



# Byproducts formation in the ethyl *tert*-butyl ether (ETBE) synthesis reaction on macroreticular acid ion-exchange resins

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## ABSTRACT

Ethyl *tert*-butyl ether (ETBE) production is one of the industrial processes of major importance today in Europe. However, the study of side reactions in this synthesis reaction appears scarcely in the open literature. Side reactions take place along with the etherification of C4 olefinic cuts with ethanol, catalyzed by acidic ion-exchange resins. In this work, byproducts formation is studied in a batch reactor. The presence of diethyl ether (DEE), ethyl *sec*-butyl ether (ESBE), dimers of isobutene (2,4,4-trimethyl-1-pentene (TMP-1) and 2,4,4-trimethyl-2-pentene (TMP-2)) and *tert*-butyl alcohol (TBA) has been studied in terms of production and selectivity. The effect of temperature, ranging from 323 to 383 K, and the influence of initial molar ratio ethanol/isobutene ( $R_{A/O}$ ), ranging from 0.5 to 2.0, on byproducts formation have been analyzed. All byproducts formation was favored by high temperatures. A low initial molar ratio ethanol/isobutene favored the formation of DEE, ESBE, TMP-1 and TMP-2, whereas high molar ratios favored TBA formation.

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## 1. Introduction

The use of ethyl tertiary-butyl ether (ETBE) became widely spread in the European Union (EU) since oxygenated ethers were selected as preferred octane enhancers due to consecutive directives regulating gasoline composition. The current Renewable Energy Directive (2009/28/EC) and Fuel Quality Directive (2009/30/EC) still are the main drivers for changes in fuel composition for the foreseeable future. These directives propose a 10% value for biofuels in the market share in the EU, by the end of 2020, and an increase in the oxygen content limit up to a 3.7 wt%, allowing a higher oxygenates content in the base pool for gasoline [1,2].

Industrially, ETBE is obtained under mild conditions by means of a heterogeneous catalytic etherification reaction of 2-methylpropene (isobutene) with ethanol, in which macroreticular ion exchange acidic resins of polystyrene-divinylbenzene matrix are used as catalysts [3–5]. Reaction between ethanol and isobutene to produce ETBE (reaction (1) in Fig. 1) is reversible and moderately exothermic (heat of reaction of  $-35\text{ kJ/mol}$  at 298 K) [6,7]. In catalytic fixed-bed tubular reactors, low inlet temperatures and a slight excess of ethanol are typical operating conditions in order to avoid possible byproducts formation. Likewise, ETBE can be formed by means of catalytic distillation technology, based on a two-step reactor design, consisting of a boiling point fixed bed

reactor followed by final conversion in a catalytic distillation column. In both units, a bed of ion exchange resin catalysts is used [8–10].

By-products formation in the industrial process is related to the feed ratio alcohol/olefin, to the sources for the two reactants and to the hot-spots that could take place within the catalytic bed, where temperatures above 373 K could be reached. With regards to the reactants sources, isobutene comes mainly from the effluent of two petrochemical processes – the fluid catalyzed cracking (FCC) and the steam cracking (SC) – along with other four-carbon compounds, resulting in what is known as the C4 cut. A typical FCC C4 cut composition includes isobutene, isobutane, butane, linear butenes and others. With respect to ethanol, currently trend is to produce it from renewable sources, as from biomass by hydrolysis and sugar fermentation. In such process, an important amount of water within the alcoholic stream can be present [11].

Main side reactions involve (Fig. 1): dimerization of isobutene to form 2,4,4 trimethyl-1-pentene (TMP-1) and 2,4,4 trimethyl-2-pentene (TMP-2), and thereof double bond isomerization (reactions (2)–(4) in Fig. 1), ethanol dehydration to form diethyl ether (DEE) and water (reaction (5) in Fig. 1), isobutene hydration to form of *tert*-butyl alcohol (TBA) (reaction (6) in Fig. 1), and formation of ethyl *sec*-butyl ether (ESBE) by reaction between ethanol and linear butenes of C4 olefinic cuts (reaction (7) in Fig. 1).

In general, byproducts are inconvenient because some of them attenuate the desired properties towards the resulting gasoline mixture (Table 1). The presence of TMP-1 and TMP-2 along with the ETBE stream product does not pose any problems for blending, since both compounds have a high octane number. However, on

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## Nomenclature

A-35	Amberlyst® A-35WET is a macroreticular, strongly acidic, cationic, polymeric catalyst by The Dow Chemical Company
$a_i$	activity of chemical specie $i$
C4	4-length hydrocarbons
CT-275	Purolite® CT275 is a macroreticular, strongly acidic, cationic, polymeric catalyst by Purolite
DEE	diethyl ether
$d_p$	particle diameter
DVB	divinyl-benzene
ESBE	ethyl <i>sec</i> -butyl ether
ETBE	ethyl <i>tert</i> -butyl ether
EtOH	ethanol
FCC	fluid catalyzed cracking
GC/MS	gas chromatographer/mass spectrophotometer
IB	2-methylpropene (isobutene)
IPTBE	isopropyl <i>tert</i> -butyl ether
$K$	thermodynamic equilibrium constant
$K_\gamma$	ratio of activity coefficients in an equilibrium reaction
$K_x$	experimental equilibrium constant based on molar fractions
MON	motor octane number
MTBE	methyl <i>tert</i> -butyl ether
$n_k$	mole of product or byproduct
$R^{\circ}_{A/O}$	feed molar ratio of alcohol to olefin
RON	research octane number
RVP	Reid vapor pressure
SC	steam cracking
$S_j^k$	selectivity of reactant $j$ toward product $k$ , expressed as a percentage
$T$	temperature [K]
TAEE	<i>tert</i> -amyl ethyl ether
TAME	<i>tert</i> -amyl methyl ether
TBA	<i>tert</i> -butyllic alcohol
TMP-1	2,4,4-trimethyl-1-pentene
TMP-2	2,4,4-trimethyl-2-pentene
$X_j$	conversion of reactant $j$ , expressed as a percentage
$x_i$	molar fraction of chemical species $i$
$w_{\text{cat}}$	catalyst weight on dry basis
<i>Greek letters</i>	
$\gamma_i$	individual activity coefficient of chemical specie $i$
$\Delta_r H_m^\circ$	standard molar enthalpy change of reaction (kJ mol <sup>-1</sup> )
$\Delta_r S_m^\circ$	standard molar entropy change of reaction (J mol <sup>-1</sup> K <sup>-1</sup> )
$\Delta_r G_m^\circ$	standard molar free energy change of reaction (kJ mol <sup>-1</sup> )

the catalyst they can originate polymers that could act as poison by accumulating in the pores and lowering the accessibility to acid centers [12]. DEE formation enhances higher blending vapor pressure that might increase undesired evaporative emissions, as its vapor pressure is higher than for the rest of possible products [13,14]. Regarding TBA, although its octane number is high, TBA presence in the gasoline blending increases its water solubility, its blending Reid vapor pressure (RVP) [15–18], and its oxygen content [19]. Finally, as ESBE has a more linear structure than ETBE, it is assumed that its octane number is lower than that of ETBE. Thus, the effect of the ESBE presence would be to reduce the octane number of the gasoline mixture [20]. Besides, byproducts

could cause some problems in the separation units, and in the later use of the unreacted C4 stream.

As literature on ETBE byproducts is very scarce, the aim of the present work is to determine the conditions of formation of DEE, isobutene dimers, TMP-1 and TMP-2, ESBE and TBA in the synthesis of ETBE on macroreticular acid resins in order to reduce their formation. Finally, as relatively fast equilibrium reactions take place within the reaction network, their corresponding pseudo equilibrium conditions were studied.

## 2. Experimental setup and procedure

### 2.1. Chemicals

As reactants, ethanol (max. water content 0.02 wt%), supplied by Panreac (Barcelona, Spain), and a synthetic C4 mixture, supplied by Abelló-Linde (Barcelona, Spain), as the isobutene source, were used. The composition of the C4 mixture was 25 wt% isobutene, 40 wt% isobutane and 35 wt% *trans*-2-butene.

TBA (99.7% G.C.) and DEE (99.5% G.C.), supplied by Panreac (Barcelona, Spain), ETBE (>95.0% G.C.) and ESBE (>99.7% G.C.), supplied by TCI (Tokio, Japan), and TMP-1 (>98% G.C.) and TMP-2 (>98% G.C.), supplied by Sigma-Aldrich Química SA (Madrid, Spain), were used for analysis purposes.

