted residual sum of squares, the weight factor being the inverse of the mean experimental reaction rate at the same temperature than that of the  $i$ -th value. It yielded practically the same results regarding the best fitted models and distribution of residuals, hence further analysis follows with  $RSS$ .

Mathematical and physicochemical criteria can be applied in sequence to reject the less likely kinetic models:

- Fitted kinetic equations that present a significantly large  $RSS$  value can be discarded, as a result of an unsatisfactory prediction of kinetic data.
- Expressions containing at least one fitted parameter with an excessive standard uncertainty should be rejected, because it indicates that the parameter is statistically not significant. This standard uncertainty can be estimated from the variance-covariance matrix for the fitted parameters. To be conservative, a model has been rejected when the standard uncertainty of at least one parameter is as large as its fitted value.
- The apparent activation energy,  $E_{\text{ap}}$ , of the etherification reaction must be positive. Since  $k'_T = -E_{\text{ap}}/R$  (Equation 5), models with a positive fitted value of  $k'_T$  should be rejected.
- Adsorption of compound  $j$  on the resin is an exothermic process, that is, its adsorption enthalpy should be negative:  $\Delta H_{\text{a},j}^o < 0$ . For models with  $\alpha_1 = 1$  in the adsorption term (Equation 11), all fitted parameters  $K_{jT}$  appearing in the model should be positive, because  $K_{jT} = -\Delta H_{\text{a},j}^o/R$ . For models with  $\alpha_1 = 0$ , this restriction does not apply, because  $K_j$  relates to a ratio of adsorption equilibrium constants, and, since  $K_{jT}$  values correspond to a subtraction of adsorption enthalpies, they are not restricted to be positive.

- On one hand, values of  $\delta_p$  have to be positive. On the other, if  $\delta_p$  depends significantly on temperature in the assayed range, then it should decrease at increasing temperature according to literature [25] and  $k_{p_T}$  must be negative (Equation 14), else  $k_{p_T} = 0$ .

The systematic proposal of kinetic models leads to mathematical similarity within groups of kinetic equations. As a consequence, it may not always be possible to obtain just one kinetic equation that stands out from the rest as the best one, but a subset of kinetic equations with a similar satisfactory prediction ability and goodness of fit. Rather than being a disadvantage, the common characteristics of this subset of best equations would allow to reach robust conclusions on the reaction mechanism.

### 3.3. Fitting kinetic data

A global overview of the ability of prediction among models can be obtained by comparing *RSS* values (Equation 15), a measure of the deviation between experimental and calculated PTBE formation rates for each fitted kinetic equation. Fig. 3 shows the inverse of *RSS* for all equations for which all fitted parameters present an estimated standard uncertainty lower than the parameter value itself. A larger  $RSS^{-1}$  value corresponds to a better prediction ability of the kinetic equation.

Next, kinetic equations whose fitted parameter values do not fulfill the physicochemical criteria listed in section 3.2 have been rejected. A subsequent reduction of the number of plausible kinetic models can be applied by selecting those whose  $RSS^{-1}$  value is within the upper quartile ( $RSS^{-1} \geq 0.147$ ). As a result, 66 kinetic equations are obtained, which differ in several aspects: number of fitted parameters, rate-determining step, compounds with a significant contribution in the adsorption term, resin-medium affinity effect, and temperature dependence (Table S1, in Supplementary material). Among these, 11 equations have been rejected, due to an excessively large value estimated for the apparent activation energy, markedly different to the rest, e.g.,  $E_{ap} > 102 \text{ kJ mol}^{-1}$  (calculated from  $k'_T = -E_{ap}/R$ ). In fact: i) the estimated  $E_{ap}$  from the Arrhenius plot (Fig. 2) equals  $(75 \pm 4) \text{ kJ mol}^{-1}$ , and ii) quoted values of  $E_{ap}$  on similar reaction systems (e.g., MTBE, ETBE or TAEE syntheses) range from 70.4 to 84  $\text{kJ mol}^{-1}$  [15,16,22]. As a result, there are 55 remaining candidate kinetic equations.

