

Liquid-phase synthesis of butyl *tert*-butyl ether catalysed by ion-exchange resins: kinetic modelling through in-depth model discrimination

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The kinetics of the butyl *tert*-butyl ether (BTBE) synthesis reaction over Amberlyst™ 35 as the catalyst has been studied at 303–356 K in the liquid phase in two different reactor systems: batch and fixed-bed. Internal mass transfer effects were detected at temperatures above 333 K for catalyst particles larger than 0.25 mm. Particles smaller than 0.08 mm did not show mass transfer limitations under the whole assayed temperature range. The best kinetic model has been searched among a large number of kinetic equations resulting from the systematic combination of all possible elementary reactions, adsorbed species, and rate-determining step based, according to the Langmuir-Hinshelwood-Hougen-Watson and the Eley-Rideal formalisms. The significance of the temperature effect on the kinetic parameters and of the effect of the interaction between the catalyst and the reaction medium on the reaction rate has been checked. All proposed kinetic equations have been fitted to experimental rate data free from mass transfer limitations. The model discrimination procedure has been based on mathematical and physicochemical criteria. The resulting kinetic model is consistent with an Eley-Rideal type mechanism where one 1-butanol molecule adsorbs on one active site of the catalyst, it reacts with one isobutene molecule from the liquid phase to give one adsorbed BTBE molecule, which finally desorbs. The rate-determining step is the surface reaction. The catalyst activity is affected by the resin-medium interaction. 1-Butanol adsorption on the catalyst is more exothermic than BTBE adsorption, and isobutene adsorption is negligible.

Introduction

Reaction between isobutene (IB) and 1-butanol (BuOH) produces butyl *tert*-butyl ether (BTBE) and can be catalysed by acidic ion-exchange resins. BTBE is an interesting alternative to methyl and ethyl *tert*-butyl ethers (MTBE and ETBE, respectively) to be used as oxygenated high-octane component in current gasoline formulations. Since 1-butanol can be obtained through fermentation of non-edible biomass,^{1,2} it would allow a reduction of the fossil fuel use and dependence in gasoline production. BTBE can be produced at industrial scale in the same reaction units than MTBE or ETBE, in contrast to the next generation biofuels (stemmed from lignocellulose, non-food materials, algal biomass, and energy crops grown on marginal lands) that these days are receiving more attention, but still being under development.^{3,4} Thus, BTBE is a feasible option to find cleaner alternatives to traditional automotive fuels in the short- and midterm. In the course of the addition of IB to BuOH to form BTBE, two side reactions can take place simultaneously depending on the operating conditions (Figure 1): isobutene hydration to form

tert-butyl alcohol (TBA), and isobutene dimerisation to form 2,4,4-trimethyl-1-pentene (TMP1) and 2,4,4-trimethyl-2-pentene (TMP2). Few literature references focused on BTBE synthesis can be found. The most significant works are devoted to the reaction thermodynamics and to the reactivity of primary alcohols with isobutene.^{5–9} No data have been found concerning the BTBE etherification kinetics, which is crucial for the potential production of BTBE in industrial units. Due to the reaction similarities, BTBE synthesis is expected to proceed through a mechanism similar to that of MTBE or ETBE and, therefore, reaction rates could be explained by means of

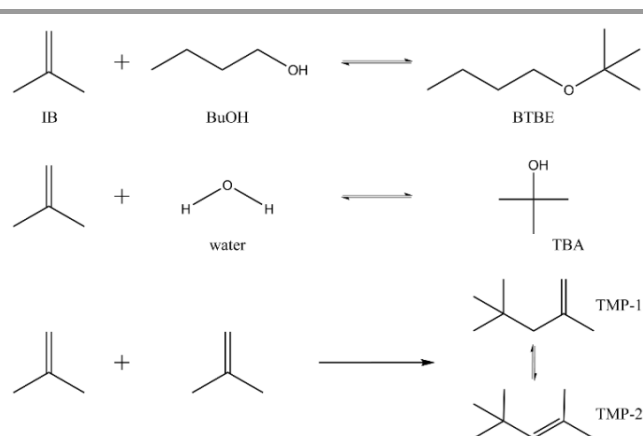


Fig. 1 Reaction scheme

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an analogous kinetic model.

MTBE and ETBE etherifications have been studied extensively throughout the years.¹⁰⁻¹⁶ More recently, the production of propyl tert-butyl ether (PTBE), the next ether in the analogous series, obtained by addition of 1-propanol to isobutene, has also been investigated.¹⁷ According to the literature, all these etherification reactions are reversible and exothermic, and the olefin-alcohol-ether mixtures behave strongly non-ideally. The reported reaction rate expressions are basically derived from Langmuir–Hinshelwood–Hougen–Watson (LHHW) or Eley–Rideal (ER) formalisms. It is expected that these reactions proceed through a similar mechanism. However, there are some discrepancies among the published works concerning mainly the number of active sites involved in the rate-determining step and the compounds that actually adsorb significantly on the resin. Possible reasons of such discrepancies are to have tested a limited number of candidate models, to have chosen a model among others with a similar goodness of fit, to have included non significant effects in the kinetic equation, or to have excluded significant effects. The present in-depth kinetic model discrimination study is motivated to assure that all plausible models are considered in the discrimination procedure, and that all parameters included in the proposed kinetic equation are significant.

Building the kinetic models

The candidate models of the BTBE synthesis have been developed from the LHHW and ER formalisms, because it is a heterogeneously catalysed system. The form of a given kinetic

equation is characterised by a set of compounds that adsorb on the catalyst, a set of elementary reactions, and the reaction step being the rate-determining step. Following the approach of our previous works,^{17,18} the search of the best kinetic model starts with the proposal of all kinetic equations to be tested. They have been obtained from the systematic combination of all possible rate-determining steps, adsorbed and non-adsorbed species on the catalyst, and significant or non-significant temperature dependence of every parameter, as well as the possible inclusion of a term accounting for the effect on rates of the interaction between the resin and the liquid mixture. The aim of this procedure is to avoid dismissing the *true model* (i.e., the one that most accurately describes the physicochemical reality of the etherification reaction) from the set of candidate models. The BTBE reacting mixture is assumed to be highly non-ideal, similarly to the analogous etherification systems. Therefore, activities were used instead of concentrations and estimated by means of the UNIFAC–Dortmund method, which is an enhancement of the widely known UNIFAC method.¹⁹

All proposed equations match the same general expression (Equation 1). Models differ in the developed form of each term in the kinetic equation (Table 1).

$$\left\{ \begin{array}{l} \text{reaction} \\ \text{rate} \end{array} \right\} = \left\{ \begin{array}{l} \text{kinetic} \\ \text{term} \end{array} \right\} \left\{ \begin{array}{l} \text{driving force} \\ \text{adsorption term} \end{array} \right\}^n \left\{ \begin{array}{l} \text{resin-medium} \\ \text{interaction} \end{array} \right\} \quad (1)$$

As seen in Table 1, the kinetic term is k' , an apparent kinetic coefficient, with the temperature dependence shown in Equation 2, since it consists of a product of the kinetic constant of the rate determining step (assumed to follow the

Table 1 Alternative forms of the kinetic equation terms (Equation 1). a stands for activity; b are binary-type variables (allowed values: 1 or 0), used to show generalised equation expressions; subscripts indices j and i refer to the involved compounds (BuOH, BTBE and IB). When the adsorption or desorption of a given compound is the reaction rate-determining step, its activity in Equation 7 or 8, if included, should be replaced by: $a_{IB} \rightarrow a_{BTBE}/a_{BuOH}$, $a_{BuOH} \rightarrow a_{BTBE}/a_{IB}$, $a_{BTBE} \rightarrow a_{IB} a_{BuOH}$

Term	Form	Observations	Equation
{kinetic term}	$k' = \exp\left(k'_1 + k'_T\left(\frac{1}{T} - \frac{1}{T_m}\right)\right)$	Arrhenius-type temperature dependence	(2)
{driving force}	$\left(a_{IB} a_{BuOH} - \frac{a_{BTBE}}{K_{eq}}\right)$	Rate-determining step: Surface reaction	(3)
	$\left(a_{BuOH} - \frac{a_{BTBE}}{K_{eq} a_{IB}}\right)$	Rate-determining step: BuOH desorption	(4)
	$\left(a_{IB} - \frac{a_{BTBE}}{K_{eq} a_{BuOH}}\right)$	Rate-determining step: IB adsorption	(5)
	$\left(a_{IB} a_{BuOH} - \frac{a_{BTBE}}{K_{eq}}\right)$	Rate-determining step: BTBE desorption	(6)
{adsorption term}	$\left(1 + \sum_j K_j a_j\right)$	$j =$ adsorbed compound	(7)
	$\left(a_i + \sum_{j \neq i} K_j a_j\right)$	$i, j =$ adsorbed compounds (derived from Eq.7 when the fraction of unoccupied sites is not significant)	(8)
{resin-medium interaction}	$\exp\left[b_p \frac{\bar{V}_M \phi_p^2}{RT} (\delta_M - \delta_p)^2\right]$	b_p is equal to 1 (interaction effect) or 0 (no interaction)	(9)

Arrhenius law), adsorption equilibrium constants and the chemical equilibrium constant (both assumed to follow the van't Hoff equation). The particular product depends on the considered mechanism. Parameters k'_1 and k'_T are the parameters to be fitted. The mean experimental temperature, T_m , is included to reduce the correlation between both parameters.

