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:

$$-r_{\mathrm{IB}} = \frac{F^{\mathrm{o}}_{\mathrm{IB}} \left(X_{\mathrm{IB,outlet}} - X_{\mathrm{IB,inlet}} \right)}{W_{\mathbf{cat}}} \qquad \text{(S1)}$$

where F^0_{IB} is the isobutene molar flow rate at null conversion, $X_{\mathrm{IB,outlet}}$ is the isobutene conversion at the reactor outlet, and $X_{\mathrm{IB,inlet}}$ 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, $X_{\mathrm{IB,inlet}} = 0$.

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:

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

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.

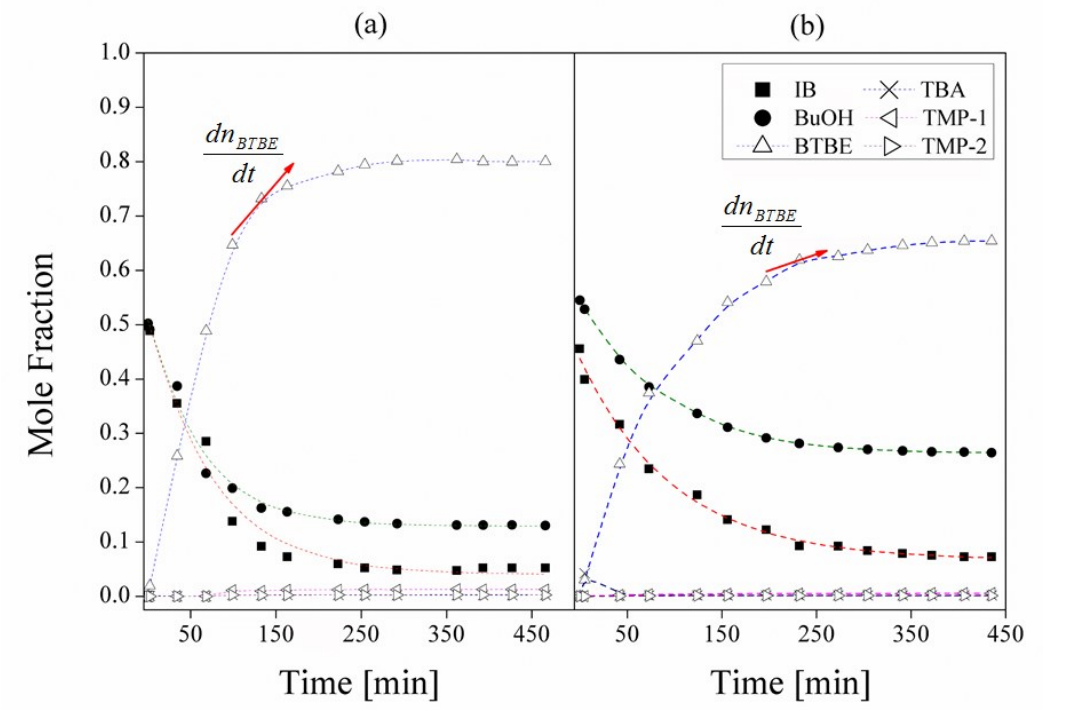

Fig. S1 Experimental mole evolution obtained in the batch reactor system under two different conditions: (a) T = 323.4 K, $R°_{BuOH/IB}$ = 1.0; (b) T = 343.5 K, $R°_{BuOH/IB}$ = 1.2. Dashed lines correspond to fitted empirical equation. Red arrows represent the derivative with respect to time, used to 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}	$x_{i\text{-butane}}$	$x_{trans\text{-}2\text{-}butene}$	$x_{cis\text{-}2\text{-}butene}$	
Plug-flow reactor	333.15	—	0.0810	0.203	0.135	0	0	0	0	0.332	0.328	0.002	1.129
	333.15	—	0.0420	0.193	0.180	0	0	0	0	0.313	0.313	0.002	1.031
	333.15	—	0.0421	0.190	0.193	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	0.666
	313.15	—	0.2080	0.520	0.480	0	0	0	0	0	0	0	0.680
	303.15	—	0.0440	0.548	0.452	0	0	0	0	0	0	0	0.255
	323.15	—	0.0217	0.490	0.510	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	1.561
	323.35	2		0.488	0.491	0.019	0.001	0	0	0	0	0	1.506
	323.35	34		0.355	0.387	0.258	0.000	0	0	0	0	0	0.844
	323.35	68		0.285	0.226	0.489	0.000	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	0.261
	323.35	133		0.092	0.162	0.732	0.002	0.010	0.002	0	0	0	0.141
	323.35	163		0.073	0.155	0.756	0.002	0.012	0.002	0	0	0	0.082
	323.35	223		0.059	0.142	0.782	0.002	0.012	0.002	0	0	0	0.028
	323.35	254		0.052	0.137	0.794	0.002	0.012	0.002	0	0	0	0.016
	323.35	292		0.048	0.134	0.801	0.002	0.012	0.003	0	0	0	0.008
	323.35	362		0.047	0.131	0.804	0.002	0.013	0.003	0	0	0	0.002