### 2.2. Catalysts

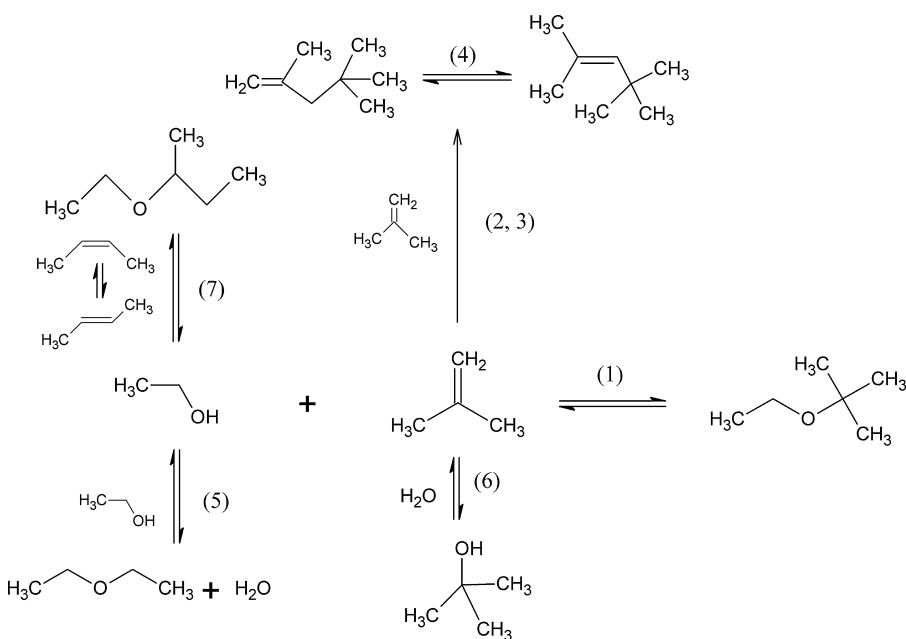
As catalysts, two ion exchange resins, namely, Amberlyst™ 35 (A-35) and Purolite® CT275 (CT-275), supplied by Rohm and Haas France SAS (Chauny, France) and Purolite (Barcelona, Spain), respectively, were used. Both resins are macroreticular, acidic, oversulfonated polymers of styrene–divinylbenze (DVB) with a permanent pore structure that makes them appropriate for a wide range of organic reactions [21,22]. Both, A-35 and CT-275 are low-swelling, strongly-acidic ion-exchange catalysts of industrial interest for etherification reactions that can be actually considered as two of the most important catalysts in use in this field. Table 2 shows the main properties of the two catalysts.

Before their use, catalyst samples were air-dried at room temperature for 48 h, introduced in an atmospheric oven, at 383 K, for 2.5 h and, afterwards, placed in a vacuum oven, at 373 K, for 12 h. Final water content in the resin beads after drying were 3–5 wt% (analyzed by Karl-Fischer titration in the laboratory). Additionally, air-dried catalyst beads were crushed and sieved in order to obtain particle diameters,  $d_p$ , ranging 0.25–0.40 mm, what ensures no internal mass transfer influence on the overall reaction rate as it was determined in previous works within this same group [7].

### 2.3. Analysis

Samples inline from the reaction medium were taken through a sampling valve (Valco A2Cl4WE.2, VICI AG International, Schenkon, Switzerland) that injected 0.2 μL of pressurized liquid into an Agilent gas-liquid chromatograph 6890 (Madrid, Spain) equipped with a HP capillary column (PONA Cross-linked Methyl Silicone Gum of 50 m × 0.2 mm × 0.5 μm, ON, Canada). A mass selective detector HP5973N was used to identify and quantify the reaction system components. The oven temperature was set at 308 K during 45 min. Helium (Abelló-Linde, Barcelona, Spain), with a minimum purity of 99.998%, was used as the carrier gas with a flow of 1.5 mL/min.

Up to 11 different chemical species, namely, ethanol, isobutene, ETBE, isobutane, *trans*- and *cis*-2-butene, TBA, DEE, ESBE, TMP-1 and TMP-2, were chromatographically identified in significant amounts depending on the experimental conditions. Besides, other minor byproducts, formed by either the hydration or the oligomerization of 2-butenes, were also detected in the experiments

**Fig. 1.** Reaction network in the ETBE synthesis using a C4 stream as isobutene source.**Table 1**

Relevant properties of involved compounds [47–49].

Category	Compound	Blending RVP [bar]	(RON + MON)/2	Boiling point [K]	Oxygen content [% wt.]	Solubility in water [g/100 g <sub>water</sub> ]
Main product	ETBE	0.34	110	345	15.7	1.2
Byproduct	TBA	0.70	101	356	21.6	Infinite
	TMP-1 and TMP-2	0.11*	~100	374.5	0	0
	DEE	0.60*	Low	308	21.6	Partially soluble in cold water
	ESBE	0.10*	Low	355	15.7	~1
Reactant	EtOH	1.25	113	351	34.7	Infinite
	IB	2.6*	Low	266.2	0	$3.88 \times 10^{-4}$

\* As blending Reid vapor Pressure (RVP) was not available, vapor pressure at 293 K is given instead.

carried out in favorable conditions (excess of olefins and highest temperature, 383 K). In particular, 2-butanol, from the hydration of 2-butene, was detected in less than 1.0% of GC area and dimers of 2-butene and/or codimers of 2-butene and isobutene were detected in less than 1.5% of GC area. These minor byproducts were never detected at other working conditions, and they were therefore not taken into further consideration in the calculations.

Fig. 2 is provided as an example chromatogram of an experiment carried out with A-35 as the catalyst, at 383 K,  $R^{\circ}\text{A/O} = 2.0$ , after 300 min of reaction.

#### 2.4. Apparatus and procedure

The experimental setup consisted in a 200 cm<sup>3</sup> stainless-steel jacketed batch reactor equipped with a six-blade magnetic stirrer (Autoclave Engineers, Pennsylvania, US). The reaction temperature range was 323–383 K, controlled within  $\pm 0.1$  K by a 1,2-propanediol–water thermostatic mixture. The system pressure

was kept at 2.0 MPa to ensure the liquid phase over the reaction system. A detailed description of the experimental setup is described elsewhere [23].

A set of 28 experiments (Table 3) was performed at four different temperatures (323, 343, 363 and 383 K) with 3 different initial alcohol/olefin molar ratio ( $R^{\circ}\text{A/O} = 0.5, 1.0$  or 2.0) in order to explore the effect of different conditions on the side reactions that take place during the ETBE synthesis reaction in industrial conditions.

For reproducibility evaluation purposes, experiments at 383 and 343 K and at  $R^{\circ}\text{A/O}$  equal to 0.5 and 2.0, as well as at intermediate conditions, were repeated at least three times. Experiments at the lowest temperature (323 K) were not repeated as they revealed scarce byproducts formation. The relative standard error for reactants conversion ranged 0.3–4.4% and the mean relative error of the mass balances was less than 3%.

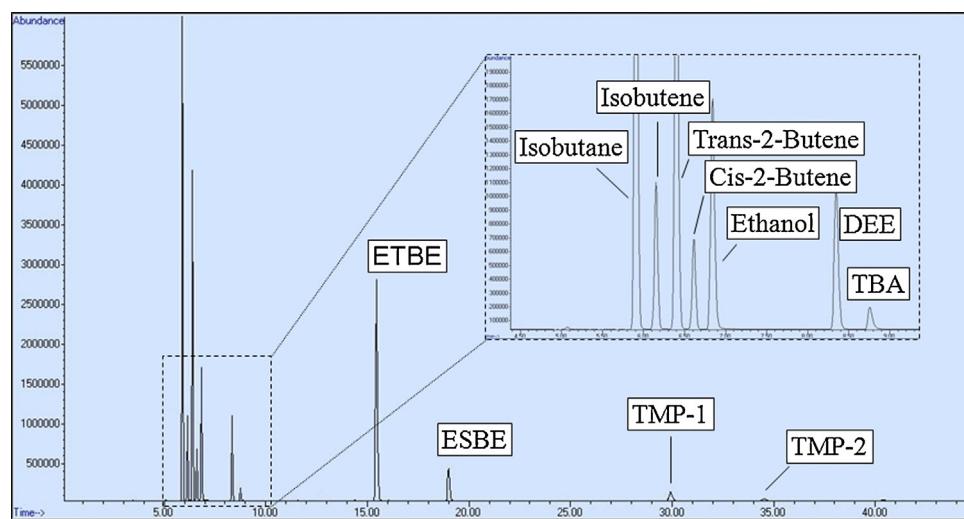
Depending on the assayed  $R^{\circ}\text{A/O}$ , a calculated amount of ethanol and  $10.08 \pm 0.02$  g of dried catalyst ( $w_{\text{cat}}$ ) were introduced in the reactor before the heating and the stirring were switched on.

**Table 2**

Catalysts properties.

Catalyst	Crosslinking <sup>a</sup>	Sulfonation	Acidity (meq H <sup>+</sup> /g)	$S_g$ <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	$V_g$ <sup>c</sup> (cm <sup>3</sup> g <sup>-1</sup> )	$d_{\text{pore}}$ <sup>d</sup> (nm)
A-35	High	Oversulfonated	5.32	34.0	0.210	23.6
CT-275	High	Oversulfonated	5.20	21.8	0.177	32.9

<sup>a</sup> High crosslinking degree: 14–25% DVB.<sup>b</sup> Specific surface area by BET method (N<sub>2</sub> for  $S_g \geq 1 \text{ m}^2 \text{ g}^{-1}$ ).<sup>c</sup> Pore volume estimated from adsorption/desorption of N<sub>2</sub> at 77 K.<sup>d</sup> Mean pore diameter.