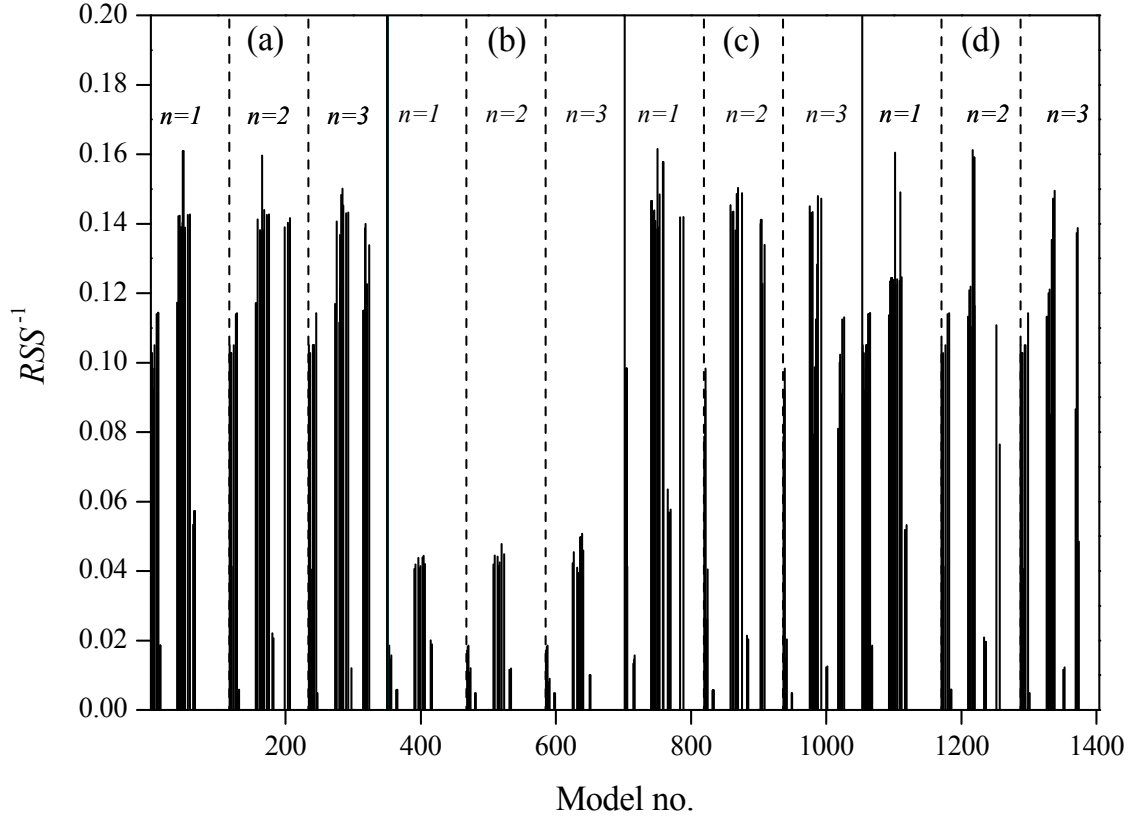


Figure 3. Inverse of  $RSS$  values for each equation fitted to PTBE reaction rates, grouped according the considered rate-limiting step and exponent  $n$ . Rate-limiting step: (a) surface reaction (Eq. 6), (b) 1-propanol adsorption (Eq. 7), (c) isobutene adsorption (Eq. 8), and (d) PTBE desorption (Eq. 9).

### 3.4. Model selection based on AIC

Given that a unique kinetic equation does not stand out clearly from the rest as the best one, a further approach is advisable. Model comparison can be easily carried out with the F-test when models are nested, that is, consecutively obtained from the simplification of a full model. However, in the present case the kinetic equations are non-nested, and an alternative method has to be applied [29].