Regarding the driving force term, four different alternatives have been considered, given the considered rate-determining step for the global reaction process, i.e., surface reaction (Equation 3), 1-butanol adsorption (Equation 4), isobutene adsorption (Equation 5), and BTBE desorption (Equation 6). The parameter K_{eq} in Equations 3 to 6 stands for the chemical equilibrium constant for the synthesis of BTBE, whose value had been determined experimentally in a previous work:⁷

$$\ln K_{eq} = 870.35 - \frac{105348}{RT} - \frac{1425.42}{R} \ln T + \frac{11.0849}{2R} T - \frac{28.316 \times 10^{-3}}{6R} T^2 + \frac{2.1305 \times 10^{-5}}{12R} T^3 \quad (10)$$

In the adsorption term, two different alternatives have been considered: whether the fraction of unoccupied active sites in the catalyst surface affects the reaction rate (Equation 7) or the number of vacant active sites is non-significant (Equation 8, derived from Equation 7 by removing the unity summand, a required mathematical issue to avoid overparameterisation in the model fit). Parameters K_j in Equation 7 correspond to the actual adsorption equilibrium constant of each species j ($K_j = K_{a,j}$, except when the rate-determining step is a compound adsorption-desorption; then, for that compound, $K_{IB} = K_{a,IB}/K_{eq}$, or $K_{BuOH} = K_{a,BuOH}/K_{eq}$, or $K_{BTBE} = K_{a,BTBE} \cdot K_{eq}$). In Equation 8, parameters K_j are quotients of adsorption equilibrium constants ($K_j = K_{a,j}/K_{a,i}$, except when the rate-determining step is a compound adsorption-desorption; then, for that compound, $K_{IB} = K_{a,IB}/(K_{a,i} \cdot K_{eq})$, or $K_{BuOH} = K_{a,BuOH}/(K_{a,i} \cdot K_{eq})$, or $K_{BTBE} = K_{a,BTBE} \cdot K_{eq}/K_{a,i}$). For the sake of clarity, Table 2 lists all alternative forms of the adsorption term.

Since K_j parameters are adsorption equilibrium constants or a quotient thereof, their temperature dependence has been expressed according to the van't Hoff equation, as follows:

$$K_j = \exp \left[K_{1,j} + K_{T,j} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \quad (11)$$

In case that the temperature dependence of K_j is not significant, the parameter $K_{T,j}$ should be taken as equal to zero and, thus, $K_{1,j}$ is the only parameter to be fitted as the K_j estimate.

Table 2 Alternative forms of the adsorption term in a LHHW or ER kinetic model for the BTBE synthesis

no.	Adsorption term	no.	Adsorption term
1	1	8	$1 + K_{BuOH} a_{BuOH}$
2	a_{BuOH}	9	$1 + K_{BTBE} a_{BTBE}$
3	a_{IB}	10	$1 + K_{IB} a_{IB}$
4	$a_{BuOH} + K_{BTBE} a_{BTBE}$	11	$1 + K_{BuOH} a_{BuOH} + K_{BTBE} a_{BTBE}$
5	$a_{BuOH} + K_{IB} a_{IB}$	12	$1 + K_{BuOH} a_{BuOH} + K_{IB} a_{IB}$
6	$a_{BTBE} + K_{IB} a_{IB}$	13	$1 + K_{BTBE} a_{BTBE} + K_{IB} a_{IB}$
7	$a_{BuOH} + K_{BTBE} a_{BTBE} + K_{IB} a_{IB}$	14	$1 + K_{BuOH} a_{BuOH} + K_{BTBE} a_{BTBE} + K_{IB} a_{IB}$

The exponent n in the adsorption term is related to the number of active sites, or clusters of active sites, involved in the reaction mechanism. Values of n of 1, 2, and 3 are the most likely, according to previous kinetic studies on similar reaction systems.^{11-13,18,20-22}

The resin-medium interaction term (Equation 9) accounts for the effect of the reaction medium on the catalyst activity promoted by the difference between the solubility parameters of the reaction medium, δ_M , and the catalyst, δ_p , as observed in analogous reaction systems where the Hildebrand solubility parameter was used.^{15,23} The binary parameter b_p is equal to 0 if the effect of the interaction between the reaction medium and the catalyst is not significant, or equal to 1 if the interaction effect is significant; then, δ_p could be constant ($k_{TP} = 0$) or linearly temperature dependent ($k_{TP} \neq 0$):^{15,23}

$$\delta_p = k_{p1} + k_{pT} (T - T_m) \quad (12)$$

where both k_{p1} and k_{pT} are the fitting parameters, and the mean temperature T_m is included to reduce the correlation between both parameters. The remaining variables in Equation 9 are the molar volume of the liquid mixture \bar{V}_M , estimated from the species concentration and the temperature,²⁴⁻²⁶ the catalyst porosity in the swollen-state ϕ_p , the Hildebrand solubility parameter of the liquid mixture δ_M , estimated as described in the literature,²⁶ and the gas constant R .

As a result of all possible combinations of the proposed forms of the general kinetic expression terms, a total of 1404 different kinetic equations are obtained, to be fitted individually to the experimental data with the aim of obtaining the best kinetic model.

Experimental section

Materials

Reactants. 1-butanol (BuOH, >99.8% GC, Sigma-Aldrich), and isobutene (IB) as pure isobutene (>99.9% GC; Air Liquide) or in a synthetic C4 mixture (25%wt isobutene, 40%wt isobutane, 35%wt trans-2-butene; Abelló-Linde). Safety & hazards: all compounds are flammable, and experiments have been carried out under pressure.

Chemical standards used for chromatographic analysis. 2-methyl-2-propanol (TBA, >99.7% GC, Panreac), 2,4,4-trimethyl-1-pentene (TMP1, >98% GC, Sigma-Aldrich), 2,4,4-trimethyl-2-pentene (TMP2, >98% GC, Sigma-Aldrich). 1-tert-Butoxybutane (butyl tert-butyl ether, BTBE, >98% GC) was synthesized and purified in our laboratory.

Catalyst. Amberlyst™35 (A35, The Dow Chemical Company, now DuPont), a sulfonic macroreticular styrene-divinylbenzene resin. Its physical properties can be found elsewhere.¹⁷

Apparatus, procedure, and analysis

Experimental runs were carried out in two different reactor setups. Most of the experiments were run in a batch stirred tank reactor, the rest in a continuously operated fixed-bed catalytic reactor. The purpose of the experiments in the fixed-bed reactor was to validate the results in the batch reactor. The initial reaction mixture in batch experiments and the

reactor feed in continuous experiments did not contain BTBE. The batch reactor experiments were carried out at 2.0 MPa and at constant temperature, in the range of 318 to 356 K. Initial alcohol to isobutene molar ratio, $R^{\circ}_{\text{BuOH/IB}}$, varied between 1.0 and 2.0, and pure isobutene was used as reactant. The catalytic fixed-bed reactor experiments were carried out at 1.5 MPa and at constant temperature, between 303 and 333 K. The isobutene source was either pure isobutene or the synthetic C_4 mixture, with an equimolar alcohol-isobutene mixture at the reactor inlet ($R^{\circ}_{\text{BuOH/IB}} = 1.0$). GC analyses of samples of the reaction medium in both setups allowed quantifying the reactants and products concentrations. Each GC was equipped with a capillary column (HP-PONA 19091S-001, J&W Scientific, Santa Clara, US; 100% dimethylpolysiloxane, 50 m \times 0.20 mm \times 0.50 μm), helium was used as the carrier gas, and the oven temperature was set at 333 K.