**Fig. 2.** Example chromatogram at  $t_{\text{exp}} = 300$  min.  $T = 383$  K,  $R^{\circ}_{\text{A/O}} = 2.0$ , A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40$  mm, 500 rpm.

Catalyst amounts correspond to a 10 wt% of the whole reacting mixture. Previous experience revealed no effect of the catalyst load below 11.3 wt% should be expected [24]. Stirring speed was set at 500 rpm to ensure no external mass transfer influence on the overall reaction rate. In previous works carried out in the same experimental apparatus, at 363 K and in the range 400–600 rpm, it was determined no influence of that physical step for the ETBE synthesis reaction [25]. Additionally, the same conclusion was achieved by other studies at 500–800 rpm stirrer speed [26,27]. Temperature ranged from 323 to 383 K, because it was considered representative of the reported temperature profiles in industrial-scale reactors, including possible hot spots. The amount of C4 mixture, determined by  $R^{\circ}_{\text{A/O}}$ , was introduced into the reactor from a pressure burette once the desired temperature inside the vessel was reached. This instant was considered as the starting point for the reaction.

**Table 3**

List of experiments. Conversion values at  $t = 300$  min, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40$  mm, 500 rpm.

Catalyst	$T$ [K]	$R^{\circ}_{\text{A/O}}$	$X_{\text{IB}}$ [%]	$X_{\text{EtOH}}$ [%]
A-35	323	0.5	88	93
		1.0	90	90
		2.0	97	47
	343	0.5	94	88
			82	75
			79	87
			78	83
		1.0	82	82
		2.0	92	46
	363		91	44
			91	45
		0.5	83	74
			84	70
		1.0	76	73
383	383	0.5	75	72
			74	71
		2.0	86	64
		0.5	90	92
			89	92
			89	92
			90	94
		1.0	74	71
		2.0	73	53
			72	52
CT-275	363	0.5	72	53
		0.5	78	75
		1.0	85	87

## 2.5. Calculations

Results were expressed in terms of conversion ( $X_j$ ) of the main reactants, ethanol and isobutene, and of selectivity ( $S_j^k$ ) of products and byproducts obtained from the two main reactants, as follows:

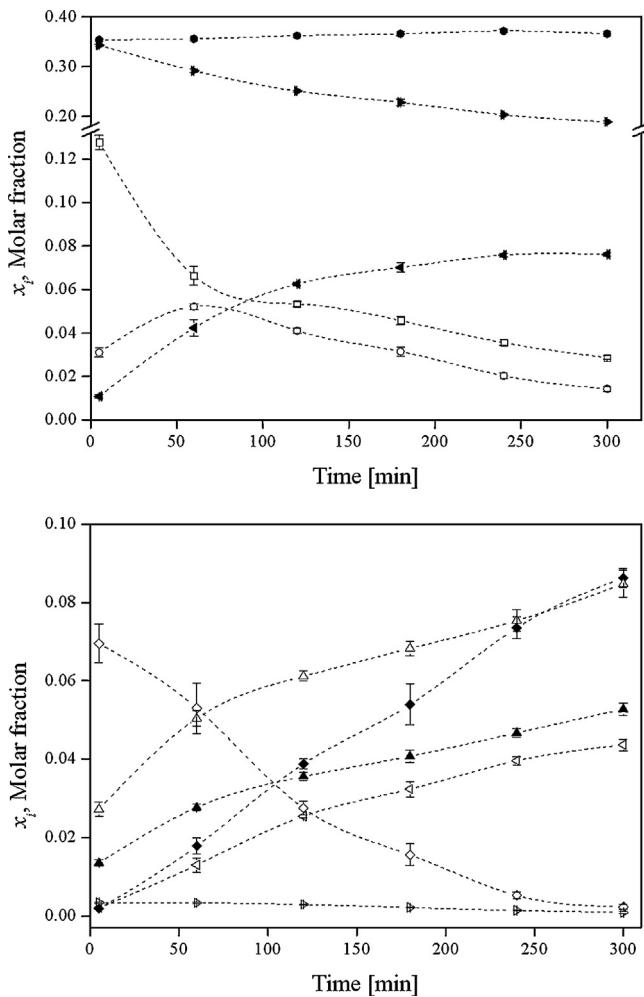
$$X_j = \frac{\text{mole of } j \text{ reacted}}{\text{mole of } j \text{ fed}} \quad (1)$$

$$S_j^k = \frac{\text{mole of } k \text{ produced}}{\text{mole of } j \text{ reacted}} \quad (2)$$

where  $k$  is the considered product or byproduct, and  $j$  is the reactant (isobutene or ethanol).

## 3. Results and discussion

**Fig. 3** plots molar fraction,  $x_i$ , evolution of the chemical species involved in a model experiment, carried out with A-35, at 383 K and  $R^{\circ}_{\text{A/O}} = 0.5$ . Under such conditions, side reactions were strongly favored. In **Fig. 3a**, molar fraction of the main reactants, ethanol and isobutene, as well as other C4 mixture components (isobutane and linear butenes) were represented. As it can be observed in **Fig. 3b**, where ETBE and byproducts molar fraction evolution is represented, byproducts appeared as soon as the reaction began. TMP-1 and TMP-2 formed quickly, and after 1 h their molar fraction increased in an almost linear trend until the end of the experiment. TBA formation was very low; it achieved a very smooth maximum concentration level within the first 60 min and then decreased to almost null values. It can be concluded that, initially, isobutene reacted swiftly with the available water in the reactive medium to approach equilibrium (see reaction (6) in **Fig. 1**) and, then, the equilibrium position shifted resulting in the observed decrease in TBA concentration, because of a higher consumption of isobutene in other simultaneous reactions (especially those of isobutene dimerization, reactions (2) and (3) in **Fig. 1**). Regarding DEE and ESBE formation, they seem to describe a linear pattern what suggests a continuous evolution towards equilibrium, both reactions being far from that point when the experiment was over. The ETBE concentration drop, reaching null values at the end of the experiment, can be explained by the multiple demands of ethanol and isobutene in the different side reactions in which they were also involved, that led to the ETBE decomposition (reaction(1) in **Fig. 1**). Note that ETBE concentration maximum level was reached within the first steps of

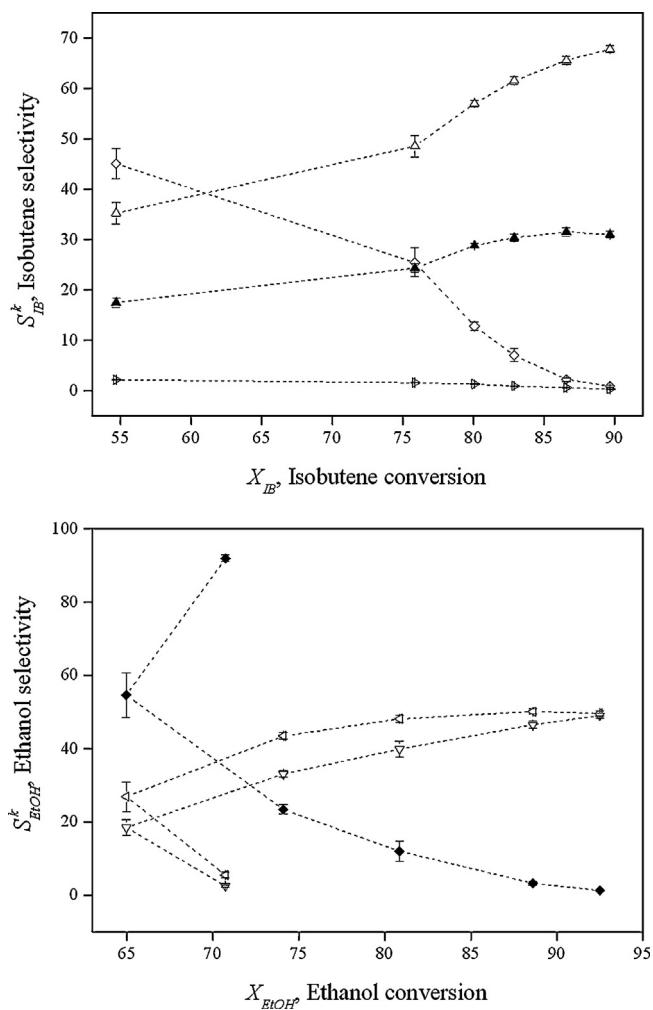


**Fig. 3.** Molar fraction evolution of major (a) and minor (b) chemical species.  $T = 383\text{ K}$ ,  $R^{\circ}_{A/O} = 0.5$ , A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40\text{ mm}$ , 500 rpm. Error bars are referred to the standard error of the mean values.  $x_{IB}$  (□),  $x_{EtOH}$  (○),  $x_{isobutane}$  (●),  $x_{trans-2-butene}$  (▲),  $x_{cis-2-butene}$  (◀),  $x_{ETBE}$  (◇),  $x_{TBA}$  (▷),  $x_{DEE}$  (◁),  $x_{ESBE}$  (◆),  $x_{TMP-1}$  (△),  $x_{TMP-2}$  (▲).

the experiment, what means that this reaction proceeded quickly, due to the high temperature and the catalyst loaded (10 wt% of the whole reacting mixture).

