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Conversion, selectivity and kinetics of the liquid-phase dimerisation of isoamylenes in the presence of C_1 to C_5 alcohols catalysed by a macroporous ion-exchange resin

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Abstract

This study evaluated the selectivity, conversion, yield, and kinetics of the liquid-phase dimerisation of 2-methyl-1-butene and 2-methyl-2-butene mixture catalysed by the acid resin Amberlyst 35 in a batch-stirred tank reactor in the temperature range 333–373 K in the presence of 10% mol alcohol content (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, *t*-butanol, and 1-pentanol). Dimers formation was favoured by increasing temperature and molecular weight of the alcohol, except for methanol. Secondary alcohols slowed dimers formation more than primary alcohols did, and for *t*-butanol, neither ether nor dimers formation was detected. The obtained isomeric mixture of diisoamylenes consisted mainly of 3,4,4,5-tetramethyl-2-hexene, 2,3,4,4-tetramethyl-1-hexene, and 3,4,5,5-tetramethyl-2-hexene. LHHW- and ER-type kinetic models were derived for the dimerisation reaction, and their parameters were estimated by fitting experimental data. The best kinetic model was that in which three active sites took part in the rate-limiting step of dimerisation, with an apparent activation energy for the dimerisation reaction in the range of 34–53 $\mathrm{kJ\,mol^{-1}}$.

Keywords: Ion-exchange resin; Isoamylenes; Alcohol; Dimerisation; Diisoamylenes; Kinetics

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1. Introduction

New regulations for gasoline establish limits for unburned hydrocarbons, carbon monoxide, nitrogen oxides, particulates, and smoke. Presently, gasoline reformulation is oriented toward achieving lower evaporative emissions and approaching complete combustion [1] by adding components such as oxygenates to gasoline or by reducing the lighter olefin content of gasoline. Regarding the latter, the C_5 reactive isoamylenes 2-methyl-1-butene (2M1B) and 2-methyl-2-butene (2M2B) of the gasoline are responsible for >90% of the total gasoline ozone formation potential due to their high atmospheric reactivity and blending Reid vapour pressure [2].

This work involves an effective alternative of reducing C_5 reactive olefins content in gasoline by means of dimerisation. This process is already used for propylene, isobutene [3], and, to a lesser extent, isoamylenes reduction [4]. The isomeric mixture of diisoamylenes consisting mainly of 2,3,4,4-tetramethyl-1-hexene (D4), 3,4,5,5-tetramethyl-2-hexene (D6), and 3,4,4,5-tetramethyl-2-hexene (D7) shows octane numbers around 96 and boiling points in the range of 147–157 °C. These data encourage the use of diisoamylenes as an octane booster in gasoline blending [5].

The mechanism and kinetics of isoamylenes dimerisation have not been extensively studied. Whitmore and Mosher [6] stated that the dimerisation of isoamylenes results from the addition of *tert*-amyl carbonium to reactive isoamylenes. Innes and Swift [7] proposed a similar mechanism for the dimerisation of isoamylenes by studying the cracking of diisoamylenes formed in the sulphuric acid extraction of isoamylenes from a C_5 refinery stream. Murphy and Lane [8] investigated the rate of oligomerization of 2M2B in the presence of H_2SO_4 and H_2SO_4–H_3PO_4 mixtures, and concluded that isoamylene was first hydrated to form *tert*-amyl alcohol (TAA) at low temperature with H_2SO_4 as catalyst, and then the alcohol dehydrates

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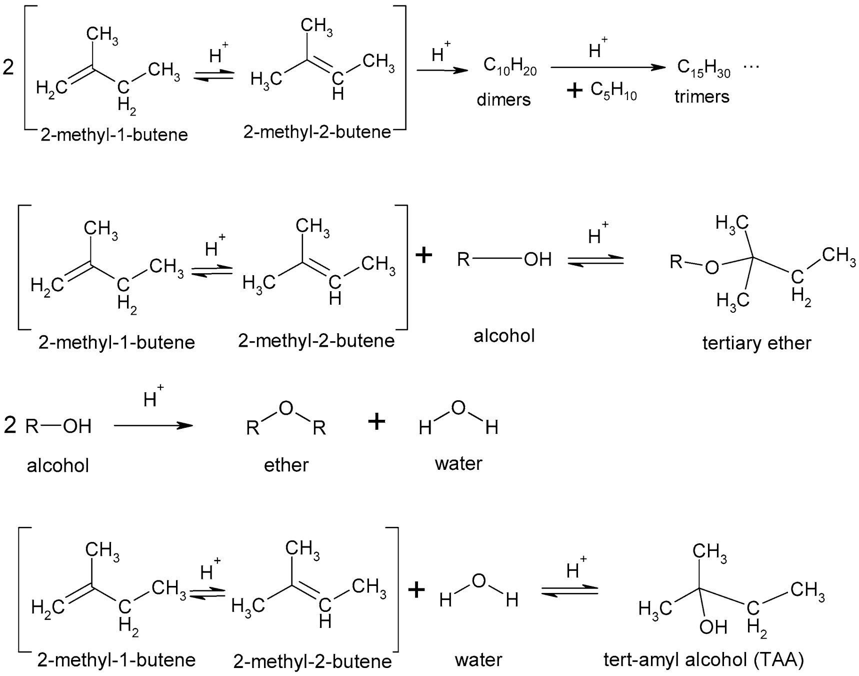

Fig. 1. Reaction scheme of isoamylenes dimerization in the presence of alcohol [15–25].

to form diisoamylenes. Murphy and Lane suggested that for both catalysts, the oligomerization rate was first order in tertiary amyl alcohol concentration and the reaction rate increased with acid concentration. De Renzi et al. [9] described the homogeneous dimerisation in batch mode of 2M2B using a platinum (II) complex in a nitro methane solution.

Shah and Sharma [10] reported the first study of isoamylenes oligomerization using a macroporous acid resin catalyst, Amberlyst 15, and an acid-treated clay in the temperature range of 333–373 K. A first-order kinetics for isoamylenes concentration was fitted, and a possible mechanism was explained on the basis of a Rideal–Eley theory for both catalysts. The yield of higher oligomers was only 2–3%, even at a isoamylenes conversion of 90%. In another early work [11], the isoamylenes dimerisation in presence of methanol was studied varying the initial methanol/isoamylenes molar ratio. The results were clearly different than those of Shah and Sharma [10], because significant amounts of trimers and cracking products were obtained when no alcohol was used. The initial methanol/isoamylenes molar ratio of 1/9 was found to show the highest selectivity for dimers. To confirm these data, the same reaction was recently studied in presence of ethanol [12]. When no ethanol was used, the yield of trimers was 17%, for an isoamylenes conversion of 73% and a dimers selectivity of 77%. In contrast, in the presence of 2.5% of ethanol, for the same isoamylenes conversion value, the dimers selectivity was 93%, with a trimers yield of only 4%. The presence of alcohol clearly improves dimers selectivity. Marchionna et al. [4] obtained similar results in the dimerisation of isobutene. Trimers formation was inhibited by feeding an alcohol at a low alcohol/olefin molar ratio. Dimers selectivity increased noticeably.

The inhibitor effect of polar components was also confirmed in dimerising isobutene by Honkela et al. [13,14] using an ion-exchange resin as the catalyst in the presence of *tert*-butyl alcohol, which was found to increase the selectivity for diisobutenes formation by reducing the activity of the sulfonic sites. Langmuir–Hinshelwood-type kinetic models were derived for the dimerisation reactions and were found to fit the experimental data quite well. The apparent activation energy for dimerisation was found to be 30 kJ mol^{-1}. Isoamylenes dimerisation in the presence of alcohol catalysed by an acid-exchange resin has been studied as a main reaction only rarely, but it frequently appears as a side reaction in the reactions of etherification and hydration of isoamylenes [15–25].

On the basis of related works, two primary reactions occur in the dimerisation of isoamylenes catalysed by an acid-resin catalyst in the presence of alcohol: isoamylenes oligomerization and isomerisation. Other possible side reactions include isoamylenes etherification, alcohol condensation, and isoamylenes hydration. The proposed reaction scheme is shown in Fig. 1.

The aim of the present work is to study the dimerisation of reactive isoamylenes using an acid resin as a catalyst in the presence of low alcohol concentrations at varying temperatures, from selectivity and reaction rate results. Several primary, secondary, and tertiary alcohols are compared. Furthermore, a kinetic model in terms of component activities for the commercial catalyst used is proposed.

