Simultaneous etherification of isobutene with ethanol and 1-butanol over ion-exchange resins

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Graphical abstract
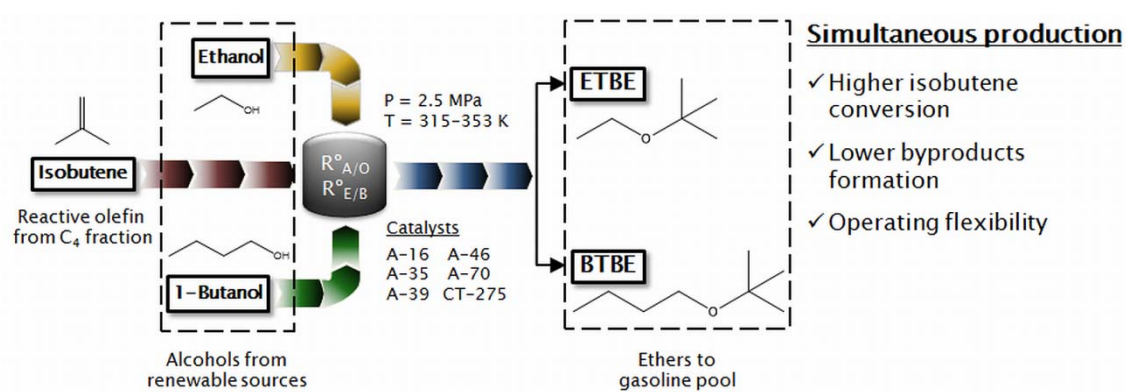
Highlights

- The catalytic performance of acidic ion-exchange resins to produce BTBE is affected by ethanol presence in the simultaneous ETBE and BTBE synthesis.

- Simultaneous etherification provides a higher isobutene conversion and lower byproducts formation using Amberlyst™ 35 compared to individual ETBE synthesis.

- The simultaneous etherification of isobutene with ethanol and 1-butanol obtained from biomass is a feasible alternative to produce biobased oxygenates for the gasoline pool.

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Abstract

The simultaneous liquid-phase etherification of isobutene with ethanol and 1-butanol to give ethyl *tert*-butyl ether (ETBE) and butyl *tert*-butyl ether (BTBE) has been studied, at temperatures in the range of 315–353 K and at 2.5 MPa, over six commercial acidic macroreticular ion-exchange resins as catalysts. The initial alcohol to isobutene molar ratio was varied in the range of 0.5–5.5 and the initial ethanol to 1-butanol molar ratio in the range of 0.5–2.0. Strongly acidic catalysts with a rigid polymer backbone structure enhance reaction rate. This fact, along with the reduced side reactions extent, makes Amberlyst™ 35 the most promising catalyst, among the tested ones, for the studied simultaneous etherification process. Irrespectively of the used catalyst, initial ETBE synthesis reaction rate is hardly sensitive to the variation of the ethanol to 1-butanol molar ratio, whereas initial BTBE synthesis reaction rate strongly diminishes at high ethanol concentration. Preferential adsorption of ethanol over 1-butanol on the catalysts active sites has been detected. As expected, both etherification reaction rates increase at increasing isobutene concentration. At 353 K, the highest temperature, both etherification rates are affected by internal mass transfer resistances due to diffusion limitations even when small catalyst beads are used. The simultaneous process has been compared to the individual syntheses of ETBE and BTBE and it has been found that the isobutene selectivity towards ethers is enhanced in the simultaneous system.

Keywords: ethyl tert-butyl ether; butyl tert-butyl ether; macroreticular ion-exchange resins; simultaneous etherification; catalyst screening

1. Introduction

Liquid-phase etherification of isobutene with ethanol over acidic ion-exchange resins to give ethyl *tert*-butyl ether (ETBE) is one of the major industrial processes to obtain oxygenate additives for automotive fuels. The current legislation struggle towards the introduction of next generation biofuels encourages biomass-based production routes using alcohols produced through fermentation processes. Although bioethanol has been the alcohol largely chosen for this purpose, the concerns about its competition with food supplies has put its production on the spot, since it is mainly obtained from edible sources.

A promising alternative is the use of biobutanol, which has experienced a renovated interest from private corporations willing to make biobutanol a keystone for next generation biofuels [1–3]. Its expected production by 2020 is around hundreds of million gallons [2]. Biobutanol production at industrial scale has been accomplished early in the 20th century in the US, until the 1980s in South Africa and the USSR, and still today in China by means of bacteria-based fermentation of sugars –in contrast to the yeast-based bioethanol production–, but it was eclipsed during the 1950s by lower-cost petrochemical routes. Direct blending of 1-butanol to the gasoline pool overcomes some of the technical issues raised by adding ethanol: 1-butanol can be processed in the existing refinery units, it is less corrosive than ethanol, it does not dissolve in or absorb water, and it does not increase fuel Reid Vapor Pressure (RVP) [1,2]. However, from an economic point of view, 1-butanol is still far from being considered a mainstream biofuel [2,3]. The indirect introduction of bioalcohols into the gasoline pool as branched ethers, through reaction with an isoolefin, constitutes an immediate alternative. The use of ethers instead of alcohols for gasoline blending is more advantageous, since ethers present significantly lower blending volatility, no significant distortion of the distillation curve, lower hygroscopicity, and they can double the octane increase per barrel at equivalent alcohol content [4].

Analogously to ETBE, etherification of isobutene with 1-butanol produces butyl *tert*-butyl ether (BTBE). Potential benefits of using BTBE as a gasoline additive are that heavier ethers have higher energy density, lower blending RVP and they allow a larger dilution effect of some harmful fuel components while still presenting a rather good octane number. In addition, previous studies indicated that BTBE synthesis is faster than ETBE synthesis [5,6], which would result in operative savings regarding its industrial production. ETBE technology is already well established and BTBE can be obtained in the same ETBE production units. Furthermore, the simultaneous production of these two ethers could be of special interest since, on one hand, it would offer to the manufacturer operating flexibility and adaptability to the market demands and stock disposal, and, on the other hand, it would allow using products from fermentative processes in which both ethanol and 1-butanol are obtained, such as the ABE fermentation (fermentation of grain to obtain acetone, 1-butanol, and ethanol) [7,8], without

further separation of the two alcohols. Therefore, studies devoted to the viability of this promising process based on extensive experimental data are of interest.

To sum up, the aim of this work is to study the simultaneous production of ETBE and BTBE. Firstly, a catalyst screening study has been carried out to identify which properties determine the catalytic performance and to select the most advantageous catalyst. Subsequently, the effect of operating conditions on reaction rates and side reactions extension, namely temperature and initial reactants concentration, has been analyzed. Finally, the performance of the simultaneous etherification has been compared to that of the individual syntheses of both ETBE and BTBE.

2. Experimental

2.1. Chemicals

Reactants were ethanol (max. water content 0.02%wt.), supplied by Panreac (Castellar del Vallès, Spain), 1-butanol (max. water content 0.005%wt.), supplied by Sigma-Aldrich (Tres Cantos, Spain), and 2-methylpropene (isobutene) (>99.9% GC), supplied by Air Liquide (Madrid, Spain). As reaction products, the following compounds were used for analytical procedures: 2-methyl-2-propanol (TBA, >99.7% GC), supplied by Panreac (Castellar del Vallès, Spain), 2,4,4-trimethyl-1-pentene (TMP-1, >98% GC) and 2,4,4-trimethyl-2-pentene (TMP-2, >98% GC), supplied by Sigma-Aldrich Química SA (Tres Cantos, Spain), 2-ethoxy-2-methylpropane (ETBE, >95.0% GC), supplied by TCI Europe (Zwijndrecht, Belgium), and 2-methyl-2-propoxybutane (BTBE, >98% GC), synthesized and purified in our laboratory.

2.2. Catalyst

Six commercial ion-exchange resins were used as catalysts: Amberlyst™ 16 (A-16), Amberlyst™ 35 (A-35), Amberlyst™ 39 (A-39), Amberlyst™ 46 (A-46), Amberlyst™ 70 (A-70), supplied by The Dow Chemical Company, and Purolite® CT275 (CT-275), supplied by Purolite. All resins are sulfonated, macroreticular polymers of styrene-divinylbenzene. Their general properties are listed in Table 1.