Fig. 4 plots selectivity vs. conversion of the two main reactants in this experiment. Note that, both in Fig. 4a and b, one can clearly distinguish the points corresponding to the first sample analyzed ( $X_{IB} \approx 55\%$  and  $X_{EtOH} \approx 71\%$ ) from the rest. This experimental fact can be explained if the side reactions taking place simultaneously are considered. It seems obvious, by observation of ETBE molar fraction evolution in Fig. 3b, that probably even before the first sample was analyzed ETBE synthesis reaction had progressed greatly. Then, ETBE decomposition to give isobutene and ethanol took place during the experiment. This is a quite acceptable hypothesis once considered the high temperature and amount of catalyst in the reacting media. In the subsequent analyses during the experiment, reactants conversion increase is due to its progressively higher consumption in side reactions.

It is worth mentioning that, as this model experiment revealed, after enough time of reaction, ETBE concentration could reach null values. As it was the aim of this paper to discuss on side reactions taking place simultaneously with ETBE production, reference time up to 300 minutes was set as the end of the experiments.



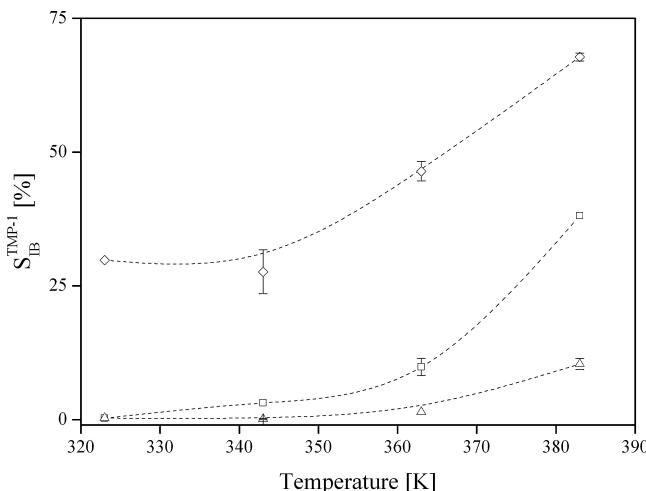
**Fig. 4.** Isobutene (a) and ethanol (b) selectivity towards products vs. total conversion.  $T = 383\text{ K}$ ,  $R^{\circ}_{A/O} = 0.5$ , A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40\text{ mm}$ , 500 rpm. Error bars are referred to the standard error of the mean values.  $S_{IB}^{ETBE}$  (◇),  $S_{IB}^{TBA}$  (▷),  $S_{IB}^{TMP-1}$  (△),  $S_{IB}^{TMP-2}$  (▲),  $S_{EtOH}^{ETBE}$  (◆),  $S_{EtOH}^{TBA}$  (▽),  $S_{EtOH}^{DEE}$  (◁),  $S_{EtOH}^{ESBE}$  (▽).

### 3.1. TMP-1 and TMP-2 formation

Isobutene dimerization (reactions (2) and (3) in Fig. 1) gives TMP-1 and TMP-2. Further oligomerization could originate trimers and tetramers. Additionally, when linear butenes are present, as it is the case of feedstocks from FCC or SC units, linear butenes could react with isobutene to form codimers giving a primary carbocation which eventually rearranged, forming other trimethylpentenes. Codimerization reactions, though, are known to be slower than isobutene dimerization, according to previous studies on the dimerization/etherification of FCC and SC C4 hydrocarbons in the presence of methanol [28]. In the present study codimers, trimers and heavier oligomers were not taken into consideration in the calculations as they were only obtained at the highest temperature in less than a 1.5% of GC area.

It has to be noted that dimers formation was the most relevant side reaction in the production of ETBE. This is in good agreement with the reported data in literature for similar systems, for instance in MTBE, TAME, TAEE, and IPTBE productions [8,12,29].

Isobutene selectivity towards TMP-1 and TMP-2 was enhanced by high temperatures and low  $R^{\circ}_{A/O}$ . This is coherent because high temperatures and isobutene concentration have been reported to be enhancers for the isobutene dimerization reaction [30,31]. As example, Fig. 5 plots the selectivity to TMP-1 against temperature at



**Fig. 5.** Variation with temperature of the isobutene selectivity towards TMP-1 at  $t_{exp} = 300$  min. A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40$  mm, 500 rpm. Error bars are referred to the standard error of the mean values.  $R_{A/O} = 0.5$  ( $\diamond$ ),  $R_{A/O} = 1.0$  ( $\square$ ),  $R_{A/O} = 2.0$  ( $\triangle$ ).

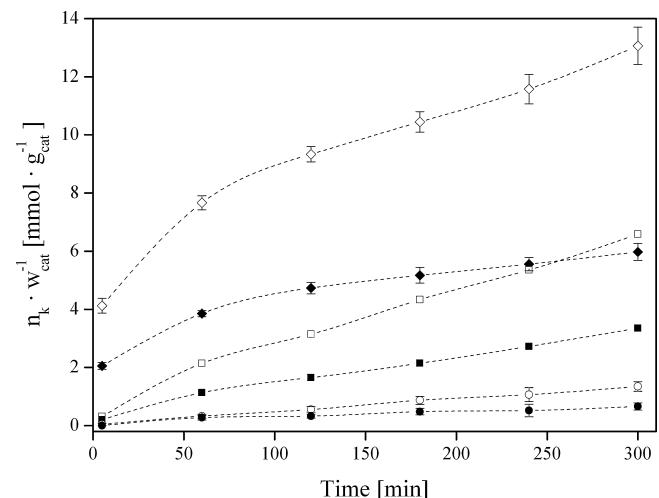
the end of the experiments ( $t = 300$  min). In that figure, a noticeable difference in isobutene selectivity to TMP-1 is observed between experiments carried out at the lowest  $R_{A/O}$  of 0.5 and that at 2.0. In the former, values of selectivity towards TMP-1 range from less than 30% at low temperatures (323 and 343 K) to more than 60% at 383 K. In the latter, though, almost null values of selectivity are observed except for the experiment carried out at the highest temperature. Experimental series with an  $R_{A/O}$  of 1.0 constitutes an intermediate situation between the others. Analogous trends were observed for the selectivity of isobutene to TMP-2, reaching a value of up to 40% at 383 K and  $R_{A/O} = 0.5$ .

The enhancement of dimers formation at low molar ratios suggests that isobutene, in a relatively high concentration, is readily adsorbed on non-dissociated sulfonic groups of the catalyst and dimerization reaction follows. This is actually a heterogeneous catalytic step, which is faster than an ionic one (specific acid catalysis), with dissociated protons due to the presence of ethanol in the surroundings of the sulfonic groups (general acid catalysis) [32–36].

With respect to the isomerization reaction between TMP-1 and TMP-2 (reaction (4) in Fig. 1), the TMP-1 to TMP-2 molar ratio was monitored throughout each experiment. In the initial stage of the reaction, this ratio quickly achieved values that ranged from 1.5 to 2.6 and remained stable onwards. Similar ratios were also reported in analogous systems involving multiple simultaneous reactions [12]. According to literature, TMP-1 is thermodynamically more favored than TMP-2, resulting in a molar ratio of about 4:1 at equilibrium in the same temperature range (323–383 K) as well as at lower temperatures [37,38] what suggests that, in the present work, isomerization had not yet reach the chemical equilibrium at the end of the experiments (300 min).

It is worth mentioning that isomerization of diisobutenes constitute an exception to the general rule in alkene isomers stability. The general rule states that the more stable alkene is the one in which the double bond is located in intermediate positions of the carbon chain, in order to produce the highest possible substitution of the double bond. However, in isobutene dimers, the more substituted isomer, the trisubstituted TMP-2, is less stable than the disubstituted TMP-1. This fact has been already explained in literature by the internal repulsion between branches in the TMP-2 molecule that arises from the *tert*-butyl group located in the *cis* position to the methyl group [38].