2. Experimental

2.1. Experimental setup

Experiments were carried out in a 200-cm^3 stainless steel-jacketed batch reactor (Autoclave Engineers). The stirring speed was set to 500 rpm, to avoid external mass transfer resistance [5,11], and the temperature was set to 60, 80, or 100 °C and controlled by a thermostatted 1,2-propanediol–water mixture within ±0.1 K. The reaction pressure was maintained with nitrogen at 1.9 MPa to ensure the liquid phase over the reaction. More detailed information about the experimental setup can be found elsewhere [5].

2.2. Reactants

The reactants used consisted of an isoamylenes mixture containing 2M2B (94 wt%) and 2M1B (6 wt%) (Fluka, Buchs, Switzerland) and alcohol:methanol (>99.9 wt%) and ethanol (>99.8 wt%) (Carlo Erba, Milano, Italy), 1-propanol (>99.9 wt%, Merck-Shuchardt, Hohenbrunn, Germany), 1-butanol (>99.7 wt%), and 2-propanol (99.9 wt%) (Romil Chemical Ltd., Shepshed, UK), 1-pentanol (>98 wt%), 2-butanol (>99.5 wt%), or *tert*-butanol (>99.7 wt%) (Fluka).

TAME (*tert*-amyl methyl ether) (>97 wt%) was supplied by Fluka, and TAA (>99 wt%) was supplied by Merck–Shuchardt. The other ethers – TAEE (*tert*-amyl ethyl ether) (>93.2 wt%), 2-methyl-2-propoxybutane (>90.2 wt%), 2-isopropyloxy-2-methylbutane (>94.6 wt%), 2-butoxy-2-methylbutane (>97.6 wt%), 2-methyl-2-(1-methyl-propyloxy)butane (>97.7 wt%), and 2-methyl-2-pentoxybutane (>97.8 %wt) – were synthesized in our laboratory. Diisoamylenes and triisoamylenes (>99.0 wt%) were also prepared in our laboratory as mixtures of dimers and trimers, respectively.

2.3. Catalyst

Acidic macroporous resin Amberlyst 35 (Rohm & Haas, Chauny, France) was used. The main physical and structural properties are summarized in Table 1. The bead size distribution was 9.4 wt% of 0.80–1.0 mm, 49.7 wt% of 0.63–0.80 mm, and 39.3 wt% of 0.40–0.63 mm.

2.4. Analytical methods

Samples were obtained through a sampling valve (Valco A2CI4WE.2) that injected 0.2 µL of pressurized liquid into a Hewlett-Packard 6890 gas chromatograph equipped with a capillary column (HP 190915-433; 5% phenyl methyl siloxane, 30.0 m × 250 µm × 0.25 µm nominal). A mass selective detector (HP 5973) was used in the gas chromatography (GC) analysis. The injector temperature was set to 250 °C, the electron source of the mass detector was set to 230 °C, and the quadrupole was set to 150 °C. Two oven temperature ramps were programmed: the first from 30 °C (isotherm during 1.5 min) to 75 °C at a 35 °C min^{-1} ramp rate, and the second from 75 °C (isotherm during 3 min) to 180 °C at a 45 °C min^{-1} ramp rate, with the final temperature of 180 °C maintained for 1 min. Helium (Air Liquide, Barcelona, Spain) with a minimum purity of 99.998% was used as a carrier gas.

2.5. Procedure

All experiments were carried out at an initial isoamylenes/alcohol molar ratio of 9/1 with the aim of avoiding the formation of trimers, tetramers, and cracking products [5,11]. Each experiment used 4 g of industrial Amberlyst 35 dried at 110 °C for 3 h in an atmospheric oven and for 5 h at 100 °C under vacuum (catalyst loading <3 wt%). The residual amount of water in the catalyst was determined by Karl Fischer method, resulting in $<3\%\ \mathrm{g_{water}\,g_{cat}^{-1}}$.

Both the isoamylenes mixture and alcohol, previously weighted, were introduced in a calibrated burette pressurized with nitrogen at 1.5 MPa. When the target temperature was reached, the reacting mixture was shifted to the reactor with nitrogen. Then the pressure was set to 1.9 MPa with nitrogen to ensure the liquid phase, and this was considered the starting point of the reaction. Samples were analysed at different time intervals with a GC/MS system connected on-line to the reactor. The maximal duration of the experiments was set to 8 h.

2.6. Calculation

For each experiment, isoamylenes conversion (X_{IA}), alcohol conversion(X_{OH}), selectivity to dimers (S_{DIA}), and diisoamylenes yield (Y_{DIA}) were calculated using the following expressions:

$$X_{\mathrm{IA}}\ (\%) = \frac{n_{\mathrm{IA}}^0 - n_{\mathrm{IA}}}{n_{\mathrm{IA}}^0} \times 100 = \frac{n_{\mathrm{ET}} + n_{\mathrm{TAA}} + 2n_{\mathrm{DIA}} + 3n_{\mathrm{TRIA}}}{n_{\mathrm{IA}} + n_{\mathrm{ET}} + n_{\mathrm{TAA}} + 2n_{\mathrm{DIA}} + 3n_{\mathrm{TRIA}}} \times 100, \quad (1)$$

$$X_{\mathrm{OH}}\ (\%) = \frac{n_{\mathrm{OH}}^0 - n_{\mathrm{OH}}}{n_{\mathrm{OH}}^0} \times 100 = \frac{n_{\mathrm{ET}}}{n_{\mathrm{OH}} + n_{\mathrm{ET}}} \times 100, \quad (2)$$

$$S_{\mathrm{DIA}}\ (\%) = \frac{n_{\mathrm{IA}\to\mathrm{DIA}}}{n_{\mathrm{IA}}^0 - n_{\mathrm{IA}}} \times 100 = \frac{2n_{\mathrm{DIA}}}{n_{\mathrm{ET}} + n_{\mathrm{TAA}} + 2n_{\mathrm{DIA}} + 3n_{\mathrm{TRIA}}} \times 100, \quad (3)$$

Table 1
Physical properties of Amberlyst 35 resin

Catalyst	Acidity (eq H$^+$ kg^{-1})	S_g[a] (m^2 g^{-1})	V_g[b] (cm^3 g^{-1})	S_g[c] (m^2 g^{-1})	V_g[c] (m^2 g^{-1})	d_{pore}[c] (m^2 g^{-1})	d_b[d] (mm)	$T_{\max}$ (°C)
A-35	5.32	34	0.28	166	0.623	329	0.51	150

[a] BET method.
[b] Determined by adsorption–desorption of N_2 at 77 K.
[c] Swollen in water (ISEC method).
[d] Determined by sieving dry industrial samples.

and

$$Y_{\mathrm{DIA}}(\%) = \frac{X_{\mathrm{IA}} S_{\mathrm{DIA}}}{100} = \frac{2n_{\mathrm{DIA}}}{n^0_{\mathrm{IA}}} \times 100 = \frac{2n_{\mathrm{DIA}}}{n_{\mathrm{IA}} + n_{\mathrm{ET}} + n_{\mathrm{TAA}} + 2n_{\mathrm{DIA}} + 3n_{\mathrm{TRIA}}} \times 100. \quad (4)$$

Trimers are included in these equations, although only very low amounts were detected under the experimental conditions in this study. Some experiments were repeated to estimate the experimental error, which was found to be $<4\%$.

3. Results and Discussion

3.1. Influence of internal mass transfer

We sieved dried catalyst to various particle sizes to allow us to study the influence of internal mass transfer on the reaction rate under reference conditions. Three alcohols (ethanol, 1-pentanol, and 2-butanol) were tested at 100 °C with unsieved commercial catalyst and with beads of 1.0–0.8, 0.8–0.63, 0.63–0.40, 0.40–0.25, and 0.25–0.16 mm. Isoamylenes conversions obtained at different reaction times were similar within the limits of experimental error. Consequently, it can be inferred that the intracatalyst mass-transfer resistance can be considered negligible for primary and secondary alcohols used in this work and that industrial bead size is suitable for obtaining the intrinsic reaction rate.

3.2. Products identification

Eighteen chromatographic peaks corresponding to diisoamylenes were detected by GC. Only eight of these peaks were considered significant (peaks $>1\%$ of the chromatographic area); five of these are outlined here. Trimers (TRIA) were detected only at long reaction times and high temperatures but always with chromatographic areas $<5\%$.