Table 1. General characteristics of ion-exchange resins used in this work.

Catalyst	Short name	Sulfonation type [a]	Acid Capacity, $[H^+]$ [b] [meq H^+ g_{cat}^{-1}]	%DVB [c]
Amberlyst 16	A-16	C	4.80	Medium
Amberlyst 35	A-35	O	5.32	High
Amberlyst 39	A-39	C	4.81	Low
Amberlyst 46	A-46	S	0.87	High
Amberlyst 70 [d]	A-70	C	2.65	Low
Purolite CT275	CT-275	O	5.20	High

[a] Oversulfonated (O): more than one sulfonic group per styrene ring; Conventionally sulfonated (C): about one sulfonic group per styrene ring; Surface sulfonated (S): sulfonated mainly at the surface of the resin microespheres. [b] Modified Fisher-Kunin titration against standard base. [c] %DVB: divinylbenzene amount. Cross-linking degree classification considered: Low (≤8%); Medium (9–14%); High (>14%). [d] In Amberlyst 70 manufacture some hydrogen atoms of the polymer chain have been substituted by chlorine atoms to increase its thermal stability.

2.3. Apparatus and procedure

Experimental runs were carried out in a 200 cm^3 stainless-steel jacketed batch reactor at constant temperature in the range of 315–353 K and at 2.5 MPa. The initial alcohol/isobutene molar ratio ($R^o_{A/IB}$) was varied from 0.5 to 5.5 and the initial ethanol/1-butanol molar ratio ($R^o_{E/B}$) from 0.5 to 2.0.

Since catalysts were supplied in wet state, the resin pretreatment consisted in reducing the water content. Catalysts were firstly dried at room temperature for 48 h to remove most of the free water from the resin beads, then placed in an atmospheric oven during a minimum of 2.5 h at 383 K to remove the bounded water molecules, and, finally, placed in a vacuum oven, at 373 K and 0.001 MPa for at least 12 h. Catalysts were then kept in the oven until the experiment was carried out. This procedure reaches a final water content in the resin beads after drying of about 3-5%wt. (analyzed by Karl-Fischer titration in the laboratory). Additionally, catalyst beads were crushed and sieved in order to obtain desired particle diameters, d_p.

The experimental procedure was as follows: a known amount of alcohols was introduced into the reactor vessel, and heating and stirring were switched on. The isobutene was introduced into the reactor impelled from a pressure burette by nitrogen. Once the reactive mixture reached the desired temperature, controlled within ±0.1 K by a 1,2-propanediol-water thermostatic mixture, the catalyst load (0.1-1.0%wt.) was injected. This instant was considered as the starting point of the reaction. Consecutive GC analyses were carried out until the experimental run was ended. Final reaction time was set at, approximately, 300 min after the starting point.

For reproducibility evaluation purposes, some experiments were replicated. Obtained mean relative standard errors were 5% for isobutene conversion and 8% for estimated reaction rate values. This can be considered an acceptable level of uncertainty and it can be assumed that the uncertainty of the experiments that were not replicated is of the same order.

2.4. Analysis

Samples were taken inline from the reaction medium every 32 min through a sampling valve that injected 0.2 µL of pressurized liquid into an Agilent gas chromatograph 6890 equipped with a capillary column (HP-PONA 19091S-001, J&W Scientific, Santa Clara, US; 100% dimethylpolysiloxane, 50 m × 0.20 mm × 0.50 µm). The GC was coupled with a mass selective detector HP5973N, which allowed identifying and quantifying the reaction system components. The oven temperature was programmed with an initial 10 min hold at 333 K followed by a 10 K/min ramp, up to 353 K, and a second hold of 11.5 min at 353 K. Helium (>99.998%, Abelló-Linde, Barcelona, Spain) was the carrier gas, and its flowrate was set to 0.6 mL/min.

2.5. Calculations

Initial reaction rates (r_j^o), conversion of reactant j (X_j), selectivity of reactant j towards product k (S_j^k), and turnover frequency (*TOF*), have been calculated as follows:

$$r_j^o = \frac{1}{W_{cat}} \frac{dn_j}{dt}\bigg|_{t=0} \tag{1}$$

where W_{cat} is the weight of dry catalyst, n_j is the number of moles of the compound j and t is the time of reaction.

$$X_j = \frac{mole\ of\ j\ reacted}{mole\ of\ j\ fed} \tag{2}$$

$$S_j^k = \frac{mole\ of\ j\ reacted\ to\ produce\ k}{mole\ of\ j\ reacted} \tag{3}$$

$$TOF = \frac{reaction\ rate}{\left[active\ sites\right]} \tag{4}$$

3. Results and discussion

3.1. Catalyst screening

The studied reaction scheme is shown in Fig. 1. Main reactions are etherification of isobutene (IB) with ethanol (EtOH) and with 1-butanol (BuOH) to produce ETBE and BTBE (R1 and R2, respectively). Under certain conditions, isobutene hydration to give TBA (R3) and isobutene dimerization to give either TMP-1 or TMP-2 (R4) took place as side reactions. As it has been discussed in the literature [9,10], other possible side reactions that could take place in the studied system are alcohols dehydration to form linear ethers, or further isobutene oligomerization to produce heavier oligomers, as trimers or tetramers, but they were not

detected in the present work. Equilibrium conditions and thermodynamics of the involved reactions can be found elsewhere [11–13].
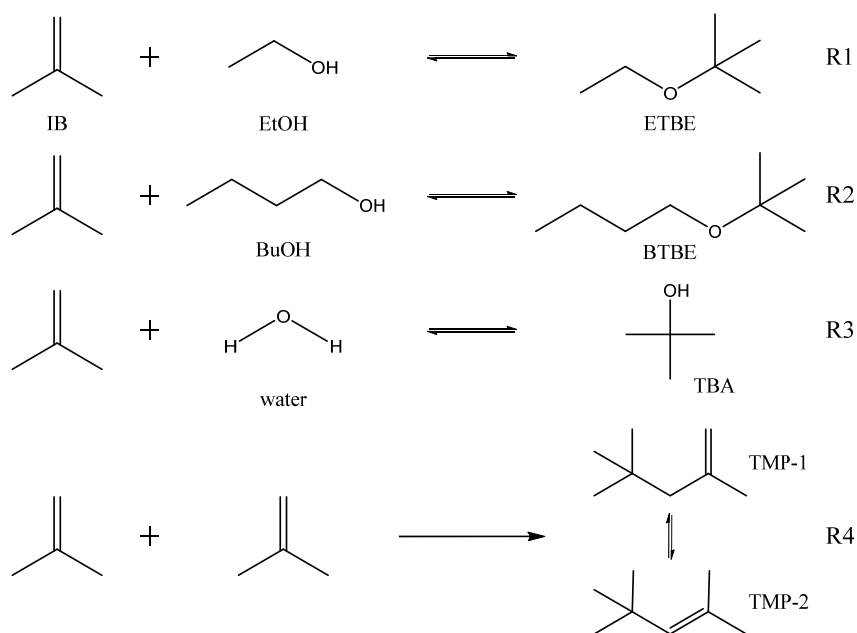

Fig. 1. Reaction scheme

The catalytic activity at 333 K was compared for all resins in the absence of reaction products. Preliminary experiments were carried out, to determine the conditions at which the effect of mass transfer limitations on the overall reaction rates could be neglected. CT-275 and A-39 were selected for these previous runs since both catalysts were considered to be representative of the range of properties of the tested resins. No significant differences in initial reaction rate values were found for experimental runs carried out with stirring speeds between 500 and 750 rpm, for each catalyst at 333 K. As for the possible effect of internal mass transfer limitations, CT-275 and A-39 beads were crushed and sieved to obtain different ranges of particle sizes, namely 0.08-0.16 mm and 0.25-0.40 mm. Again, no significant differences in the measured reaction rates were observed at 333 K. Therefore, all further experiments were done at 750 rpm and with 0.25-0.40 mm catalyst particles, unless otherwise is indicated.

The initial alcohol/isobutene molar ratio, $R^\circ_{A/IB}$, was set at 1.0 and the initial ethanol/1-butanol molar ratio, $R^\circ_{E/B}$, was varied in the range 0.5-2.0. Since the tested resins presented large differences in terms of activity, the catalyst load was varied accordingly in order to achieve conversion levels far above detection limits. The possible effect of the catalyst load (0.1-1.0%wt.) was considered as negligible, given that previous studies found it non-significant when catalyst load were up to 1.4%wt. in similar systems [14].