With regards of dimerization reaction rate at high temperatures, it can be observed in Fig. 6, where number of moles,  $n_k$ ,

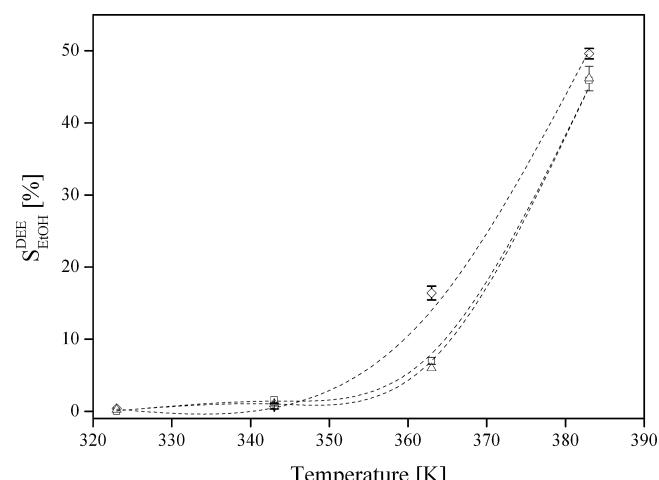


**Fig. 6.** TMP-1 and TMP-2 formation vs. time at different  $R_{A/O}$ .  $n_k$  is referred to number of moles.  $T = 383$  K, A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40$  mm, 500 rpm. Error bars are referred to the standard error of the mean values. Open symbols: TMP-1 ( $R_{A/O} = 0.5$  ( $\diamond$ ),  $R_{A/O} = 1.0$  ( $\square$ ),  $R_{A/O} = 2.0$  ( $\circ$ )). Solid symbols: TMP-2 ( $R_{A/O} = 0.5$  ( $\blacklozenge$ ),  $R_{A/O} = 1.0$  ( $\blacksquare$ ),  $R_{A/O} = 2.0$  ( $\bullet$ )).

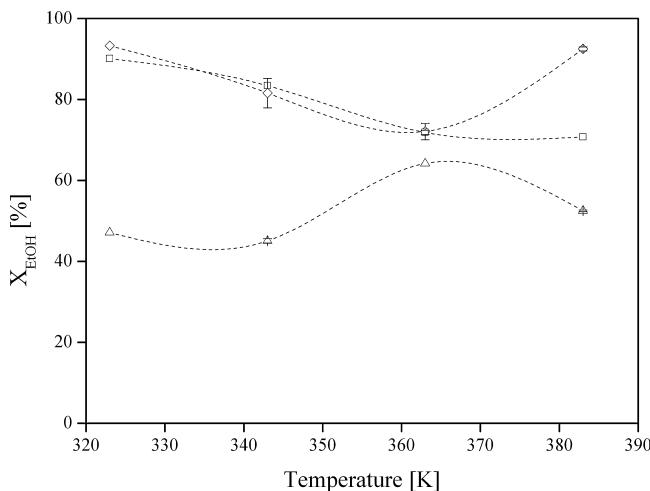
evolution is presented- that TMP-1 was formed swifter than TMP-2. The shape of both dimers production against time suggests irreversible reactions. Reaction rate of the isobutene dimerization decreased as  $R_{A/O}$  increased, achieving its maximum values at 383 K and at  $R_{A/O} = 0.5$ .

### 3.2. DEE formation

Regarding ethanol dehydration (reaction (5) in Fig. 1), Fig. 7 reveals that high temperatures greatly enhanced the selectivity of ethanol towards diethyl ether, reaching levels of almost 50%. At low temperatures (323 and 343 K), no difference in selectivity towards DEE was observed at different  $R_{A/O}$ . At high temperatures (363 and 383 K), low alcohol concentration ( $R_{A/O} = 0.5$ ) led to higher selectivity to DEE whereas no difference in selectivity was observed between experiments carried out under stoichiometric conditions ( $R_{A/O} = 1.0$ ) or when an excess of ethanol was fed to the reactor ( $R_{A/O} = 2.0$ ). This fact might seem counterintuitive, because an excess of ethanol could be expected to constitute an enhancer



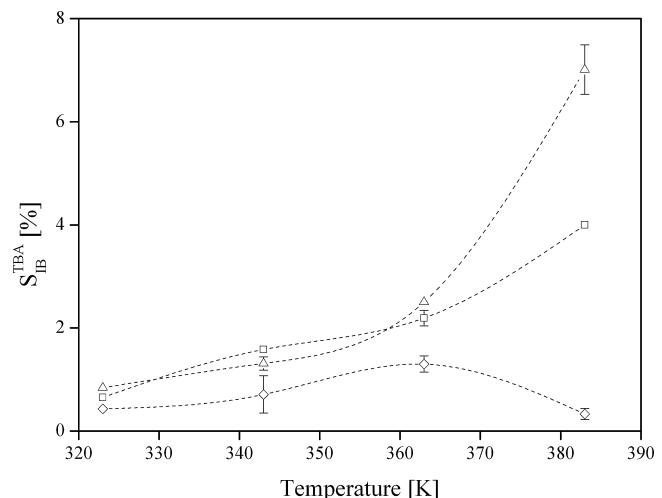
**Fig. 7.** Variation with temperature of the ethanol selectivity towards DEE at  $t_{exp} = 300$  min. A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40$  mm, 500 rpm. Error bars are referred to the standard error of the mean values.  $R_{A/O} = 0.5$  ( $\diamond$ ),  $R_{A/O} = 1.0$  ( $\square$ ),  $R_{A/O} = 2.0$  ( $\triangle$ ).



**Fig. 8.** Ethanol conversion at  $t_{\text{exp}} = 300$  min against temperature at different  $R^{\circ}_{\text{A}/\text{O}}$ . A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40$  mm, 500 rpm. Error bars are referred to the standard error of the mean values.  $R^{\circ}_{\text{A}/\text{O}} = 0.5$  ( $\diamond$ ),  $R^{\circ}_{\text{A}/\text{O}} = 1.0$  ( $\square$ ),  $R^{\circ}_{\text{A}/\text{O}} = 2.0$  ( $\triangle$ ).

of the DEE formation. But as Fig. 8 illustrates, when an excess of alcohol was fed, ethanol conversion was lower than operating at other  $R^{\circ}_{\text{A}/\text{O}}$ .

In terms of DEE production at the end of every experiment, temperature plays a much more important role than  $R^{\circ}_{\text{A}/\text{O}}$  as a DEE promoter. To illustrate it, consider the experiments at 363 K and lower temperatures depicted in Fig. 9, none of which showed significant differences in terms of DEE production with respect to  $R^{\circ}_{\text{A}/\text{O}}$ . Nevertheless, at 383 K, an increase in DEE formation is observed as increasing  $R^{\circ}_{\text{A}/\text{O}}$ . The increase of the reaction medium polarity due to the excess of ethanol affects the catalytic behavior of the catalyst in several ways [39,40] and can account for the increase in the DEE production. Polar molecules, as ethanol, can break the hydrogen network that binds the sulfonic groups and, as a consequence, more inner active centers become accessible to the reactants. When ethanol dehydration takes place, the water released as the reaction proceeds would even enhance this effect. On the contrary, a polar medium solvates the acidic protons of those active centers which present a lower acid strength than the protons bound to the sulfonic groups, thus reducing the reaction rate on each catalytic center [41]. Taking into account these opposed



**Fig. 10.** Variation with temperature of the isobutene selectivity towards TBA at  $t_{\text{exp}} = 300$  min. A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40$  mm, 500 rpm. Error bars are referred to the standard error of the mean values.  $R^{\circ}_{\text{A}/\text{O}} = 0.5$  ( $\diamond$ ),  $R^{\circ}_{\text{A}/\text{O}} = 1.0$  ( $\square$ ),  $R^{\circ}_{\text{A}/\text{O}} = 2.0$  ( $\triangle$ ).

factors, the enhancing effect might be more important than the inhibiting one in the ethanol dehydration reaction at 383 K.

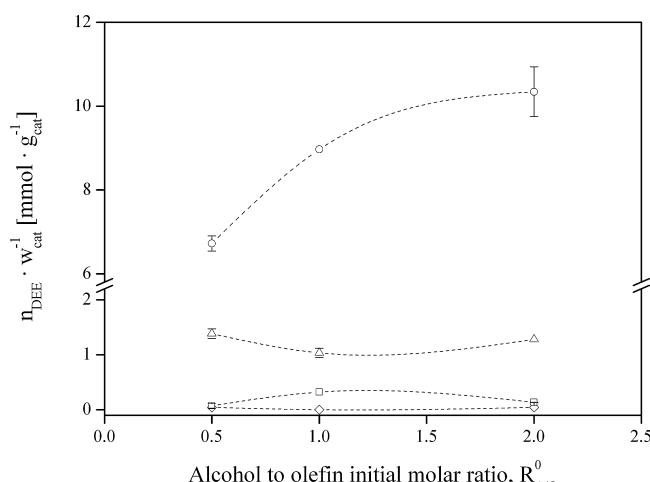
### 3.3. TBA formation

Reaction between water and isobutene led to TBA formation (reaction (6) in Fig. 1). For the present work, water could stem from different sources: the amount of water contained within the ethanol (200 ppm), the remaining moisture hold in the catalyst (3–5 wt%), and the chemically-produced molecules of water proceeding from the dehydration of ethanol.