To confirm the structure of the five predominant dimers, electronic impact mass spectrometry and ^{13}C magnetic nuclear resonance were applied. The diisoamylenes obtained consisted mainly of D4, D6, and D7, with $>70\%$ of the total dimers weight. D4 was formed predominantly in the initial reaction period, but it gradually isomerised to the others. The results agree with those obtained in earlier works [5,11] and with dimer identification achieved by others [7,9,10].

3.3. Effect of temperature and alcohol type on conversion and selectivity

The reaction of isoamylenes in the presence of alcohol was found to be highly selective toward dimers at 60, 80, and 100 °C. Detected amounts of trimers were always $<5\%$ of the chromatographic area, and no tetramers formation or cracking products were observed. These results satisfactorily agree with the results of previous studies [5,11] of the dimerisation reaction catalysed by macroporous and microporous resins in the presence of ethanol and methanol. All of the runs where performed at a 10% mol alcohol content and 4 g of dried Amberlyst 35. Under these conditions, the ratio (eq H^+ R–OH)/(eq H^+ catalyst) is approximately 10, and therefore it can be assumed that initially the alcohol is adsorbed on the catalyst and prevents isoamylenes dimerisation. Besides alcohol, there is residual water from the drying process ($<3\%\ \mathrm{g_{water}\,g_{cat}^{-1}}$) on catalyst active sites; consequently, at low reaction times, isoamylenes hydration reactions also occur preferentially over the dimerisation reaction. Only when those reactions approach the equilibrium, which occurs extremely rapidly, isoamylenes can adsorb on the free active sites, and then dimerisation becomes the main reaction.

The ether formed initially was observed to slowly decompose to isoamylenes and alcohol due to the consumption of isoamylenes by the dimerisation reaction, giving rise to a slight continuous ether equilibrium displacement. The processes of alcohol adsorption and etherification and hydration reactions appear to be extremely rapid compared with the dimerisation reaction. Therefore, it seems that the effect of the remaining alcohol is to reduce the strength of the acid sites. Consequently, the rate of the oligomerization reaction to trimers is greatly reduced, and the selectivity to dimers increases.

Results at 60, 80, and 100 °C with all the alcohols after 7.2 h of reaction, necessary to reach a pseudostationary state (with composition practically constant), are compared in Table 2. The highest alcohol conversion corresponds to methanol, and the best results were obtained using 1-pentanol at 100 °C, with 80% isoamylenes conversion, 95% dimers selectivity, and 82% dimers yield. Comparative effects of $\mathrm{C_1}$–$\mathrm{C_5}$ alcohols are shown in Figs. 2 and 3, where isoamylenes conversion and diisoamylenes selectivity, respectively, are plotted as functions of time at 100 °C. Dimers formation increases with temperature and the molecular weight of the alcohol, and different behav-

Table 2
Isoamylenes and alcohol conversion (X_{IA}, X_{OH}), selectivity to diisoamylenes (S_{DIA}), and yield (Y_{DIA}) after 7.2 h of reaction

T (°C)	Alcohol	X_{IA} (%)	X_{OH} (%)	S_{DIA} (%)	Y_{DIA} (%)
60	MetOH	50.9 ± 1.6	92.8 ± 0.2	79.2 ± 1.5	40.4 ± 2.2
	EtOH	37.6	83.9	62.7	22.2
	1-PropOH	47.2	72.1	73.7	32.7
	2-PropOH	14.9	17.3	28.9	2.8
	1-ButOH	59.9 ± 1.1	90.6 ± 0.1	83.0 ± 0.2	49.8 ± 0.8
	2-ButOH	13.1	9.2	49.1	4.8
	1-PentOH	61.8	86.1	84.8	52.7
80	MetOH	60.8 ± 0.1	92.3 ± 0.1	89.1 ± 0.1	55.7 ± 0.1
	EtOH	43.1 ± 0.4	79.4 ± 0.5	72.1 ± 0.2	30.0 ± 0.3
	1-PropOH	55.8	72.5	84.6	47.0
	2-PropOH	14.8 ± 0.9	25.0 ± 2.8	48.0 ± 4.2	4.8 ± 0.9
	1-ButOH	62.3	84.2	88.2	56.9
	2-ButOH	16.0 ± 0.2	24.5 ± 0.6	68.6 ± 0.2	11.0 ± 0.1
	1-PentOH	71.7 ± 0.9	78.1 ± 0.1	88.9 ± 0.4	64.7 ± 1.4
100	MetOH	62.5	90.5	95.8	63.2
	EtOH	49.1	75.3	86.4	43.6
	1-PropOH	62.7 ± 1.1	68.0 ± 0.4	90.6 ± 0.1	58.2 ± 0.9
	2-PropOH	26.1	29.2	86.5	18.2
	1-ButOH	72.3 ± 0.2	76.9 ± 0.5	94.0 ± 0.2	72.2 ± 0.4
	2-ButOH	18.7	61.7	79.2	18.7
	1-PentOH	80.5	68.0	95.4	81.6

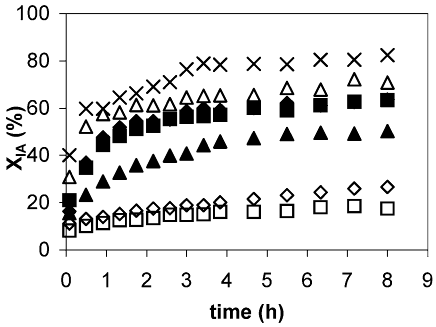

Fig. 2. Conversion of isoamylenes as a function of time with 10% mol alcohol using Amberlyst 35 at 100 °C. MetOH (◆), EtOH (▲), 1-PropOH (■), 2-PropOH (◇), 1-ButOH (△), 2-ButOH (□), 1-PentOH (×).

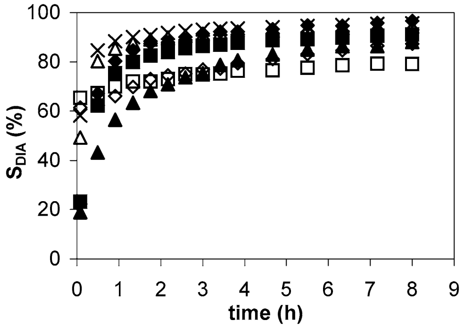

Fig. 3. Selectivity of diisoamylenes as a function of time with 10% mol alcohol using Amberlyst 35 at 100 °C. MetOH (◆), EtOH (▲), 1-PropOH (■), 2-PropOH (◇), 1-ButOH (△), 2-ButOH (□), 1-PentOH (×).

iours were observed depending on the type of alcohol used (primary or secondary). Among primary alcohols, methanol showed an unexpected trend, being located between 1-propanol and 1-butanol instead of below ethanol, as expected. A possible explanation for this abnormal effect is given later in the paper.

The secondary alcohol systems appear to be less selective to dimers formation, and reaction proceeds slower than with primary alcohols. The stronger inhibitory effect of secondary alcohols over the dimerisation reaction can be associated with the steric hindrances caused by the OH position; the farther the OH group is from the primary carbon, the more difficult the etherification reaction, and then unreacted alcohol remains adsorbed and hinders the isoamylenes adsorption. This hypothesis was assessed when *tert*-butyl alcohol (the only tertiary alcohol tested) was used; neither ether nor dimers formation was detected.

Water in an isoamylenes/water molar ratio of 9/1 was also tested, and TAA was the only product quantified. This was an expected result, because water has a high affinity for the active sites and avoids reactions other than isoamylenes hydration. Based on these results, we decided to eliminate water and *tert*-butyl alcohol experiments in the comparisons.

The dimerisation inhibitory trend of the alcohols with varying substitution degrees (primary, secondary, or tertiary) but the same OH group position depends to a great extent on the interactions between the alcohol and the polymeric catalyst structure. To characterize the degree of affinity of the alcohols with the acid ion-exchange catalyst, the Hildebrand individual solubility parameter δ_i is compared with the polymer solubility parameter δ_p [26,27]. The more similar both parameters are, the more alcohol adsorbs on the resin backbone.