As it is shown in Fig. 2, A-35 was the most active catalyst for the two etherification reactions irrespectively of $R^\circ_{E/B}$. Initial ETBE reaction rates were hardly affected by reactants composition, whereas initial BTBE rates strongly diminished for all resins when the amount of

ethanol increased. The relative decrease of initial BTBE rates was about 80% from $x^o_{EtOH} = 0.17$ to $x^o_{EtOH} = 0.33$ ($R^o_{E/B} = 0.5$ and $R^o_{E/B} = 2.0$, respectively, and $R^o_{A/IB} = 1.0$). This fact suggests a preferential adsorption of ethanol over 1-butanol that could take place on all the tested catalysts, which affects more significantly BTBE synthesis than ETBE synthesis.
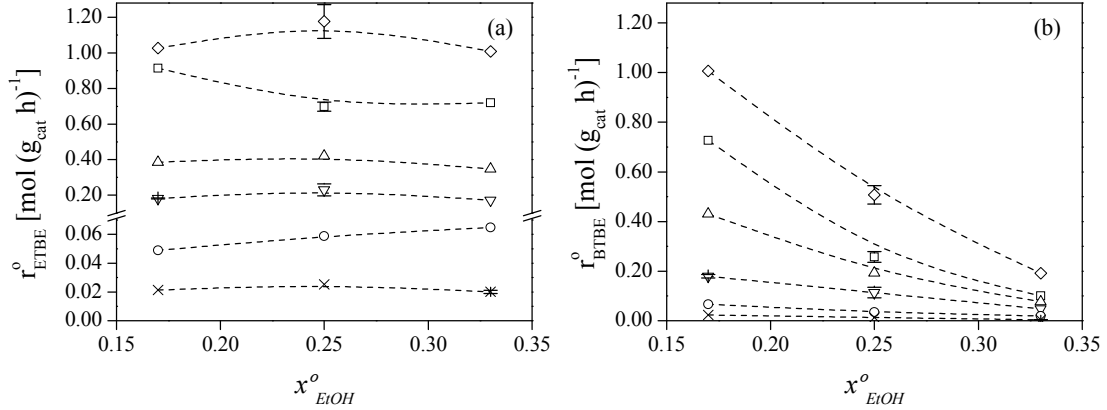

Fig. 2. Initial ETBE (a) and BTBE (b) reaction rate vs. initial ethanol molar fraction.
Error bars refer to the standard error for replicated experiments. T = 333 K, $R^o_{A/IB} = 1.0$, $d_p = 0.25$-0.40 mm, 750 rpm. A-35 ($\diamond$), CT-275 ($\square$), A-16 ($\triangle$), A-39 (∇), A-70 ($\circ$) and A-46 ($\times$)

Resins catalytic activity followed the relative order A-35 > CT-275 > A-16 > A-39 > A-70 > A-46. This relative order of activity can be globally explained by the relative order of resins acid capacity, shown in Table 1, except for resins A-16 and A-39, whose acidity is almost coincident, but they have significantly different activity. For instance, A-16 presents larger and wider pores than A-39 (Table 2). Therefore, the catalytic activity level cannot be explained only on terms of acid capacity, what suggests that other factors from resins morphology should be taken into consideration.

Table 2. Morphological characteristics of the assayed resins in both dry and water-swollen state.

| Catalyst | ρ [a] [g cm^{-3}] | Dry state: adsorption-desorption of N$_2$ at 77 K [b] | | | | Swollen in water (ISEC method) | | | |
| | | | | | | Macro-mesopores | | | Gel phase |
		S_{BET} [c] [m^2 g^{-1}]	S_g [m^2 g^{-1}]	V_g [d] [cm^3 g^{-1}]	$d_{m,pore}$ [e] [nm]	S_{area} [m^2 g^{-1}]	V_{pore} [cm^3 g^{-1}]	d_{pore} [e] [nm]	V_{SP} [cm^3 g^{-1}]
A-16	1.401	1.69	1.75	0.013	29.7	46.2	0.188	16.3	1.129
A-35	1.542	29.0	35.6	0.21	23.7	199	0.720	14.5	0.613
A-39	1.417	0.09	0.065	0.0003	17.6	56.1	0.155	11.1	1.624
A-46	1.137	57.4	54.8	0.263	19.2	186	0.470	10.1	0.523
A-70	1.514	0.018				66.1	0.220	13.3	1.257
CT-275	1.506	20.3	30.2	0.377	50.1	209	0.772	14.7	0.806

[a] Skeletal density. Measured by helium displacement (Accupic 1330). [b] Samples dried at vacuum (0.001 MPa, 383 K). [c] BET method (Brunauer-Emmett-Teller). [d] Volume of N$_2$ adsorbed at relative pressure (P/P$_0$) = 0.99. [e] $d_{m,pore} = 4V_g/S_g$ or $d_{pore} = 4V_{pore}/S_{area}$, respectively.

The dependence of initial reaction rates on the morphological characteristics of the tested resins, in both dry and water-swollen state (Table 2), has been checked. As discussed in the literature, dry state properties of the resins do not show a clear correlation with the displayed activity level

[15]. Since resins swell significantly in the reaction medium, dry state properties would not be an accurate picture of the actual resin morphology under reacting conditions [16]. Swollen-state morphological properties have been found to better describe the real resin morphology, and therefore they should be better related to its catalytic behavior [15,17]. As shown in Fig. 3, a linear relationship can be observed between the resins activity, in terms of initial reaction rates, and the active sites concentration in the resins gel-type phase, that is, the ratio between acid capacity, $[H^+]$, and the specific swollen polymer volume, V_{SP}, determined by Inverse Steric Exclusion Chromatography (ISEC) [18,19].
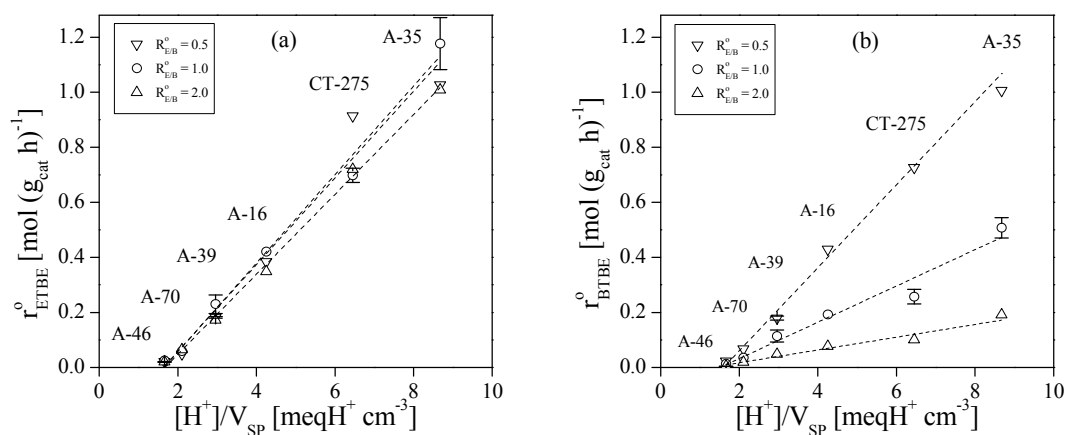

Fig. 3. Dependence of the initial ETBE (a) and BTBE (b) reaction rate on the acid sites density in the swollen gel phase volume. Error bars refer to the standard error for replicated experiments. T = 333 K, $R^\circ_{A/O}$ = 1.0, d_p = 0.25-0.40 mm, 750 rpm.

From these results, it can be stated that the water-swollen state morphology of the resins is directly related to their actual morphology in the reactive medium, although the swelling of the gel-type phase would differ somewhat from that measured in water [20]. In the ETBE synthesis, the catalytic activity is not affected by the alcohol ratio, $R^\circ_{E/B}$. On the contrary, BTBE synthesis is sensitive to the alcohol ratio: at every and $R^\circ_{E/B}$, a different clear linear dependence is observed between initial reaction rate and $[H^+]/V_{SP}$.