Multimodel procedures allow to obtain robust inferences from several models in a set, rather than from a unique model chosen as the best one [30]. For that purpose, model averaging techniques have been applied, specifically the Akaike Information Criterion (AIC), whose estimator can be calculated as follows [31]:

$$AIC = m \ln \left( \frac{RSS}{m} \right) + 2k \quad (16)$$



where  $m$  is the number of experimental points, and  $k$  is the number of fitted parameters in the model. The first summand is a measure of goodness of fit and the second summand is related to the model complexity. Among the proposed models, the preferred one would present the lowest  $AIC$  value. When the sample size  $m$  is small compared to the number of parameters ( $m/k < 40$ ), as in the present case, the use of a second-order corrected  $AIC$  ( $AICc$ ) is recommended as an unbiased estimator [30,31]:

$$AICc = AIC + \frac{2k(k+1)}{m-k-1} \quad (17)$$

The relative quality of the  $i$ -th model can be evaluated by means of the  $AICc$  difference:  $\Delta_i = AICc_i - AICc_{\min}$ , where  $AICc_{\min}$  is the minimum  $AICc$  among all models. As a rule of thumb, the level of empirical support for a given model is considered as substantial when its  $\Delta_i$  value is lower than 3; models with  $\Delta_i$  values in the range 4-7 are considered to provide useful information on the modeled process, but their level of empirical support is considerably low; models whose  $\Delta_i$  values are larger than 10 might be omitted from further consideration [30,31].

Finally, Akaike weights,  $w_i$ , are a measure of the probability for each model being the best model, given the data and a set of  $R$  candidate models. This value can be computed for each model  $i$  as [30]:

$$w_i = \frac{\exp(-\Delta_i/2)}{\sum_{r=1}^R \exp(-\Delta_r/2)} \quad (18)$$

Table 4 shows the results obtained for the four best ranked kinetic models fitted to experimental reaction rates, sorted by  $\Delta_i$  or  $w_i$ . Clearly, models #751, 49 and 166 stand out as the most plausible ones, since their  $\Delta_i$  values are in the range 0-2; the following models present a significantly larger  $\Delta_i$  value larger than 10. All three models are very similar in form and their parameter values fulfill the physicochemical criteria. They agree with: i) the significant temperature dependence of the kinetic term; ii) the significant contribution of 1-PrOH and PTBE adsorption, and no relevant contribution of vacant sites and IB in the adsorption term; iii) the significant temperature dependence of the  $K_{PTBE}$

parameter in the adsorption term; and iv) the significant effect of the resin–medium interaction on reaction rate, with a constant  $\delta_p$  value within the assayed temperature range. The most remarkable differences among these models are: i) the rate-determining step is the surface reaction for equations #49 and 166 (relative importance weight:  $\Sigma w=0.530$ ), but isobutene adsorption for equation #751 ( $w=0.457$ ), and ii) the exponent of the adsorption term,  $n=1$  for equations #751 and 49 ( $\Sigma w=0.801$ ), and  $n=2$  for equation #166 ( $w=0.186$ ). Their kinetic equation and fitted parameter values are listed in Table 5.

Table 4. Best ranked PTBE kinetic equations fitted to experimental reaction rates

No.	$k'$ (mol/g h)		{driving force} <sup>a</sup>	{adsorption term}				$\delta_p$ (MPa <sup>1/2</sup> )						
	$k'_j$	$k'_T$		1 <sup>st</sup> Ads <sup>b</sup>	$K_{PTBE_j}$	$K_{PTBE_T}$	$K_{IB_j}$	$K_{IB_T}$	$n$	$k_{p_j}$	$k_{p_T}$	RSS	$\Delta_i$	$w_i$
751	0.0183	-9,541	(c)	$a_{1-PrOH}$	-1.420	-9,378	–	–	1	16.6	–	6.190	0	0.457
49	0.369	-9,025	(a)	$a_{1-PrOH}$	-1.370	-9,038	–	–	1	20.5	–	6.214	1	0.344
166	0.0208	-9,503	(a)	$a_{1-PrOH}$	-2.102	-8,291	–	–	2	16.6	–	6.264	2	0.186
742	0.528	-8,264	(a)	$a_{1-PrOH}$	0.3342	–	–	–	1	–	–	6.826	11	0.002