Table 3
δ_i, ε and MW of the primary alcohols

	MetOH	EtOH	1-PropOH	1-ButOH	1-PentOH
δ_i 10^{-3} $(\mathrm{J\,m^{-3}})^{1/2}$ 60 °C	27.8	24.8	23.3	22.3	21.6
δ_i 10^{-3} $(\mathrm{J\,m^{-3}})^{1/2}$ 80 °C	26.6	23.7	22.4	21.6	20.9
δ_i 10^{-3} $(\mathrm{J\,m^{-3}})^{1/2}$ 100 °C	25.4	22.6	21.5	20.8	20.2
ε	32.6	24.3	20.1	17.8	13.9
MW $(\mathrm{g\,mol^{-1}})$	32	46	60	74	88

For each alcohol, δ_i is defined by [28]

$$\delta_i = \sqrt{\frac{\Delta H_{\mathrm{VAP},i} - RT}{V_i^{\mathrm{L}}}}, \tag{5}$$

where $\Delta H_{\mathrm{VAP},i}$ is the molar enthalpy of vaporisation and V_i^{L} is the liquid molar volume for the component i. Parameters obtained for primary alcohols at 60, 80, and 100 °C, along with the molecular weight and the dielectric constant ε [24], are given in Table 3. As a rule, when the molecular weight increases, the individual solubility parameter and the polarity decrease.

An estimation of the resin solubility parameter is obtained from a group contribution method by [29]

$$\delta_{\mathrm{p}} = \sqrt{\frac{\sum_i x_i E_{\mathrm{coh},i}}{\sum_i x_i V_i}}, \tag{6}$$

where x_i, $E_{\mathrm{coh},i}$, and V_i are the molar fraction, energy cohesion and molar volume, respectively, of the structural group contribution i. The δ_{p} value calculated for Amberlyst 35 was 25.3 $(\mathrm{MPa})^{1/2}$.

It is noteworthy that this value obtained by a group contribution method was estimated at 25 °C. The polymer solubility parameter has been shown to be slightly temperature-dependent and to decreases quasi-linearly with increasing temperature [27]. Thus, this value would be expected to be slightly lower in the studied temperature range of 60–100 °C. For resin Bayer K-2631, the decrease in polymer solubility parameter was reportedly $<6\%$ [27] compared with the values obtained at 100 °C. The solubility parameter for the polyethylene molecules with approximately 1000 units of carbon atoms at 166 °C was found to be 17.8 $(\mathrm{MPa})^{1/2}$ using pressure-volume-temperature methods, and in the range of 15.8–17.1 $(\mathrm{MPa})^{1/2}$ using the prediction of the group additivity method at 25 °C [30]. In this framework, for the purpose of evaluating the affinity between the used alcohols and the resin backbone, we can assume the polymer solubility parameter to be constant with temperature. A similar approximation was used in previous studies that developed inverse GC techniques to evaluate the intermolecular contact interactions between solvents and polymers [31].

Fig. 4 shows diisoamylenes yield as a function of the individual solubility parameter for each primary alcohol at 60, 80, and 100 °C. The vertical line at $\delta = 25.3$ represents the polymer solubility parameter. As mentioned earlier, chemical species with a solubility parameter close to that of the catalyst (alcohols in

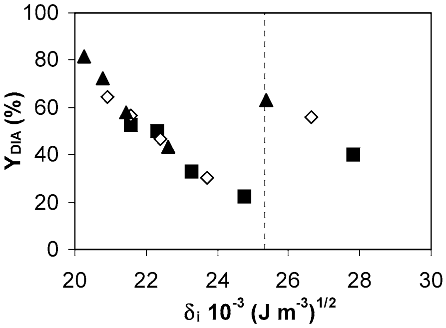

Fig. 4. Diisoamylenes yield after 7.2 h as a function of individual solubility parameter for primary alcohols at 60, 80 and 100 °C. 60 °C (■), 80 °C (◇), 100 °C (▲), A-35 (- - -).

this work) should have better affinity to the resin backbone and should hinder accessibility to the active sites for species with a different δ value (e.g., isoamylene molecules). Consequently, a major dimerisation reaction should be achieved when increasing the difference between the alcohol and polymer solubility parameters. As shown in Fig. 4, this hypothesis agrees with our results, except for methanol. The diisoamylenes yield appears to increase from a minimum of 20% at δ near the polymer solubility parameter for small alcohols with high polarity to a maximum of 80% for large alcohols with low polarity. The three points of the plot lying outside the general curve correspond to methanol yields at 60, 80, and 100 °C, with higher yields than should be expected from methanol's solubility value.

Although etherification equilibrium was not studied in detail in this work, published studies on the reaction of isobutylene with various alcohols [24] assert that the reaction equilibrium constant decreases with increasing size of the alcohol. For example, at 50 °C, the equilibrium constants for the etherification of isobutene are 79 for methanol, 40 for ethanol, 30 for 1-propanol, and 2.6 for 2-propanol, and when etherifying 2M1B, the equilibrium constants at 50 °C are 61 for methanol [19] and 31 for ethanol [15]. Therefore, it can be assumed that with increasing alcohol molecular weight, the equilibrium constant decreases and the concentration of unreacted alcohol at equilibrium increases. At the same time, less-polar alcohols demonstrate less capacity to occupy the active sites, facilitating access of the reactive olefin to the active sites and allowing the dimerisation and isomerisation reactions. In contrast, with decreasing alcohol molecular weight, more alcohol is consumed in the etherification reaction, and less free alcohol remains unreacted.

When using methanol at low temperatures (60 °C), the alcohol conversion in etherification reaction is the highest of all the alcohols tested. Moreover, at this temperature, the solubility of methanol is to some extent different than that of the polymer, as shown in Table 3. Subsequently, these facts may explain why at 60 °C the diisoamylenes yield is greater in the presence of methanol than in the presence of ethanol and 1-propanol. At higher temperatures, the conversion of methanol would decrease, due to the decreased equilibrium constant, as occurs with the other alcohols, but, as shown in Table 2, methanol conversion remains approximately constant, in such a way that methanol seems to be consumed in some other reaction than etherification.

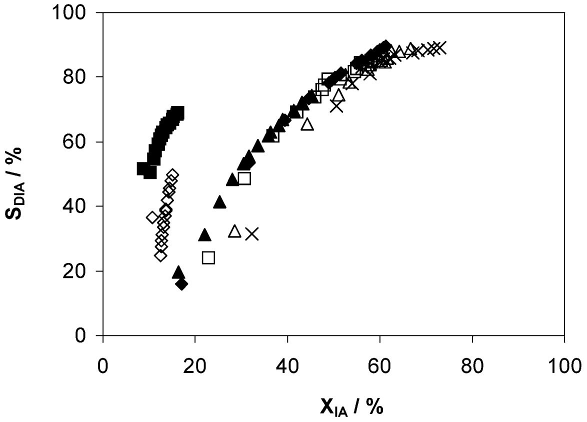

Fig. 5. Selectivity for diisoamylenes as a function of isoamylenes conversion with A-35 at 80 °C. MetOH (◆), EtOH (▲), 1-PropOH (□), 2-PropOH (◇), 1-ButOH (△), 2-ButOH (■), 1-PentOH (×).

The formation of dimethyl ether (DME) from alcohol condensation has been detected. DME formation is favoured by high temperatures and high alcohol content. At low alcohol content, methanol dehydration appears to be faster than for the ethanol system [18,32]. As shown in Table 2, methanol is the only alcohol tested with conversion values close to 1 independent of the reaction temperature instead of decreasing with temperature as would be expected. Under these conditions, the low content of free methanol in the active sites of the catalyst and the high temperature allow isoamylenes to dimerise easily. As a result, the activity of the system to dimerisation is even higher for the 1-propanol system, for which the etherification equilibrium constant is lower.

The selectivity for diisoamylenes as a function of isoamylenes conversion for each tested alcohol is plotted in Fig. 5. The results were obtained at an initial isoamylenes/alcohol molar ratio of 9/1, and the various values of selectivities and conversions for each alcohol correspond to their variation over time. Diisoamylenes selectivity appears to increase with isoamylenes conversion.

An earlier study of the influence of polar components in the dimerisation of isobutene [14] found that dimer selectivity decreased with increasing isobutene conversion. This behaviour differs from what was obtained in isoamylenes dimerisation, but it can be readily explained due to the different activity of the system, which can be related to the alcohol content and catalyst amount. In isobutene dimerisation, methanol content ranged from 18 to 2% with a catalyst loading of 3%. At the lowest alcohol concentrations, ether formation could be neglected, trimers being the main byproduct. With increasing isobutene conversion, trimerization increased as well, resulting in decreased dimers selectivity. In contrast, in this work 10% mol alcohol and 3% catalyst loadings were used. The global activity of the system was lower, with ether being the main byproduct formed. A trimerization reaction was practically unobserved. Etherification was initially the main reaction observed, but as isoamylenes conversion increased, ether formation approximated the equilibrium state and dimers selectivity improved.

These results demonstrate that a maximum dimer selectivity can be found between the maximum ether selectivity and the maximum trimers selectivity.