Higher reaction rates are obtained with catalysts that present a high acidity and a relatively rigid structure, what suggests that it is important to maintain high active sites concentration in the gel phase and that an excessive swelling of the polymer backbone has a detrimental effect on etherification rates. From a manufacturer standpoint, resins with high acid capacity and crosslinking degree (>14% DVB) are more prone to exhibit higher catalytic activity. For instance, among the highly-crosslinked resins, i.e., A-35, A-46 and CT-275, the higher the acid capacity, the faster the reaction rate, and among the highly acidic resins, i.e., A-16, A-35, A-39 and CT-275, a higher crosslinking degree leads to faster reaction rates.

On the other hand, since the activity level of the tested resins is far from being similar, the specific activity, or turnover frequency (TOF), can be used to compare resins activity per acid group. TOF is often calculated as the ratio between the overall reaction rate and the acid

capacity, under the assumption that all active sites are accessible to reactants. Even though such an assumption may not be valid for ion-exchange resins in non-polar media, TOF can be considered a fair indication of the overall effectiveness of the active sites for each resin and it would include the effect of the active site accessibility. As seen in Fig. 4, the relative order of specific activity was A-35 > CT-275 > A-16 > A-39 > A-46 $\geq$ A-70, irrespectively of $R^\circ_{E/B}$. This order reinforces the idea that high local concentrations of active sites enhance etherification rates, because A-35 and CT-275 presented superior specific activity. Resins with similar acidity, but more flexible structures, i.e., A-39 compared to A-16, were drastically less active. Special attention should be paid to resins A-70 and A-46, since the latter, with a more rigid structure, presented a level of specific activity at least equal to that of A-70, whose acid capacity triples that of A-46.
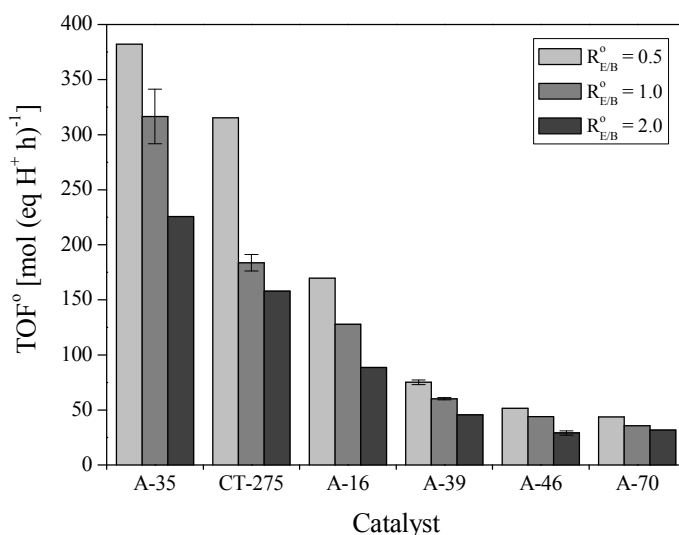

Fig. 4. *TOF°* displayed by each catalyst. Error bars refer to the standard error for replicated experiments. T = 333 K, $R^\circ_{A/IB}$ = 1.0, d_p = 0.25-0.40 mm, 750 rpm.

It is also observed that, for all resins, a higher 1-butanol concentration leads to a higher specific activity. This fact can be explained by assuming that the longer hydrocarbon chain of 1-butanol could interact with the hydrophobic polymer backbone of the resins, whereas the interaction between ethanol and the polymer would be mainly restricted to its hydroxyl group. As a result of the 1-butanol interaction, resins would experience a higher swelling, a larger number of active sites would become accessible to reactants and, hence, their specific activity would increase.

As for the products distribution, Table 3 lists the isobutene selectivity towards products at the end of the experimental runs (t = 300 min). In general, no significant differences in isobutene selectivity towards ethers were detected among the tested catalysts, irrespectively of the initial reactants concentration. As an exception, the least active resin, A-46, presented slightly higher

values of selectivity towards ETBE than the other catalysts. Selectivity values towards TBA were null or rather low. The isobutene selectivity towards dimers, when produced, generally increased at higher initial ethanol concentration, except for resin A-39, for which the opposite results were observed. From values in Table 3, the most active resin, A-35, presented scarce byproducts formation, which makes A-35 the most appropriate catalyst for the simultaneous etherification.

Table 3. Isobutene selectivity towards products and byproducts at t = 300 min. Standard error for replicated experiments is presented.

Catalyst	Catalyst Load [%wt.]	$R^{\circ}_{E/B}$	Isobutene selectivity towards main products and byproducts, S^k_{IB} [%]				
			ETBE	BTBE	TBA	TMP-1	TMP-2
A-16	0.20	0.5	41.8	56	0	1.7	0.4
		1.0	59.5	38.1	0	1.9	0.5
		2.0	75.5	19.5	0	4	1
A-35	0.15	0.5	39.2	58.9	0	1.5	0.4
		1.0	60.9 ± 1.7	37 ± 1	0.2 ± 0.04	1.5 ± 0.5	0.3 ± 0.1
		2.0	77.6	19.7	0	2.2	0.5
A-39	0.26	0.5	40.8 ± 0.1	48.6 ± 5.5	0	8 ± 4	2 ± 1
		1.0	58 ± 1	35.5 ± 1.7	0.1 ± 0.1	5.3 ± 1.7	1.4 ± 0.5
		2.0	75.6	21.5	0	2.4	0.6
A-46	0.40	0.5	48.4	51.6	0	0	0
		1.0	66.7	33.3	0	0	0
		2.0	82.8 ± 0.9	17.2 ± 0.9	0	0	0
A-70	0.25	0.5	44.8	55.2	0	0	0
		1.0	62.4	37.6	0	0	0
		2.0	77.5	22.5	0	0	0
CT-275	0.15	0.5	41.0	54.2	0	3.8	1
		1.0	64 ± 2	30 ± 2	0.3 ± 0.1	5 ± 2	1.2 ± 0.4
		2.0	73.9	14.3	0	9.2	2.5

The particular behavior of A-39 with respect to higher selectivity towards dimers should be explained as a basis of its properties. A-39 presents the highest swelling capacity among the tested resins, because of its low amount of DVB. Therefore, A-39 would be more affected by swelling and, as a result, the observed increase of isobutene selectivity towards dimers in A-39 could be explained by a larger number of inner active sites that become accessible at higher 1-butanol concentration, which would have a more pronounced effect in A-39 than in the other catalysts.

3.2. Effect of the initial concentration on the simultaneous etherification

To study the effect that different reactants concentration could have on the simultaneous etherification reaction performance, initial reactants composition was varied as follows: at initial equimolar amount of alcohols ($R^{\circ}_{E/B} = 1.0$), the initial molar ratio alcohol/isobutene ($R^{\circ}_{A/IB}$) was varied from 0.5 (excess of isobutene) to 5.5 (large excess of alcohols); and, at stoichiometric initial composition alcohol/isobutene ($R^{\circ}_{A/IB} = 1.0$), the initial molar ratio ethanol/1-butanol

($R^\circ_{E/B}$) was varied between 0.5 (high initial concentration of 1-butanol) and 2.0 (high initial concentration of ethanol). All further experiments were carried out using A-35 as catalyst, since it has been considered as the most promising catalyst among the tested ones.