A detailed description of the experimental setup and procedure can be found elsewhere.¹⁷ Further details on the calculation of experimental reaction rates are shown in Section A of the Electronic Supplementary Information, and a list of all experimental conditions and calculated reaction rates in Section B.

Results and discussion

Experimental results

In order to focus the present study on the BTBE synthesis kinetics, the experimental conditions were chosen to minimize the side reactions extension, based on previous works on similar systems.^{24,25} Since the amount of byproducts at the end of the experiments was always below 5%wt, they have been further dismissed from the kinetic analysis. Other side reactions, such as 1-butanol dehydration or further isobutene oligomerisation, were not detected. Obtaining a kinetic model from experimental data requires that the calculated reaction rates are intrinsic kinetics, that is, free from mass and heat transfer effects. The consequence of such effects is to increase the resistance of the global reaction process, so the measured reaction rate would be lower than the reaction rate in the absence of transfer effects. In heterogeneous catalysis, external transfer effects can take place between the fluid bulk phase and the catalyst surface, so they can be avoided by sufficiently reducing the thickness of the film surrounding the catalyst: by increasing the stirring speed in a batch reactor, or by increasing the fluid flow rate in a fixed-bed reactor. In the present reaction system, external mass transfer effects are avoided with stirring speeds of 750 rpm in the batch reactor, and flow rates of 0.031 g/s in the fixed-bed setup, as determined in previous works.^{16,26,27}

Internal mass transfer effects occur inside the catalyst. They become more noticeable at larger catalyst bead size and at higher reaction temperature. Assuming that there are not external transfer effects, internal mass transfer effects can be easily checked by plotting the logarithm of measured reaction rates obtained at the same composition vs the temperature

inverse (Figure 2). If a straight line is obtained, internal mass transfer effects are negligible. For this purpose, a set of experiments was carried out at different temperatures in both reactor systems, i.e., batch and fixed-bed, with the same reactants composition ($R^{\circ}_{\text{BuOH/IB}} = 1.0$) in the absence of product, and with 0.25–0.40 mm catalyst bead size (solid symbols in Figure 2). Experimental points deviate at temperature higher than 333 K ($1/T < 3.0 \cdot 10^{-3} \text{ K}^{-1}$ in Figure 2), what indicates a significant effect of mass transfer resistances above 333 K. Additional experiments at the same composition and at about 343K and 353K were carried out using smaller catalyst particles (< 0.08 mm, open symbols in Figure 2), which resulted well aligned with those obtained at lower temperatures, thus free of mass transfer resistance. In the further kinetic analysis, reaction rates affected by transfer effects were dismissed. From the slope of the solid straight line in Figure 2, the apparent activation energy, E_{app} , for the BTBE formation reaction has been estimated as $(67 \pm 2) \text{ kJ mol}^{-1}$. This value is in the same range of those quoted in the literature for similar reaction systems using A35.^{10,17,18,28–30}

Fitting kinetic models to experimental rate data

The first step in the search of the kinetic model was to fit each of the 1404 built equations to all experimental reaction rates free from mass transfer limitations at once by optimisation of the parameter values. The Levenberg-Marquardt algorithm was used to minimize the residual sum of squares (RSS), defined as:

$$RSS = \sum_i^N (r_{\text{exp}} - r_{\text{calc}})_i^2 \quad (13)$$

where r_{exp} is the experimental reaction rate, r_{calc} is the calculated value, and N is the number of experimental data ($N = 136$). Weighted residual sum of squares, with different

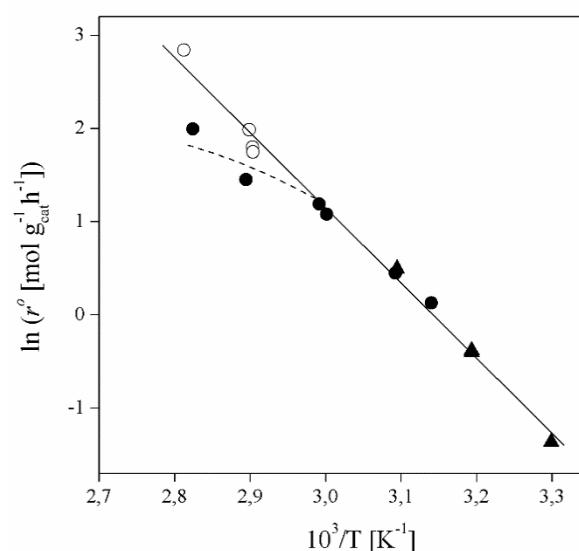


Fig. 2 Arrhenius plot of BTBE formation rates with $R^{\circ}_{\text{BuOH/IB}} = 1.0$ and pure isobutene. Solid symbols: catalyst bead size 0.25–0.40 mm, batch reactor (●) and fixed-bed reactor (▲). Open symbols: catalyst bead size < 0.08 mm, batch reactor (○)

weighting factors, were also tested, resulting in similar model ranking, distribution of residuals and parameter values. Therefore, further analysis refers to *RSS*.

The discrimination of kinetic models has been carried out by applying the following mathematical and physicochemical criteria to conservatively discard inadequate models:

1. Fitted kinetic equations presenting large *RSS* values do not provide a satisfactory description of all experimental kinetic data. Figure 3 shows the obtained *RSS*, where kinetic equations are ordered from lowest to highest *RSS* values. Consequently, equations presenting *RSS* values larger than 100 have been rejected.
2. In a suitable kinetic expression, all fitted parameter values should be statistically significant. Their standard error can be estimated from the covariance matrix of the parameters at the optimum. In this regard, models with at least one parameter with an associated standard uncertainty as large as the fitted value have been discarded.
3. Only kinetic equations producing positive values for the apparent activation energy, E_{ap} , can be accepted, because of the experimental evidence that the reaction rate increases with temperature (Figure 2), so models with positive fitted values for k'_T (Equation 2) are directly discarded. In addition, positive E_{ap} values clearly inconsistent with previously reported E_{ap} for similar reaction systems (in the range of 69.3 to 84 kJ mol⁻¹ for MTBE, ETBE, PTBE, and TAE syntheses over A35)^{10,17,18,28–30} can also be rejected. In particular, E_{ap} values well above 100 kJ mol⁻¹ (i.e., $k'_T < -13\ 000\ K^{-1}$) or below 45 kJ mol⁻¹ (i.e., $k'_T > -5\ 000\ K^{-1}$) have been rejected.
4. The adsorption process of a given compound on the resin is an exothermic process ($\Delta_a H_j^0 < 0$). For models with a significant number of unoccupied active sites (Equation 7), K_j is the adsorption equilibrium constant of compound j , and $K_{T,j}$ (Equation 11) corresponds to $-\Delta_a H_j^0/R$, thus it should be positive. Models whose range of any $K_{T,j}$ and its

uncertainty clearly falls in negative values have been discarded. Models where all active sites are considered as occupied (Equation 8) are not affected by this condition, because K_j is defined as a ratio of adsorption equilibrium constants and, therefore, $K_{T,j} = -(\Delta_a H_j^0 - \Delta_a H_i^0)/R$, so it can be either positive or negative.

5. From its definition, the resin solubility parameter δ_p must be positive. In models where δ_p is temperature dependent, and it is expected to decrease with temperature,¹⁹ so the range of k_{pT} and its uncertainty cannot fall completely in positive values. Models that do not meet these conditions have been discarded.
6. The Akaike Information Criterion (*AIC*), i.e., the relative likelihood of every model, can be used to rank a number of S kinetic equations from more to less plausible upon the basis of robust multimodel inferences.^{31,32} The following expressions apply in the Akaike procedure:

$$AIC = m \left[\ln \left(\frac{RSS}{m} \right) \right] + 2k \quad (14)$$

$$AICc = AIC + \frac{2k(k+1)}{m-k-1} \quad (15)$$

$$\Delta_i = AICc_i - AICc_{\min} \quad (16)$$

$$w_i = \frac{\exp \left(-\frac{\Delta_i}{2} \right)}{\sum_{s=1}^S \exp \left(-\frac{\Delta_s}{2} \right)} \quad (17)$$

where m is the number of experimental points, k is the number of parameters in the fitted equation, $AICc$ is the bias-corrected reduced *AIC* for situations with low m/k values (i.e., $m/k < 40$, like in the present case), Δ_i is an estimator of the level of empirical support for a given model (the lowest Δ_i value corresponds to the most plausible candidate model), $AICc_{\min}$ is the minimum *AICc* among all models, and w_i accounts for the relative likelihood of model i out of the S candidate models.^{31,32} Lower Δ_i and higher w_i values are an indication of a better model.