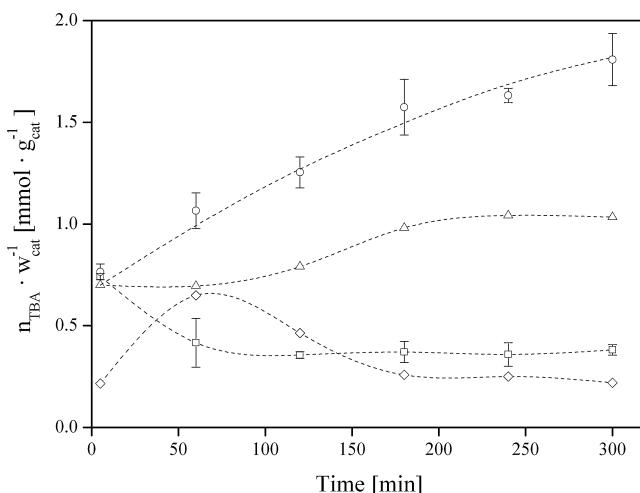
Fig. 10 reveals that, at  $R^{\circ}_{\text{A}/\text{O}}$  other than 0.5, isobutene selectivity towards TBA at the end of the experiments increased with temperature. At low temperatures (363 K and lower), no significant differences in the selectivity to TBA can be distinguished between experiments at  $R^{\circ}_{\text{A}/\text{O}} = 1.0$  and 2.0, whereas for the experiments at  $R^{\circ}_{\text{A}/\text{O}} = 0.5$  the selectivity was slightly lower. At the highest temperature (383 K), the higher the molar ratio, the higher the selectivity towards TBA was. These facts suggest that more polar media enhanced selectivity to TBA.

Fig. 11 plots the evolution of the TBA production at  $R^{\circ}_{\text{A}/\text{O}} = 2.0$ , that is when the highest amounts of TBA were detected, and at different temperatures. While at lowest temperatures, namely 323 K and 343 K, the TBA content decreased after a maximum value, at highest temperatures (363 K and 383 K) no maximum value was yet achieved by the time the experiment ended. The former behavior can be explained by assuming that, as TBA is known to reach the equilibrium swiftly [42], water present in the medium reacted readily with isobutene at the initial steps of the experiment and, afterwards, the reverse reaction proceeded since isobutene was consumed by other competitive side reactions, mainly dimerization. The later behavior can be related to the major extent of the dehydration reaction of ethanol at high temperatures, what produced water that subsequently reacted with isobutene to form more TBA.

As reported in literature, water shows a strong inhibitor effect on the ETBE production, even at low contents [42]. This inhibitor effect would disappear progressively as water was consumed to yield TBA, which was produced quickly. However, the simultaneous dehydration of ethanol enhanced by high temperatures, could lead to higher water production that would account for a sustained consumption of isobutene. This feasible explanation would imply



**Fig. 9.** DEE formation at  $t_{\text{exp}} = 300$  min against  $R^{\circ}_{\text{A}/\text{O}}$  at different temperatures. A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40$  mm, 500 rpm. Error bars are referred to the standard error of the mean values.  $T = 323$  K ( $\diamond$ ),  $T = 343$  K ( $\square$ ),  $T = 363$  K ( $\triangle$ ),  $T = 383$  K ( $\circ$ ).



**Fig. 11.** TBA formation in time at different temperatures.  $R^{\circ}_{A/O} = 2.0$ , A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40\text{ mm}$ , 500 rpm. Error bars are referred to the standard error of the mean values.  $T = 323\text{ K}$  ( $\diamond$ ),  $T = 343\text{ K}$  ( $\square$ ),  $T = 363\text{ K}$  ( $\triangle$ ),  $T = 383\text{ K}$  ( $\circ$ ).

that, depending on the experimental conditions, some water can be redelivered to the reactive media, what arises as a potentially modifier factor of the catalytic conditions throughout an experiment. The high polarity of water leads to a combined effect of, potentially, reducing the activity of sulfonic groups, and simultaneously swelling the resin, what allows reactants to access to active centers that were initially unreachable [43].

#### 3.4. ESBE formation

Etherification of linear butenes with ethanol occurs when linear butenes are present in the C4 cut used as isobutene source, leading to ESBE formation (reactions (7) in Fig. 1). In the present work, *trans*-2-butene was included in the synthetic C4 mixture in order to emulate the presence of these linear butenes in typical sources of isobutene, such as FCC or SC C4 cuts. It is worth noting that isomerization of *trans*-2-butene present in the initial mixture to *cis*-2-butene was detected. Amounts of *cis*-2-butene reached levels up to 7% of GC area that were taken into account in the calculations. According to literature, *trans*-2-butene is thermodynamically more stable than *cis*-2-butene [44,45].

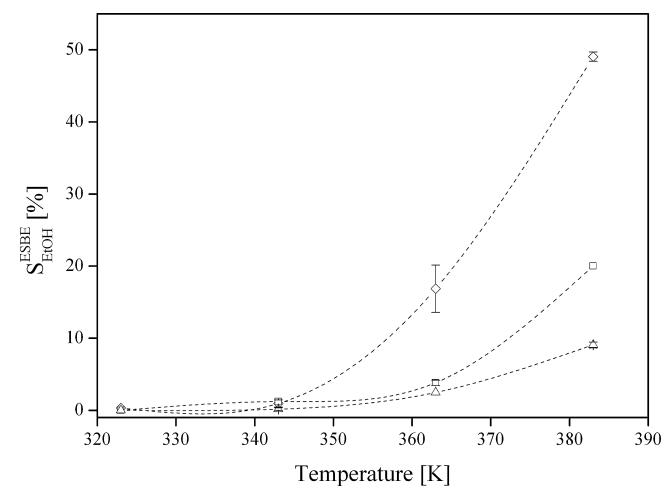
As shown in Fig. 12, selectivity to ESBE was strongly favored by high temperatures and low  $R^{\circ}_{A/O}$ . At low temperatures ( $T = 343\text{ K}$  and lower) no significant amounts of ESBE were detected, but at  $363\text{ K}$  and higher, the selectivity to TBA values achieved by experiments at  $R^{\circ}_{A/O} = 0.5$  were far higher than those achieved under stoichiometric or in excess of alcohol conditions ( $R^{\circ}_{A/O} = 1.0$  or 2.0, respectively).

Fig. 13 reveals that ESBE production evolved linearly with time under the most favorable condition ( $R^{\circ}_{A/O} = 0.5$ ), what suggests that the reaction was far from the equilibrium within the assayed temperature range.

Similar to the one described for the dimers formation at low  $R^{\circ}_{A/O}$ , a heterogeneous catalytic step can be assumed again. Linear butenes would be able to take the proton directly from the sulfonic groups, because they would be less dissociated due to the lack of ethanol [32–36]. This assumption was already adopted in a similar study on the side reactions taking place along with the MTBE synthesis [29].

#### 3.5. Catalysts comparison

In order to compare possible differences in terms of global behavior of the reaction system due to the catalyst, three

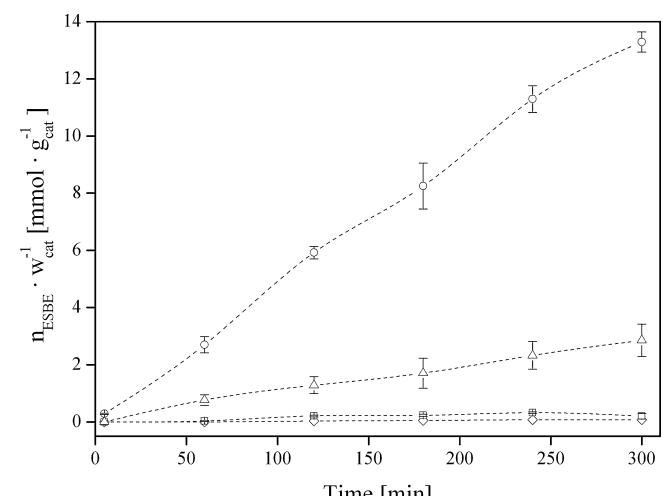


**Fig. 12.** Variation with temperature of the ethanol selectivity towards ESBE at  $t_{exp} = 300$  min. A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40\text{ mm}$ , 500 rpm. Error bars are referred to the standard error of the mean values.  $R^{\circ}_{A/O} = 0.5$  ( $\diamond$ ),  $R^{\circ}_{A/O} = 1.0$  ( $\square$ ),  $R^{\circ}_{A/O} = 2.0$  ( $\triangle$ ).

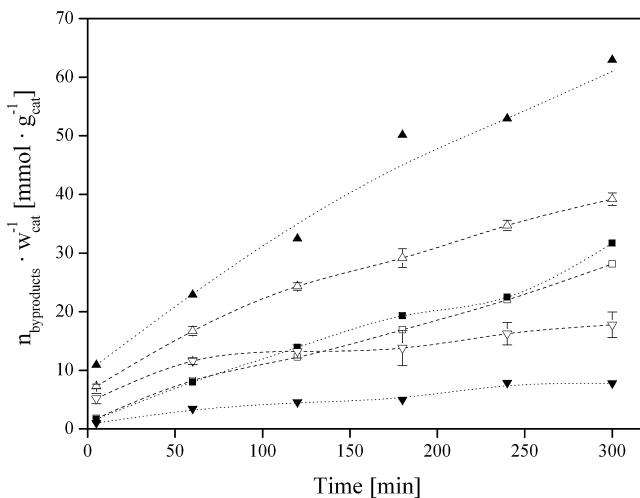
representative experiments carried out with A-35 were repeated with CT-275. These experiments were performed at high temperatures (363 and 383 K), in order to favor side reactions, and in excess of olefins and under stoichiometric conditions ( $R^{\circ}_{A/O} = 0.5$  and 1.0, respectively), in order not to mask a possible influence of  $R^{\circ}_{A/O}$  by choosing only one initial feed composition. In general, significant differences between both catalysts were observed in terms of ETBE production, total byproducts formation and product distribution, depending on the assayed conditions.