	323.35	393		0.052	0.131	0.800	0.002	0.012	0.003	0	0	0	0.001
	323.35	427		0.052	0.131	0.800	0.002	0.013	0.003	0	0	0	0.001
	323.35	466		0.052	0.130	0.800	0.002	0.012	0.003	0	0	0	0.000
Batch reactor	318.45	0	0.5100	0.492	0.508	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	1.217
	318.45	33		0.403	0.436	0.150	0.002	0.009	0.002	0	0	0	0.853
	318.45	63		0.316	0.392	0.268	0.002	0.017	0.004	0	0	0	0.599
	318.45	93		0.246	0.343	0.379	0.002	0.024	0.005	0	0	0	0.420
	318.45	125		0.208	0.311	0.445	0.002	0.028	0.006	0	0	0	0.288
	318.45	156		0.180	0.272	0.509	0.002	0.031	0.007	0	0	0	0.199
	318.45	187		0.143	0.252	0.564	0.002	0.032	0.007	0	0	0	0.138
	318.45	217		0.120	0.229	0.608	0.002	0.033	0.007	0	0	0	0.097
	318.45	248		0.107	0.219	0.631	0.002	0.034	0.007	0	0	0	0.067
	318.45	287		0.087	0.193	0.684	0.002	0.028	0.006	0	0	0	0.042
	318.45	313		0.068	0.196	0.692	0.002	0.035	0.008	0	0	0	0.031
	318.45	345		0.058	0.190	0.707	0.002	0.035	0.008	0	0	0	0.021
	318.45	450		0.043	0.184	0.727	0.002	0.036	0.008	0	0	0	0.006
	318.45	480		0.041	0.179	0.734	0.002	0.036	0.008	0	0	0	0.004
	318.45	547		0.039	0.179	0.736	0.002	0.037	0.008	0	0	0	0.002
	318.45	580		0.037	0.177	0.740	0.002	0.035	0.008	0	0	0	0.001
	318.45	621		0.035	0.177	0.742	0.002	0.036	0.008	0	0	0	0.001
Batch reactor	344.95	0	0.1296	0.492	0.508	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	7.653
	344.95	19		0.396	0.463	0.124	0.001	0.013	0.003	0	0	0	5.593
	344.95	35		0.329	0.420	0.225	0.001	0.020	0.005	0	0	0	4.088
	344.95	51		0.261	0.381	0.325	0.001	0.025	0.007	0	0	0	2.988
	344.95	66		0.212	0.356	0.395	0.001	0.028	0.007	0	0	0	2.227
	344.95	82		0.168	0.341	0.452	0.002	0.029	0.008	0	0	0	1.628
	344.95	100		0.149	0.313	0.498	0.001	0.031	0.008	0	0	0	1.144
	344.95	116		0.118	0.298	0.543	0.001	0.031	0.008	0	0	0	0.836
	344.95	138		0.094	0.286	0.577	0.002	0.033	0.009	0	0	0	0.543
	344.95	168		0.084	0.281	0.591	0.001	0.033	0.009	0	0	0	0.302
	344.95	187		0.071	0.288	0.599	0.001	0.033	0.008	0	0	0	0.208
	344.95	220		0.074	0.274	0.608	0.001	0.033	0.009	0	0	0	0.109
	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