The consideration of the mathematical and physicochemical criteria applied in a conservative way allowed to reduce the number of candidate equations from 1404 to only a few. The best ranked models, their optimal parameter values and ranking criteria (*RSS*, Δ_i , and w_i) are listed in Table 3, sorted from best to worst.

A model is considered as substantially supported by empirical evidence when its Δ_i value is lower than 3.^{31,32} The first ranked model (Model 49) stands out as the most plausible one, because of its high probability ($w_{\text{Model49}} = 93.7\%$) and $\Delta_{\text{Model49}} = 0$ value, far from the second ranked model ($w_{\text{Model48}} = 2.1\%$, $\Delta_{\text{Model48}} = 8$). In addition, some common features are observed among the first ranked models that support the choice of Model 49: i) none of the equations includes the isobutene contribution in the adsorption term ($\Sigma w_i = 0$), whereas the 1-butanol and BTBE effect appears in the adsorption term for most of the candidate equations ($\Sigma w_i = 0.993$ and $\Sigma w_i \approx 1$, respectively); ii) there is a high probability that the first summand in the adsorption term is

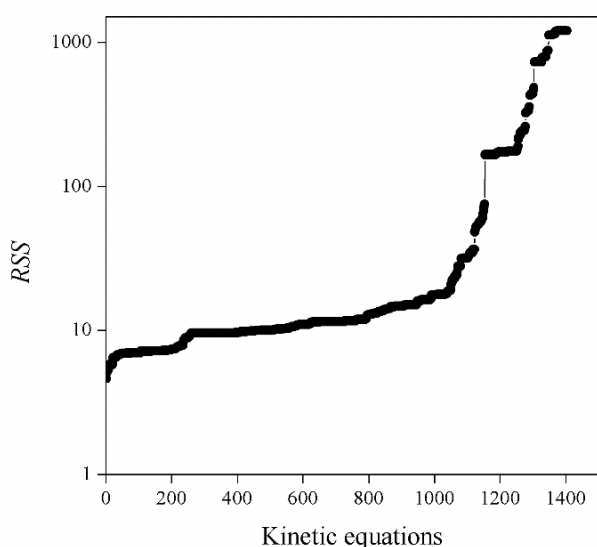


Fig. 3 *RSS* values of fitted kinetic equations.

Table 3 Parameter values for the best fitting BTBE kinetic equations. A “–” sign indicates that the related effect is not included in the model.

Model no.	k' (mol/g h)		{driving force} ^a	{adsorption term}						δ_p (MPa ^{1/2})		RSS	Δ_i	w_i		
	k'_1	k'_T		1^{st} Ads ^b	$K_{1,BuOH}$	$K_{T,BuOH}$	$K_{1,IB}$	$K_{T,IB}$	$K_{1,BTBE}$	$K_{T,BTBE}$	n				k_{p1}	k_{pT}
49	0.320	-9171	(a)	a_{BuOH}	–	–	–	–	-1.119	-4039	1	24.51	–	6.497	0	0.937
48	0.395	-9031	(a)	a_{BuOH}	–	–	–	–	-0.540	–	1	24.18	–	6.981	8	0.021
290	1.917	-8986	(a)	1	-0.334	–	–	–	-0.810	–	3	24.61	–	6.948	9	0.010
173	2.072	-8994	(a)	1	0.332	–	–	–	-0.144	–	2	24.53	–	6.954	9	0.009
56	3.408	-9019	(a)	1	2.951	–	–	–	2.491	–	1	24.32	–	6.977	10	0.007
174	2.230	-8498	(a)	1	0.495	530	–	–	-0.096	–	2	24.50	–	6.920	11	0.004
978	0.412	-9033	(c)	1	–	–	–	–	-1.178	–	3	24.06	–	7.155	11	0.004
291	1.975	-8707	(a)	1	-0.272	308	–	–	-0.804	–	3	24.60	–	6.933	11	0.004
861	0.428	-9042	(c)	1	–	–	–	–	-0.761	–	2	23.94	–	7.185	11	0.003
166	0.088	-9318	(a)	a_{BuOH}	–	–	–	–	-1.655	-3039	2	22.56	–	7.327	16	<0.001
751	0.121	-9346	(c)	a_{BuOH}	–	–	–	–	-0.981	-3650	1	22.24	–	7.429	18	<0.001
759	17.46	-6477	(c)	1	17.34	2813	–	–	16.51	–	1	22.36	–	7.454	21	<0.001
165	0.144	-9196	(a)	a_{BuOH}	–	–	–	–	-1.207	–	2	22.26	–	7.749	22	<0.001
750	0.182	-9218	(c)	a_{BuOH}	–	–	–	–	-0.451	–	1	21.89	–	7.888	24	<0.001
2	1.170	-9770	(a)	1	–	–	–	–	–	–	1	20.06	–	9.566	48	<10 ⁻¹⁰

^a Form of the driving force: (a) surface reaction (Equation 3) and (c) isobutene adsorption (Equation 5). ^b First summand of the adsorption term

a_{BuOH} ($\Sigma w_i = 0.959$) in front of being 1 ($\Sigma w_i = 0.041$); iii) the exponent in the adsorption term is likely to be $n = 1$ ($\Sigma w_i = 0.966$); iv) the resin-medium interaction term is suitable ($\Sigma w_i \approx 1$); and v) the most likely rate-determining step is the surface reaction ($\Sigma w_i = 0.993$; driving force type (a) in Table 3). Figure 4 shows the adequacy of the prediction of experimental reaction rates by Model 49, the low sensitivity of the model output due to the uncertainty of the fitted parameters and the randomly distributed residuals for each experimental point. Model 49 predicts simultaneously well the experimental data obtained in both batch and fixed-bed reactor systems.

Selected kinetic model

The proposed kinetic equation Model 49, its parameter estimates, and their standard error are:

$$r = k' \frac{\left(a_{IB} a_{BuOH} - \frac{a_{BTBE}}{K_{Eq}} \right)}{a_{BuOH} + K_{BTBE} a_{BTBE}} \exp \left(\frac{\bar{V}_M \phi_p^2}{RT} (\delta_M - \delta_p)^2 \right) \quad (18)$$

where:

$$k' \left[\frac{\text{mol}}{\text{g h}} \right] = \exp \left[(0.32 \pm 0.02) - (9.17 \pm 0.03) \cdot 10^3 \left(\frac{1}{T} - \frac{1}{329.4} \right) \right]$$

$$K_{BTBE} = \frac{K_{a,BTBE}}{K_{a,BuOH}} = \exp \left[-(1.12 \pm 0.06) - (4.0 \pm 0.3) \cdot 10^3 \left(\frac{1}{T} - \frac{1}{329.4} \right) \right]$$

$$\delta_p \left[\text{MPa}^{1/2} \right] = (24.51 \pm 0.18)$$

This expression derives from an ER reaction mechanism consisting of the following steps: i) one molecule of 1-butanol adsorbs on a resin active site (or cluster of active sites); ii) it reacts with one isobutene molecule from solution to give one molecule of adsorbed BTBE; and iii) the BTBE molecule