Fig. 14 plots the evolution of the total byproducts formation in those experiments. Under stoichiometric conditions ( $R^{\circ}_{A/O} = 1.0$ ) no significant differences between both catalysts were detected. At 363 K and  $R^{\circ}_{A/O} = 0.5$ , A-35 led to more byproducts formation than CT-275. At the same  $R^{\circ}_{A/O}$  and 383 K, byproducts formation increased for both catalysts, as expected, but with a larger production for CT-275. A similar fact has been reported in the oligomerization reaction of 1-hexene for the same resins [46].

According to literature [28], A-35 is expected to be more active than CT-275 due to its higher acid capacity, regardless the difference might be scarce. Accordingly, the higher the activity of a catalyst, the higher the total formation of products and/or



**Fig. 13.** ESBE formation vs. time at different temperatures.  $R^{\circ}_{A/O} = 0.5$ , A-35, catalyst load = 10 wt%,  $d_p = 0.25\text{--}0.40\text{ mm}$ , 500 rpm. Error bars are referred to the standard error of the mean values.  $T = 323\text{ K}$  ( $\diamond$ ),  $T = 343\text{ K}$  ( $\square$ ),  $T = 363\text{ K}$  ( $\triangle$ ),  $T = 383\text{ K}$  ( $\circ$ ).



**Fig. 14.** Total byproducts formation vs. time with two different catalysts. Catalyst load = 10 wt%,  $d_p$  = 0.25–0.40 mm, 500 rpm. Error bars are referred to the standard error of the mean values. Open symbols: A-35 ( $R^o_{A/O} = 0.5$ ,  $T = 363$  K ( $\nabla$ );  $R^o_{A/O} = 0.5$ ,  $T = 383$  K ( $\triangle$ );  $R^o_{A/O} = 1.0$ ,  $T = 383$  K ( $\square$ )). Solid symbols: CT-275 ( $R^o_{A/O} = 0.5$ ,  $T = 363$  K ( $\blacktriangledown$ );  $R^o_{A/O} = 0.5$ ,  $T = 383$  K ( $\blacktriangle$ );  $R^o_{A/O} = 1.0$ ,  $T = 383$  K ( $\blacksquare$ )).

byproducts should be expected. Nonetheless, in this particular case, this premise was not accomplished in the experiments at the highest temperature.

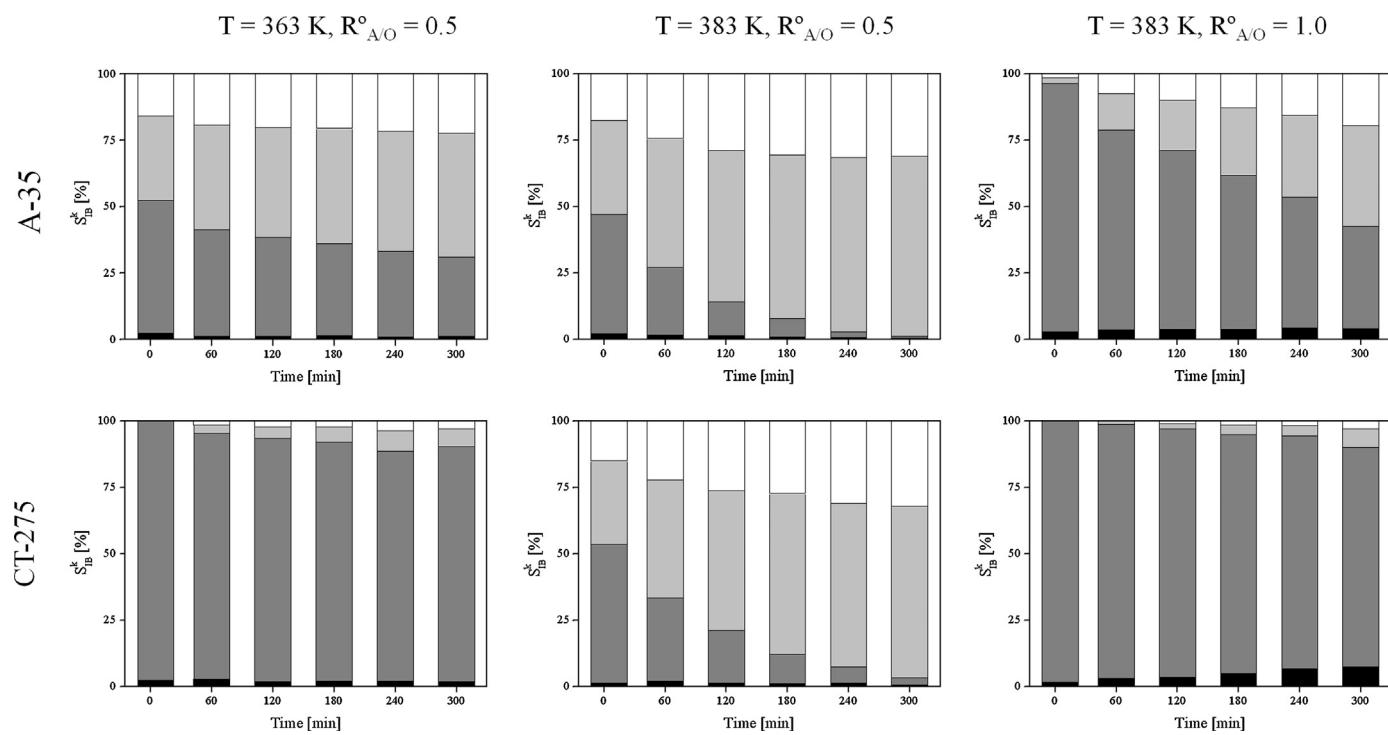
After analyzing each byproduct individually, it was determined that the shift of the most active catalyst in the byproducts formation from A-35 to CT-275 as temperature was raised from 363 to 383 K was mainly due to an increase in the isobutene dimers production as well as, though in minor extension, in the ESBE production. This shift could be explained by morphological differences between both catalysts. A-35 would experience internal diffusion problems due to its small pore diameter that would become apparent at higher temperature that is when dimerization is more favored. A

sufficiently high amount of dimers would block partially the pores of A-35 and, therefore, hinder the species diffusion, especially for larger molecules as TMP-1, TMP-2 and ESBE. Such phenomenon would not occur, or it could occur in a much lower extension, with CT-275 because it presents a larger pore size (Table 2).

With respect to isobutene selectivity towards products (Fig. 15), strong differences were detected between both resins at 363 K and  $R^o_{A/O} = 0.5$ , where A-35 clearly favored isobutene dimerization compared to CT-275. This difference was reduced by increasing the temperature to 383 K, at the same  $R^o_{A/O} = 0.5$ , where both catalysts presented similar isobutene selectivity towards each byproduct. Consequently, a higher temperature reduces the effects of the structural catalyst properties on selectivity. Finally, at 383 K and  $R^o_{A/O} = 1.0$ , isobutene selectivity towards dimers was more enhanced by A-35 than by CT-275. Selectivity towards TBA was higher for CT-275 than for A-35, what can be explained by the lesser consumption of isobutene due to the competitive irreversible reaction of dimerization. Evolution of ethanol selectivity towards products showed similar trends to those described here.

In order to give an explanation to the results plotted in Fig. 15, it has to be considered that at high temperatures, namely 363 and 383 K, the fastest reversible reactions, ETBE and TBA, could reach positions close to chemical equilibrium conditions rapidly, irrespectively of the used catalyst. Then, as slower side reactions proceeded, the reversible reactions could move to the left side, leaving free isobutene that can dimerize. Therefore, Fig. 15 shows an increasing selectivity towards TMP-1 and TMP-2 through the experiments.

From the catalysts properties standpoint, it is necessary to bear in mind that the most active catalyst for the main reaction is also the most active one for side reactions. So, in general, A-35 was progressively more selective than CT-275 towards larger molecules, as TMP-1 and TMP-2. Additional explanation for such phenomenon could be the higher specific surface area and pore volume of A-35 that could lead to a more suitable spatial distribution of acid centers to form isobutene dimers. To support this hypothesis,



**Fig. 15.** Product distribution evolution in terms of isobutene selectivity to TBA (■), ETBE (▨), TMP-1 (□), TMP-2 (□) with A-35 and CT-275. Catalyst load = 10 wt%,  $d_p$  = 0.25–0.40 mm, 500 rpm.

literature data showed that, operating under the same temperature range (343–383 K), in the isobutene dimerization reaction in the presence of *tert*-butyl alcohol, the more selective ion-exchange catalyst assayed for the isobutene dimerization was the one with the highest specific surface area [47]. However, more than two catalysts should be assayed in order to establish a proper correlation between the chemical reaction and the catalyst properties.