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}	$x_{i\text{-butane}}$	$x_{trans\text{-}2\text{-}butene}$	$x_{cis\text{-}2\text{-}butene}$	
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	7.273
	344.35	20		0.451	0.517	0.009	0.022	0	0	0	0	0	6.664
	344.35	37		0.431	0.504	0.033	0.031	0	0	0	0	0	6.073
	344.35	53		0.409	0.488	0.064	0.038	0	0	0	0	0	5.565
	344.35	70		0.388	0.472	0.097	0.042	0.001	0	0	0	0	5.071
	344.35	86		0.371	0.459	0.125	0.043	0.001	0	0	0	0	4.646
	344.35	110		0.356	0.442	0.155	0.045	0.001	0	0	0	0	4.075
	344.35	127		0.326	0.431	0.193	0.048	0.001	0	0	0	0	3.714
	344.35	143		0.320	0.422	0.208	0.047	0.002	0	0	0	0	3.403
	344.35	159		0.291	0.414	0.240	0.053	0.001	0	0	0	0	3.118
	344.35	176		0.278	0.403	0.262	0.054	0.002	0	0	0	0	2.841
	344.35	194		0.265	0.393	0.285	0.055	0.002	0	0	0	0	2.575
	344.35	211		0.261	0.389	0.293	0.054	0.002	0	0	0	0	2.346
	344.35	229		0.236	0.384	0.318	0.060	0.002	0	0	0	0	2.127
	344.35	251		0.232	0.375	0.332	0.058	0.003	0.001	0	0	0	1.886
	344.35	268		0.218	0.372	0.346	0.060	0.003	0.001	0	0	0	1.718
	344.35	285		0.213	0.369	0.354	0.061	0.003	0.001	0	0	0	1.566
	344.35	303		0.195	0.368	0.374	0.059	0.003	0.001	0	0	0	1.419
	344.35	318		0.193	0.361	0.379	0.062	0.004	0.001	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	16.042
	355.55	33		0.259	0.309	0.422	0.002	0.006	0.002	0	0	0	4.300
	355.55	51		0.181	0.249	0.558	0.002	0.007	0.002	0	0	0	2.002
	355.55	67		0.154	0.224	0.609	0.002	0.008	0.002	0	0	0	1.015
	355.55	83		0.134	0.213	0.641	0.002	0.008	0.002	0	0	0	0.514
	355.55	101		0.133	0.209	0.645	0.002	0.008	0.002	0	0	0	0.239
	355.55	118		0.127	0.207	0.652	0.002	0.009	0.002	0	0	0	0.116
	355.55	134		0.122	0.207	0.657	0.002	0.009	0.003	0	0	0	0.059
	355.55	154		0.128	0.208	0.650	0.002	0.009	0.002	0	0	0	0.025
	355.55	175		0.130	0.212	0.645	0.002	0.009	0.002	0	0	0	0.010
	355.55	194		0.126	0.210	0.649	0.002	0.010	0.003	0	0	0	0.005
	355.55	232		0.124	0.213	0.648	0.002	0.010	0.003	0	0	0	0.001
Batch reactor	334.25	0	0.3530	0.500	0.500	0	0	0	0	0	0	0	3.396
	334.25	3		0.492	0.496	0.012	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	1.773
	334.25	65		0.249	0.298	0.439	0.002	0.010	0.002	0	0	0	0.980
	334.25	98		0.181	0.235	0.568	0.002	0.011	0.003	0	0	0	0.522
	334.25	128		0.135	0.194	0.654	0.002	0.012	0.003	0	0	0	0.294
	334.25	165		0.139	0.143	0.710	0.000	0.007	0.000	0	0	0	0.145
	334.25	197		0.114	0.133	0.745	0.000	0.007	0.001	0	0	0	0.079
	334.25	229		0.085	0.148	0.749	0.002	0.014	0.003	0	0	0	0.043
	334.25	286		0.078	0.143	0.760	0.002	0.014	0.003	0	0	0	0.014
	334.25	365		0.079	0.139	0.763	0.002	0.014	0.003	0	0	0	0.003
	334.25	413		0.075	0.140	0.766	0.002	0.014	0.003	0	0	0	0.001
	334.25	440		0.077	0.140	0.764	0.002	0.014	0.003	0	0	0	0.001
	334.25	470		0.079	0.140	0.762	0.002	0.014	0.003	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	3.306
	333.15	33		0.404	0.431	0.146	0.001	0.015	0.003	0	0	0	2.215
	333.15	67		0.303	0.372	0.290	0.001	0.027	0.007	0	0	0	1.447
	333.15	99		0.244	0.325	0.386	0.001	0.035	0.009	0	0	0	0.970
	333.15	131		0.198	0.289	0.464	0.001	0.039	0.010	0	0	0	0.650
	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

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}	$x_{i\text{-butane}}$	$x_{trans\text{-}2\text{-}butene}$	$x_{cis\text{-}2\text{-}butene}$	
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 δ_P = 20.85 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	{adsorption term}							δ_P included	*RSS*	Δ_i	w_i
	k'_1	k'_T	force}[a]	1st Ads[b]	$K_{1,BuOH}$	$K_{T,BuOH}$	$K_{1,IB}$	$K_{T,IB}$	$K_{1,BTBE}$	$K_{T,BTBE}$	*n*	(Equation 9)			
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
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
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.