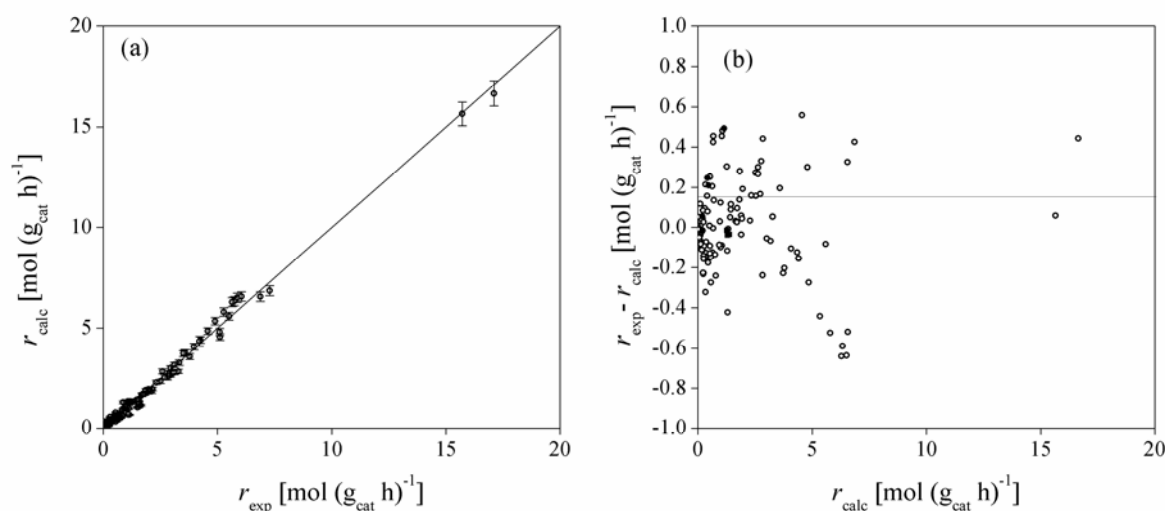


Fig. 4 Comparison between experimental and calculated BTBE reaction rates for Model 49 (a), and residuals distribution (b). Symbols: Experimental rates obtained in the batch reactor (\circ), in the fixed-bed reactor using the C_4 as isobutene source (\bullet), and in the fixed-bed reactor using pure isobutene (\blacksquare). Error bars in (a) correspond to the sensitivity (standard deviation) of the model output due to the parameters uncertainty (see section C in Electronic Supplementary Information).

desorbs. The surface reaction step is the rate-limiting step of the overall reaction process. This mechanism is in agreement with previous works on analogous reaction systems, e.g., syntheses of MTBE,²⁸ ETBE,¹⁵ or PTBE.¹⁰

Since the exponent of the adsorption term n is 1, is equal to the apparent kinetic coefficient k' is equal to the intrinsic kinetic constant k , as follows:

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

and, therefore, the true activation energy of the reaction E_a is equal to the apparent one E_{ap} . Since $k'_T = -(9.17 \pm 0.03) \cdot 10^3 \text{ K}$, then $E_a = (76.3 \pm 0.3) \text{ kJ mol}^{-1}$.

The parameter K_{BTBE} in the adsorption term of Equation 18 corresponds to the ratio between the adsorption equilibrium constants of BTBE and 1-butanol, i.e., $K_{a,\text{BTBE}}/K_{a,\text{BuOH}}$. It is related to adsorption thermodynamic properties as follows:

$$\begin{aligned} \ln K_{\text{BTBE}} &= \ln \frac{K_{a,\text{BTBE}}}{K_{a,\text{BuOH}}} = \frac{-(\Delta_a G_{\text{BTBE}}^{\circ} - \Delta_a G_{\text{BuOH}}^{\circ})}{RT} \\ &= \frac{-(\Delta_a H_{\text{BTBE}}^{\circ} - \Delta_a H_{\text{BuOH}}^{\circ})}{RT} + \frac{\Delta_a S_{\text{BTBE}}^{\circ} - \Delta_a S_{\text{BuOH}}^{\circ}}{R} \end{aligned} \quad (20)$$

where $K_{a,\text{BTBE}}$ is the adsorption equilibrium constant of BTBE, and $\Delta_a G_j^{\circ}$, $\Delta_a H_j^{\circ}$ and $\Delta_a S_j^{\circ}$ are the adsorption Gibbs free energy, enthalpy and entropy changes of compound j , respectively. The adsorption enthalpy and entropy changes of individual compounds cannot be obtained from the parameter estimates of the kinetic model. Instead, parameters provide differences between BTBE and 1-butanol adsorption enthalpy and entropy changes: $\Delta_a H_{\text{BTBE}}^{\circ} - \Delta_a H_{\text{BuOH}}^{\circ} = (34 \pm 2) \text{ kJ mol}^{-1}$ and $\Delta_a S_{\text{BTBE}}^{\circ} - \Delta_a S_{\text{BuOH}}^{\circ} = (93 \pm 7) \text{ J mol}^{-1} \text{ K}^{-1}$. Consequently, 1-butanol adsorption on the resin is more exothermic than BTBE adsorption, and the entropic loss due to adsorption for 1-butanol is larger than for BTBE. A positive difference between the adsorption enthalpies is consistent with values reported in a previous work on adsorption equilibrium of BTBE and 1-butanol on A35, but in the gas phase: $\Delta_a H_{\text{BTBE}}^{\circ} = -21.8 \text{ kJ mol}^{-1}$ and $\Delta_a H_{\text{BuOH}}^{\circ} = -41.8 \text{ kJ mol}^{-1}$.³³ The estimate of the Hildebrand solubility parameter of A35, δ_p (Equation 12), can be considered as constant in the assayed temperature range and equal to $(24.51 \pm 0.18) \text{ MPa}^{1/2}$. This value is slightly larger than the published δ_p values for this catalyst in similar reaction systems, also being constant: $(20.5 \pm 0.3) \text{ MPa}^{1/2}$ in the PTBE synthesis,¹⁰ $(20.9 \pm 2.0) \text{ MPa}^{1/2}$ in the ETBE synthesis,²⁹ and $(21.16 \pm 0.12) \text{ MPa}^{1/2}$ in the simultaneous synthesis of ETBE and TAEE.¹⁷ However, it fully agrees with the Hildebrand solubility parameter estimated by means of the Hoftyzer and van Krevelen group contribution method,³⁴ resulting in $\delta_p = 25.45 \text{ MPa}^{1/2}$ at 298 K. The Hansen solubility parameter, which is considered as a refinement of the Hildebrand parameter, has also been estimated from group contribution,³³ resulting in $\delta_p = 25.54 \text{ MPa}^{1/2}$ at 298 K. With the aim of checking whether the choice of the selected model, and thus the reaction mechanism, would be affected in case that δ_p were roughly estimated, all kinetic equations have been fitted again to experimental rate data, but taking δ_p as a fixed value equal to $20.85 \text{ MPa}^{1/2}$ (the average of the estimated values quoted in literature)^{10,17,29} if appearing in the

model. The best ranked models obtained with this constraint are listed in Table S2 (section D in Electronic Supplementary information). Globally, the residual sum of squares (RSS) is now slightly higher due to the reduction of the degrees of freedom of the fit, but the group of best ranked models is coincident with the non-restricted case, and Model 49 is again the most plausible one ($w_{\text{Model49}} = 44.7\%$, followed by $w_{\text{Model166}} = 8.9\%$). This result reinforces the choice of the selected kinetic equation Model 49 as the best one.

Conclusions

The kinetics of the liquid-phase etherification reaction of isobutene with 1-butanol to produce butyl *tert*-butyl ether using Amberlyst™35 as the catalyst has been studied at 303–356 K in the liquid phase. Significant internal mass transfer limitations have been detected at temperatures above 333 K using 0.25–0.40 mm catalyst bead size, but this effect was not noticeable for bead size smaller than 0.08 mm. Reaction rates free from mass transfer effects obtained in two reaction setups (a batch reactor and a differential tubular reactor) have been used to fit a large number of candidate kinetic equations, each derived from a different mechanism and rate-determining step, based on the Langmuir-Hinshelwood-Hougen-Watson and Eley-Rideal formalisms. The possible effects of the reaction medium on the catalyst activity, and of the temperature on the parameters of the kinetic equations have also been considered. Discrimination of models has been accomplished by applying mathematical and physicochemical criteria in a conservative manner. The Akaike Information Criterion has been used to rank the reliability of the kinetic models. The best model is derived from an Eley-Rideal type mechanism, where one molecule of 1-butanol adsorbed on one active site reacts with one isobutene molecule from the liquid phase to form one BTBE molecule that, finally, desorbs. The rate-determining step is the surface reaction. The adsorption of 1-butanol on the resin is more exothermic than BTBE adsorption. The interaction between the reaction medium and the resin has a significant effect on the catalytic activity.

Conflicts of interest

There are no conflicts to declare.