<sup>a</sup> Form of the driving force: (a) surface reaction (Eq. 6) and (c) isobutene adsorption (Eq. 8).  
<sup>b</sup> First summand of the adsorption term

Table 5. Kinetic equations, parameters values, with their standard uncertainty, and estimated apparent activation energy for the best models

No.	Kinetic expression	Parameters values	$E_{ap}$ [kJ mol <sup>-1</sup> ]
751	$r = k' \frac{\left( a_{IB} - \frac{a_{PTBE}}{K_{Eq} a_{1-PrOH}} \right) \exp \left[ \frac{\bar{V}_M \phi_p^2}{RT} (\delta_M - \delta_p)^2 \right]}{a_{1-PrOH} + K_{PTBE} a_{PTBE}}$	$k' \left[ \frac{\text{mol}}{\text{g h}} \right] = \exp \left[ (0.018 \pm 0.014) - (9.54 \pm 0.08) \cdot 10^3 \left( \frac{1}{T} - \frac{1}{327.7} \right) \right]$ $K_{PTBE} = \exp \left[ -(1.42 \pm 0.07) - (9.4 \pm 0.3) \cdot 10^3 \left( \frac{1}{T} - \frac{1}{327.7} \right) \right]$ $\delta_p \left[ \text{MPa}^{1/2} \right] = (16.6 \pm 0.4)$	$79.3 \pm 0.7$
49	$r = k' \frac{\left( a_{IB} a_{1-PrOH} - \frac{a_{PTBE}}{K_{Eq}} \right) \exp \left[ \frac{\bar{V}_M \phi_p^2}{RT} (\delta_M - \delta_p)^2 \right]}{a_{1-PrOH} + K_{PTBE} a_{PTBE}}$	$k' \left[ \frac{\text{mol}}{\text{g h}} \right] = \exp \left[ (0.369 \pm 0.014) - (9.03 \pm 0.08) \cdot 10^3 \left( \frac{1}{T} - \frac{1}{327.7} \right) \right]$ $K_{PTBE} = \exp \left[ -(1.37 \pm 0.07) - (9.0 \pm 0.4) \cdot 10^3 \left( \frac{1}{T} - \frac{1}{327.7} \right) \right]$ $\delta_p \left[ \text{MPa}^{1/2} \right] = (20.5 \pm 0.3)$	$75.0 \pm 0.7$
166	$r = k' \frac{\left( a_{IB} a_{1-PrOH} - \frac{a_{PTBE}}{K_{Eq}} \right) \exp \left[ \frac{\bar{V}_M \phi_p^2}{RT} (\delta_M - \delta_p)^2 \right]}{(a_{1-PrOH} + K_{PTBE} a_{PTBE})^2}$	$k' \left[ \frac{\text{mol}}{\text{g h}} \right] = \exp \left[ (0.021 \pm 0.015) - (9.50 \pm 0.08) \cdot 10^3 \left( \frac{1}{T} - \frac{1}{327.7} \right) \right]$ $K_{PTBE} = \exp \left[ -(2.10 \pm 0.06) - (8.3 \pm 0.3) \cdot 10^3 \left( \frac{1}{T} - \frac{1}{327.7} \right) \right]$ $\delta_p \left[ \text{MPa}^{1/2} \right] = (16.6 \pm 0.4)$	$79.0 \pm 0.7$