Fig. 5 shows that, for experiments at $R^\circ_{E/B} = 1.0$, initial reaction rates increased at increasing the initial isobutene molar fraction, x°_{IB} (which, in the assayed experimental conditions, corresponds to a decrease in $R^\circ_{A/IB}$). The same behavior can be observed for both reactions, and it agrees with results reported in literature on different alcohol/isobutene systems, in which methanol, ethanol, or 1-butanol were considered [5,21,22].
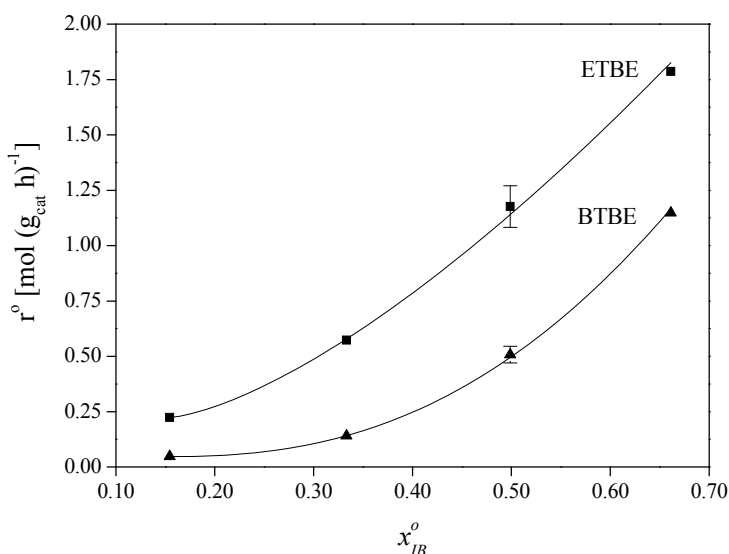
Fig. 5. Initial etherification rate vs. initial isobutene molar fraction. Error bars refer to the standard error for replicated experiments. A-35, $R^\circ_{E/B} = 1.0$, T = 333 K, d_p = 0.25-0.40 mm, 750 rpm. ETBE (■), BTBE (▲)

It has been shown in the previous section that ETBE rate is hardly affected by the initial alcohols ratio, whereas BTBE rate strongly diminishes as ethanol concentration increases (Fig. 2). This fact can be related to a preferential adsorption of ethanol over 1-butanol on the catalyst active sites, what hinders BTBE formation. To check it, some adsorption experiments were performed using A-35 at 333 K and atmospheric pressure. 10 mL of commercial size beads, previously pretreated to reduce their water content (catalyst dry weight was about 3.6 g), were introduced into test tubes containing 20 mL of alcohol mixtures, submerged in a thermostatic bath. Five different alcohol mixtures were used, whose initial ethanol/1-butanol ratio, $R^\circ_{E/B}$, ranged from 8.4 to 0.10. Then, the liquid-phase composition was analyzed by means of repeated GC analyses. The evolution in time of the ethanol/1-butanol molar ratio of the liquid phase is represented in Fig. 6 for the different mixtures. As seen in the figure, ethanol/1-butanol molar ratios decreased progressively for all $R^\circ_{E/B}$, what, in absence of reaction (since no products were detected in the GC analyses), indicates a preferential adsorption of ethanol compared to 1-butanol. These results are in agreement with literature data on the adsorbed concentration of

alcohols on the ion-exchange resin Amberlyst 35 in liquid-phase experiments [23], where it was found that the amount of ethanol adsorbed by the resin is higher than that of 1-butanol.
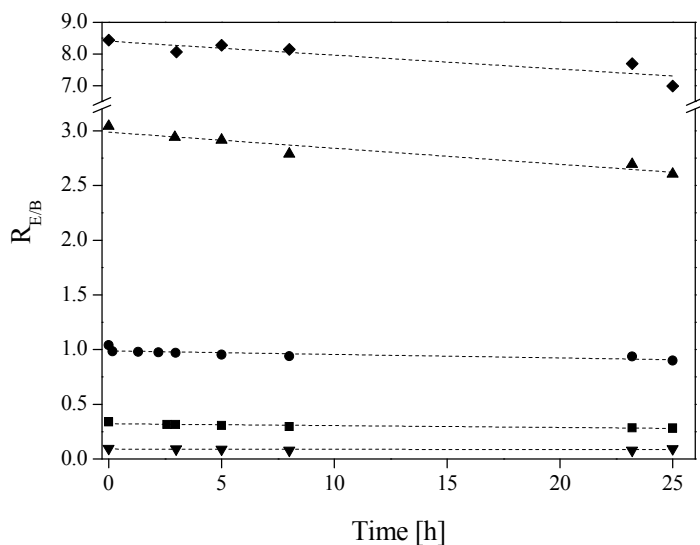

Fig. 6. Evolution in time of the liquid-phase ethanol/1-butanol molar ratio in contact with A-35 at T = 333 K. $R^{\circ}_{E/B}$ = 8.4 (♦), $R^{\circ}_{E/B}$ = 3.04 (▲), $R^{\circ}_{E/B}$ = 1.03 (●), $R^{\circ}_{E/B}$ = 0.34 (■), $R^{\circ}_{E/B}$ = 0.10 (▼).

With regards to byproducts formation at $R^{\circ}_{E/B}$ = 1.0, dimerization of isobutene was notably favored when isobutene was in excess ($R^{\circ}_{A/IB}$ = 0.5, which, in the assayed experimental conditions, corresponds to x°_{IB} = 0.66). Under these conditions and after 300 min, isobutene selectivity values towards TMP-1 and TMP-2 were up to 18% and 5%, respectively. In large excess of alcohols ($R^{\circ}_{A/IB}$ = 5.5, which, in the assayed experimental conditions, corresponds to x°_{IB} = 0.15) no dimers were detected. On the other hand, higher amounts of TBA were formed when alcohols were in excess (isobutene selectivity towards TBA was up to 0.8% at t = 300 min with $R^{\circ}_{A/IB}$ = 5.5), which can be related to the water content present as alcohols impurities.

The enhancement of dimers formation when isobutene is in excess is known to be caused by the adsorption of isobutene, albeit reduced, on non-dissociated sulfonic groups, typically associated to a concerted mechanism (general acid catalysis) [24]. In this type of mechanism, the rate determining step is the surface reaction either between adsorbed molecules or between adsorbed and non-adsorbed molecules, as would be the case of the isobutene dimerization [5,6,25,26]. This mechanism is faster than the ionic one (specific acid catalysis), which is characteristic of large excess of a polar compound, e.g., water and alcohols, and can account for the decrease of etherification rates observed at high $R^{\circ}_{A/IB}$.

The effect of $R^{\circ}_{A/IB}$ and $R^{\circ}_{E/B}$ on isobutene selectivity towards ETBE and BTBE at increasing isobutene conversion is shown in Fig. 7 and Fig. 8. As it is seen in Fig. 7, at $R^{\circ}_{E/B}$ = 1.0 a high alcohol content enhances isobutene selectivity towards ETBE over BTBE. Results at $R^{\circ}_{A/IB}$ = 1.0, which are shown in Fig. 8, show that a high concentration of ethanol ($R^{\circ}_{E/B}$ = 2.0) favors

12

ETBE production over that of BTBE. In the range of the assayed initial compositions, overall isobutene selectivity towards ethers was about 97% for the highest isobutene conversion values, except for the experiment at $R°_{A/IB} = 0.5$ and $R°_{E/B} = 1.0$, in which the isobutene selectivity towards ethers dropped to around 80% because of the already commented enhancement of isobutene dimerization.
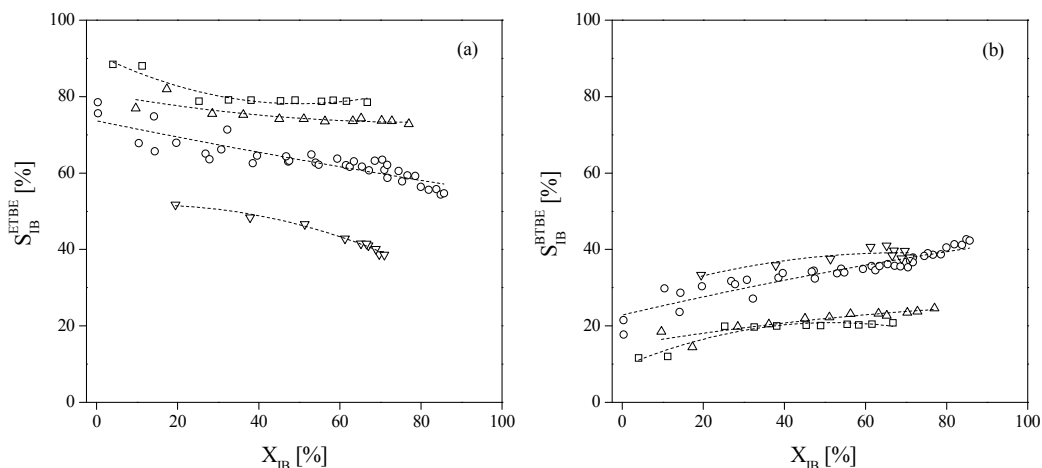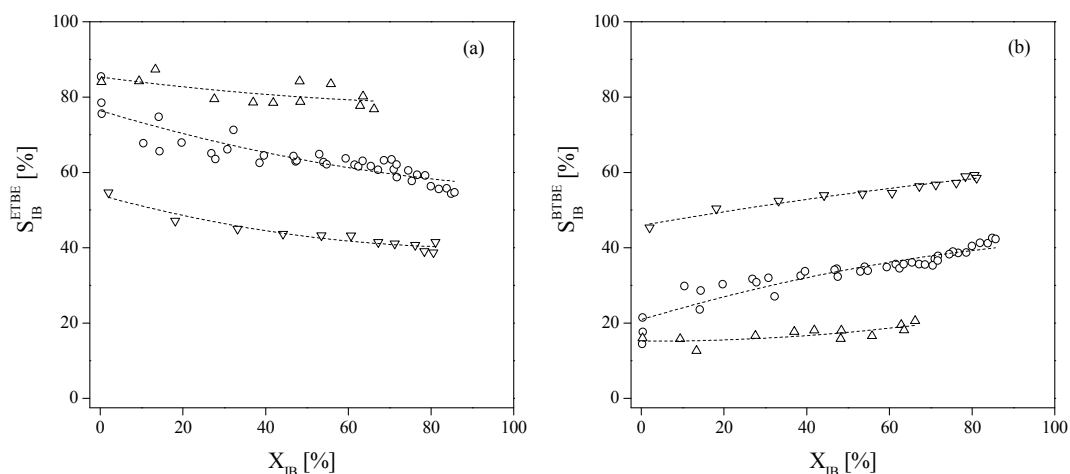