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Liquid-phase synthesis of butyl *tert*-butyl ether catalysed by ion-exchange resins: kinetic modelling through in-depth model discrimination

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Electronic Supplementary Information (ESI)

A. Calculation of experimental reaction rates

In the present work, two different reactor setups have been used: a fixed-bed reactor and a batch reactor. In the fixed-bed reactor, one experimental run provides only one measured reaction rate, calculated from the composition change between the reactor inlet and at outlet at the steady state. Since the reactor operated under differential regime, i.e., at low conversion, the reaction rate can be assumed to be constant along the reactor. The experimental isobutene consumption rate was calculated as follows:

$$-r_{\text{IB}} = \frac{F_{\text{IB}}^0 (X_{\text{IB,outlet}} - X_{\text{IB,inlet}})}{W_{\text{cat}}} \quad (\text{S1})$$

where F_{IB}^0 is the isobutene molar flow rate at null conversion, $X_{\text{IB,outlet}}$ is the isobutene conversion at the reactor outlet, and $X_{\text{IB,inlet}}$ is the inlet isobutene conversion, and W_{cat} is the mass of dry catalyst in the reactor bed. In particular, the reactor inlet stream was only composed of reactants and, therefore, $X_{\text{IB,inlet}} = 0$.

In the batch reactor system, the evolution of the reaction medium composition was obtained from samples taken at different times. For each experimental run, the progress of the isobutene molar content was used to fit an empirical function that allowed calculating its slope at the sampled times, which is related with the experimental formation rate of compound j , r_j , as follows:

$$r_j = \frac{1}{W_{\text{cat}}} \left(\frac{dn_j}{dt} \right) \quad (\text{S3})$$

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

As an illustrative example, Figure S1 shows the result of two different experimental runs carried out in the batch reactor system and how the experimental reaction rate was calculated at instants where samples were taken.

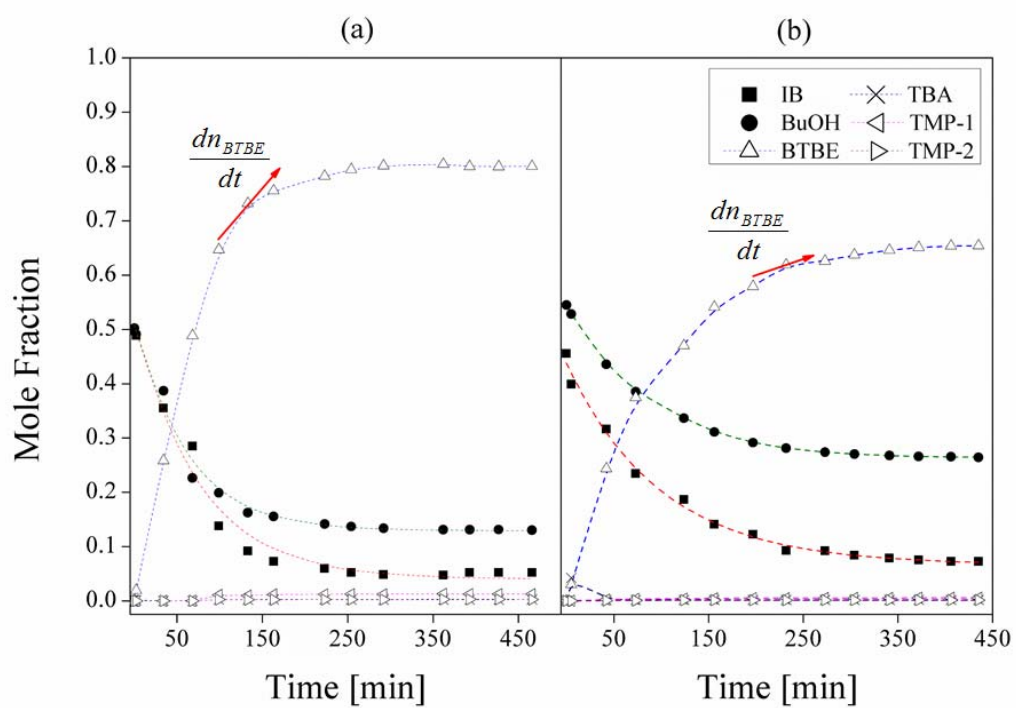


Fig. S1 Experimental mole evolution obtained in the batch reactor system under two different conditions: (a) $T = 323.4 \text{ K}$, $R^0_{\text{BuOH/IB}} = 1.0$; (b) $T = 343.5 \text{ K}$, $R^0_{\text{BuOH/IB}} = 1.2$. Dashed lines correspond to fitted empirical equation. Red arrows represent the derivative with respect to time, used to calculate experimental reaction rates at those instants.

B. Experimental conditions and calculated reaction rates

Table S1. Experimental conditions and calculated experimental rates considered in the fit of the kinetic equations

Exper. setup	T (K)	t (min)	W _{cat} (g)	Mole fraction									r _{BTBE} [mol/g h]		
				x _{IB}	x _{BuOH}	x _{BTBE}	x _{TBA}	x _{TMP-1}	x _{TMP-2}	x _{i-butane}	x _{trans-2-butene}	x _{cis-2-butene}			
Plug-flow reactor	333.15	—	0.0810	0.203	0.135	0	0	0	0	0	0.332	0.328	0.002	1.129	
	333.15	—	0.0420	0.193	0.180	0	0	0	0	0	0.313	0.313	0.002	1.031	
	333.15	—	0.0421	0.190	0.193	0	0	0	0	0	0.311	0.305	0.002	1.212	
	313.15	—	0.1685	0.488	0.512	0	0	0	0	0	0	0	0	0.666	
	313.15	—	0.2080	0.520	0.480	0	0	0	0	0	0	0	0	0.680	
	303.15	—	0.0440	0.548	0.452	0	0	0	0	0	0	0	0	0.255	
	323.15	—	0.0217	0.490	0.510	0	0	0	0	0	0	0	0	1.640	
Batch reactor	323.35	0	0.7200	0.498	0.502	0	0	0	0	0	0	0	0	1.561	
	323.35	2		0.488	0.491	0.019	0.001	0	0	0	0	0	0	0	1.506
	323.35	34		0.355	0.387	0.258	0.000	0	0	0	0	0	0	0	0.844
	323.35	68		0.285	0.226	0.489	0.000	0	0	0	0	0	0	0	0.457
	323.35	99		0.138	0.199	0.647	0.002	0.011	0.002	0	0	0	0	0	0.261
	323.35	133		0.092	0.162	0.732	0.002	0.010	0.002	0	0	0	0	0	0.141
	323.35	163		0.073	0.155	0.756	0.002	0.012	0.002	0	0	0	0	0	0.082
	323.35	223		0.059	0.142	0.782	0.002	0.012	0.002	0	0	0	0	0	0.028
	323.35	254		0.052	0.137	0.794	0.002	0.012	0.002	0	0	0	0	0	0.016
	323.35	292		0.048	0.134	0.801	0.002	0.012	0.003	0	0	0	0	0	0.008
	323.35	362		0.047	0.131	0.804	0.002	0.013	0.003	0	0	0	0	0	0.002
	323.35	393		0.052	0.131	0.800	0.002	0.012	0.003	0	0	0	0	0	0.001
	323.35	427		0.052	0.131	0.800	0.002	0.013	0.003	0	0	0	0	0	0.001
	323.35	466		0.052	0.130	0.800	0.002	0.012	0.003	0	0	0	0	0	0.000
Batch reactor	318.45	0	0.5100	0.492	0.508	0	0	0	0	0	0	0	0	1.261	
	318.45	3		0.489	0.503	0.008	0.001	0	0	0	0	0	0	0	1.217
	318.45	33		0.403	0.436	0.150	0.002	0.009	0.002	0	0	0	0	0	0.853
	318.45	63		0.316	0.392	0.268	0.002	0.017	0.004	0	0	0	0	0	0.599
	318.45	93		0.246	0.343	0.379	0.002	0.024	0.005	0	0	0	0	0	0.420
	318.45	125		0.208	0.311	0.445	0.002	0.028	0.006	0	0	0	0	0	0.288
	318.45	156		0.180	0.272	0.509	0.002	0.031	0.007	0	0	0	0	0	0.199
	318.45	187		0.143	0.252	0.564	0.002	0.032	0.007	0	0	0	0	0	0.138
	318.45	217		0.120	0.229	0.608	0.002	0.033	0.007	0	0	0	0	0	0.097
	318.45	248		0.107	0.219	0.631	0.002	0.034	0.007	0	0	0	0	0	0.067
	318.45	287		0.087	0.193	0.684	0.002	0.028	0.006	0	0	0	0	0	0.042
	318.45	313		0.068	0.196	0.692	0.002	0.035	0.008	0	0	0	0	0	0.031
	318.45	345		0.058	0.190	0.707	0.002	0.035	0.008	0	0	0	0	0	0.021
	318.45	450		0.043	0.184	0.727	0.002	0.036	0.008	0	0	0	0	0	0.006
	318.45	480		0.041	0.179	0.734	0.002	0.036	0.008	0	0	0	0	0	0.004
	318.45	547		0.039	0.179	0.736	0.002	0.037	0.008	0	0	0	0	0	0.002
	318.45	580		0.037	0.177	0.740	0.002	0.035	0.008	0	0	0	0	0	0.001
318.45	621	0.035	0.177	0.742	0.002	0.036	0.008	0	0	0	0	0	0.001		
Batch reactor	344.95	0	0.1296	0.492	0.508	0	0	0	0	0	0	0	0	8.116	
	344.95	3		0.480	0.501	0.017	0.001	0.001	0	0	0	0	0	0	7.653
	344.95	19		0.396	0.463	0.124	0.001	0.013	0.003	0	0	0	0	0	5.593
	344.95	35		0.329	0.420	0.225	0.001	0.020	0.005	0	0	0	0	0	4.088
	344.95	51		0.261	0.381	0.325	0.001	0.025	0.007	0	0	0	0	0	2.988
	344.95	66		0.212	0.356	0.395	0.001	0.028	0.007	0	0	0	0	0	2.227
	344.95	82		0.168	0.341	0.452	0.002	0.029	0.008	0	0	0	0	0	1.628
	344.95	100		0.149	0.313	0.498	0.001	0.031	0.008	0	0	0	0	0	1.144
	344.95	116		0.118	0.298	0.543	0.001	0.031	0.008	0	0	0	0	0	0.836
	344.95	138		0.094	0.286	0.577	0.002	0.033	0.009	0	0	0	0	0	0.543
	344.95	168		0.084	0.281	0.591	0.001	0.033	0.009	0	0	0	0	0	0.302
	344.95	187		0.071	0.288	0.599	0.001	0.033	0.008	0	0	0	0	0	0.208
	344.95	220		0.074	0.274	0.608	0.001	0.033	0.009	0	0	0	0	0	0.109