At this point, from the combination of both sources of information, i.e., models with superior empirical support and multimodel inferences regarding the relative importance of every variable,

model #49 is the one that meets the most plausible characteristics and, therefore, it has been selected as the best model for the PTBE kinetics. Moreover, in Table 5 it can be seen that the relative uncertainty for the same parameter among the listed equations is similar, except for  $k'_1$ , which is remarkably lower for model #49 (below 4%), in contrast to model #751 (70%) and model #166 (79%). Finally, the calculated value for  $E_{ap}$  in model #49 results in  $(75.0 \pm 0.7) \text{ kJ mol}^{-1}$ , which is coincident with the previously estimated value from experimental reaction rates in the absence of ether,  $(75 \pm 4) \text{ kJ mol}^{-1}$  (Figure 2). The fit of equation #49 to the experimental reaction rate data, and the distribution of residuals are shown in Fig. 4, where a satisfactory prediction of experimental reaction rates is observed for both batch and fixed-bed reactor systems.

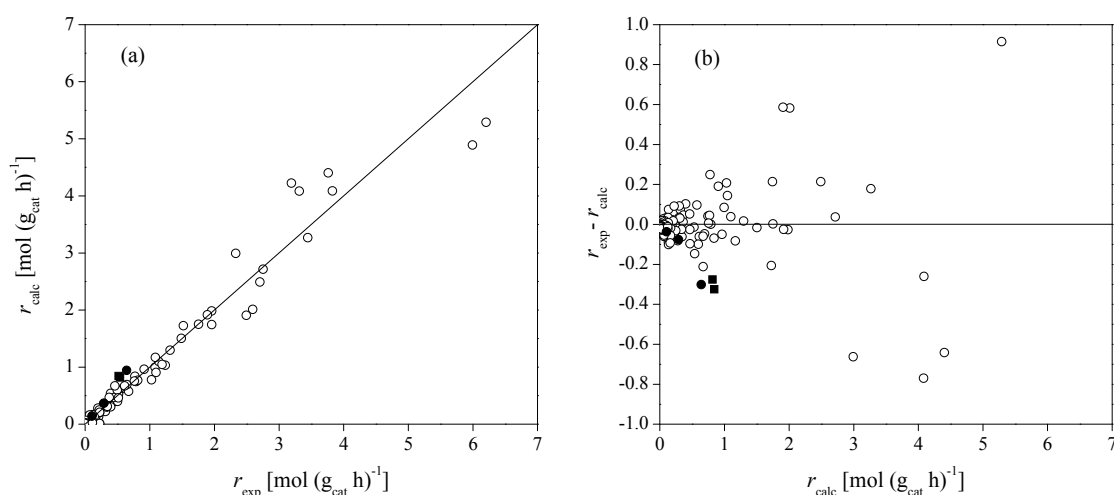


Figure 4. Comparison between experimental and calculated PTBE reaction rates from equation #49 (a), and residuals distribution (b). Symbols: Experimental rates obtained in the batch reactor ( $\circ$ ), in the fixed-bed reactor using the C<sub>4</sub> as isobutene source ( $\bullet$ ), and in the fixed-bed reactor using pure isobutene ( $\blacksquare$ ).

### 3.5. Analysis of the selected kinetic model

The finally selected model #49 is consistent with an ER mechanism where one molecule of 1-propanol adsorbed on one active site reacts with one isobutene molecule from the liquid phase to give one adsorbed molecule of PTBE, the surface reaction being the rate-determining step. The obtained result is consistent with previous works on similar reaction systems, e.g., syntheses of MTBE [8], ETBE [7] or simultaneous ETBE and TAEE synthesis [16]. Since  $n=1$ , the apparent kinetic constant,  $k'$ , corresponds to the actual kinetic constant,  $k$ :