The dependence between dimers selectivity and isoamylenes conversion also indicates a different trend depending on the substitution degree of alcohol (primary or secondary). The only difference is their differing polarity and sterical hindrance to react for etherification. For the same alcohol family, it can be inferred that a smaller amount of the compound with higher polarity is required to get the same selectivity compared with another compound with lower polarity; thus, most polar alcohols should be used to a lesser extent to increase dimers selectivity.

3.4. *Effect of temperature and alcohols on dimer distribution*

As mentioned above, the isomeric mixture of diisoamylenes consisted mainly of 2,3,4,4-tetramethyl-1-hexene (D4), 3,4,5,5-tetramethyl-2-hexene (D6), and 3,4,4,5-tetramethyl-2-hexene (D7). Figs. 6–8 plot the selectivity toward these three dimers at 7.2 h versus temperature for each primary alcohol tested.

From the preceding discussion, it can be deduced that increasing the molecular weight of the alcohol results in major catalyst activity, similar to the effect of a higher reaction temperature. Keeping this fact in mind, different behaviours for the three major diisoamylenes obtained can be observed in Figs. 6–8.

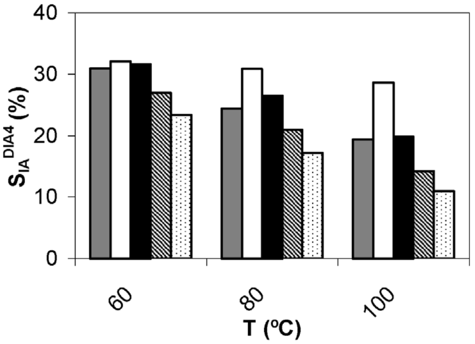

Fig. 6. Selectivity for 2,3,4,4-tetramethyl-1-hexene, D4, as a function of temperature for primary alcohols at 7.2 h. MetOH (▣), EtOH (□), 1-PropOH (■), 1-ButOH (▨), 1-PentOH (⊡).

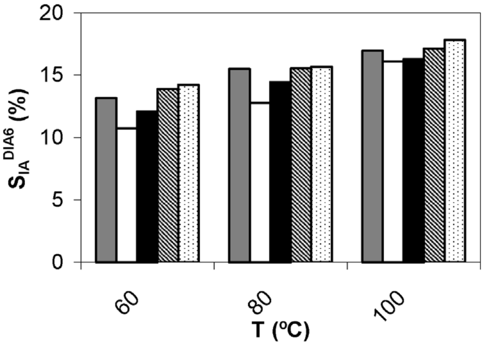

Fig. 7. Selectivity for 3,4,5,5-tetramethyl-2-hexene, D6, as a function of temperature for primary alcohols at 7.2 h. MetOH (▣), EtOH (□), 1-PropOH (■), 1-ButOH (▨), 1-PentOH (⊡).

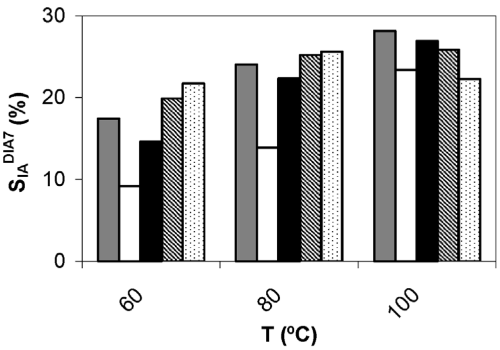

Fig. 8. Selectivity for 3,4,4,5-tetramethyl-2-hexene, *D*7, as a function of temperature for primary alcohols at 7.2 h. MetOH (▣), EtOH (□), 1-PropOH (■), 1-ButOH (▨), 1-PentOH (⊡).

D4 selectivity shows a maximum selectivity of about 30% at low temperatures (60 °C) and low alcohol molecular weight (EtOH). With increasing catalyst activity, D4 selectivity decreases. These results confirm that D4 was the first dimer to appear in the reaction medium and that it progressively isomerised to other diisoamylenes [5,7,9–11]. Comparing dimers D6 and D7, the observed trend was completely opposite. Selectivity toward both dimers increased with increasing temperature and molecular weight of the alcohol, indicating that these products were formed mainly from D4 isomerisation.

3.5. *Kinetic model of the dimerisation reaction*

Because the dimerisation reaction in the presence of secondary alcohols under the study conditions was found to be insignificant for kinetic calculation, only primary alcohol systems were considered for modeling purposes. Diisoamylenes and triisoamylenes formation were the experimentally observed oligomerization reactions. However, triisoamylenes formation was not been considered in the modeling, because TRIA formation was always <5% of the chromatographic area.

The etherification reaction appeared to be very rapid under the study conditions; equilibrium was reached in the first minutes of the reaction. Therefore, this reaction was not considered in the modeling of dimerisation.

Selectivity for diisoamylenes appears to depend on the presence and type of alcohol used in the dimerisation reaction. This effect can be explained by the preferential adsorption of the alcohol on the active sites, which determines the number of free active sites and, consequently, the catalyst activity. The increased selectivity is correlated with lower activity. Hence, in kinetic modelling, the effect of the interaction of alcohol and ether with the resin was taken into account by including the terms of adsorption and desorption for alcohol and ether, respectively.

Because of the complexity of the system, to simplify the kinetic modeling for dimerisation reactions, we decided to lump all of the dimers together. Similar considerations had been assumed in isobutene dimerisation in previous works with successful results [13,33]. Consequently, the experimental reaction

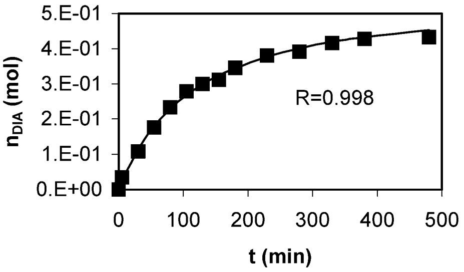

Fig. 9. Diisoamylenes mols evolution using 1-propanol at 80 °C. Experimental values (■).

Table 4
Experimental dimerization reaction rates ($\mathrm{mol\,g^{-1}\,h^{-1}}$) in the presence of 1-propanol at 60, 80 and 100 °C

t (h)	r_{DIA}		
	60 °C	80 °C	100 °C
0	0.018	0.075	0.136
0.1	0.017	0.069	0.117
0.5	0.016	0.047	0.063
0.9	0.014	0.034	0.039
1.3	0.013	0.025	0.027
1.8	0.012	0.020	0.020
2.2	0.011	0.016	0.015
2.6	0.011	0.013	0.012
3.0	0.010	0.010	0.009
3.4	0.009	0.009	0.008
3.8	0.009	0.007	0.006
4.7	0.008	0.005	0.005
5.5	0.007	0.004	0.004
6.3	0.007	0.003	0.003
7.2	0.006	0.002	0.002
8.0	0.006	0.002	0.002

rates of dimerisation were obtained by computing the derivative of the plot of the number of mols of all of the dimers lumped together versus time. As an example, Fig. 9 plots the number of mols of dimers versus time using 1-propanol at 80 °C, and Table 4 gives the dimerisation reaction rates obtained using 1-propanol.

Before kinetic modeling, the nonideality of the reaction mixture was considered, because an initial kinetic fit to data using concentrations proved unsatisfactory. Furthermore, a kinetic model in activities was used acceptably in isobutene dimerisation [13]. The activity coefficients were calculated by the Dortmund-modified UNIFAC method [34] and were found to vary between 1.07 and 0.97 for DIA and IA, between 0.84 and 1.04 for the ethers, between 8.0 and 23.9 for MetOH, between 6.3 and 13.5 for EtOH, between 5.3 and 9.7 for 1-PropOH, between 4.6 and 11.5 for 1-ButOH, and between 4.0 and 9.5 for PentOH. Consequently, the system seems to behave nonideally, and thus we decided to express the kinetic model in terms of activities.