Exper. setup	T (K)	t (min)	W _{cat} (g)	Mole fraction									r _{BTBE} [mol/g h]	
				x _{IB}	x _{BuOH}	x _{BTBE}	x _{TBA}	x _{TMP-1}	x _{TMP-2}	x _{i-butane}	x _{trans-2-butene}	x _{cis-2-butene}		
	344.95	237		0.073	0.273	0.611	0.001	0.033	0.009	0	0	0	0.078	
	344.95	254		0.065	0.268	0.622	0.001	0.035	0.009	0	0	0	0.056	
Batch reactor	344.35	0	0.0353	0.478	0.522	0	0	0	0	0	0	0	7.434	
	344.35	4		0.476	0.521	0.001	0.002	0	0	0	0	0	0	7.273
	344.35	20		0.451	0.517	0.009	0.022	0	0	0	0	0	0	6.664
	344.35	37		0.431	0.504	0.033	0.031	0	0	0	0	0	0	6.073
	344.35	53		0.409	0.488	0.064	0.038	0	0	0	0	0	0	5.565
	344.35	70		0.388	0.472	0.097	0.042	0.001	0	0	0	0	0	5.071
	344.35	86		0.371	0.459	0.125	0.043	0.001	0	0	0	0	0	4.646
	344.35	110		0.356	0.442	0.155	0.045	0.001	0	0	0	0	0	4.075
	344.35	127		0.326	0.431	0.193	0.048	0.001	0	0	0	0	0	3.714
	344.35	143		0.320	0.422	0.208	0.047	0.002	0	0	0	0	0	3.403
	344.35	159		0.291	0.414	0.240	0.053	0.001	0	0	0	0	0	3.118
	344.35	176		0.278	0.403	0.262	0.054	0.002	0	0	0	0	0	2.841
	344.35	194		0.265	0.393	0.285	0.055	0.002	0	0	0	0	0	2.575
	344.35	211		0.261	0.389	0.293	0.054	0.002	0	0	0	0	0	2.346
	344.35	229		0.236	0.384	0.318	0.060	0.002	0	0	0	0	0	2.127
	344.35	251		0.232	0.375	0.332	0.058	0.003	0.001	0	0	0	0	1.886
	344.35	268		0.218	0.372	0.346	0.060	0.003	0.001	0	0	0	0	1.718
	344.35	285		0.213	0.369	0.354	0.061	0.003	0.001	0	0	0	0	1.566
344.35	303	0.195	0.368	0.374	0.059	0.003	0.001	0	0	0	0	1.419		
344.35	318	0.193	0.361	0.379	0.062	0.004	0.001	0	0	0	0	1.308		
Batch reactor	355.55	0	0.1238	0.503	0.497	0	0	0	0	0	0	0	17.464	
	355.55	2		0.495	0.491	0.014	0.001	0	0	0	0	0	0	16.042
	355.55	33		0.259	0.309	0.422	0.002	0.006	0.002	0	0	0	0	4.300
	355.55	51		0.181	0.249	0.558	0.002	0.007	0.002	0	0	0	0	2.002
	355.55	67		0.154	0.224	0.609	0.002	0.008	0.002	0	0	0	0	1.015
	355.55	83		0.134	0.213	0.641	0.002	0.008	0.002	0	0	0	0	0.514
	355.55	101		0.133	0.209	0.645	0.002	0.008	0.002	0	0	0	0	0.239
	355.55	118		0.127	0.207	0.652	0.002	0.009	0.002	0	0	0	0	0.116
	355.55	134		0.122	0.207	0.657	0.002	0.009	0.003	0	0	0	0	0.059
	355.55	154		0.128	0.208	0.650	0.002	0.009	0.002	0	0	0	0	0.025
	355.55	175		0.130	0.212	0.645	0.002	0.009	0.002	0	0	0	0	0.010
	355.55	194		0.126	0.210	0.649	0.002	0.010	0.003	0	0	0	0	0.005
	355.55	232		0.124	0.213	0.648	0.002	0.010	0.003	0	0	0	0	0.001
	Batch reactor	334.25		0	0.3530	0.500	0.500	0	0	0	0	0	0	0
334.25		3	0.492	0.496		0.012	0	0	0	0	0	0	0	3.206
334.25		34	0.353	0.372		0.266	0.001	0.007	0.001	0	0	0	0	1.773
334.25		65	0.249	0.298		0.439	0.002	0.010	0.002	0	0	0	0	0.980
334.25		98	0.181	0.235		0.568	0.002	0.011	0.003	0	0	0	0	0.522
334.25		128	0.135	0.194		0.654	0.002	0.012	0.003	0	0	0	0	0.294
334.25		165	0.139	0.143		0.710	0.000	0.007	0.000	0	0	0	0	0.145
334.25		197	0.114	0.133		0.745	0.000	0.007	0.001	0	0	0	0	0.079
334.25		229	0.085	0.148		0.749	0.002	0.014	0.003	0	0	0	0	0.043
334.25		286	0.078	0.143		0.760	0.002	0.014	0.003	0	0	0	0	0.014
334.25		365	0.079	0.139		0.763	0.002	0.014	0.003	0	0	0	0	0.003
334.25		413	0.075	0.140		0.766	0.002	0.014	0.003	0	0	0	0	0.001
334.25		440	0.077	0.140		0.764	0.002	0.014	0.003	0	0	0	0	0.001
334.25		470	0.079	0.140		0.762	0.002	0.014	0.003	0	0	0	0	0.000
Batch reactor	333.15	0	0.2060	0.501	0.499	0	0	0	0	0	0	0	3.347	
	333.15	1		0.500	0.499	0.001	0	0	0	0	0	0	0	3.306
	333.15	33		0.404	0.431	0.146	0.001	0.015	0.003	0	0	0	0	2.215
	333.15	67		0.303	0.372	0.290	0.001	0.027	0.007	0	0	0	0	1.447
	333.15	99		0.244	0.325	0.386	0.001	0.035	0.009	0	0	0	0	0.970
	333.15	131		0.198	0.289	0.464	0.001	0.039	0.010	0	0	0	0	0.650