Fig. 7. Effect of $R°_{A/IB}$ on isobutene selectivity towards ETBE (a) and BTBE (b) as a function of isobutene conversion. A-35, $R°_{E/B} = 1.0$, T = 333 K, $d_p = 0.25\text{-}0.40$ mm, 750 rpm. $R°_{A/IB} = 5.5$ (□), $R°_{A/IB} = 2.0$ (△), $R°_{A/IB} = 1.0$ (○), $R°_{A/IB} = 0.5$ (▽).

Fig. 8. Effect of $R°_{E/B}$ on isobutene selectivity towards ETBE (a) and BTBE (b) as a function of isobutene conversion. A-35, $R°_{A/IB} = 1.0$, T = 333 K, $d_p = 0.25\text{-}0.40$ mm, 750 rpm. $R°_{E/B} = 2.0$ (△), $R°_{E/B} = 1.0$ (○), $R°_{E/B} = 0.5$ (▽).

From an industrial standpoint, these results point out that the overall performance of the simultaneous etherification can be adapted to the market demands and stock disposal by selecting the reactants composition. For instance, given that byproducts are not desirable, $R°_{A/IB}$ should be near 1.0 or slightly higher, and, if production of one ether is preferred over the other, the corresponding alcohol concentration should be increased. If an increased overall ethers production is required, $R°_{E/B}$ should be below 1.0, because the production of BTBE is lowered at

low concentrations of 1-butanol in a larger extent than ETBE at low concentrations of ethanol, in both terms of reaction rate and selectivity.

3.3. Effect of temperature on the simultaneous etherification

The effect of temperature on the simultaneous etherification process performance was assessed by carrying out experiments in the temperature range of 315 to 353 K, at $R°_{A/IB} = 1.0$, $R°_{E/B} = 1.0$, and using A-35 as the catalyst.

The isobutene selectivity towards ethers at different isobutene conversion levels is depicted in Fig. 9 as a function of temperature. As it is observed, isobutene selectivity towards ETBE is higher than towards BTBE. Both selectivity values approach as temperature and conversion increase.
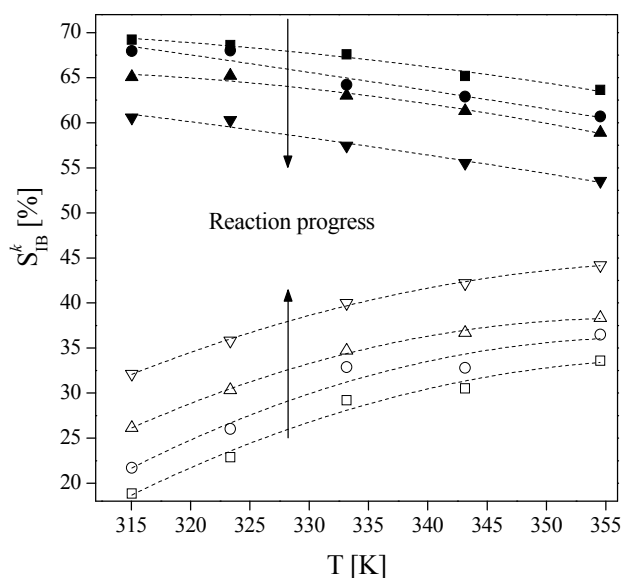

Fig. 9. Isobutene selectivity towards main products as a function of temperature for a given isobutene conversion level. A-35, $R°_{A/IB} = 1.0$, $R°_{E/B} = 1.0$, $d_p = 0.25$-0.40 mm, 750 rpm.
Solid symbols: S_{IB}^{ETBE} at $X_{IB} = 20\%$ (■), $X_{IB} = 40\%$ (●), $X_{IB} = 60\%$ (▲), and $X_{IB} = 80\%$ (▼);
Open symbols: S_{IB}^{BTBE} at $X_{IB} = 20\%$ (□), $X_{IB} = 40\%$ (○), $X_{IB} = 60\%$ (△), $X_{IB} = 80\%$ (▽).

With regards to the sensitivity of etherification rates to temperature variations, the Arrhenius plot of initial etherification reaction rates is shown in Fig. 10. As seen, rates at the highest assayed temperature (around 353 K) are not aligned with the rest. It indicates that, at 353 K, some transport limitations affect the overall reaction rate. As it can be assumed that there was no significant effect of the external mass transfer, since the stirring speed was large enough (750 rpm), the observed depletion in the Arrhenius plot would indicate that the catalyst bead size used for these experiments ($d_p = 0.25$-0.40 mm) was large enough for diffusion resistance through the pores to become non-negligible at that temperature. Thus, an additional experiment was performed, using a smaller particle size ($d_p = 0.08$-0.16 mm) at 353 K, also included in Fig. 10 as open symbols, which gives reaction rate values aligned with lower-temperature rates,

within the margin of experimental error. The latter experimental result confirms the effect of the internal mass transport limitations at 353 K.
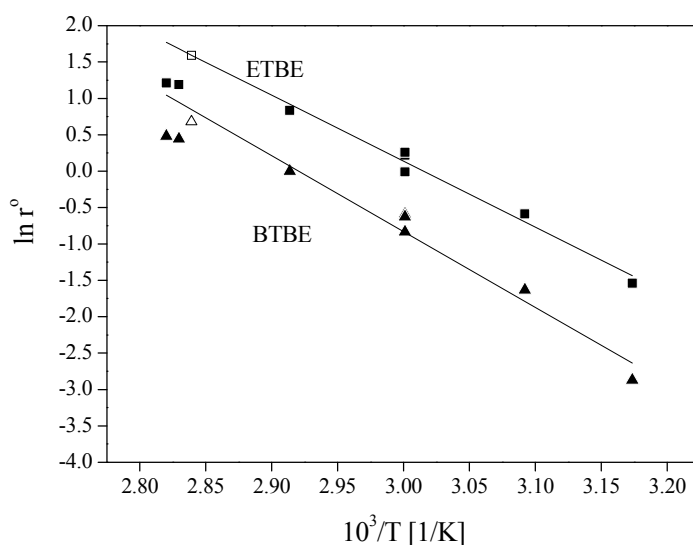

Fig. 10. Arrhenius plot of the initial etherification rates. Solid lines represent the fit of rate data to straight lines. Open symbols represent rate data using bead size range of 0.08-0.16 mm. A-35, $R°_{A/IB} = 1.0$, $R°_{E/B} = 1.0$, $d_p = 0.25$-0.40 mm, 750 rpm. ETBE (■), BTBE (▲).