Kinetic equations based on the Langmuir–Hinshelwood–Hougen–Watson (LHHW) formalism and on its derived form, the Eley–Rideal (ER) formalism, were used. Considering the adsorption–reaction–desorption process, with n being the possible number of actives sites that may participate in the surface reaction step, a mechanism applying LHHW formalism is

$$\mathrm{IA} + \sigma \leftrightarrow \mathrm{IA}\sigma,$$
$$\mathrm{OH} + \sigma \leftrightarrow \mathrm{OH}\sigma,$$
$$2\mathrm{IA}\sigma + (n-2)\sigma \rightarrow \mathrm{DIA}\sigma + (n-1)\sigma,$$
$$\mathrm{DIA}\sigma \leftrightarrow \mathrm{DIA} + \sigma,$$

and

$$\mathrm{ET}\sigma \leftrightarrow \mathrm{ET} + \sigma,$$

or the analogue er formalism, which differs only in the surface reaction step, in which one isoamylene molecule would react directly from the liquid phase with one adsorbed isoamylene molecule,

$$\mathrm{IA}\sigma + \mathrm{IA} + (n-1)\sigma \rightarrow \mathrm{DIA}\sigma + (n-1)\sigma.$$

For both mechanisms, the rate-limiting step was assumed to be the surface reaction in which one or more additional active sites could take part. The LHHW formalism leads to the following rate equation:

$$r_{\mathrm{LHHW}} = \frac{\hat{k}_1 K_{\mathrm{a,IA}}^2 a_{\mathrm{IA}}^2}{(1 + a_{\mathrm{IA}} K_{\mathrm{a,IA}} + a_{\mathrm{DIA}} K_{\mathrm{a,DIA}} + a_{\mathrm{ET}} K_{\mathrm{a,ET}} + a_{\mathrm{OH}} K_{\mathrm{a,OH}})^n}. \tag{7}$$

When the ER formalism is applied, the following reaction rate equation is obtained:

$$r_{\mathrm{ER}} = \frac{\hat{k}_1 K_{\mathrm{a,IA}} a_{\mathrm{IA}}^2}{(1 + a_{\mathrm{IA}} K_{\mathrm{a,IA}} + a_{\mathrm{DIA}} K_{\mathrm{a,DIA}} + a_{\mathrm{ET}} K_{\mathrm{a,ET}} + a_{\mathrm{OH}} K_{\mathrm{a,OH}})^n}. \tag{8}$$

The number of active sites that participate in the surface reaction step was assumed to be two or three; however, models with $n = 1$ have been also considered for ER models. Based on Eqs. (7) and (8), all possible derived equations were considered and grouped into two classes, depending on the number of unoccupied active sites: (i) class I, for which the number of unoccupied active centres is considered negligible (which implies that the 1 in the denominator [the adsorption term] can be removed) and (ii) class II, where the above hypothesis is rejected.

Subsequently, the adsorption terms are considered alternately negligible. The models obtained are listed in Table 5. For models of class I, the surface reaction kinetic constant, $\hat{k}$, and adsorption equilibrium constants, $K_{\mathrm{a,I}}$, $K_{\mathrm{a,DIA}}$, $K_{\mathrm{a,OH}}$, and $K_{\mathrm{a,ET}}$, have been grouped into factors, called A, B, C, and D for mathematical fitting purposes. The particular form in which constants are grouped depends on the mechanism (LHHW or ER) and the neglected adsorption terms, if any. For the models of class II, k_1 is equal to $\hat{k} K_{\mathrm{a,IA}}^2$ for LHHW models and to $\hat{k} K_{\mathrm{a,IA}}$ for ER models.

The kinetic models proposed in Table 5 were fitted to experimental data and compared. Parameters for models were found by minimizing the sum of squares of the residuals between the measured and calculated data using the Marquardt–Levenberg method [35,36]. Temperature dependence of the reaction rate

Table 5
Kinetic models tested for liquid-phase dimerization of isoamylenes, with n values ranging from 1 to 3

Type	Model class I	Model class II
1	$r = Aa_{\mathrm{I}}^{2-n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{IA}}k_{\mathrm{a,IA}})^n}$
2	$r = A\frac{a_{\mathrm{IA}}^2}{a_{\mathrm{DIA}}^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{DIA}}k_{\mathrm{a,DIA}})^n}$
3	$r = A\frac{a_{\mathrm{IA}}^2}{a_{\mathrm{OH}}^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{OH}}k_{\mathrm{a,OH}})^n}$
4	$r = A\frac{a_{\mathrm{IA}}^2}{a_{\mathrm{ET}}^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{ET}}k_{\mathrm{a,ET}})^n}$
5	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{IA}}+Ba_{\mathrm{DIA}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{IA}}k_{\mathrm{a,IA}}+a_{\mathrm{DIA}}k_{\mathrm{a,DIA}})^n}$
6	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{IA}}+Ba_{\mathrm{OH}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{IA}}k_{\mathrm{a,IA}}+a_{\mathrm{OH}}k_{\mathrm{a,OH}})^n}$
7	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{IA}}+Ba_{\mathrm{ET}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{IA}}k_{\mathrm{a,IA}}+a_{\mathrm{ET}}k_{\mathrm{a,ET}})^n}$
8	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{DIA}}+Ba_{\mathrm{OH}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{DIA}}k_{\mathrm{a,DIA}}+a_{\mathrm{OH}}k_{\mathrm{a,OH}})^n}$
9	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{DIA}}+Ba_{\mathrm{ET}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{DIA}}k_{\mathrm{a,DIA}}+a_{\mathrm{ET}}k_{\mathrm{a,ET}})^n}$
10	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{OH}}+Ba_{\mathrm{ET}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{OH}}k_{\mathrm{a,OH}}+a_{\mathrm{ET}}k_{\mathrm{a,ET}})^n}$
11	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{IA}}+Ba_{\mathrm{DIA}}+Ca_{\mathrm{OH}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{IA}}k_{\mathrm{a,IA}}+a_{\mathrm{DIA}}k_{\mathrm{a,DIA}}+a_{\mathrm{OH}}k_{\mathrm{a,OH}})^n}$
12	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{IA}}+Ba_{\mathrm{DIA}}+Ca_{\mathrm{ET}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{IA}}k_{\mathrm{a,IA}}+a_{\mathrm{DIA}}k_{\mathrm{a,DIA}}+a_{\mathrm{ET}}k_{\mathrm{a,ET}})^n}$
13	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{IA}}+Ba_{\mathrm{OH}}+Ca_{\mathrm{ET}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{IA}}k_{\mathrm{a,IA}}+a_{\mathrm{OH}}k_{\mathrm{a,OH}}+a_{\mathrm{ET}}k_{\mathrm{a,ET}})^n}$
14	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{OH}}+Ba_{\mathrm{DIA}}+Ca_{\mathrm{ET}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{(1+a_{\mathrm{OH}}k_{\mathrm{a,OH}}+a_{\mathrm{DIA}}k_{\mathrm{a,DIA}}+a_{\mathrm{ET}}k_{\mathrm{a,ET}})^n}$
15	$r = \frac{Aa_{\mathrm{IA}}^2}{(a_{\mathrm{I}}+Ba_{\mathrm{DIA}}+Ca_{\mathrm{OH}}+Da_{\mathrm{ET}})^n}$	$r = \frac{k_1 a_{\mathrm{IA}}^2}{\left(1+a_{\mathrm{IA}}k_{\mathrm{a,IA}}+a_{\mathrm{DIA}}k_{\mathrm{a,DIA}}+a_{\mathrm{OH}}k_{\mathrm{a,OH}}+a_{\mathrm{ET}}k_{\mathrm{a,ET}}\right)^n}$

and adsorption equilibrium constants were assumed to follow the equations:

$$\hat{k} = \exp(b_1)\exp\left[-b_2\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right] \tag{9}$$

and

$$K_i = \exp(d_1)\exp\left[-d_2\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right], \tag{10}$$

where T_{ref} is the reference temperature, taken as 353 K, the mean experimental temperature to minimize the parameter correlation. Fitted parameters were b_1, b_2, d_1, and d_2. From Eqs. (9) and (10), it can be inferred that any combination (multiplication or division) of kinetic and adsorption equilibrium constants should follow the same temperature dependence. Parameter values also must be thermodynamically consistent; at increasing temperature, the kinetic constant must increase and the adsorption equilibrium constants must decrease, because the activation energy must be positive and the adsorption enthalpies and entropies must be negative.