$$k' = k K_{a,1-PrOH}^{-(n-1)} = k \quad (19)$$

where  $K_{a,1-PrOH}$  is the 1-PrOH adsorption constant. Therefore, the activation energy of the PTBE formation reaction equals the apparent activation energy, i.e.,  $(75.0 \pm 0.7)$  kJ mol<sup>-1</sup>. The parameter in the adsorption term,  $K_{PTBE}$ , corresponds to the ratio between adsorption equilibrium constants of the formed ether and the alcohol, i.e.,  $K_{a,PTBE}/K_{a,1-PrOH}$ :

$$\begin{aligned} \ln K_{PTBE} &= \ln \frac{K_{a,PTBE}}{K_{a,1-PrOH}} = \frac{-\left(\Delta G_{a,PTBE}^{\circ} - \Delta G_{a,1-PrOH}^{\circ}\right)}{RT} \\ &= \frac{-\left(\Delta H_{a,PTBE}^{\circ} - \Delta H_{a,1-PrOH}^{\circ}\right)}{R} \frac{1}{T} + \frac{\Delta S_{a,PTBE}^{\circ} - \Delta S_{a,1-PrOH}^{\circ}}{R} \end{aligned} \quad (20)$$

Consequently, individual compound adsorption enthalpies and entropies cannot be estimated, but their differences:  $(\Delta H_{a,PTBE}^{\circ} - \Delta H_{a,1-PrOH}^{\circ}) = (75 \pm 2)$  kJ mol<sup>-1</sup>, and  $(\Delta S_{a,PTBE}^{\circ} - \Delta S_{a,1-PrOH}^{\circ}) = (218 \pm 8)$  J (mol K)<sup>-1</sup>. Clearly, these values are very high for physical adsorption, which usually ranges between 0 and – 40 kJ mol<sup>-1</sup> for an individual compound. It would be due to the fact that they have been obtained from the fit of kinetic data. However, these values can be taken as indicative. In this way, it follows that 1-PrOH adsorption on the resin is more exothermic than PTBE adsorption, and the adsorption entropic loss for PTBE is larger than for 1-PrOH. It is expected that specific adsorption equilibrium experiments would be more appropriate to obtain accurate values. To date, only some results can be found in the literature regarding the liquid-phase adsorption of alcohols and 2-methyl-2-butene on A35, including 1-propanol, for which estimated adsorption enthalpy and entropy were –7.0 kJ mol<sup>-1</sup> and –2.9 J (mol K)<sup>-1</sup>, respectively [32]. In the same work, adsorption enthalpies on A35 in the gas-phase were estimated as –38.9 kJ mol<sup>-1</sup> for 1-PrOH, and –20.9 kJ mol<sup>-1</sup> for PTBE, which results also in  $(\Delta H_{a,PTBE}^{\circ} - \Delta H_{a,1-PrOH}^{\circ}) > 0$ .

With respect to the solubility parameter,  $\delta_P$ , its estimate for A35 is  $(20.5 \pm 0.3)$  MPa<sup>1/2</sup>. This value is coincident with previously reported estimates for the same catalyst in analogous liquid-phase etherifications:  $(20.9 \pm 2.0)$  MPa<sup>1/2</sup> in the ETBE synthesis [15] and  $(21.16 \pm 0.12)$  MPa<sup>1/2</sup> in the simultaneous synthesis of ETBE and TAEE [16], in both cases also without a significant effect of the

temperature within the experimental range. Consequently, the appropriateness to include the resin-medium interaction factor in the kinetic equation is reinforced.