Exper. setup	T (K)	t (min)	W _{cat} (g)	Mole fraction									r _{BTBE} [mol/g h]
				X _{IB}	X _{BuOH}	X _{BTBE}	X _{TBA}	X _{TMP-1}	X _{TMP-2}	X _{i-butane}	X _{trans-2-butene}	X _{cis-2-butene}	
	333.15	163		0.164	0.261	0.523	0.001	0.042	0.010	0	0	0	0.435
	333.15	199		0.142	0.236	0.565	0.001	0.044	0.011	0	0	0	0.278
	333.15	231		0.120	0.222	0.601	0.001	0.046	0.011	0	0	0	0.186
	333.15	275		0.105	0.208	0.627	0.001	0.048	0.011	0	0	0	0.107
	333.15	309		0.091	0.199	0.651	0.002	0.046	0.012	0	0	0	0.070
Batch reactor	344.45	0	0.1200	0.490	0.510	0	0	0	0	0	0	0	7.125
	344.45	2		0.488	0.506	0.006	0	0	0	0	0	0	6.895
	344.45	36		0.341	0.444	0.183	0.002	0.024	0.006	0	0	0	3.946
	344.45	56		0.285	0.391	0.282	0.002	0.032	0.008	0	0	0	2.841
	344.45	91		0.185	0.324	0.441	0.002	0.038	0.010	0	0	0	1.599
	344.45	109		0.177	0.282	0.485	0.002	0.044	0.011	0	0	0	1.190
	344.45	130		0.151	0.260	0.530	0.002	0.046	0.012	0	0	0	0.843
	344.45	146		0.129	0.252	0.559	0.002	0.046	0.012	0	0	0	0.648
	344.45	163		0.115	0.242	0.579	0.002	0.049	0.013	0	0	0	0.490
344.45	180		0.121	0.232	0.590	0.002	0.043	0.012	0	0	0	0.371	
Batch reactor	343.45	0	0.1520	0.455	0.545	0	0	0	0	0	0	0	4.974
	343.45	5		0.399	0.528	0.030	0.042	0	0	0	0	0	4.643
	343.45	42		0.316	0.436	0.243	0.001	0.002	0.001	0	0	0	2.790
	343.45	73		0.234	0.386	0.374	0.002	0.003	0.001	0	0	0	1.821
	343.45	124		0.186	0.337	0.470	0.002	0.004	0.001	0	0	0	0.903
	343.45	156		0.141	0.311	0.541	0.002	0.004	0.001	0	0	0	0.581
	343.45	197		0.122	0.291	0.579	0.002	0.005	0.001	0	0	0	0.331
	343.45	232		0.092	0.281	0.619	0.002	0.005	0.001	0	0	0	0.204
	343.45	273		0.092	0.274	0.626	0.002	0.005	0.001	0	0	0	0.116
	343.45	304		0.084	0.270	0.637	0.002	0.005	0.001	0	0	0	0.076
	343.45	341		0.079	0.267	0.646	0.002	0.005	0.001	0	0	0	0.046
	343.45	372		0.075	0.266	0.651	0.002	0.006	0.001	0	0	0	0.030
	343.45	406		0.073	0.265	0.654	0.002	0.006	0.001	0	0	0	0.019
	343.45	435		0.073	0.265	0.654	0.002	0.006	0.001	0	0	0	0.013

C. Sensitivity analysis of the parameters on the selected kinetic model

The sensitivity analysis of the parameters on the reaction rate predicted by the selected model (Model 49, Equation 18) has been evaluated by means of the Monte Carlo method. It accounts for the effect of the parameter uncertainty on the model output. The applied procedure consists of 3 steps:

- 1) Random generation of a set of parameters: Parameters in the model were assumed to follow a normal distribution with mean equal to its optimal value and standard deviation equal to its standard error, both estimated from the fit. For each parameter, a random value was generated according to its normal distribution. As a result, a set of random parameters was obtained and it was used to calculate the reaction rates at the conditions of each experimental point using Equation 18.
- 2) For each experimental point, the previous step was repeated 1000 times to obtain 1000 calculated reaction rates values. They followed a normal distribution. Its mean corresponds to the reaction rate predicted with Equation 18 using the optimal parameter values. Its standard deviation is a measure of the model sensitivity due to the uncertainty of the parameters.
- 3) Error bars in Figure 4(a) show the model output sensitivity, expressed as the standard deviation of the calculated reaction rates given the standard error of the fitted parameters.

D. Best models ranking obtained with the fixed resin solubility parameter value

TABLE S2. Optimal parameter values for BTBE kinetic equations with the restriction that $\delta_p = 20.85 \text{ MPa}^{1/2}$, when δ_p is included. A “–” sign indicates that the related effect is not included in the model.

Model #	k' (mol/g h)		{driving force} ^a	{adsorption term}								n	δ_p included (Equation 9)	RSS	Δ_i	w_i
	k'_1	k'_T		$1^{\text{st}} \text{ Ads}^b$	$K_{1,\text{BuOH}}$	$K_{T,\text{BuOH}}$	$K_{1,\text{IB}}$	$K_{T,\text{IB}}$	$K_{1,\text{BTBE}}$	$K_{T,\text{BTBE}}$						
49	0.686	-9570	(a)	a_{BuOH}	–	–	–	–	-1.890	-4991	1	Yes	7.364	0	0.447	
151	0.231	-9491	(a)	a_{BuOH}	–	–	–	–	-1.862	-3199	2	Yes	7.541	3	0.089	
48	0.709	-9440	(a)	a_{BuOH}	–	–	–	–	-1.096	–	1	Yes	7.687	4	0.071	
736	0.233	-9487	(c)	a_{BuOH}	–	–	–	–	-1.150	-3711	1	Yes	7.581	4	0.062	
156	3.641	-9396	(a)	1	1.350	–	–	–	0.103	–	2	Yes	7.606	4	0.050	
273	3.121	-9393	(a)	1	0.370	–	–	–	-0.884	–	3	Yes	7.616	5	0.046	
964	0.712	-9429	(c)	1	–	–	–	–	-1.673	–	3	Yes	7.786	5	0.030	
847	0.712	-9426	(c)	1	–	–	–	–	-1.248	–	2	Yes	7.787	5	0.030	
730	0.714	-9420	(c)	1	–	–	–	–	-0.497	–	1	Yes	7.792	6	0.028	
157	3.941	-8540	(a)	1	1.559	597.6	–	–	0.209	–	2	Yes	7.563	6	0.024	
741	1.237	-9380	(c)	1	0.075	–	–	–	0.198	–	1	Yes	7.701	6	0.021	
858	1.124	-9388	(c)	1	-1.028	–	–	–	-0.873	–	2	Yes	7.711	6	0.020	
975	1.093	-9391	(c)	1	-1.549	–	–	–	-1.378	–	3	Yes	7.715	6	0.019	
274	3.199	-9004	(a)	1	0.425	277.0	–	–	-0.874	–	3	Yes	7.599	6	0.018	
150	0.256	-9354	(a)	a_{BuOH}	–	–	–	–	-1.355	–	2	Yes	7.895	7	0.012	
742	15.10	-6558	(c)	1	14.88	3040	–	–	13.828	–	1	Yes	7.654	7	0.011	
859	1.158	-9287	(c)	1	-0.935	270.7	–	–	-0.857	–	2	Yes	7.705	8	0.007	
976	1.116	-9314	(c)	1	-1.485	225.7	–	–	-1.371	–	3	Yes	7.711	8	0.007	
735	0.260	-9339	(c)	a_{BuOH}	–	–	–	–	-0.568	–	1	Yes	7.974	9	0.006	
56	707.6	-9696	(a)	1	706.9	–	–	–	705.8	–	1	Yes	7.887	9	0.004	
2	1.116	-9694	(a)	1	–	–	–	–	–	–	1	Yes	9.692	33	<10 ⁻⁶	

^a Form of the driving force: (a) surface reaction (Equation 3) and (c) isobutene adsorption (Equation 5). ^b First summand of the adsorption term.