The sum of squares of residuals (SQ) was evaluated for the various kinetic models listed in Table 5 and separately for all of the primary alcohols tested. For each alcohol, the ratio $\mathrm{SQ_{min}/SQ}$ was compared for each model to quantify the goodness of fit. The more similar to unity the ratio $\mathrm{SQ_{min}/SQ}$ is, the better the fit. Figs. 10 and 11 compare the goodness of fit of kinetic models of classes I and II, respectively, in terms of $\mathrm{SQ_{min}/SQ}$, plotted with 1-butanol used as a selectivity enhancer. Similar results were obtained for the other primary alcohols. As the figures show, models with $n = 3$ show the minimum SQ value, suggesting that three active sites may take part in the reaction mechanism. Among these, models I-5, I-11, I-12, I-15, II-5, II-11, II-12, and II-15 show the best mathematical fit, with $\mathrm{SQ_{min}/SQ}$ values approximately equal to unity. These eight models appear to have isoamylenes and diisoamylenes

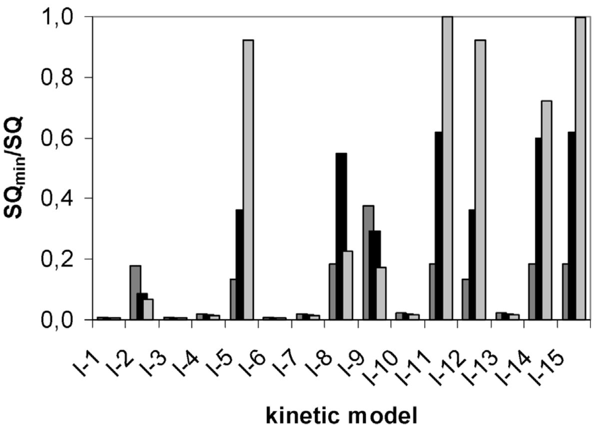

Fig. 10. Comparison of the goodness of fit of class I models in terms of $\mathrm{SQ_{min}/SQ}$ when 1-butanol is used. The best fit corresponds to the maximum $\mathrm{SQ_{min}/SQ}$ value, equal to unity. $n = 1$ (☐), $n = 2$ (■), $n = 3$ (▨).

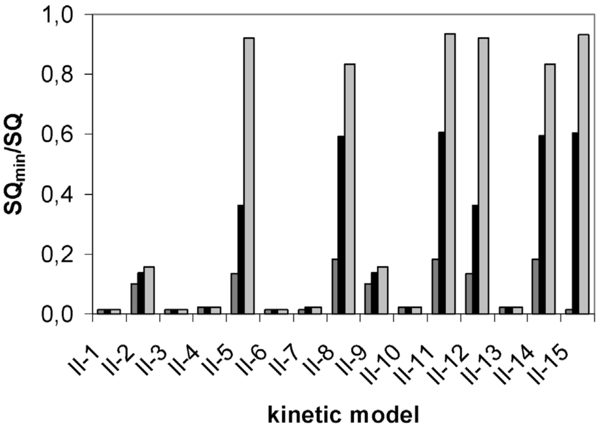

Fig. 11. Comparison of the goodness of fit of class II models in terms of SQ_{min}/SQ when 1-butanol is used. The best fit corresponds to the maximum SQ_{min}/SQ value, equal to unity. $n = 1$ (□), $n = 2$ (■), $n = 3$ (▨).

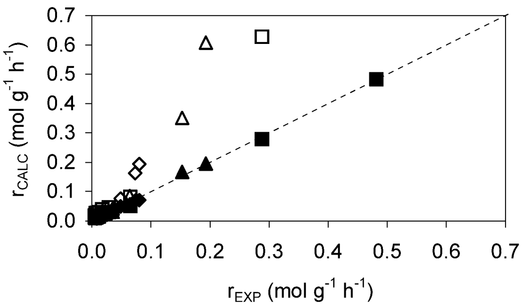

Fig. 12. Correspondence between experimental and calculated reaction rates at all temperatures using 1-butanol with model I-11 ($n = 3$). 60 °C (◆), 80 °C (▲), 100 °C (■) and model II-11 ($n = 3$). 60 °C (◇), 80 °C (△), 100 °C (□).

adsorption contribution terms. Consequently, only these eight models are considered in what follows.

Model I-5 has the fewest parameters, as shown in Table 5, and is the preferred candidate for the best model. Models I-11 and I-12 are similar to model I-5, but they include the contribution of alcohol and ether, respectively, in the adsorption terms. This contribution is about 10^{-6}% of the total, so it can be considered insignificant. Model I-15 includes the adsorption terms for all of the components, but convergence problems found during the calculation caused an excessive number of parameters, and thus this model was rejected. Therefore, adsorption of alcohol and desorption of ether seem to have no significant affect on the adsorption terms, due to their low concentration in the reaction medium.

Models II-5, II-11, II-12, and II-15 were rejected, because the fit of the experimental data showed large errors at short durations of reaction and low temperatures compared with models I-5, I-11, I-12, and I-15, as can be deduced from Fig. 12, which plots calculated reaction rates versus experimental reaction rates for 1-butanol and models I-11 and II-11. This finding implies that the 1 present in the denominator (the adsorption term) can be removed. Thus, free active centres are negligible compared with the other absorption terms of monomers and dimers, but they are not nil. Finally, model I-5 with $n = 3$ was selected as the best kinetic model; this model can be written as

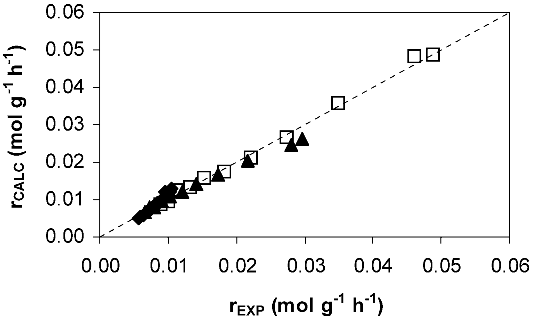

Fig. 13. Comparison of experimental and calculated reaction rates at all temperatures using ethanol with model I-5 ($n = 3$). 60 °C (◆), 80 °C (▲), 100 °C (□).

Table 6
Estimated parameters for every primary alcohol with kinetic model I-5 $n = 3$

Alcohol	b_1	b_2	d_1	d_2
MetOH	-2.642 ± 0.073	6372 ± 644	0.94 ± 0.17	492 ± 1372
EtOH	-3.681 ± 0.021	4086 ± 101	1.369 ± 0.024	-1649 ± 225
1-PropOH	-2.859 ± 0.036	5314 ± 212	0.995 ± 0.075	386 ± 664
1-ButOH	-1.6621 ± 0.0040	5924 ± 80	1.140 ± 0.020	649 ± 269
1-PentOH	-1.326 ± 0.023	4144 ± 292	1.131 ± 0.057	-1717 ± 527

Table 7
Correlation matrix of estimated parameters using 1-pentanol

	b_1	b_2	d_1	d_2
b_1	1	0.620	0.649	0.293
b_2	0.620	1	0.353	0.601
d_1	0.649	0.353	1	0.046
d_2	0.293	0.601	0.046	1

$$r = \frac{A a_{\mathrm{IA}}^2}{(a_{\mathrm{IA}} + B a_{\mathrm{DIA}})^3}, \tag{11}$$

with A and B following the temperature dependence demonstrated in Eqs. (9) and (10) respectively, where A is equal to $\hat{k}/K_{\mathrm{a,IA}}$ and B is the relative adsorption constant of diisoamylenes to isoamylenes. As example, results of the fit for ethanol are presented by plotting calculated reaction rates versus experimental reaction rates in Fig. 13. Similar plots were obtained using Eq. (11) as the kinetic model for the other primary alcohols, and thus the goodness of fit is satisfactory.

Table 6 presents parameter values with standard errors evaluated using the jackknife method [37] for each alcohol. The largest error is associated with the adsorption parameter d_2, with methanol and 1-propanol the systems with the greatest uncertainty. For each alcohol, correlation among parameters was computed using their correlation matrix. Results when using 1-pentanol are given in Table 7. As this table shows, all of the values of the matrix are <0.65, and thus it can be assumed that there is no significant correlation for the estimated parameters. Similar results where obtained for the other primary alcohol except methanol and 1-propanol, for which the most important correlation was found for the d_1 and d_2 parameters (<0.95).