With regards to the experiments at 383 K and  $R^{\circ}\text{A}/\text{O} = 0.5$ , also in Fig. 15, the almost identical product distribution evolution experienced by both catalysts evidences that given such favoring conditions –in terms of dimerization reaction– morphological differences between the catalysts were not significant enough so as to lead to different behavior. Perhaps, in excess of olefin, the resins structures could be partially collapsed and the advantages of A-35 towards dimerization were not showed because the accessibility to its acid centers decreased more than for CT-275.

Considering the three experiments, it has to be pointed out that CT-275 led to higher productions of ETBE than A-35, within the experimental conditions assayed. At 383 K, though, CT-275 also produced more byproducts than A-35. Notwithstanding, to quantify the effects of temperature and initial molar ratio on the two catalysts more experimental work is needed.

### 3.6. Equilibrium data

In the previous discussion it has been affirmed that some equilibrium reactions could be relatively fast enough to assume that they were in a pseudo equilibrium state in such a way that the equilibrium point shifted accordingly to the changes in composition of the species involved in other reactions. In order to check if this hypothesis was realistic, activities relation corresponding to each equilibrium reaction were calculated for each experimental point. The following relation of activities for the ETBE synthesis is shown as example.

$$K = \left( \frac{a_{\text{ETBE}}}{a_{\text{IB}} \cdot a_{\text{EtOH}}} \right) = \left( \frac{x_{\text{ETBE}}}{x_{\text{IB}} \cdot x_{\text{EtOH}}} \right) \cdot \left( \frac{\gamma_{\text{ETBE}}}{\gamma_{\text{IB}} \cdot \gamma_{\text{EtOH}}} \right) = K_x \cdot K_y \quad (3)$$

The individual activity coefficients of all the species involved in the equilibrium reactions considered were calculated by the modified UNIFAC (Dortmund) method [48].

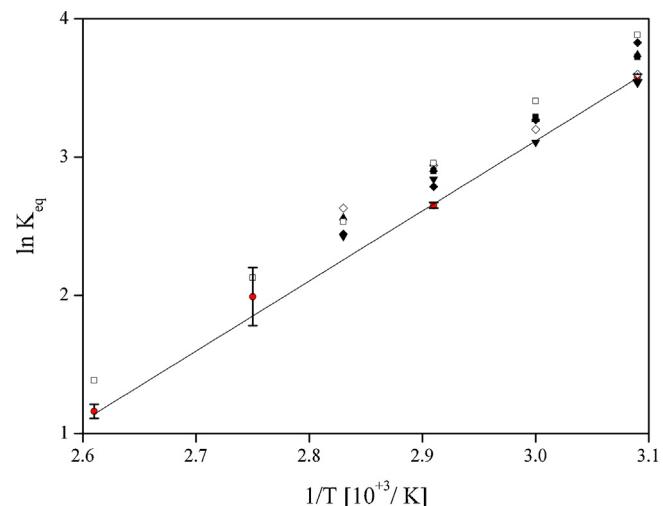
Equilibrium reaction syntheses of ETBE and TBA, as well as the isomerization reaction of isobutene dimers, can be considered to be in pseudo equilibrium situations in a number of experiments, as it can be inferred by the evolution of the implicated species relation of activities.

Experimental values of the ETBE pseudo equilibrium constant fit well, within the margin of experimental error, with previously reported expressions for the temperature dependence of the chemical equilibrium constant such as Eqs. (4) and (5) [42,49,50]:

$$\begin{aligned} \ln(K_{\text{ETBE}}) &= 1140.876 - 14583.2 T^{-1} - 232.873 \ln(T) \\ &\quad + 1.086489 T - 1.11385 \times 10^{-3} T^2 + 5.53858 \\ &\quad \times 10^{-7} T^3 \end{aligned} \quad (4)$$

$$K_{\text{ETBE}} = 7.4 \times 10^{-5} \exp \left[ \frac{4226.21}{T} \right] \quad (5)$$

Experimental values of  $K$  (Fig. 16), as well as estimates of standard enthalpy, entropy and free energy change of the synthesis of ETBE were calculated for comparative purposes. It is worth noting that, except for the experiments at 383 K and  $R^{\circ}\text{A}/\text{O} = 0.5$  (that is, in the conditions at which isobutene dimerization was more favored), the calculated values showed a rather good agreement



**Fig. 16.** ETBE equilibrium constant values from literature data and from the present work. A-35, catalyst load = 10% wt.,  $d_p = 0.25\text{--}0.40\text{ mm}$ , 500 rpm. Error bars are referred to the standard error of the mean values. The line corresponds to the relation between  $\ln K$  and  $1/T$  achieved experimentally in the present work. Françoise and Thyrrion [6] ( $\blacklozenge$ ), Vila et al. [50] ( $\blacktriangle$ ), Cunill et al. [42] ( $\blacksquare$ ), Izquierdo et al. [49] ( $\diamond$ ), Jensen and Datta [51] ( $\square$ ), Gómez et al. [53] ( $\blacktriangledown$ ), Present work ( $\bullet$ ).

with published literature data on ETBE equilibrium [6,42,49–53]. This suggests that, despite side reactions taking place simultaneously, ETBE synthesis reaction was fast enough to reach a pseudo equilibrium state. The dependence of  $K$  was estimated by integration of the van't Hoff equation, and the reaction enthalpy change was considered a function of temperature (Kirchoff equation).

At 298.15 K we obtain the following values:

$$\Delta_r H_m^\circ = -38.5 \pm 6.0 [\text{kJ mol}^{-1}]$$

$$\Delta_r S_m^\circ = -89.3 \pm 17.3 [\text{J mol}^{-1} \text{K}^{-1}]$$

$$\Delta_r G_m^\circ = -11.8 \pm 6.1 [\text{kJ mol}^{-1}]$$

Deviations of the calculated equilibrium constant due to pressure effects can be considered as negligible, as it was determined by calculation of the Poynting factor [54]. In the whole experimental conditions range, the Poynting factor was always close to the unity (always higher than 0.9998).

With regards of TBA formation, experimental pseudo equilibrium constant values were far lower than the ones reported as chemical equilibrium constants [55]. It has to be highlighted that actual amounts of water in the reacting system were estimated by means of the water initially fed to the reactor (the sources of which were the remaining moisture of catalysts and the water content in ethanol) and the extension of the reactions in which water was involved (namely, dehydration of ethanol and isobutene hydration). So, in relative terms, the indetermination associated to the water quantification was severe. Therefore, the commented deviation in the calculated pseudo equilibrium constants can be explained by its high sensitivity towards the water quantification indetermination because, accordingly with the low quantity of water in the reacting system throughout the experiments, very high activity coefficients of water were achieved that, subsequently account for this low values of TBA pseudo equilibrium constant.

As for DEE and ESBE formations, their mole production evolution in time at all conditions (Fig. 3b and 13, for instance) revealed linear patterns, what suggests far from equilibrium situations for both reactions through all the experiments.

#### 4. Conclusions

Dimerization of isobutene, giving TMP-1 and TMP-2, was the most relevant side reaction. Low molar ratios and high temperatures enhance this reaction. High temperatures enhanced DEE formation. Excess of ethanol produced scarcely more DEE than low molar ratios and that was related to slow kinetics of the ethanol dehydration reaction. At the conditions assayed, TBA was produced in very low quantities. Although at low temperatures, selectivity towards TBA at the end of the experiment was almost zero, at high temperatures, the higher the molar ratio, the higher the selectivity towards TBA was. Possible explanation implies a combined effect of the dehydration of ethanol, what produces water, and the readiness with which isobutene reacts with this water. There was a strong effect of the loaded water over this side reaction. ESBE formation was detected only at high temperatures but the selectivity towards it achieved values up to 50%. Low feed molar ratios also enhanced this side reaction.

Finally, it can be stated that high temperatures strongly enhance the formation of all the byproducts studied – kinetics of the side reactions are strongly affected by temperature – whereas initial molar ratios have a strong influence on the nature of side reactions that are favored.

Concerning the catalysts comparison, CT-275 led to higher productions of ETBE than A-35, within the experimental conditions assayed. However, at 383 K, CT-275 also produced more byproducts than A-35.

Minimum ETBE production was detected in experiments at high temperatures and low molar ratios. Selectivity of the two reactants towards ETBE was slightly higher at  $R^{\circ}\text{A/O} = 2.0$  than at  $R^{\circ}\text{A/O} = 1.0$ . However, at  $R^{\circ}\text{A/O} = 2.0$ , part of the ethanol did not react. Then, in order to minimize side reactions along with the ETBE reaction synthesis, it is advisable to control the cooling system -so hot-spots should be minimized-, to work with molar ratios slightly higher than the stoichiometric one and to keep the feedstock as free of water as possible.

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