From the slope of the solid lines shown in Fig. 10, the calculated apparent activation energies in the simultaneous synthesis result in (75 ± 4) kJ mol^{-1} and (85 ± 7) kJ mol^{-1} for the ETBE and BTBE syntheses, respectively. ETBE apparent activation energy agrees with literature data, which has been reported to be in the range of 72 to 83 kJ mol^{-1} using A-35 as catalyst [27]. Data for the BTBE synthesis activation energy were not found in the open literature. Therefore, some additional experiments were carried out in the temperature range between 303 and 353 K in the BTBE system. Experimental conditions concerning this set of experiments were: $R°_{A/IB} = 1.0$, A-35 as catalyst, 0.25-0.40 mm beads (the same particle size range was used for comparison purposes), and stirring speed of 750 rpm. Literature rate data regarding ETBE rate dependence on temperature were also retrieved from a previous study where it was determined the experimental conditions that ensured no significant mass transfer limitations [28]. The logarithm of the isobutene consumption rate for these three systems –i.e., ETBE synthesis, BTBE synthesis, and simultaneous ETBE and BTBE syntheses– is plotted against the inverse temperature in Fig. 11.
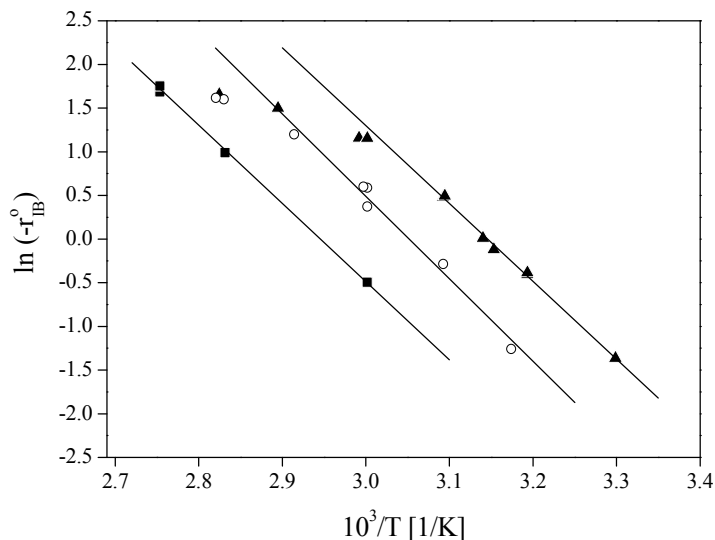
15

Fig. 11. Dependence of initial rates on temperature. Solid lines represent the fit of rate data free from mass transfer effects to straight lines. A-35, d_p = 0.25-0.40 mm, 750 rpm, $R°_{A/IB}$ = 1.0, and $R°_{E/B}$ = 1.0 (only simultaneous synthesis). ETBE (■), BTBE (▲), simultaneous synthesis (○).

Results in Fig. 11 allow inferring that the isobutene consumption rate dependence on temperature is analogous for the three systems, given that the slopes of the straight lines are almost equal. From these slopes, apparent activation energies are (74 ± 1) kJ mol^{-1} and (74 ± 2) kJ mol^{-1} for the individual syntheses of ETBE and BTBE, respectively. Notice that the estimated values of ETBE apparent activation energy in both the simultaneous synthesis and the individual one are the same, within the margin of experimental error, whereas there is a slight increase of the BTBE apparent activation energy in the simultaneous system compared to that of the individual synthesis. This fact could suggest that ETBE synthesis reaction rate would not be affected by the presence of 1-butanol, but that BTBE reaction rate could be influenced by the presence of ethanol molecules in the simultaneous system.

Isobutene consumption rates at a given temperature follow the order: BTBE > ETBE + BTBE > ETBE, when internal mass transfer effects on overall reaction rates are negligible. At temperatures higher than 333 K, and using A-35 particles of d_p = 0.25-0.40 mm, rate limitations due to internal mass transfer on the BTBE synthesis become non-negligible. Likewise, these effects are significant at temperatures higher than 343 K for the simultaneous system. No significant mass transfer limitations on rates were detected in the ETBE system at temperatures as high as 363 K, using the same catalyst and particle size range.

From these results, efficiency factors using 0.25-0.40 mm beads of A-35 can be calculated as the quotient between actual initial rates and initial rates free from mass transfer effects. Efficiency factors for the BTBE synthesis are about 0.5 and 0.3 at 343 K and 353 K, respectively. For the simultaneous system, efficiency is slightly over 0.6 at 353 K. Within the assayed temperature range, 0.25-0.40 mm particles of A-35 would present efficiency factor

16

values close to unity for the individual synthesis of ETBE at all temperatures. Thus, rate limitations due to diffusion through the pores are more accused in the BTBE synthesis than they are in the ETBE synthesis. Given that the difference between these two systems is the size of the involved compounds, it seems reasonable to assume that BTBE formation is hindered by internal mass transport limitations because of the steric effects caused by either 1-butanol or the formed ether. Results also point out that mass transport limitations on ETBE rate, when produced simultaneously with BTBE, also arise, whereas these limitations are not observed in the absence of 1-butanol. This fact suggests that the presence of 1-butanol increases the resistance to the mass transport within the resin for both 1-butanol and ethanol and reduces accessibility to the inner active sites.

3.4. Comparison between simultaneous system and individual syntheses

Finally, the performance of the etherification reaction of each individual synthesis was compared to that of the simultaneous process by means of three analogous experimental runs (one with ethanol, one with 1-butanol, and one with the two alcohols as reactants). Experimental conditions regarding these runs were as follows: $T = 333$ K, A-35 as catalyst, catalyst load = 0.16%wt., $d_p = 0.25$-0.40 mm, stirring speed = 750 rpm, and $R^o_{A/IB} = 1.0$. Initial concentrations could not be the same, since no diluents were added. Therefore, to maintain the initial alcohol/isobutene molar ratio ($R^o_{A/IB}$) at 1.0, the initial molar ratios were 1:1 (isobutene:alcohol) in the individual syntheses, and 2:1:1 (isobutene:ethanol:1-butanol) in the simultaneous process. Figs. 12 and 13 show the mole evolution in time of the main compounds for the three systems. Fig. 12a corresponds to the reaction between isobutene and ethanol, and Fig. 12b to the reaction with 1-butanol. In Fig. 13, the mole evolution for an experiment with both ethanol and 1-butanol as reactants is presented.
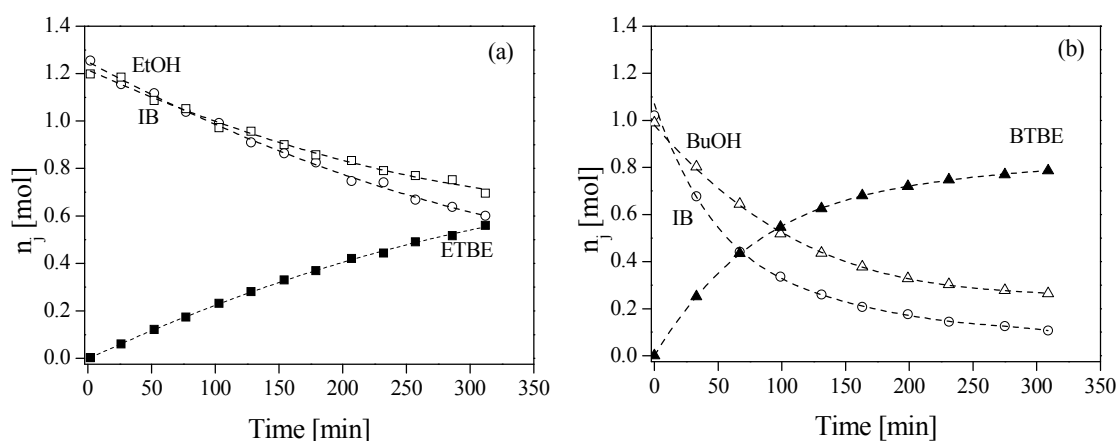