Apparent activation energies and the adsorption enthalpy and entropy values for isoamylenes and diisoamylenes were

Table 8
Apparent dimerization activation energy and adsorption enthalpies and entropies of isoamylenes and diisoamylenes with their corresponding standard deviations

Alcohol	E_a (kJ mol^{-1})	$\Delta H_{DIA} - \Delta H_{IA}$ (kJ mol^{-1})	$\Delta S_{DIA} - \Delta S_{IA}$ (J K^{-1} mol^{-1})
MetOH	53 ± 5	4 ± 11	8 ± 1
EtOH	34.0 ± 0.8	-14 ± 2	11.4 ± 0.2
1-PropOH	44 ± 2	3 ± 6	8.3 ± 0.6
1-ButOH	49.3 ± 0.7	5 ± 2	9.5 ± 0.2
1-PentOH	34 ± 2	-14 ± 4	9.4 ± 0.5

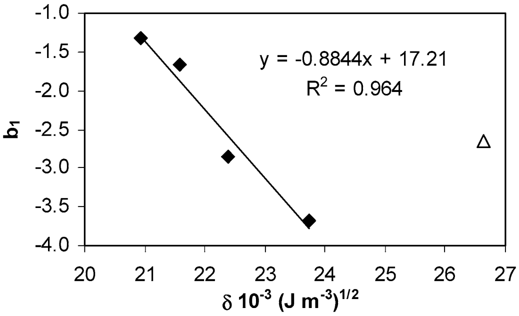

Fig. 14. Correlation between parameter b_1 and individual solubility parameter for primary alcohols at 80 °C. ROH (◆), methanol (△).

derived from the parameter values; results are given in Table 8. Because of the kinetic model chosen, adsorption enthalpies and entropies could not be estimated independently for diisoamylenes and isoamylenes, respectively, because only differences between them can be obtained. The d_1 values were all positive, suggesting higher values of ΔS_{IA} than of ΔS_{DIA}. However, for enthalpy values, the associated error was rather high, and the general trend cannot be predicted. Nonetheless, due to the higher molecular weight of dimers, it can be assumed that adsorption equilibrium constants are higher for diisoamylene than for isoamylenes. Unfortunately, no references values for adsorption terms can be found in the literature.

In contrast, our results for apparent activation energy were in the range of the values given in the literature. In the dimerisation of isobutene using acid ion-exchange resin, Honkela et al. [13] obtained a very low activation energy value, about 30 kJ mol^{-1}. Rehfinger and Hoffmann [38] also obtained an apparent activation energy value on the order of 40 kJ mol^{-1} using Amberlyst 15. They attributed this low activation energy to the influence of gel-phase diffusion. Hagg [39] reported an activation energy value of 66.6 kJ mol^{-1}, and Hauge et al. [33] obtained an apparent activation energy of 48 kJ mol^{-1}. Shah and Sharma [10] performed the sole study of isoamylenes dimerisation to date, using Amberlyst 15 as the acid-resin catalyst and evaluating the dimerisation activation energy, reporting a value of 48 kJ mol^{-1}.

Apparent activation energy values for dimerisation reaction showed no trend for the various alcohols used. However, parameter b_1 appeared to decrease with increasing molecular weight of the alcohol used. Consequently, it can be stated that the inhibition effect of the alcohol affects the preexponential factor of the Arrhenius equation. Fig. 14 shows the correlation between parameter b_1 and the individual solubility parameter for all of the alcohols used. As can be seen, there is a linear-type relation between the b_1 parameter and the individual solubility parameters of the alcohols, except for methanol. From these results, it can be concluded that the b_1 parameter of the dimerisation kinetic model depends linearly on the individual solubility parameter of the alcohol used, decreasing as the solubility parameter decreases; that is, the oligomerization process is faster with decreasing affinity of the alcohol for the catalyst.

4. Conclusion

The dimerisation of isoamylenes was carried out successfully in the presence of alcohol catalysed by the acid-exchange resin Amberlyst 35 in the temperature range of 60–100 °C. Selectivity values were between 62 and 95%, depending on the alcohol used. 3,4,4,5-Tetramethyl-2-hexene, 2,3,4,4-tetramethyl-1-hexene, and 3,4,5,5-tetramethyl-2-hexene were the main dimers found, representing $>70\%$ of the total dimers.

In this reaction, alcohols improved the selectivity for diisoamylenes. Trimers, tetramers, and cracking products were not detected under the assay conditions. Almost all of the primary and secondary alcohols reacted in the initial reaction stages to form ether, but with differing behaviours.

With primary alcohols, diisoamylenes selectivity and isoamylenes conversion increased with increasing carbon number atoms of alcohol and temperature. The best results were obtained for 1-pentanol at 100 °C, with a dimers selectivity of 95% and a yield of 82%. Methanol behaviour did not follow the general trends, being located between 1-propanol and 1-butanol. The dimethyl ether formation reduces the alcohol concentration increasing the dimers formation much more than could have been expected.

In contrast, secondary alcohols behaved differently from the primary alcohols. Isoamylenes conversion and diisoamylenes yields were much lower than with primary alcohols, due to the steric hindrances to ether formation; fewer isoamylenes react in etherification, and more free alcohol inhibits the diisoamylenes reaction. Confirming this hypothesis, in the presence of *tert*-butyl alcohol (the only tertiary alcohol tested), neither ether nor dimer formation was detected. Water in an isoamylenes/water molar ratio of $9/1$ was also tested, and TAA was the only product found.

A kinetic model based on activities in which the surface reaction between two adsorbed isoamylene molecules is the rate-limiting step has been found to describe the kinetic data for all of the primary alcohol systems quite well. The apparent activation energy for the dimerisation reaction with primary C_1–C_5 alcohols was in the range of 34–53 kJ mol^{-1}.

Nomenclature

2M1B	2-Methyl-1-butene;
2M2B	2-Methyl-2-butene;
A	$\hat{k}/K_{a,IA}$;
a_i	Activity of compound i;
ΔH_i	Molar enthalpy of compound i (kJ mol^{-1});

$\Delta H_{\mathrm{VAP},i}$	Molar vaporisation enthalpy of compound i ($\mathrm{kJ\,mol^{-1}}$);
ΔS_i	Molar entropy of compound i ($\mathrm{J\,K^{-1}\,mol^{-1}}$);
B	$K_{\mathrm{a,DIA}}/K_{\mathrm{a,IA}}$;
$b_1,\ b_2$	Kinetic model fitted parameters;
$d_1,\ d_2$	Kinetic model fitted parameters;
D4	2,3,4,4-Tetramethyl-1-hexene;
D6	3,4,5,5-Tetramethyl-2-hexene;
D7	3,4,4,5-Tetramethyl-2-hexene;
d_{b}	Average particle size (mm);
DIA	Diisoamylenes;
DME	Dimethyl ether;
d_{pore}	Pore diameter (Å);
δ_i	Individual solubility parameter of compound i $(\mathrm{J\,m^{-3}})^{1/2}$;
δ_{p}	Polymer solubility parameter $(\mathrm{J\,m^{-3}})^{1/2}$;
E_{a}	Molar activation energy ($\mathrm{kJ\,mol^{-1}}$);
$E_{\mathrm{coh},i}$	Cohesion energy of the structural group contribution i ($\mathrm{cal\,mol^{-1}}$);
ER	Eley–Rideal formalism;
ET	Ether;
ε	Dielectric constant;
GC/MS	Gas chromatograph coupled to mass selective spectrometer;
IA	Isoamylenes;
$\hat{k}$	Intrinsic rate coefficient ($\mathrm{mol\,g_{cat}^{-1}\,h^{-1}}$);
k_i	Apparent rate coefficient ($\mathrm{mol\,g_{cat}^{-1}\,h^{-1}}$);
K_i	Adsorption equilibrium constant of compound i;
LHHW	Langmuir–Hinshelwood–Hougen–Watson formalism;
MW	Molecular weight ($\mathrm{g\,mol^{-1}}$);
n	Number of active sites that take part in the surface reaction step;
n_i	Number of mols of compound i (mol);
OH	Alcohol;
r	Reaction rate ($\mathrm{mol\,g_{cat}^{-1}\,h^{-1}}$);
S_{DIA}	Diisoamylenes selectivity;
SQ	Sum of squares of residuals;
S_g	Catalyst surface area ($\mathrm{m^2\,g^{-1}}$ catalyst);
TAA	*tert*-Amyl alcohol (2-methyl-2-butanol);
TAEE	*tert*-Amyl ethyl ether (2-ethoxy-2-methyl butane);
TAME	*tert*-Amyl methyl ether (2-methoxy-2-methyl butane);
T_{ref}	Reference temperature, taken as 353 K;
TRIA	Triisoamylenes;
V_i	Molar volume of the structural group contribution i ($\mathrm{m^3\,mol^{-1}}$);
V_i^L	Liquid molar volume of compound i ($\mathrm{m^3\,mol^{-1}}$);
V_{g}	Catalyst pore volume ($\mathrm{cm^3\,g_{cat}^{-1}}$);
x_i	Molar fraction;
X_{IA}	Isoamylenes conversion;
X_{OH}	Alcohol conversion;
Y_{DIA}	Diisoamylenes yield.

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