#### **4. Conclusions**

The kinetic study of the liquid-phase etherification reaction of isobutene with 1-propanol to produce propyl *tert*-butyl ether catalyzed by Amberlyst™ 35 has been carried out. Reaction rates free from mass transfer effects have been measured in two different reaction setups: a batch reactor and a differential tubular. They have been used all at once to fit an exhaustive list of kinetic equations obtained from the Langmuir-Hinshelwood-Hougen-Watson and Eley-Rideal formalisms, based on different mechanisms and rate-determining step, taking into account the possible effect of reaction medium on the catalyst activity, and the possible non-significant dependence of fitted parameters on temperature. Discrimination using mathematical and physico-chemical criteria has yielded a subset of plausible equations. Finally, the Akaike Information Criterion has been applied to obtain the best kinetic equation. It corresponds to an Eley-Rideal type mechanism where one molecule of 1-propanol adsorbed on one active site reacts with one isobutene molecule from the liquid phase to form one PTBE molecule that, finally, desorbs. The reaction medium has been found to have a significant effect on the catalytic activity.

#### **Acknowledgement**

The authors thank The Dow Chemical Company for providing the ion exchange resin used in this work.

#### **Funding sources**

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

#### **References**

- [1] B. Torck, A. Convers, L. Asselineau, M. Hellin, Process for manufacturing and recovering methyl *tert*-butyl ether, US Patent 4310710, 01/12/1982.

- [2] F. Ancillotti, G. Oriani, E. Pescarollo, Process for the production of methyl tert-butyl ether , US Patent 4071567, 01/31/1978.
- [3] C. W. Zahn, Etherification process, US Patent 5245087, 09/14/1993.
- [4] A. Gicquel, B. Torck, Synthesis of methyl tertiary butyl ether catalyzed by ion-exchange resin. Influence of methanol concentration and temperature, *J. Catal.* 83 (1983) 9-18.
- [5] O. Françoisse, F. C. Thyron, Kinetics and mechanism of ethyl *tert*-butyl ether liquid-phase synthesis, *Chem. Eng. Process.* 30 (1991) 141-149.
- [6] A. Rehfinger, U. Hoffmann, Kinetics of methyl tertiary butyl ether liquid phase synthesis catalyzed by ion exchange resin—I. Intrinsic rate expression in liquid phase activities, *Chem. Eng. Sci.* 45 (1990) 1605-1617.
- [7] C. Fité, M. Iborra, J. Tejero, J. F. Izquierdo, F. Cunill, Kinetics of the liquid-phase synthesis of ethyl tert-butyl ether (ETBE), *Ind. Eng. Chem. Res.* 33 (1994) 581-591.
- [8] D. Parra, J. Tejero, F. Cunill, M. Iborra, J. F. Izquierdo, Kinetic study of MTBE liquid-phase synthesis using C4 olefinic cut, *Chem. Eng. Sci.* 49 (1994) 4563-4578.
- [9] C. Fité, J. Tejero, M. Iborra, F. Cunill, J. F. Izquierdo, Enhancing MTBE rate equation by considering reaction medium influence, *AIChE J.* 44 (1998) 2273-2279.
- [10] K. Sundmacher, R. S. Zhang, U. Hoffmann, Mass transfer effects on kinetics of nonideal liquid phase ethyl tert-butyl ether formation, *Chem. Eng. Technol.* 18 (1995) 269-277.
- [11] K. Srirangan, L. Akawi, X. Liu, A. Westbrook, E. J. Blondeel, M. G. Aucoin, M. Moo-Young, C. P. Chou, Manipulating the sleeping beauty mutase operon for the production of 1-propanol in engineered *Escherichia coli*, *Biotechnol. Biofuels* 6 (2013) 139-153.
- [12] R. Jain, Y. Yan, Dehydratase mediated 1-propanol production in metabolically engineered *Escherichia coli*, *Microb. Cell Fact.* 10 (2011) 97-107.
- [13] P. M. Słomkiewicz, The gas phase *n*-propyl-*tert*-butyl ether synthesis, *Appl. Catal. A Gen.* 313 (2006) 74-85.
- [14] J. A. Linnekoski, A. O. I. Krause, A. Holmen, M. Kjsetså, K. Moljord, Etherification of isobutene with 1-propanol and 2-propanol, *Appl. Catal. A Gen.* 174 (1998) 1-11.
- [15] R. González, Performance of Amberlyst<sup>TM</sup>35 in the Synthesis of ETBE from Ethanol and C<sub>4</sub>