Fig. 12. Mole evolution in time of the main compounds for (a) ETBE and (b) BTBE individual syntheses
A-35, catalyst load = 0.16%wt., $d_p = 0.25$-0.40 mm, 750 rpm, $R^o_{A/IB} = 1.0$, T = 333 K
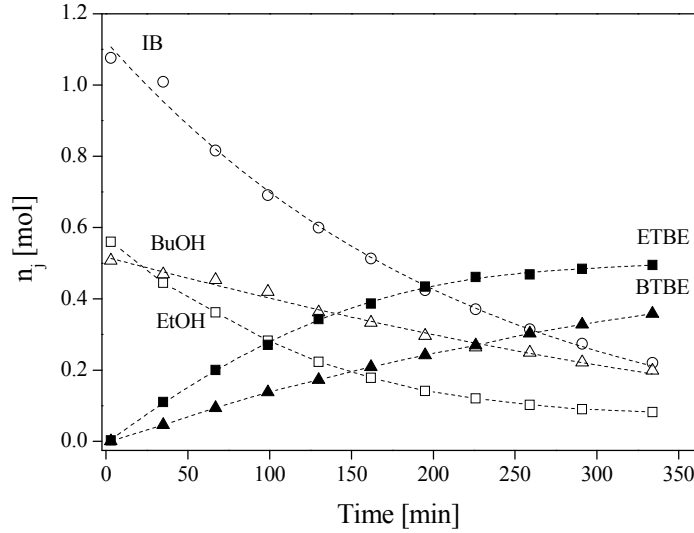IB (○), EtOH (□), BuOH (△), ETBE (■), BTBE (▲)

Fig. 13. Mole evolution in time of the main compounds in the simultaneous synthesis
A-35, catalyst load = 0.16%wt., d_p = 0.25-0.40 mm, 750 rpm, $R°_{A/IB}$ = 1.0, $R°_{E/B}$ = 1.0, T = 333 K
IB (○), EtOH (□), BuOH (△), ETBE (■), BTBE (▲)

As it can be seen in Fig. 12, the individual BTBE production proceeds much faster and in a larger extent than that of ETBE. This fact is consistent with the higher reactivity of larger primary alcohols with isobutene already reported in literature [5,29,30]. In contrast, in the simultaneous system (Fig. 13), the opposite situation was observed, which can be explained by the previously discussed preferential adsorption of ethanol compared to 1-butanol on the resin active sites.

With regard to the side reactions extension in the studied systems, isobutene selectivity values (Table 4) towards ethers and byproducts were almost the same for the two individual syntheses, reaching selectivity values towards ether over 91% in both cases. On the other hand, overall isobutene selectivity towards ethers in the simultaneous system reached values of about 97% at t = 300 min, what would imply a significant advantage in industrial operation. The higher overall selectivity towards ethers in the simultaneous process is consistent with a larger number of accessible active sites occupied by alcohol molecules compared to individual syntheses.

Table 4. Reactants initial concentration and conversion and selectivity at t = 300 min for individual and simultaneous processes. A-35, catalyst load = 0.16%wt., d_p = 0.25-0.40 mm, 750 rpm, T = 333 K.

Reactants initial concentration [mol L^{-1}]			Reactants conversion and selectivity [%]							
isobutene	ethanol	1-butanol	X_{IB}	X_{EtOH}	X_{BuOH}	S_{IB}^{ETBE}	S_{IB}^{BTBE}	S_{IB}^{TMP-1}	S_{IB}^{TMP-2}	S_{IB}^{TBA}
6.1	6.1		48.9	42.8		91.3		6.8	1.6	0.3
5.1		5.1	88.0		73.6		91.3	6.9	1.7	0.2
5.5	2.8	2.8	76.3	84.6	60.5	57.5	39.3	2.5	0.5	0.2

Fig. 14 depicts initial etherification rates as a function of the initial ethanol molar fraction at $R°_{A/IB} = 1.0$ for the whole range of possible $R°_{E/B}$. Values $x°_{EtOH} = 0, 0.17, 0.25, 0.33,$ and 0.50 correspond respectively to $R°_{E/B} = 0$ (absence of ethanol), 0.5, 1.0, 2.0, and ∞ (absence of 1-butanol). As seen in the figure, ETBE formation rates show little variation in the range of $x°_{EtOH}$ from 0.17 to 0.50, and BTBE rates follow an almost exponential-like depletion as the initial ethanol concentration decreases, that is, as the initial 1-butanol concentration increases.
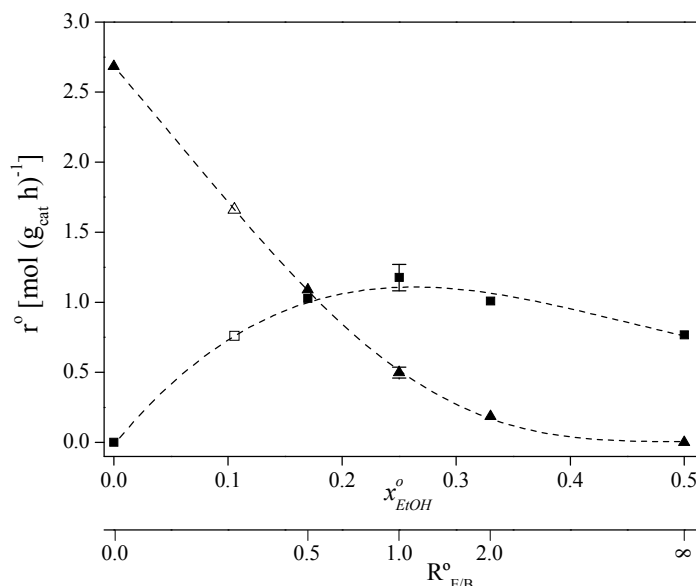

Fig. 14. Effect of the ethanol concentration in the intial reactant mixture on the initial ETBE and BTBE formation rate. $R°_{A/IB} = 1.0$, T = 333 K, A-35, catalyst load = 0.16%wt., d_p = 0.25-0.40 mm, 750 rpm. Solid symbols: experimental rates, $r°_{ETBE}$ (■), $r°_{BTBE}$ (▲). Open symbols: estimated rates, $r°_{ETBE}$ (□), $r°_{BTBE}$ (△)

Fig. 14 allows to estimate the result of using a certain raw alcohol mixture, which is of interest from an industrial standpoint. An ABE fermentation unit yields acetone:1-butanol:ethanol mixtures with a typical weight ratio 3:6:1 [31,32]. After separation of acetone, an alcohol mixture with $R°_{E/B} = 0.27$ would be obtained. The corresponding estimates of initial etherification rates at $R°_{A/IB} = 1.0$ ($x°_{EtOH} = 0.11$) are shown in Fig. 14 as open symbols. As it can be seen, a high BTBE production rate and satisfactory ETBE rates could be obtained under those conditions.

4. Conclusions

Several aspects of the syntheses of ETBE and BTBE by means of the simultaneous etherification of isobutene with ethanol and 1-butanol over acidic macroreticular ion-exchange resins have been studied. From the screening study in which six different ion-exchange resins were tested, A-35 stands out as the most appropriate catalyst for the simultaneous etherification process, because it yields low byproducts formation and high reaction rates.

Experimental reaction rates have been found to increase linearly with the resin active sites concentration in the swollen gel phase volume of six different resins. Strongly acidic catalysts with high crosslinking degrees achieve faster reaction rates, what implies that some rigidity of the polymer backbone is required to avoid excessive swelling in order to maintain a high active sites density in the catalyst gel phase.

Both ethers formation rates increase at high initial isobutene concentration, but dimers are produced in a larger extent. ETBE reaction rate is hardly affected by variation of the initial alcohols molar ratio, whereas BTBE production rate strongly diminishes when ethanol concentration is higher than that of 1-butanol. A preferential adsorption of ethanol over 1-butanol on the tested resins has been observed.

In the simultaneous etherification process, ETBE and BTBE apparent activation energies are (75 ± 3) kJ mol^{-1} and (81 ± 5) kJ mol^{-1}, respectively, and, in the individual processes, (74 ± 1) kJ mol^{-1} and (74 ± 2) kJ mol^{-1}, respectively. The apparent activation energy for the ETBE synthesis is not modified by the 1-butanol presence, while that of BTBE synthesis slightly increases by the ethanol presence. Since ethanol adsorbs preferentially on the catalyst, its presence reduces noticeably the BTBE formation rate, below the ETBE formation rate at equal initial molar concentration. The effect on rates of the internal mass transport is stronger for the simultaneous syntheses than it is for the individual ETBE synthesis. Finally, the simultaneous syntheses of ETBE and BTBE present high reactants conversion and selectivity towards the desired products. The simultaneous process produces less byproducts than each of the individual syntheses.

Acknowledgements

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