- Cuts, PhD Thesis, University of Barcelona, 2011.
- [16] R. Soto, C. Fité, E. Ramírez, R. Bringué, F. Cunill, Chem. Eng. J. Kinetic modeling of the simultaneous etherification of ethanol with C4 and C5 olefins over Amberlyst™ 35 using model averaging, 307 (2017) 122-134.
- [17] K. Jeřábek, Determination of pore volume distribution from size exclusion chromatography data, Anal. Chem. 57 (1985) 1595-1597.
- [18] K. Jeřábek, Characterization of swollen polymer gels using size exclusion chromatography, Anal. Chem. 57 (1985) 1598-1602.
- [19] J. H. Badia, C. Fité, R. Bringué, E. Ramírez, M. Iborra, Relevant properties for catalytic activity of sulfonic ion-exchange resins in etherification of isobutene with linear primary alcohols, J. Ind. Eng. Chem. 42 (2016) 36-45.
- [20] M. Umar, A.R. Saleemi, S. Qaiser, Synthesis of ethyl *tert*-butyl ether with *tert*-butyl alcohol and ethanol on various ion exchange resin catalysts, Catal. Commun. 9 (2008) 721-727.
- [21] J. A. Linnekoski, A. O. I. Krause, L.K. Rihko, Kinetics of the heterogeneously catalyzed formation of *tert*-amyl ethyl ether, Ind. Eng. Chem. Res. 36 (1997) 310-316.
- [22] Ó. Santín, Estudio del control de las etapas físicas en las síntesis de MTBE y ETBE, MSc Thesis, University of Barcelona, 2005.
- [23] J. Gmehling, J. Li, M. Schiller, A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties, Ind. Eng. Chem. Res. 32 (1993) 178-193.
- [24] J. H. Badia, C. Fité, R. Bringué, E. Ramírez, F. Cunill, Thermodynamic analysis of the experimental equilibria for the liquid-phase etherification of isobutene with C1 to C4 linear primary alcohols, J. Chem. Eng. Data 61 (2016) 1054-1064.
- [25] C. Fité, J. Tejero, M. Iborra, F. Cunill, J. F. Izquierdo, D. Parra, The effect of the reaction medium on the kinetics of the liquid-phase addition of methanol to isobutene, Appl. Catal. A Gen. 169 (1998) 165-177.
- [26] R. C. Reid, J. M. Prausnitz, B. E. Poling, The Properties of Gases and Liquids, forth ed., McGraw-Hill, New York, 1987.
- [27] B. E. Poling, J. M. Prausnitz, J. P. O'Connell, R. C. Reid, The Properties of Gases and Liquids,

- fifth ed., McGraw-Hill, New York, 2001.
- [28] C. L. Yaws, *Thermophysical Properties of Chemicals and Hydrocarbons*, William Andrew, Norwich, NY, 2008.
- [29] H. Motulsky, A. Christopoulos, *Fitting Models to Biological Data Using Linear and Nonlinear Regression: A Practical Guide to Curve Fitting*, Oxford University Press, New York, 2004.
- [30] K. P. Burnham, D.R. Anderson, *Model Selection and Multimodel Inference: A Practical Information-Theoretic Approach*, second ed., Springer-Verlag, New York, 2002.
- [31] M. R. E. Symonds, A. Moussalli, A brief guide to model selection, multimodel inference and model averaging in behavioural ecology using Akaike's information criterion, *Behav. Ecol. Sociobiol.* 65 (2011) 13-21.
- [32] R. Soto, N. Oktar, C. Fité, E. Ramírez, R. Bringué, J. Tejero, Adsorption of C1–C4 alcohols, C4–C5 isoolefins, and their corresponding ethers over Amberlyst™35, *Chem. Eng. Technol.* 40 (2017) 889-899.